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X RAYS AND CRYSTAL STRUCTURE

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AND
CRYSTAL STRUCTURE

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PREFACE TO THE FIRST EDITION

IT is now two years since Dr. Laue conceived the idea of employing a crystal as a 'space diffraction grating' for X-rays. The successful realisation of the idea by Messrs. Friedrich and Knipping has opened up a wide field of research in which results of great interest and importance have already been obtained. On the one hand the analysis of X-rays which has been rendered possible has led to remarkable conclusions concerning the atoms which emit them under the proper stimulus, and has thrown an entirely fresh light on problems of atomic structure. On the other hand the architecture of crystals has been laid open to examination; crystallography is no longer obliged to build[1] only on the external forms of crystals, but on the much firmer basis of an exact knowledge of the arrangement of the atoms within. It seems possible also that the thermal movements of the atoms in the crystal will be susceptible not only of observation but even of exact measurement.

In order to grasp the meaning and progress of the new science, it is necessary to have some knowledge both of X-ray phenomena and of crystallography. As these branches of science have never been linked together before, it is to be expected that many who are interested in the new development find themselves hampered by a tantalising ignorance of one or other of the essential contributory subjects. In this little book my son and I have first made an attempt to set out the chief facts and principles relating to X-rays and to crystals, so far as they are of importance to the main subject. We have devoted the remaining and larger portion

of the book to a brief history of the progress of the work, and an account of the most important of the results which have been obtained.

The book is necessarily an introduction rather than a treatise. The subject is too new and too unformed to justify a more comprehensive treatment. We have tried to draw its main outlines for the use of those who wish to understand its general bearings, and we hope that our statement may even be of some service to those who wish to make its acquaintance practically and to share in the fascinating research work which it offers. No doubt the latter will consult also the original papers.

Considering the purpose which we have had in view we have refrained from the discussion of a number of interesting points of contact with other sciences and with older work, such as for example the remarkable investigations of Pope and Barlow. We have not even given a complete account of all the experimental investigations that have been made in connection with the subject itself, and have been content with the merest allusion to the serious mathematical discussions which it has received at several hands.

The publication of the book has been delayed by the difficulties of these times, which have also hindered the continuance of some researches and the publication of others that are almost or quite complete. A few results which could not be included in the book itself are given in supplementary notes at the end.

The same circumstances have left me to write this preface alone. Probably, however, I should have demanded the privilege in any case. I am anxious to make one point clear, viz., that my son is responsible for the ' reflection ' idea which has made it possible to advance, as well as for much the greater portion of the work of unravelling crystal structure to which the advance has led.

W. H. BRAGG.

January, 1915.

PREFACE TO THE FOURTH EDITION

WHEN this book was written, analysis of crystal structure by means of X-rays was a new subject of which no connected account was in existence. We had it in mind to describe it in such a way that anyone who was interested in the new field which it opened up might become generally acquainted with its methods. It seemed especially necessary to make the attempt because, in the first place, the subject demanded a little knowledge of many subjects which were not usually combined in any one person's acquaintance, and, in the second, because the same catholicity promised a general usefulness to many different sciences.

During the last eight years, the subject has been greatly studied and widely extended. The treatises of Dauvillier, Ewald and others are witness to the increase in the ground that has been covered. A large book would be required to treat, in any detail, of all the work that has been done and of the new fields of research which have been opened up.

This new edition does not aim at being such a comprehensive treatise : we have thought it best to keep to our original purpose. We have, of course, rewritten most of it, in order that some account might be given of the developments that have been made, and of the position in which the subject now stands. But we hope, as before, that the main usefulness of the book will lie in giving to the students of the different sciences a general idea of methods that bear upon a very wide range of enquiry. It was best, we have thought, to sketch the main lines of advance and to leave it to everyone interested in following up any special

point, to do so by the study of such researches as, dealt with it more particularly.

It is curiously difficult, in writing of this subject, to use words which remain suitable in face of a succession of new researches. For instance, on page 10 we have said that " there can be no such thing as a surface reflexion of X-rays " and on page 40 that " scattered radiation has the same wave length as the original." The very recent work of A. H. Compton, to which we have referred later in the book, imposes a certain qualification on these phrases. We hope, however, that on the whole we have given a reasonably faithful sketch of the subject as it stands to-day.

In our description of the determination of crystal structure we have often adopted a historical method. We have used the original measurements when they might have been replaced by the more accurate determinations that are now made easily. The accuracy of the earlier data was amply sufficient for the purposes to which they were applied, and it seemed better to leave them as they were. The results of more exact measurements are given when required.

We would express our grateful thanks to many kind helpers : to M. de Broglie, to Messrs. Debye and Scherrer, and to Mr. Hull for the gift of photographs, to Dr. Hutchinson for corrections of crystallographic references, to Mr. James for preparing an index, to Mr. Buckley for help in writing the appendix, and to many others.

W. H. B.
W. L. B.

December, 1923.

NOTE TO FIFTH EDITION

OPPORTUNITY has been taken of the necessity for a further reprint to make a few corrections and to extend with the help of Mr. Astbury the bibliography at the end of the volume.

March, 1925.

CONTENTS

LIST OF PLATES

CHAPTER I

INTRODUCTORY

FROM the year 1895, when Rontgen discovered the rays which bear his name, to the year 1912, when v. Laue showed that they could be diffracted by a crystalline structure, their relation to other forms of radiation was the subject of the keenest investigation. In many respects the rays resembled light. They moved in straight lines and cast sharp shadows, they traversed space without any obvious transference or intervention of matter, they acted on a photographic plate, excited certain materials to phosphorescence, and could bring about the ionisation of a gas. In other respects the rays seemed to differ from light. The mirrors, prisms and lenses which deflected light had no such action on X-rays; gratings as ordinarily constructed did not diffract them ; neither double refraction, nor polarisation was produced by the action of crystals. If the velocity of X-rays could have been shown without question to have been the same as that of light, it would have been a most important piece of evidence. E. Marx of Leipzig devoted the greatest skill and perseverance to the attempt to measure the velocity, and claimed that he had overcome all the many acute objections brought against his work. His results led him to assert the equality of the velocities of the two kinds of rays ; but the difficulties of the experiment were so great that his work did not bring universal conviction.

Undoubtedly the strongest evidence of the similarity of nature of light and X-rays was supplied by the discovery of a form of polarisation of the latter rays. Barkla showed

that the X-rays issuing from a bulb and impinging upon matter were less scattered by the matter in a direction parallel to the stream of cathode rays in the bulb than in directions at right angles to the stream. A pencil of rays selected from the scattered radiation, though more difficult to work with than primary rays, showed the same effect to a much higher degree.

These facts were in accordance with the theory of the electromagnetic origin of X-rays due to Schuster, Wiechert, Stokes, J. J. Thomson, and others. Cathode particles, whose flight was suddenly arrested by impact on the anti-cathode, should send out ether pulses in which the vibrations would tend to be parallel to the direction of the cathode-ray stream. Such vibrations, impinging on matter and scattered thereby, would give rise to less radiation in the direction of the vibrations than in any other direction.

The strongest evidence *against* the similarity of nature of light and X-rays arose from considerations of the transference of energy by means of the latter. Cathode rays impinging on the anti-cathode gave rise to X-rays : it was found that these in turn gave rise to cathode rays, *i.e.* swiftly moving electrons, when they encountered matter of any kind. It was very remarkable that the speed of the secondary electron which the X-ray produced was of the same order as that of the primary electron which produced the X-ray. That was so, no matter what the intensity of the X-rays might be, nor how far from the bulb the production of the secondary X-ray took place, nor what the nature of the matter from which the secondary electron seemed to spring.

It seemed almost imperative that we should consider the **X-ray** to have transferred so much energy from the one electron to the other, and this involved the conception of **a** ' quantum' of energy radiation travelling through space without alteration of form or content. The idea was and is quite foreign to orthodox conceptions of the transference of radiation energy. No one has been able to suggest how it is to be reconciled with the older hypotheses.

It had, however, become increasingly clear, even prior to v. Laue's discovery, that the phenomenon which appeared so irreconcilable with light theory must in some way be made to fit in. The 'photo-electric action' was found, on closer investigation, to be of exactly the same kind as the X-ray action which has just been described. The difficulty in connection with the apparent transference of energy by X-rays could not be avoided by asserting that X-rays and light were of different nature, and were not to be compared with each other.

The whole aspect of the problem was changed when v. Laue showed that on the classical theory of electromagnetic radiation, a crystal should be able to diffract X-rays, certain subsidiary conditions being satisfied, and when his forecast was verified by Friedrich and Knipping. We now know that light and X-rays are identical in nature. The identity is even closer than we had imagined because we are precluded from ascribing differences in character to anything else than mere differences in wave-length. The new knowledge narrows the question but broadens the field of its application.

In the second place, we have a new and powerful method of analysing a stream of X-radiation. We are placed in the same position with regard to X-rays as we may conceive ourselves to have been in the case of light if we had, up to a certain time, been able to analyse light only by observing the absorbing powers of various screens, and had then been presented with a spectrometer.

Again, we have a new means of investigating the structure of crystals. Instead of guessing the internal arrangement of the atoms from the outward form assumed by the crystal, we find ourselves able to measure the actual distances from atom to atom. In doing so we seem certain to acquire, indeed we have already acquired, knowledge of great importance to all the sciences and to their applications.

Dr. v. Laue's proposal was based on a brilliant extrapolation. A large proportion of our knowledge of the

phenomena of light is derived from investigations suggested by the undulatory theory. Our most useful instrument is the spectrometer, and especially that form of it which makes use of the diffraction grating. The essential feature of the use of the grating is the absolute measurement of the wave-length which it renders possible. The grating consists, as is well-known, of an arrangement of parallel and equidistant straight lines ruled in great numbers on a glass or metal surface. The spacing of the lines must in practice be of the same order as the wave-length to be measured. Sodium light, which has a wave-length of .0000589 cm., is diffracted through about 24^0 by a grating which has 7000 lines to the centimetre, *i.e.* a spacing of .000143 cm.

On various grounds it had been known for some time that the length of the X-ray wave, if there were such a thing, should be about 10^{-8} cm. or 10^{-9} cm., *i.e.* about ten thousand times smaller than the wave-length of sodium light. To construct a grating of appropriate spacings was unthinkable, because the spacings would need to be of the order of the distances between the molecules of a solid.

v. Laue conceived the idea of using the ordered arrangements of atoms or molecules in a crystal as a proper 'grating' for the investigation of X-rays. The spacings of the atoms or molecules were of the right order of magnitude. The diffraction problem was not so simple as in the case of the grating, because the regularity of arrangement of the atoms of the crystal extended over three dimensions instead of one. v. Laue was, nevertheless, successful in his attack upon the mathematical side of the problem. He showed that if a pencil of X-rays was made to traverse a crystal, diffracted pencils would be formed, arranged about the primary beam in a regular pattern according to laws which he formulated. A photographic plate placed perpendicular to the primary rays and behind the crystal would show a strong central spot where the primary rays struck it, and other spots arranged in regular fashion round the central spot in the places struck by the diffracted pencils. The experiment

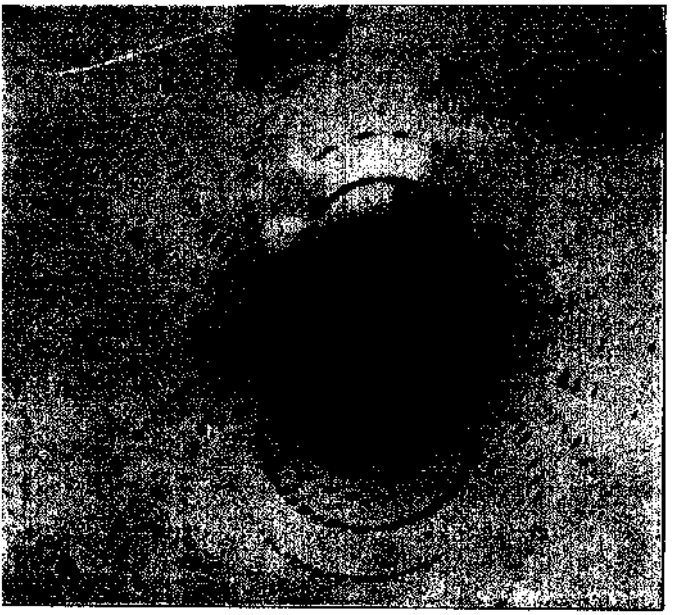
was carried out by Messrs. Friedrich and Knipping in the spring of 1912, and was immediately successful. Since then the authors have pursued their investigations vigorously, and their diagrams have attained the most admirable clearness. Examples are given in Plate I. The beautiful geometrical arrangement of the pattern is in reality a manifestation of the regularity of crystal structure.

We shall not discuss the mathematical investigation of the theory of the space-grating. Experience has shown that there is an exceedingly simple method of attacking the question which differs in form, though of necessity not in essence, from the original method of v. Laue. The newer method leads also to a simple and useful mode of experimental procedure. It will be convenient to follow it for the present.

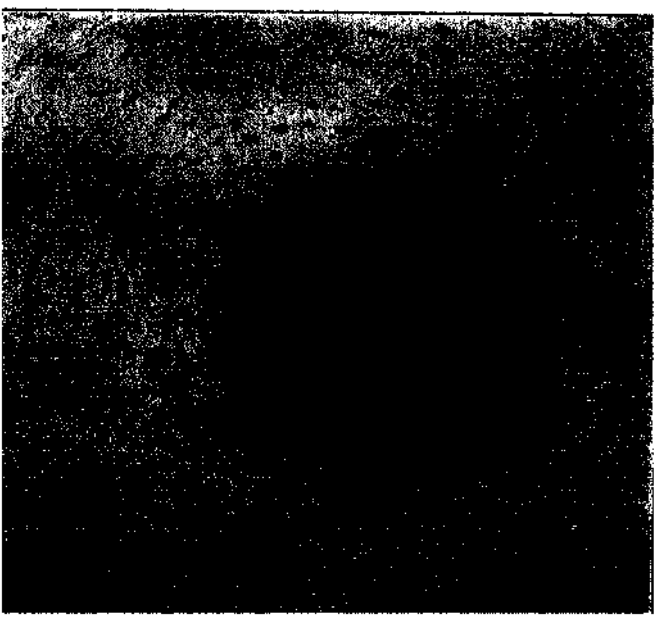
CHAPTER II

DIFFRACTION OF WAVES

WHEN X-rays are scattered by an amorphous body, the scattering takes place in a continuous manner all round the body. In the case of the photographs obtained by Laue, however, by far the greater part of the scattering takes place in certain directions only, and the scattered rays are grouped into separate pencils which leave their impression on the photographic plate in a series of isolated spots as shown in Plate I. The arrangement of these spots shows, both by its regularity and by the form which the regularity takes, that the effect is intimately connected with the crystal structure. It must be connected, moreover, with the fundamental pattern of the structure, and not with any accidental consequences of the crystal growth. For example, in the first case the crystal of Nickel sulphate is so oriented that the X-ray beam falling on it is parallel to a two-fold symmetry axis of the crystal structure, and the corresponding photograph shows this two-fold symmetry in the arrangement of the spots on the pattern. In the second case, the incident beam is parallel to the six-fold axis of symmetry of the hexagonal Beryl crystal, and the pattern has the same six-fold symmetry, slightly distorted owing to a small error in the orientation of the crystal slip. It is natural to suppose that the Laue pattern owes its origin to the interference of waves diffracted at a number of centres which are closely connected with the atoms or molecules of which the crystal is built, and are therefore arranged according to the same plan. The crystal is, in fact, acting as a diffraction grating.



NICKEL, SULPHATE



BERYL.

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The diffraction of waves by such a grating is a more complex effect than the diffraction of waves by the ordinary line grating, such as is used in spectroscopy. The latter owes its power of analysing a complex beam of light into its component wave-trains to the system of parallel lines which are ruled upon its surface at exactly equal intervals, many thousands going to the inch. When a train of waves falls on the system, each line acts as a fresh centre from which a diffracted train of waves spreads out, and it is the interaction of the similar wave trains from all the lines which gives rise to the diffraction effects. This type of grating is the simplest possible, for it consists of a single series of lines repeated one after the other in a plane. A crystal, on account of its regular structure, also forms a grating, but one of a more complicated type. A molecule, or a small group of molecules, forms the unit of the crystal pattern, and this unit is repeated throughout the whole volume. The line grating has regularity in one dimension only, whereas in the crystal the pattern is repeated regularly in all three dimensions in space. The waves of very short wave-length fall on the grating, and from each element, consisting of the unit of pattern as described above, an identical train of waves is diffracted, the interference of these trains giving rise to the diffraction effects.

In his original paper on the newly discovered effect, Laue obtained a mathematical expression which gave the intensity at all points due to the diffraction of waves of known wave-length incident on a set of particles arranged on a space lattice. A study of this expression showed that the spots on his photographs were in positions agreeing with the supposition that they were due to diffraction, and so proved the all-important nature of the new discovery. Treated in the direct manner, the analysis is somewliat complex, and in order to simplify the conception of the effect it will be viewed in what follows from a different standpoint. Both ways of attacking the problem lead to the same conclusions.

Let us suppose that we have a series of particles which all lie in one plane, these particles representing the atoms or other units which scatter the waves. When a pulse passes over these atoms, each emits a diffracted pulse which spreads spherically around it. Fig. 1 illustrates the result of the passage of the pulse *PP* over the atoms in the plane *A A*. The circles represent the pulses sent out by atoms in the plane. It is clear that all the diffracted wavelets touch a reflected wave front P'P'; in fact we have only repeated

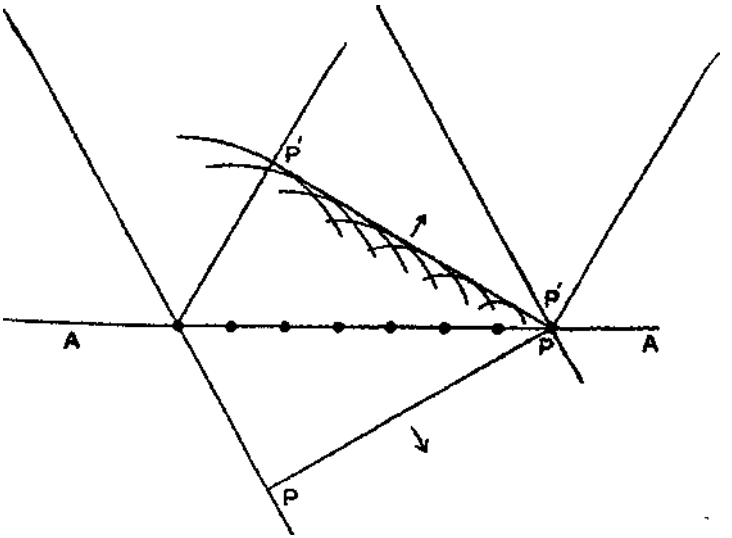


FIG. I.

Huygens[1] construction for the wave front reflected from a plane surface. It does not matter how the particles are arranged on the plane *AA*, as long as they lie exactly on that plane.

Thus, when the pulse passes over a set of particles which lie in a plane, the diffracted pulges combine to form a wave front which obeys the laws of reflection from the plane.

Turning now to the crystal, it is evident that its atoms may be considered as arranged in planes in an infinite number of ways. Fig. 2 represents a crystal, everything being drawn in two dimensions as in the last figure. It is

the natural arrangement of the particles in planes which gives rise to the plane faces of crystals, just as the form of the crystal in Fig. 2 is a polygon bounded by straight lines. It has been seen that, if a wave passes over the crystal, all the particles in any plane combine to reflect it with respect to that plane. Therefore, if we choose any one way of arranging the crystal particles in planes, corresponding to the lines *pp* in Fig. 2, and then find the direction in which a wave would be reflected by these parallel planes, this

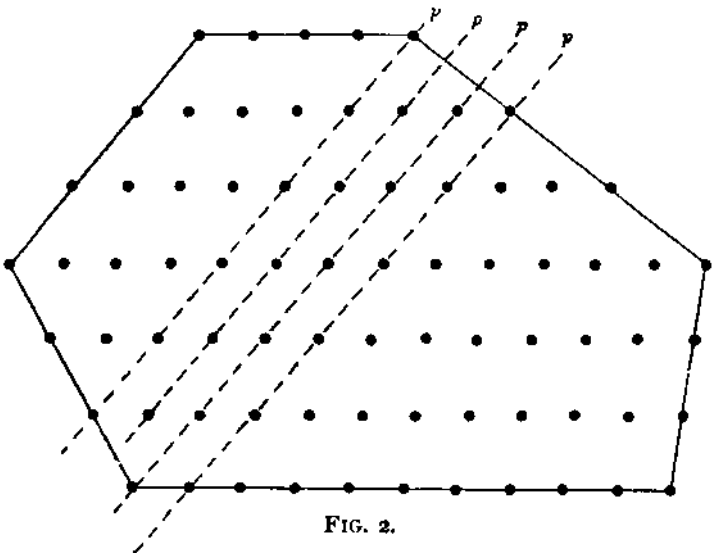


FIG. 2.

direction will be one in which to expect an interference maximum. There are an infinite number of ways of choosing such planes, but the most effective planes are those which are most thickly studded with particles, and which have correspondingly a wide spacing between successive planes; Study of crystal forms has shown that the natural faces which crystals exhibit can be explained as being on the whole those of a simple type, on which the particles are distributed with the greatest density. Therefore one might say, to sum up, that when a pulse passes over the crystal its scattered energy is concentrated into definite beams, and that these beams may be regarded as faint reflections of the

pulse on planes parallel to possible faces in the interior of the crystal.

The reflection does not depend upon the existence of any polished surface on the outside of the crystal, it depends upon an arrangement of planes within. It is this difference between what is here called the 'reflection' and the true reflection of ordinary light on surfaces which may make the analogy somewhat puzzling. When we talk of the X-rays being reflected by the crystal, it must be borne in mind that the term is only used in order to simplify the conception of the effect. There can be no such thing as a surface reflection of X-rays. The surface reflection of light is an effect concerned with the external form of the reflecting body alone. As long as the reflecting film is more than a few wave-lengths thick the full reflection is obtained. But when X-rays fall on a crystal face, the first few layers of atoms cannot diffract an appreciable proportion of the rays, for experiment shows that the rays must pass through some millions of layers before the X-ray beam is appreciably absorbed. Reflection takes place on all the layers, the only limitation being that if a layer is too deep within the body of the crystal, the absorption by the superincumbent layers reduces its contribution to an amount that is negligible. To the comparatively long waves of light the atomic structure is so fine grained that the medium is practically continuous. The X-rays are so short, on the other hand, that a crystal is to them a series of widely separated and regularly arranged particles, each of which diffracts a very small proportion of their energy.

If the waves may be regarded as reflected in the crystal planes, this idea should be capable of explaining the Laue photographs. When Laue employed zincblende to obtain his original photographs, the exact arrangement of the atoms in the crystal was unknown. However, the fact that zincblende crystals belong to the cubic system makes it possible to determine the orientation of the planes with respect to the incident X-ray pencil, and so to find the

directions of the reflected beams. A comparison shows that the spots in Laue's diffraction pattern for zincblende can be regarded very simply as the partial reflection of the incident beam by the principal planes of the crystal structure.

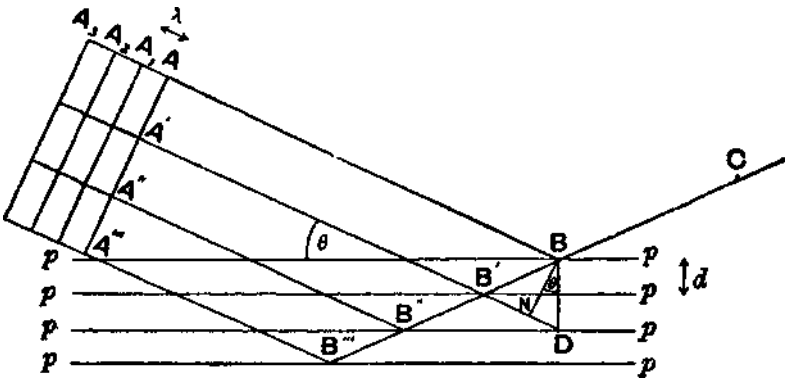
Let us suppose that we have a crystal with a large natural face on it, one of its important faces. From what has been said of the crystal structure in connection with Fig. 2, it is clear that this implies a possible arrangement of the particles in a series of planes parallel to this face. Therefore, as a pulse falls on this face, it will appear to be reflected from the face itself, though it is not at the face, but inside the crystal, that reflection is occurring. Yet, since the rays do not usually penetrate more than a millimetre in depth into the crystal, and often much less than a millimetre, it is only a thin layer parallel to the face which is engaged in the reflection. In future we shall, for brevity, describe a reflection of this kind as reflection by the face.

So far we have considered the reflection of a single pulse. We may now proceed to consider the reflection of a regular train of waves. Each plane reflects the wave train as a wave train, but when the reflected trains are in the same phase, that is to say, are so arranged that they fit on to each other exactly, crest to crest, and hollow to hollow, the reflected energy is far greater than if this condition is imperfectly fulfilled, even if the want of fit is exceedingly small.

Let the crystal structure be represented in Fig. 3 by the series of planes, *p, p, p, d* being their common distance apart or ' spacing.' *A, A_1, A_2, A_3* ... compose a train of advancing waves of wave length *X*. Consider those waves which, after reflection, join in moving along *BC,* and compare the distances which they must travel from some line such as *A A'"* before they reach the point C. The routes by which they travel are *ABC, A'B'C, A"B"C* and so on. Draw *BN* perpendicular to *A'B'*. Produce *A'B'* to *D,* where *D* is the image of *B* in the plane through *B'*. Since *B'B=B'D,* and

A'N—AB, the difference between *A'B'C* and *ABC* is equal to *ND,* that is to *2d* sin *d.* Similarly *A"B"C* is greater than *A'B'C* by the same distance, and so on.

If *DN* is equal to the length of the wave, or is any whole multiple of that length, all the wave trains reflected by the planes *p, p, p,* are in the same phase and their amplitudes are added together. If *DN* differs but slightly from the wave length, say by a thousandth part, the many thousand reflections bear all sorts of phase relations with each other, and the resultant amplitude is practically zero. When,



therefore, a monochromatic wave train is allowed to strike the face of the crystal, it is only when the glancing angle has certain values that reflection takes place. These values are given by

$$\lambda = 2d \sin \theta_1,$$
$$2\lambda = 2d \sin \theta_2,$$
$$3\lambda = 2d \sin \theta_3, \text{ etc.}$$

The reflection at the angle Θ_1 is called the reflection of the first order, that at the angle Θ_2 reflection of the second order, and so on.*

If the crystal is slowly turned round in such a way that the glancing angle steadily increases, in general there is no

*** By analogy with the spectra given by a line grating, these reflections are often called ist, 2nd, and 3rd spectra.**

reflected beam. But as the angle assumes the values Θ_1, Θ_2, Θ_3, there is a reflection of the rays. Passing now to another face of the crystal, which has a different spacing, *d'*, the monochromatic rays will only be reflected when

$$\lambda = 2d' \sin \theta_1',$$
$$2\lambda = 2d' \sin \theta_2', \text{ etc.}$$

If, therefore, we measure the angles Θ_1, Θ_2, Θ_3, at which reflection occurs, it gives us a relation between A, the wave length and *d,* the constant of the grating. By employing the same crystal face, the wave lengths of different monochromatic vibrations can be compared. By using the same wave length, the distance *d* can be compared for different crystals and different faces of the same crystal.

In this way we may, on the one hand, investigate the structure of crystals, and on the other hand analyse a beam of X-rays. An instrument which detects and measures the reflection from a crystal face may be called an X-ray spectrometer. The next chapter will be devoted to a description of such instruments ; we are here concerned merely with the theoretical explanation of the reflection. In order, however, to gain some idea of the dimensions of the quantities involved, we may assume some of the results obtained with the spectrometer, and take as an example the reflection of palladium rays *(i.e.* the rays emitted by a palladium anticathode) by rock-salt. It will be proved later that the planes parallel to the face of a cube of rock-salt are equally spaced at intervals 2.81×10^{-8} centimetres. When the palladium rays are reflected from such a face there is a series of angles (5° 59', 12° 3', 18° 14' ... , in a certain experiment), at which the reflection is exceptionally strong. It is clear that a monochromatic radiation is diffracted as 1st, 2nd, and 3rd spectra at these angles, for the sines of these angles are in the ratio 1:2:3. The wave length being given by the equation $n\lambda = 2d \sin \theta$, we have therefore, considering the first spectrum only,

$$\lambda = 2 \times 2.81 \times 10^{-8} \sin 5° 59' = .586 \times 10^{-8} \text{ centimetres.}$$

It is important to notice the relative magnitude of the grating constant d and the wave length λ. If the spacing d is less than one half the wave length, no value of d will satisfy the equation $\lambda = 2d \sin\theta$. In the case we have considered, there is a wide margin. The value of the spacing is some five times larger than the wave length. The planes we have chosen are densely packed with atoms, and the spacing between them is large. As one proceeds, however, to consider the reflection from more complex planes of the structure, the spacing becomes smaller and smaller until finally d is so small that it is impossible to find an angle which satisfies the condition for reflection. The conditions under which the reflection of monochromatic X-rays can take place are therefore very restricted indeed. Reflection is possible only when the spacing of the planes is large enough, and when the planes are inclined at exactly the right angle to the primary beam. It is because we are dealing with the complicated case of a three dimensional grating that all these conditions must be satisfied in order to obtain a ' spectrum ' of monochromatic waves.

We may now sum up the analysis which has been made. When a pulse passes over the crystal it will be more or less strongly reflected by all the sets of planes on which the crystal particles can be pictured as arranged. Its scattered energy will be concentrated in the special directions which correspond. If a series of pulses falls on the crystal this will be true for each of them, so that on the whole the X-rays, if of this nature, will be diffracted along the ' reflection ' directions. The series of pulses may be regarded as radiation composed of trains of all wave lengths over a certain range, just as a hot body gives off light which forms a continuous spectrum. However the crystal is oriented, the ' white ' radiation is reflected as a number of fine pencils. A crystal in one fixed position can reflect rays in many directions, because the reflection is not a surface effect, but takes place throughout the whole body of the crystal. The rays forming each diffracted pencil will no longer contain all

wave lengths, but will consist only of those wave lengths which satisfy the relation for reflection. The crystal selects for reflection certain components of the general radiation.

When the light falling on the crystal is monochromatic, the effect is more restricted. For each set of planes it is now only at certain definite angles that reflection can take place at all, these being determined by the equation $n\lambda = 2d \sin \theta$.

It is this extra condition which distinguishes the crystal grating from the ordinary line grating. The latter, at whatever angle the incident rays fall on it, gives a series of spectra. The crystal must be held at exactly the right angle, and even then can only give a spectrum of one order at a time. The reflection of the monochromatic vibration in this way gives more information about the crystal structure than the reflection of the white radiation. By observing the angles of reflection, we get a relation between λ and d, and by doing this for various faces of a crystal we gain an important insight into its structure. It is in this way that it has been possible to determine the absolute wave lengths of various types of X-radiation and the arrangement of the atoms in crystals.

CHAPTER III

THE X-RAY SPECTROMETER

THE X-ray spectrometer is an instrument designed to make use of the reflection principle which we have just discussed. Plate II. shows the instrument as first constructed, and will still serve to illustrate the essential principles.

The X-ray bulb is completely enclosed in a wooden box coated with lead, only one side of the box being shown. Good screening is, of course, an absolute necessity, for the sake not only of the experiment but also of the operator. We have used a thickness of 2 mm. over the whole box and a special shield of 5 mm. in places where the direct rays might do harm. With anticathodes of rhodium, palladium or molybdenum, and with applied potentials of 30,000 to 50,000 volts, this amount of protection seems to be sufficient; but it would be much too little if very high potentials were employed. The bulb shown in Fig. 4 is now generally replaced by a Coolidge tube of special form, in which a heavy molybdenum block is shaped so as to present a target nearly at right angles to the incident cathode rays. The wave length of MoK_a is .712 A.u., a size which is convenient for most crystal measurements, because the angles at which this ray is reflected by spacings of common occurrence are of the right size for measurement. The angles of reflection of shorter waves are too small, either for accuracy or for convenience, and longer waves are too much absorbed by the materials they must traverse. When, however, the crystal does not contain heavy atoms, and when as in organic substances the spacings may be 10 A.u., and more,

a longer wave, such as that of CuK_a, 1.54 A.u. (see p. 57), is often more convenient. One or other of the slits at *A* and *B* may be used to define the pencil of rays, and both assist in intercepting stray radiation. When the latter slit is used

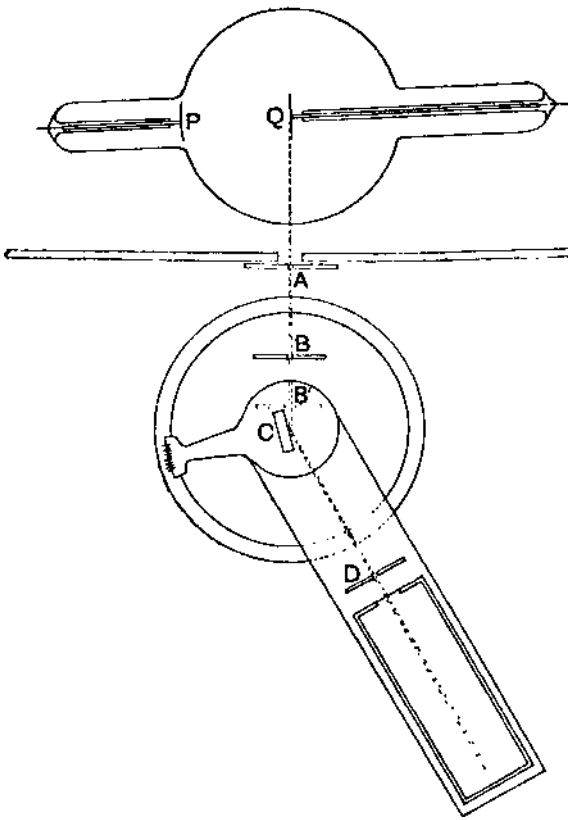


FIG. 4.

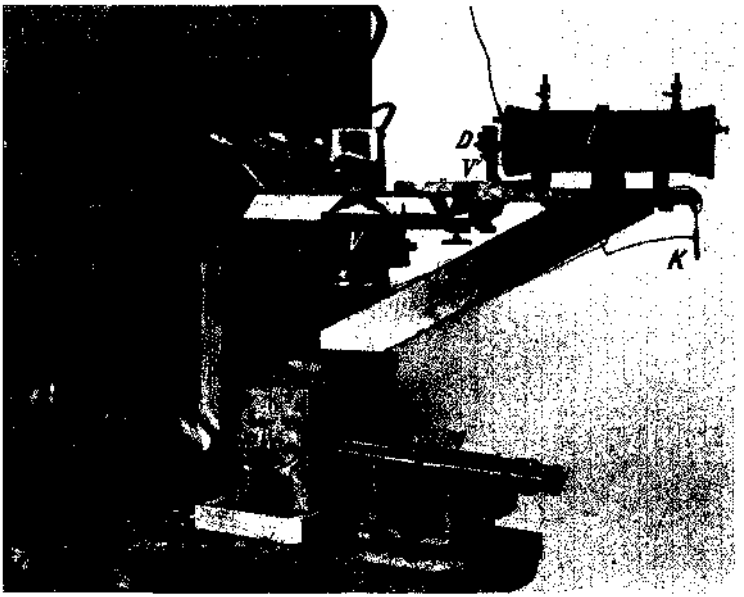
to define the rays it is generally placed as near the crystal as possible, and is for that reason mounted on a slider. The crystal *C*—in the figure, a very large crystal of rock-salt—is mounted on a revolving table carrying an arm, at the end of which is a vernier working in conjunction with a graduated circle. On the table various crystal holders can be placed, each furnished with three supports : two of the latter rest in a groove which runs round the crystal table,

the third rests on the table surface. In this way a holder can be removed and so replaced that, when the table is turned, the crystal revolves about the same axis as before. At the same time the crystal and its holder can be turned on the crystal table, so that a plane or planes can be brought into any desired angular position with respect to the vernier arm. This is a convenient arrangement when it is desired to measure the angle between a pair of reflecting planes and the vernier is not to be put into some position where it is awkward to read it.

The reflected pencil of X-rays passes into an ionisation chamber mounted so as to be capable of revolving about the same vertical axis as the crystal chamber. An adjustable slit *D* stands in front of the ionisation chamber. The chamber consists of a closed lead cylinder 15 cm. long and 5 cm. in diameter. A hole in the centre of the lead plate at one end is covered by a thin sheet of aluminium which transmits the reflected rays without much loss. The opening is large enough to take in a pencil 1 cm. wide ; but the width can be limited to very small dimensions by the slit at D.

The chamber is filled with a gas which absorbs the X-rays strongly, and so yields a large ionisation current. In the earliest experiments $S0_2$ was used, but methyl bromide is better for Mo, Rh or Pd rays. The chamber is insulated and raised to a high potential by a battery of storage cells. An electrode is mounted in the cylinder, just out of the way of the stream of rays that enters it, and is connected through a mounting in an amber plug with a fine wire leading to some form of electroscope. We have used the Wilson tilted electroscope and also the string electrometer of Edelmann, and found both satisfactory.

The wire is connected to the electroscope at a point immediately below and on the continuation of the axis of the instrument. The photograph will make this clear. The object of this arrangement is to make it possible to turn the ionisation chamber about the axis without straining the connection with the electroscope. The connecting wire of



X-RAY SPECTROMETER.

LLL, Lead box.
A, B, D, Slits.
C, Crystal.
I, Ionisation chamber.
V, Vernier of crystal table.
V, Vernier of ionisation chamber.
K, Earthing key.
£, Electroscope.
M, Microscope.

Facing page **18,**

the electroscope is electrically shielded by stout metal casings which are earthed.

The arm of the chamber also carries a vernier which works on the same scale as that of the revolving table.

The mode of using the spectrometer for crystal analysis depends upon the nature of the crystal and upon the information that is required. In general we require measurements of the angles at which the principal planes of the crystal reflect the monochromatic X-ray; and also of the angles which these planes make with one another. We may also require to know the relative intensities of the different orders of reflection by any plane.

The resolving power of the spectrometer increases rapidly as the reflecting angle approaches 90° ; for, since $n\lambda = 2d \sin\theta$,

$$\frac{d\theta}{d\lambda} = \frac{n}{2d} \sec\theta.$$

The curve in Fig. 5 shows the result of observations of the lines Ka_1 and Ka_2 in the rhodium spectrum of the fourth

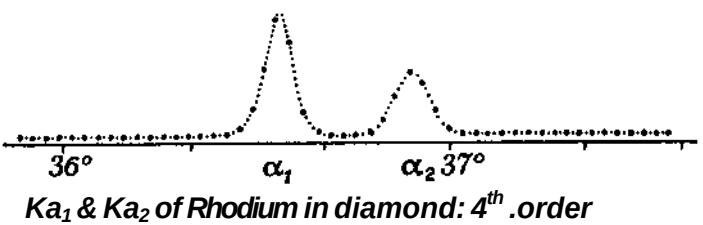


FIG. 5.

(Proceedings of the Physical Society of London, 1920.)

order, diamond being the crystal employed. The angles of reflection, which are the angular settings of the crystal table are plotted as abscissae : the two lines lie between 36^0 and 37^0. Any error of scale zero is eliminated by making a corresponding set of observations on the negative side. The wave lengths of the lines are .6163 A.U. and .6121, so that the separation in the figure is due to a difference of .0042 A.u. only.

When a substance can be obtained in the form of a single crystal, weighing a few milligrammes and not too much

extended *in* any one direction, the procedure is very simple and convenient. The crystal is mounted on a stand resembling part of the equipment of a goniometer ; such a stand is illustrated in Fig. 6. All slits are opened wide : the crystal itself is an effective slit since its dimensions limit

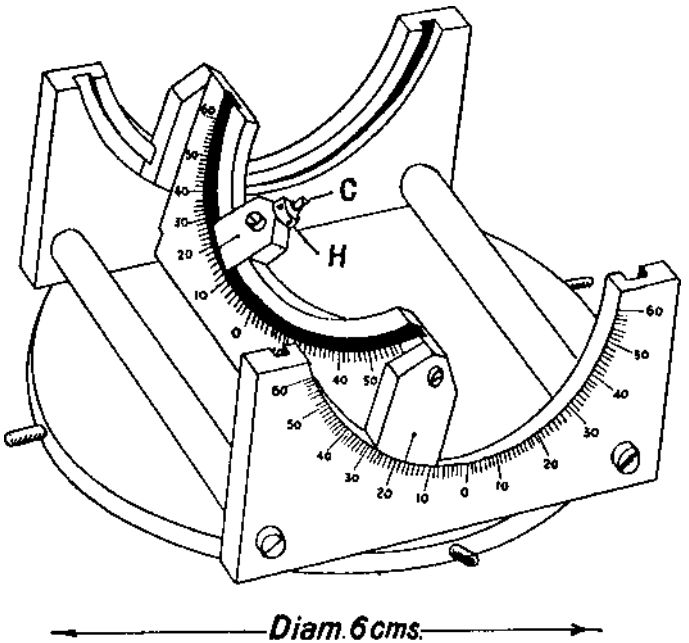


FIG. 6.

The crystal at *C*, which is generally quite small, is attached by a small pellet of wax to a holder *H* which can be turned on its own axis. The figure shows how the crystal on the holder can be rocked in two directions at right angles to one another. The whole apparatus as shown stands on the crystal table of the spectrometer.

the pencil of X-rays very narrowly. The crystal is so placed that an important zonal axis is vertical. If faces can be seen on the crystal this is readily done by eye with sufficient preliminary accuracy ; exact adjustment can, if required, be made by means of the X-ray measurements. If only one good face is visible, and this face is placed in the vertical plane, it is generally easy to find a zonal axis by searching for reflections from some plane other than that which is

visible : the intersection of the two planes is an axis. Reflecting angles often have values lying between 3^0 and 6°; if the ionisation chamber is set with wide open slit at successively 6°, 8°, 10°, 12^0, or thereabouts, the crystal table may then be turned gently round over as wide a range as is convenient, in the hope that a reflection will suddenly flash out. If this happens, a zonal axis has been found, and the road is plain. If no reflection is found, the crystal is turned a few degrees in the plane of the visible face, and the search is renewed. A few minutes generally bring success. If the crystal has no visible face, the groping takes somewhat longer.

When a zonal axis has been found, the crystal is adjusted until the axis is vertical within one or two degrees. This is done by turning the crystal in the plane of the visible face, and observing the extreme positions at which the reflection fails to enter the ionisation chamber. The crystal is then set in the mean position.

The reflecting planes belonging to the zone are then examined in turn. Each plane is made to reflect, first to the right, then to the left ; and measurement is made of that angular setting of the crystal table which in each case gives the maximum reflection. From the two maximum readings are at once found the glancing angle and the orientation of the reflecting plane with respect to the crystal table. A second plane being similarly examined, the positions of all the other reflecting planes belonging to the same zone can be calculated as well as their spacings ; and the reflections can be looked for in their proper places. If, for instance, it is found that two reflecting planes having spacings a and c respectively, make an angle Θ with each other, a figure can be drawn to represent these facts. All the points *ABC*... which lie at the intersections of the two sets of parallels (Fig. 7), may or may not represent points in the fundamental lattice of the figure ; it may be that only some of them do so, as for example *B, F, H, D*. The point is settled at once by examining the spacings of other planes such as

those parallel to *BF*, *BJ*, *BG*, or *BD*. The figure gives information as to how the crystal table is to be set to find the corresponding reflections, and suggests values for the spacings which are either equal to, or some very simple multiple or submultiple of, the actual values.

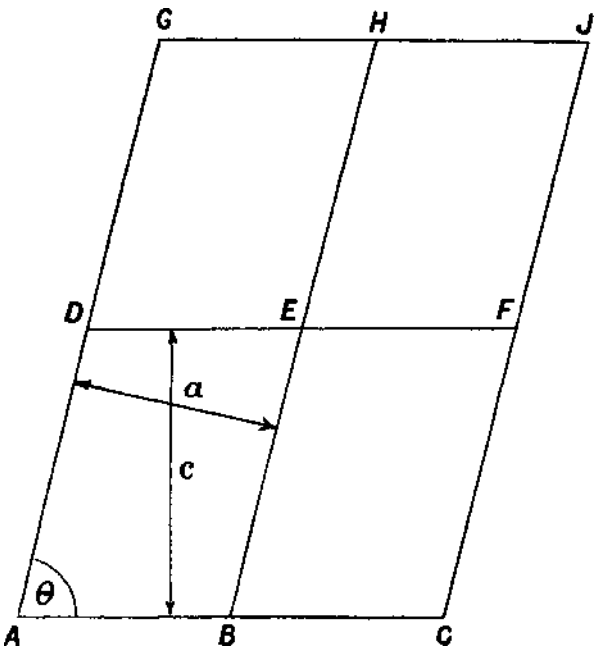


FIG. 7.

When a sufficient examination has been made in this way of the planes belonging to a zonal axis lying in the crystal face that has been placed vertical, a second zonal axis may be looked for in the same face. The examination of two zones gives the space lattice of the crystal. The most important face of the crystal naturally contains the most important zonal axes; and in general all the planes from which reflections can be obtained belong to one or other of a very small number of zonal systems, whose axes lie in an important face. For instance, nearly all the planes in diamond which give reflections of a wave greater than half an Angstrom unit belong to one zonal system ; its axis joins

any atom in the tetrahedral plane to its nearest neighbour in that plane (see p. 100).

This method of examining a crystal is more direct than any other. For the essential subject of measurement of the spectrometer is the angle of reflection ; and it is here determined directly by the angular setting of the crystal table. The angular setting of the ionisation chamber is only a secondary consideration, and does not enter into the calculations. There are no measurements of length to be made. The crystal is assumed, of course, to be so small that the portions of it which are concerned in the two reflections, right and left, are essentially the same. A very high standard of accuracy is obtainable; measurements can be made with at least as much precision as in any other X-ray determination ; and in wave-length measurements which have been carried out with great care errors have been limited to a few seconds of arc in many degrees. Such a standard of accuracy is not generally required in crystal determinations : it is enough to be able to distinguish from one another spacings which differ by one or two per cent., so as to be able to recognise the similarity, or the reverse, of two planes occurring in different parts of the crystal.

When a crystal is in the form of a thin flake or needle, as is so often the case with organic substances, it may be necessary to use one of the slits in order to limit the pencil of reflected X-rays. The *B* slit is convenient for the purpose, and may be pushed up towards the crystal. Otherwise, the procedure is as before. A crystal of this kind which shows principal faces or axes prominently may conveniently be attached to a circular celluloid disc as in Fig. 8, the latter being simply mounted so as to be capable of revolution only in its own plane.

The method which has just been described fails when the substance under examination cannot be obtained in the form of crystals of sufficient size. This is the case with a very large number of crystalline substances ; and it is clearly of great importance that they should be brought within the

range of X-ray analysis. It has been shown independently by Debye* and by Hull † that a crystalline substance when reduced to the form of a fine powder can be examined

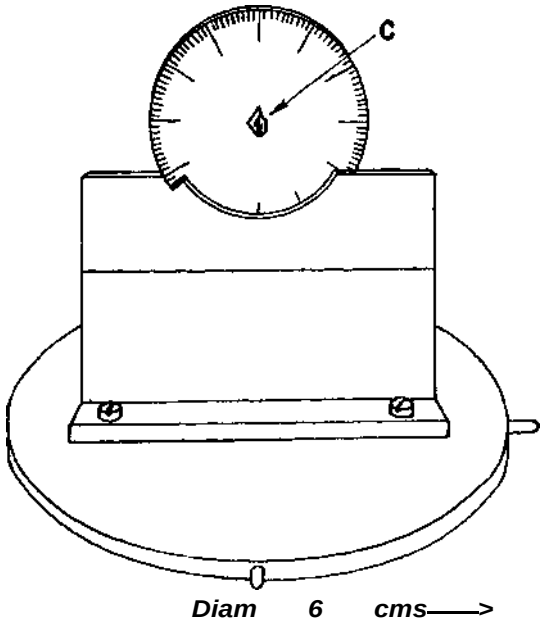


FIG. 8.

with satisfactory results. Their work is described later in this book (Chap. X.) ; and some of their records, which are always photographic, are reproduced (Plates V. and VI.).

A simple variation of their method has been found to give good results with the ionisation spectrometer. The substance is mounted on the crystal table in the form of a flat plate replacing the crystal of Fig. 4: the disposition is shown in Fig. 9. The plate may be prepared, if necessary, by grinding down the material, and pasting it, using a little adhesive, upon a sheet of glass or other material which has no obvious crystalline structure of its own.

***Debye and Scherrer, *Kgl. Ges. d. Wiss.* Gottingen; Dec. 1915. *Phys.-Zeit,* July 1, 1916, p. 277.**

† Hull, *Phys. Rev.,* Jan. 1917, p. 84. Paper read before American Physical Society, Oct. 1916.

Rays proceeding from the source 5 and incident on the plate at *A* are sure to find close to the surface some crystals so oriented as to reflect into the ionisation chamber through the slit at *C*, provided that the angle *SAC* is the supplement of twice the glancing angle appropriate to the wave length of the rays and some spacing of the crystal. If the face of the plate *AB* is parallel to *SC*, *S* and *C* being equally distant from the mean position on the face *AB*, rays of the same wave length, proceeding in the direction *SB*, will also be reflected to *C*, since an angle such as *SAC* changes very little as the point of reflection moves over the plate from *A* to *B*. If, then, the angular setting of the ionisation chamber be progressively altered, and the crystal table be turned so as to follow at half the rate of movement of the chamber, a spectrum is mapped out which shows all the glancing angles at which each set of monochromatic X-rays is reflected by the various crystal planes. The special form of X-ray bulb described on p. 33 is very well adapted to this method of measurement because the slit at *S*, Fig. 9, which may be considered to be the effective source of the rays, can be brought close to the actual source on the anticathode. The beam of rays which passes through the slit is then sufficiently divergent to cover a large area of the crystal block. The result is not so complex as might at first appear, because the number of crystal planes which

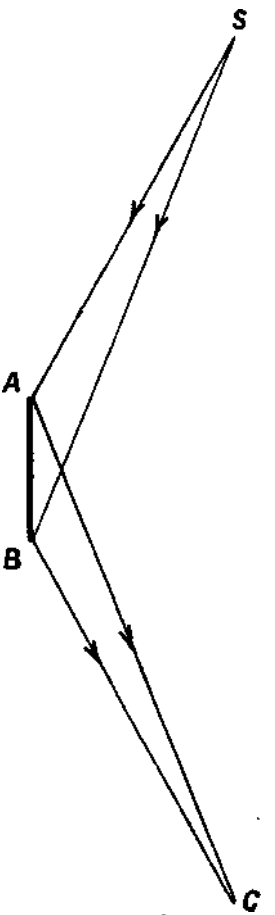


FIG. 9.
Rays diverging from 5 fall upon the powdered crystal spread over the plate *AB* and are reflected to the spectrometer holder at C.

can reflect a given X-ray is limited by the fact that the glancing angle cannot be greater than a right angle. Examples of this method are shown in Fig. 10. The interpretation is similar to that of the photographic results of Debye and Scherrer and Hull which are described in Chap. X.

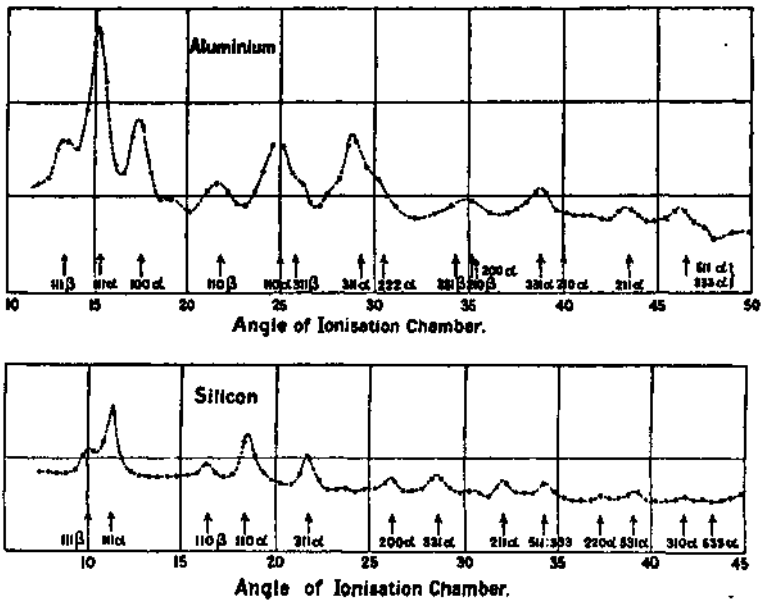


FIG. 10.

(From the *Proceedings of the Physical Society of London,* 1921.) ,

The angular setting of the crystal table is in this method of secondary importance : it is the angular setting of the ionisation chamber which is recorded. The method, in common with other ' powder' methods, measures glancing angles only : it gives no information as to the angles between reflecting planes. This is a somewhat serious defect unless the crystal has the simplest of forms, because two planes are indistinguishable if they have the same spacing though they may belong to entirely different zones. It has, however, the great advantage of being applicable where the other method fails. Moreover, its measurements of intensity of reflection are probably more capable of interpretation than

those of any other method, provided that the ionisation method is used rather than the photographic ; this point is fully considered later (Chap. XIII.).

The crystal which is so small that it may be considered perfect, and yet is large enough to give readable results, may be considered as in antithesis to the wholly disordered array of minute crystals. Each is perfect in its way. The larger crystals which were the subject of all the first experiments and are still usefully employed for many purposes, may be considered to lie between the extreme cases, for they are neither perfect crystal nor perfectly disordered.

Large crystals are mounted in wax on the crystal table so that the face to be investigated, whether natural or prepared, takes the position shown in Fig. 4; a template is generally used to ensure the adjustment of the face in the vertical plane which contains the axis of the table. So placed, the focussing action illustrated in Fig. 9 comes into play; the results are recorded in terms of the angular setting of the ionisation chamber. In this way, the imperfections so generally shown by large crystals, consisting of want of alignment of the various small crystals of which the whole is composed, are prevented from doing any serious injury to the measurements.

So far we have considered the X-ray spectrometer as an instrument used for the purpose of determining the structure of crystals. It is now necessary to consider its application to the study of X-ray spectra, but we shall limit ourselves to a brief survey for reasons already given in the preface.

In this part of the work the crystal is merely an essential portion of the spectrometer. The spacing of the reflecting plane should be of convenient magnitude, and the reflection should be intense. The crystal should be as nearly perfect as possible, and should be readily obtainable so that the results of different workers may be directly comparable. Rock-salt and calcite fulfil most of these requisites except that the former is not always to be obtained of sufficient

perfection. Too little attention has perhaps been paid to the diamond. The spacings of rock-salt and calcite have been measured with very great care.

All absolute measurements of crystal spacings involve, however, not only determinations of angles by the spectrometer but also determinations of specific gravity, and of the actual weights of the atoms, and it is probable that of the two sets of determinations the first can be carried out more accurately than the last. It is convenient to assume—when reducing observations—that the spacing of NaCl(ioo) is 2.814 A.u. and of $CaC0_3$(100) is 3.028 A.u. These figures are no doubt slightly in error,* more so absolutely than relatively to each other; but for most purposes relative wave lengths are the principal requirement, and it is important that all observers should have the same standard of reference. It is a fortunate circumstance that there are never any variations in the crystal spacings, except with temperature or pressure ; at any rate, nothing of the kind has yet been recorded.

Measurements are generally made by photography : the technique has been studied very thoroughly and great accuracy is now attained (see Chap. VI.). Duane has used ionisation methods, however, and claims, with apparent reason, that they are at least as accurate as the other. It is to be observed that photographic methods are less direct, since they necessitate measurements of distances on the plate and of the distances from the crystal to the plate ; calculation then gives an angle, which the ionisation method measures directly, as has been explained above. The greatest source of inaccuracy lies in the uncertainty as to the position of the point in the crystal at which reflection takes place, especially because the rays penetrate the crystal and are reflected within. Although the thickness of the active layer may be only a small fraction of a millimetre the effect can be felt seriously in the very accurate measurements of

* W. P. Davey has recently made careful measurements of the crystals of the alkali halides. *Phys. Rev.*, 21, p. 143, 1923.

to-day. The difficulty does not arise in any method which depends only on the measurements of angular settings of the crystal table. An ingenious method of avoiding this difficulty has been devised by Uhler and Cooksey,* in which

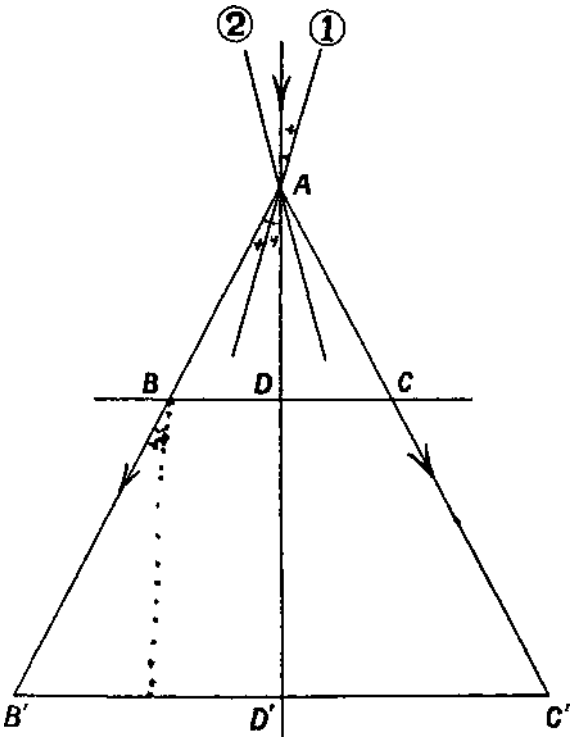


FIG. 11.

The crystal plane can be placed in either of the positions (i) or (2). The reflected rays are *ABB′* and *ACC* respectively.

photographs of the same spectrum are taken with the same plate placed successively in the positions shown in Fig. 11. The value of the reflection angle is found from the formula

$$\tan 2\Theta = (B'C' - BC)/2DD'.$$

In yet another method the crystal is ground to a very thin film whose faces are parallel to the reflecting plane :

* Uhler and Cooksey, *Phys. Rev.,* Dec. 1917. Cooksey, *Phys. Rev.,* **Oct. 1920.**

Dershem used rock-salt slips of .2 mm. in thickness.* Or again, a thin slip may be placed perpendicular to rays which have been limited by a fine slit; the slip is so oriented in its own plane that the rays are reflected by a plane which is perpendicular to the slip. Some of the needle-like organic crystals, *e.g.* dibenzyl (101), give very strong reflections from planes which include the axis of the needle, and such a crystal might give good results in spectrum work without the help of any definition of the rays by means of slits.

When the wave length is large the X-rays are highly absorbed even by air, and it is necessary to carry out the whole of the operation in a vacuum. Moseley was the first to construct a vacuum spectrograph when, during his classic survey of the spectra of the elements, he measured the wave length characteristic of the low atomic weights. Friman, Maimer, Siegbahn and Stenstrom have also used the vacuum spectrograph in a very important series of researches on the *M* series and other long waves (see p. 61), and have brought the instrument to a high pitch of perfection.

* *Phys. Rev.*, June, 1918, p. 464.

CHAPTER IV

THE PRODUCTION OF X-RAYS

ACCORDING to electromagnetic theory any acceleration in the motion of a charged particle causes a pulse to travel away through space, with the velocity of light, carrying energy with it. When X-rays were discovered, that is to say, when it was found that a hitherto unknown form of radiation was issuing from a plate on which the electrons of the cathode stream were impinging, it was natural to explain it as due to the arrest of the motion of the electrons by the matter of the plate. The most widely accepted theory of the action supposed that the arrest of each electron originated a single pulse, and that the difference in the quality of X-rays was due to a difference in the pulse width. The fact that the most penetrating rays were due to the action of the swiftest electrons was explained by supposing that their arrest took place in a shorter space of time and that the pulses were therefore thinner.

These explanations now seem to us inadequate; X-rays possess the properties of wave trains, not of single pulses, and there are other features which the classical theories are unable to explain. Nevertheless, we do not reject the older conceptions in their entirety; for, in some ways, their predictions have been fulfilled extraordinarily well. We merely hold judgment in suspense, knowing that there must be a way of amending or enlarging the classical theories without replacing them altogether.

We still, therefore, ascribe the origin of X-rays to the arrest of the cathode particles by matter, though we have

no clear ideas as to the mechanism which is at work. We have replaced the somewhat vague idea of the relation between electron velocity and pulse thickness by very precise discoveries as to the relations between electron energy and wave frequency, and must for the time be content to describe the new laws without explanation.

The X-ray bulb or tube is simply a convenient apparatus in which a vacuum is maintained so that the electron stream may be directed with sufficient velocity and without hindrance against the target or anticathode which arrests the motion. The driving force is supplied by an induction coil, or, as is common in the most powerful modern installations, by a transformer. Occasionally the source of power has been an immense battery of accumulators whose steadiness has, for some special experiment, been worth the cost : batteries of normal size have been used when exceptional low potentials have been required. Statical electrical machines have also been employed. The applied potentials have varied from 10 volts to 200,600 volts, with correspondingly varying quality in the X-ray product.

The bulbs take a variety of shapes, depending on the purpose for which they are required. Those which are used in X-ray spectrometry should give a fine line source of rays, and for this reason the target is placed square on to the cathode stream as in Fig. 4. It should be observed that the emission from any one point in the target is approximately equal in all directions towards the front, and so also is the total quantity of radiation, which is the sum at any one moment of the radiation from a number of points. The problem is not the same as that of the illumination due to a luminous disc, which at any point is proportional to the solid angle subtended by the disc at the point; but it corresponds to that of the radiation of *a* rays by an extremely thin layer of radioactive substance, or to the light received by an observer from a number of small lamps dotted all over a wall. There is, therefore, no loss in total radiation consequent on taking the rays from the target at a glancing

angle. The angle must not however be too fine, or else the emission of X-rays is hindered by absorption in the material of the target itself.

The electrons in the older tubes were supplied in a somewhat complicated way from the ionisation of the rarefied gas in the tube ; and as the action was due to the discharges the process was of a cyclic character, and self-maintaining under correct conditions. In the form designed by Coolidge the cathode consists of a fine tungsten wire which is heated by a battery to a very high temperature. It then emits electrons copiously ; the rate of supply can be nicely adjusted by regulating the current in the wire. The gas in the tube is entirely removed, being no longer required as a source of electrons, and being otherwise a hindrance to the working of the tube. The Coolidge bulb is extremely convenient for work with the ionisation spectrometer, both because it is steady and powerful, and also because the quantity and the quality of its output are under control.

The heat which is unavoidably generated is disposed of by radiation from the large surface of the block, or by conduction to heat radiators outside the bulb, or by a circulating stream of water. The current through the bulb need not exceed two or three milliamperes.

The material of the target used in the X-ray analysis of crystals is usually molybdenum, rhodium, palladium, copper, or other substance of the same order of atomic weights, since each of them gives a convenient spectrum. For the study of X-ray spectra the target may be made of the substance under investigation ; and for some spectroscopic work the ordinary tungsten target serves very well.

Observers have sometimes found it convenient to make up tubes of special pattern. Fig. 12 shows a form which is a variant of a design described by Siegbahn *(Phil. Mag.,* June 1919), and by Muller *(Phil. Mag.,* Sept. 1921), which we find to work very well. It has the advantage of giving a fine line source behind and close up to a thin aluminium window. In this way a very strong radiation can be obtained which

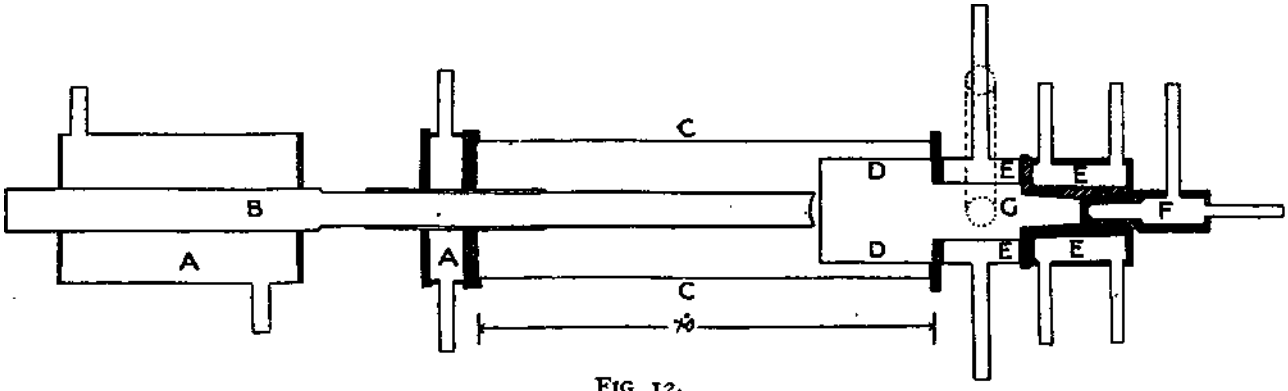
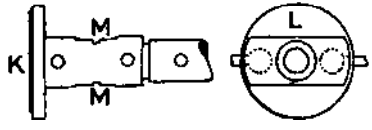


FIG. 12.



See also Fig. 106, p. 295.)

A. A. Insulated water jackets.
B. Cathode—solid aluminium rod, the part inside the X-ray tube being covered with brass tube.
C. Glass tube, insulating cathode from anticathode.
D. Brass shielding tube.
E. E. Water jackets, through which water is circulated from mains.
F. Water-cooled anticathode (copper or iron, etc.).
G. Brass tube connecting to pumps.
K. Section of anticathode end perpendicular to plane of paper.
L. Section of anticathode end perpendicular to length of tube.
M, M. Windows covered with .001 aluminium.

All glass-metal and any metal-metal joints which may require dismantling are made air-tight with sealing wax. The anticathode end is earth connected.

The tube is kept connected to a mercury vapour pump, and the gas pressure in the tube is controlled by means of a shunt from the low vacuum of the mercury pump to the high vacuum side. A clip on pressure tubing on this shunt admits of the pressure in the tube being kept steadily at any desired value.

is most useful when a crystal is to be examined by one of the 'powder' methods. The tube is kept in permanent connection with a vacuum pump, and has cooling arrangements for all parts of its construction.*

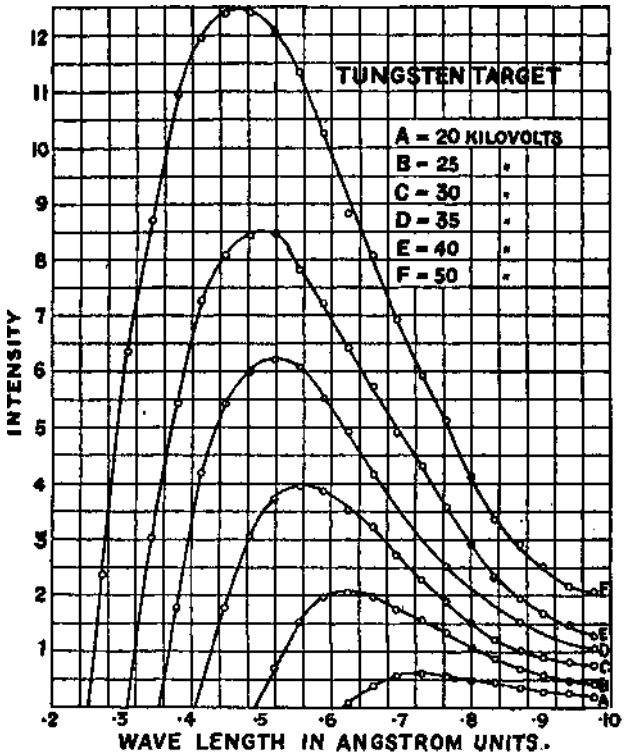


FIG. 13.
(Physical Review, May 1918.)

The quality of the X-ray output depends on the potential applied to the tube. This is best illustrated by reference to a set of curves such as are given in Fig. 13. These represent the results of a spectrometric analysis by Ulrey *(Phys. Rev.,* May 1918, p. 401) of the radiation issuing from a tube working under different constant potentials, the power being supplied by a very large battery of accumulators. It will be observed that the radiation in each case

*** A drawing of a tube used by Scherrer is given on p. 127.**

covers a wide range of wave lengths, though there is a genera] shift towards the shorter wave as the potential rises. A remarkable feature of each curve is the steep descent to the axis on the left; which means that for each potential there is a limit to the shortness of the waves that are generated, and that this limit can be accurately measured. It is found that the maximum frequency ν of the radiation ($\nu\lambda$ = velocity of light) is connected with the potential V applied to the tube by the simple relation $h \cdot \nu = e \cdot V$ = the energy imparted to the electron by the applied potential before it strikes the target. The quantity A is a constant, and $h\nu$ is known as the ' quantum ' energy associated with the frequency ν. The nature of the target has no influence on this result. This very remarkable relation is of the greatest importance, and we shall return later to its consideration (Chap. VI).

The total amount of the energy emitted in the form of X-rays is not easily measured with accuracy, because so much is lost in transmission ; also, the loss falls very differently on the different wave lengths. It is certain, however, that the X-ray energy emitted is only a very small fraction, of the order of a thousandth, of the energy applied to the tube. It increases approximately as the square of the applied potential, and is proportional, other things.being equal, to the atomic number of the element forming the target. But these statements do not apply to the characteristic radiations of the target (see later, Chap. VI). A summary of the work done on these points is given by A. Dauvillier, ' Thèse de Doctorat,' Paris, 1920.*

It is also found that the form of the curve showing the distribution of the energy between the various wave lengths is wholly independent of the intensity" of the current in the cathode stream, that is to say of the number of electrons striking the target in a second. *(La Physique des Rayons X,* by Ledoux-Lebard et Dauvillier, p. 36). This result goes with the relation already stated to show that the actions of the electrons are entirely separate. No two conspire to

* See also *La physique des Rayons X,* Ledoux-Lebard et A. Dauvillier.

produce a radiation which one could not produce by itself. In fact, it is difficult to conceive such an action. For, if 10 milliamperes of current were carried by electrons striking a target over an area of a square millimetre, then the number of electrons striking per second will be about 6×10^{16}, and the number of atoms in the surface of the target on which they fall about 10^{13}. Each atom is hit on the average 6000 times a second. Even if two impacts succeeded one another at the interval of a hundred-thousandth of a second, and if both were effective (which must very rarely be the case because the electrons on the average penetrate some distance into the target, crossing thousands of atoms), and if each started a train of a hundred million waves, having a total breadth of one centimetre, the first train would be 3×10^{5} centimetres away before the second started. The form of the energy distribution curves (Fig. 13) actually shows the proportion of waves of various kinds due to the single electron.

In the experiments illustrated by Fig. 13 the potential applied to the X-ray bulb was constant, and all the electrons must have possessed the same velocity at the moment of striking the target. There is nothing surprising, nevertheless, in the wide distribution of wave lengths which is shown by the curves. It is known that the electrons penetrate the metal; and they retain the power of producing X-rays until their energy disappears in the process of ionisation of the metal atoms. At any time the whole, or possibly a part, of the remaining energy of an electron may be converted into X-ray energy. As we have already seen, the frequency cannot be higher than is given by equating $h\nu$ to the electron energy. For this reason alone a variety of wave lengths must appear in the radiation excited by a cathode stream, even when the impact velocity of the electrons is uniform.

When an induction coil or transformer is used, the applied potential is no longer constant, and the curves of distribution vary accordingly. A greater proportion of the energy is found among the longer wave lengths, and the point of

maximum energy shifts somewhat in the same direction. But the change is not great: it would appear that the electrons of maximum speed are the most effective in impressing their character on the radiation, and if the maximum velocity is the same in the two cases, viz. when the applied potential is steady, and when it is variable, the results do not differ much from each other.

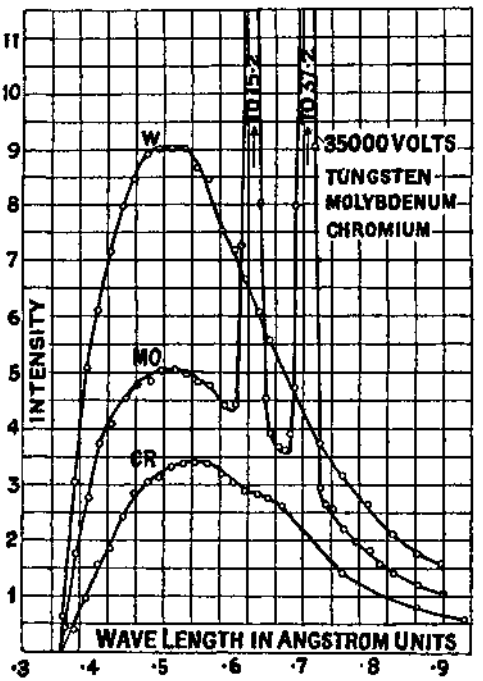


FIG. 14.
(*Physical Review*, May 1918.)

It will be observed that there is no evidence in the curves given above of the characteristic radiations of the target. The reason is that the applied potentials are not great enough to excite the *K* series of the tungsten target, and the wave lengths of the *L* series are too great to be included in the figure.

In Fig. 14, which is also due to Ulrey *(Physical Review,* Dec. 1918), the characteristic rays occur in the radiation

from a molybdenum target. The tungsten curve, as before, shows none. It is very remarkable that the characteristic rays appear to be a superposition upon the continuous spectrum ; in fact, the outputs of energy are proportional in the two cases to the atomic numbers, when no account is taken of the considerable energy of the characteristic rays. The two radiations are produced independently. The high frequency waves in the continuous spectrum of molybdenum must themselves add something to the characteristic rays, but the effect is too small to be seen. Such a very small fraction of the whole number is concerned in the production of either set of X-rays that the two processes do not interfere with each other.

The processes differ remarkably in respect to efficiency of production. The total output of the continuous spectrum increases as we have seen with the square of the applied voltage ; but the output of characteristic rays does not set in until the voltage reaches a critical value V_c, depending on the nature of the target, and is then proportional to $(V - V_c)^{3/2}$, according to Webster and Clark *(Physical Review,* June 1917, p. 571), who worked with the *K* series of Rhodium and the *L* series of Platinum. Wooten *(Physical Review,* p. 71, January 1919) found the output to be proportional to $(V - V_0)^2$ for the *K* rays of molybdenum and palladium. Thus, as the voltage is increased beyond the critical point the output of characteristic rays at first rises very rapidly, relatively to that of the continuous radiation. For this reason, when using the characteristic rays, it is advisable to apply a potential considerably in excess of the critical value. The *K* rays of molybdenum appear as soon as the applied voltage exceeds 20,000, but it is well to employ 40,000 in order to obtain a satisfactory supply.

CHAPTER V

THE ABSORPTION OF X-RAYS

A BEAM of X-rays loses energy as it traverses matter. Part of the loss is due to the *scattering* action of the electrons and other charged particles over which the radiation passes. This effect can be explained by the classical electromagnetic theory; and, in particular, the facts that the scattered radiation has the same wave length as the original and that it is partially polarised. Another fraction of the energy is transformed into energy of X-rays of different wave length, and of electrons in motion. The frequency of the new X-rays is always less than that of the original; and the energy of any one electron is always less than the quantum energy of the same radiation. These effects are to be classed with the parallel effects which occur in the case of light, and are grouped under the title of fluorescence and photoelectricity. It appears that classical electromagnetic theory cannot explain the phenomena attending these interchanges of energy.

No doubt the whole energy of the original X-ray beam is finally converted into heat: mainly, if not entirely, through the agency of the electrons which are set into motion by X-rays of every kind, and of the ionisation which such electrons produce. But these two processes, of scattering and of transformation, may be looked on as different ways in which the energy of the primary beam is dispersed, and it is important to distinguish them from one another both for theoretical and for practical reasons.

Unless the atomic weight is small, and the wave length

also, the scattering effect is negligibly small compared to the transformation effect.

If the original beam of X-rays is homogeneous, or, at least, if the wave lengths of the radiation which it contains lie so closely about one wave length that they cannot conveniently be resolved, the loss of energy in crossing a thin layer of matter of thickness σt may be put equal to $(\sigma + T)Idt$, where / stands for the amount of energy before entering the layer; a is the 'scattering coefficient,' and τ the 'transformation coefficient.' The sum of a and τ is the total absorption coefficient, and may be denoted by μ. We then have $\sigma I = -\mu / \sigma t$; $I = I_0 e^{-\mu t}$.

The second equation gives the value of the energy of the beam in terms of the original energy I_0 after traversing a layer of thickness t. In the case of a homogeneous beam equal increases in thickness of the layer absorb equal fractions of the energy remaining.

Sometimes this principle is used in the converse sense: it is assumed that because certain successive equal increases in thickness of screen produce equal fractional reductions the beam is homogeneous. It seems that in practice the test is not very sure, probably because it is difficult either to realise the proper experimental conditions or to apply the test over a sufficient range.

It is important that the values of these coefficients should be found for the whole range of substances and of X-ray wave lengths. Such a task might seem endless, but there are circumstances which simplify it greatly. Most striking of these is the fact that the transformation coefficient of an atom is independent of its physical and chemical condition over a wide range of wave lengths. Of pourse this may cease to be true when the wave lengths approach those of visible light, and there may also be special and minute exceptions such as that described by Forman *(Physical Review,* April 1914, and Jan. 1916), who found the absorption coefficient of iron for X-rays to alter by one part in six

hundred when the iron was placed in a field of 3500 gauss. Bergengren * finds a very small difference between the behaviour of black and red phosphorus. But for wave lengths less than 10 Angstrom Units, at any rate, the absorption coefficient of any compound can be calculated very exactly from a knowledge of the absorption coefficients of its constituent atoms : no other factor having any influence.

From this it follows that the task of determining all absorption coefficients is reduced to the task of determining them for the various elements. Also, it is simpler to express the coefficient in terms of mass traversed rather than of length, since it is the amount of matter which determines the absorption and not its distribution in space. The weight per square centimetre of the absorbing screen is used in place of the thickness, and the coefficients used are μ/ϱ, σ/ϱ, τ/ϱ, where Q is the density of the material. A still more fundamental constant can be obtained by multiplying the mass absorption coefficient μ/ϱ by the weight of the atom, obtaining in this way an atomic absorption coefficient which expresses the loss of energy of a pencil of X-rays in crossing a layer of material containing one atom to the square centimetre. All this is true of σ and τ separately, and therefore also of their sum, μ.

It is found that the relation between the transformation coefficient and variables defining the radiation and the atom respectively may be expressed to a first approximation at least by a formula of the form

Atomic transformation coefficient $\propto CN^4\lambda^3$,

or Mass transformation coefficient $\frac{\tau}{\varrho} = \frac{C'N^4\lambda^3}{w}$,

where N is the atomic number of the' element forming the absorbing screen, w is the atomic weight and λ the wave length of the radiator. C is a constant which may have one of two or three values, according to certain conditions involving N and λ.

* *C.R.*, 1920, p. 624. Bergengren has also found a remarkable effect in the case of sulphur.

If for a given value of N, λ does not exceed a certain critical value, the constant C of the upper formula =.0225, λ being measured in centimetres. Thus, for example, the atomic absorption coefficient of the wave length .586 A.U., which is one of the principal lines in the K series of *Pd*, by copper, for which N=29, w=63.6, is

$$.0225 \times (29)^4 \times (.586)^3 \times 10^{-24} = 32 \times 10^{-22}.$$

In the other formula the value of C is .0136 if λ is measured in Angstrom Units, and we have

$$\frac{\tau}{\varrho} = \frac{.0136 \cdot (29)^4 \cdot (.586)^3}{63.6} = 30.4.$$

The latter figure can be derived from the former by dividing by the weight of the atom. In the case of copper this is equal to $63.6 \times 1.662 \times 10^{-24} = 1.048 \times 10^{-22}$.

The critical value for λ for each absorbing element, *i.e.* for each value of N, can be determined with great precision as we shall see; and it is found that all the corresponding values of λ and N are connected approximately by the relation $\lambda(N-3.5)^2 = 900$, λ being in Angstrom Units. So long as this number is not exceeded either of the formulae given above may be applied. ' The range thus allowed covers all practicable wave lengths when Al is the absorber; for zinc there is a maximum at 1.29 A.u. ; for lead at 0.140 A.u., which means that lead is outside the limit for all ordinary X-rays.

When this limit is passed a new value of the constant C (or C) is immediately applicable : we now have C =.0031 or C =.00188. The new values hold until the above limit of 900 is extended to about 6000. In this extended range are to be found most transformation coefficients except on the one hand those in the first range, and on the other those which refer to the action of the heavy elements such as lead on wave lengths greater than 1 A.U. These last belong to yet another range in which the constants are now about .0006 and 0004 respectively ; beyond this are other ranges, but there is no information as to the values the constants now take.

In order to see these points more clearly it is convenient to consider such a diagram as that in Fig. 15, where the lines represent the variations of $(\tau/\rho)^{\frac{1}{3}}$ with λ in the cases of a few substances as calculated from the formula. The curves of the heavier elements show two critical points represented by what are known as the *K* and the *L* critical

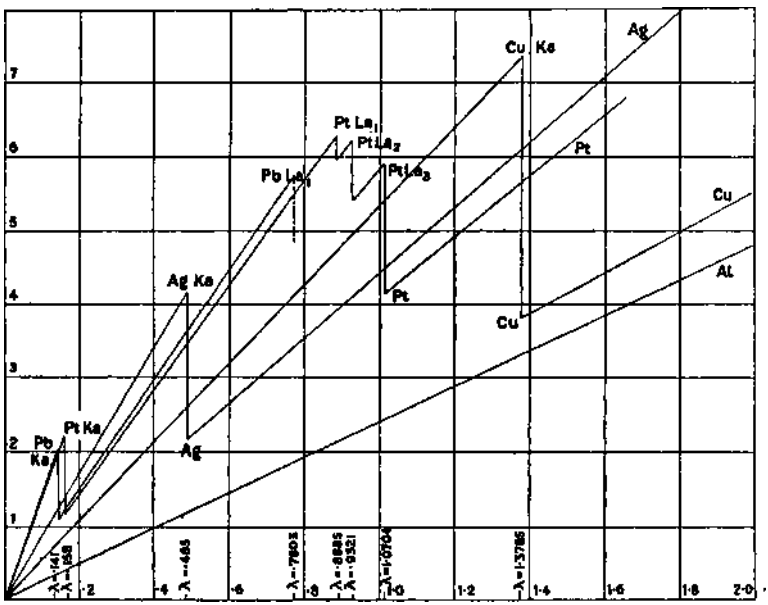


FIG. 15.

values of the wave length. The *L* critical value is complex ; there are three breaks close together as shown in the platinum curve; the exact amount of the drop at each break is uncertain. Elements of medium weight represented by Ag and Cu show a *K* point only. There is no critical point on the Al curve. If the figure had included wave lengths up to 10 the heavy elements would have shown *M* points as well, and the *L* points of some of the lighter elements would also have appeared in the figure.

Such a figure cannot do more than give a general idea of the dependence of absorption coefficients upon wave length and atomic number. If the actual value of any

absorption coefficient is required, the best way is to find first in what region, *K*, or *KL* or *LM*, the effect lies. This must be done by reference to the tables of critical absorption values on pp. 63-67. The formulae stated above, p. 43, will then give the absorption coefficient with an accuracy of about 5 per cent.

These critical points are of great interest because we can establish a connection between them and the characteristic radiation. The sudden increase in the value of the transformation coefficient, which occurs when the wave length of the rays passes—diminishingly—through one of these critical points, occurs simultaneously with the acquisition of the power to excite one of the series characteristic of the atoms of the absorbing screen. For instance, the value of τ/ρ for Ag at $\lambda = .48$ is nearly 70, but at $\lambda = .50$ it is 10; the latter rays cannot excite the *K* series of rays, the former can. The series consists of wave lengths ranging from .486 to .567; we shall consider them more fully in the next chapter. The emission of all these waves by the silver absorber begins when, and not until, the wave length of the incident ray shortens and passes through the critical value .485; and it is the increase of energy which is required to produce them that causes the sudden change. The positions of the critical points and of the wave lengths of the series belonging to each can be determined with great precision. They involve measurements differing so much from measurements of transformation coefficients, both in method and in accuracy, that it is convenient to consider them separately (Chap VI.).

In what we may call the *K* region the rays can excite all the characteristic rays of the absorber; in the *KL* region the *K* rays are not excited, but all other series are still excited. In the *LM* region the *L* rays drop out, and so on.

The evidence on which the truth of this formula is based is sufficient to show that it is quite correct over small portions of the whole field in which it is to be applied, and, at least, a fair approximation over the remainder. There are in

reality very few accurate determinations on which to found a formula, and much investigation is still required. We may consider, briefly, the principal measurements that have been made and see how closely the formulae given are in agreement with them.

Soon after the discovery of X-rays Barkla commenced a long series of researches on the absorption coefficients, during the course of which he discovered the secondary or characteristic radiations, and also the discontinuities in their emission by the various elements. Finding that these radiations were far more homogeneous than the primary rays of the X-ray bulb, he used them as sources of radiation, and with various collaborators obtained a table of absorption coefficients the main features of which are reproduced in Table I.

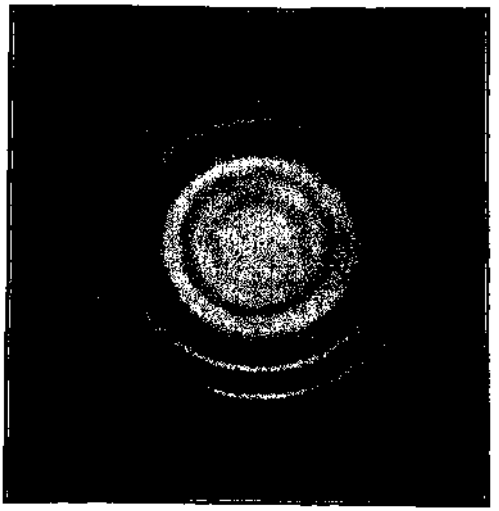
TABLE I.

MASS ABSORPTION COEFFICIENTS (λ/ρ).

Radiator.	ABSORBER.										
	C.	Mg.	Al.	Fe.	Ni.	Cu.	Zn.	Ag.	Sn.	Pt.	Au.
Cr	153	126.5	136	103.8	129	143	I70.5	580.5	713.7	[516.8]	[507+]?
Fe	I0.I	80	88.5	66.1	83.8	95.1	112.5	381	472	340	367
Co	7.96	63.5	71.6	67.2	67.2	75.3	91.5	314	392	281	306
Ni	6.58	51.8	59.1	314	56.3	61.8	74.4	262	328	236.	253
Cu	5.22	41.4	47.7	268	62.7	53.o	60.9	214	272	194	210
Zn	4.26	34.7	39.4	221	265	55.5	50.1	175	225	162.5	178.2
As	2.49	19.3	22.5	134	166	176	203.5	105.3	I3I.5	105.7	106.1
Se	2.O4	157	18.9	116/3	141.3	149.8	174.6	87.5	112	930	100.0
Ag	.41	2.2	2.5	174	22.7	24.3	27.1	13.3	16.5	56.5	61.4

The analysis of the characteristic radiations had not then been made. It is now known that each of the radiators mentioned in the first column of the Table emits, when struck by the primary radiation, not one ray but a series of rays. The transformation coefficients are, therefore, composite and cannot be referred to any one wave length. Approximately, however, they may be supposed to refer to a wave length at about the centre of gravity of the actual

SPECTRUM OF MOLYBDENUM CRYSTAL IN POWDERED FORM.
(By Hull.)
X-ray studies: General Electric Company, Schenectady, 1919, p. 221.



SPECTRUM OF ALUMINIUM CRYSTAL TO POWDERED FORM.
X-ray studies : General Electric Company, Schenectady, 1919, p. 221.

spectrum; and on this understanding the values given by the formula represent the values in the Table fairly well, especially those within the *K* limit. As a rule the values given by the formula are somewhat the lower.

The X-ray spectrometer has made it possible to work with monochromatic rays. Very few measurements have yet been made, however. Bragg and Peirce, using the principal rays of the Ag, Pd, and Rh spectra, obtained a series of measurements for the range $\lambda = .491$ to $\lambda = .615$ and the metals Al, Fe, Ni, Cu, Zn, which are contained in the first six lines of the following table. The range of λ in these experiments

TABLE II.

MASS ABSORPTION COEFFICIENTS.

Anticathode and ray.	Wave Length $\lambda \times 10^8$	ABSORBING ELEMENT.									
		AL	Fe.	Ni.	Cu.	Zn.	Pd.	Ag.	Sn.	Pt.	Au.
Silver	.491	1.94	14.2	17.8	20.9	21.8	58 +	10.3	12.2	46.9	48.0
ßPalladium „	.508	2.25	17.7	21.6	22.4	25.0	11.4	12.4	152	52.3	58.0
Rhodium „	•537	2.73	19.3	234	25.3	28.1	12.8	14.0	16.7	55.1	57.7
Silver a	•554	2.70	20.4	25.0	26.7	30.3	13.6	14.3	18.1	64.1	65.8
Palladium „	•576	3.16	23.1	28.9	30.9	34.0	16.2	16.9	20.0	744	75.4
Rhodium „	.615	353	26.0	32.1	34.6	38.8	18.0	19.8	233	75.9	78.5
Platinum C	•95	xi.4	80		115			71.8	78		
B	1.10	20.8	125	167	186			86	107	92	98
A	1.32	30.8	205	250	273	39.1		152.5		145	
Atomic „ numbers		13	26	28	29	30	46	47	50	79	80

was not great enough to furnish an accurate determination of the index to λ, but the range of *N* was much wider, and the results showed clearly that the atomic transformation coefficient varied with the fourth power of the atomic number. The observations lie within the *K* limit; and are accurately expressed by the formula already given for that range, except that the variation with wave length is not quite rapid enough.

Hull and Rice *(Phys. Rev.,* Sept. 1916) measured the

absorption coefficients of Al and Cu for a range **of wave** lengths $\lambda = .147$ to $\lambda = .294$, and found

$$\left(\frac{\tau}{\rho}\right)\text{Al} = 14.9\lambda^3; \quad \left(\frac{\tau}{\rho}\right)\text{Cu} = 150\lambda^3.$$

Richtmeyer and Kerr Grant *(Phys. Rev.,* June 1920), also using monochromatic rays, found :

$$\left(\frac{\tau}{\rho}\right)\text{Al} = 14.45\lambda^3; \quad \lambda = .08 \text{ to } .48,$$

and $\left(\frac{\tau}{\rho}\right)\text{Cu} = 162\lambda^3$, between the same limits.

Siegb-hn and Wingardh *(P.Z.,* Feb. 1920), using the spectremeter with a rather wide slit so that the rays were some what heterogeneous, found the mass absorption coefficients

$$\left(\frac{\mu}{\rho}\right)\text{Cu} = 162\lambda^3,$$

between the limits $\lambda = .48$ and $.78$.

Now, if in our formula $\tau/\rho = .0136 \times N^4 \times \lambda^3/w$, we put $N = 13$ and $w = 27$, we obtain :

$$\left(\frac{\tau}{\rho}\right)\text{Al} = 14.2\lambda^3.$$

Putting $N = 29$ and $w = 64$, we find

$$\left(\frac{\tau}{\rho}\right)\text{Cu} = 150\lambda^3,$$

so that these measurements also are well represented by the formula.

C. D. Miller *(Phys. Rev.,* Oct. 1916), using very long waves obtained from an iron anticathode and purified by filters, found

$$\left(\frac{\mu}{\rho}\right)\text{Al} = 19.4\lambda^{2.77},$$

up to values of λ as great as 5 A.u.

Owen *(P.R.S.,* Vol. 94, p. 516, 1918), has measured the absorption coefficients of the elements up to Br **for** the wave length .586 and has found them to satisfy very exactly the relation:

Atomic transformation coefficient $= 441 \times 10^{-27} \times N^4$,

Putting λ=.586, and C=.0225 in the first form of our formula we find :

Atomic transformation coefficient = $4.50 \times 10^{-27} \times N^4$.

The formula, therefore, represents Owen's results very well.

If we now pass on to the region lying outside the critical values given by $\lambda(N-3.5)^2 = 900$, the region in which the *K* rays are no longer excited by the incident radiation in the absorbing screen, we find very little evidence on which the accurate determination of the formula can be based. A portion of Table I. belongs to the region between the *K* and the *L* boundaries : it is outlined so as to distinguish it from the rest. A portion of Bragg and Peirce's table also refers to this region : the figures contained in it are represented very well—except for the one or two determinations with longer waves—by the formula if we put C=.oo3i in the first form and *C* =.0019 in the second. This also applies to Owen's redetermination of some of the figures in this table. Hull and Rice give a set of values which fall within the *KL* region, viz.

$$\left(\frac{\tau}{\rho}\right) \text{Pb} = 430\lambda^3,$$

for $\lambda = .147$ to $\lambda = .294$.

Putting N = 82 and C' = .0019 we find from the formula

$$\left(\frac{\tau}{\rho}\right) \text{Pb} = \frac{.0019(82)^4\lambda^3}{207} = 415\lambda^3.$$

The formula also is a fair agreement with Barkla's tables for the shorter waves but not for the longer.

It should be observed that Barkla and White *(Phil, Mag.* Oct. 1917), using short waves which they obtained from characteristic radiation, and which were much shorter than the waves characteristic of the absorber, found that the index of the λ should be 3 ; but that when the two sets were more nearly similar the index might fall to 5/2. The few figures which Bragg and Peirce obtained for longer wave lengths in the *KL* region show the same thing.

A recent research by Richtmeyer (*P.R.*, July, 1921), establishes still further the formulae given above. The absorbers experimented with were Ag, Al, Cu, Mo, and Pd, and the wave lengths ranged from .1 to .7 A.u. Within the *K* range, as defined above, the value of *C* is given, after alteration to suit the units of our formula, as .0229 and as .0033 in the *KL* region.

This practically completes the evidence as to the behaviour of τ/ϱ in the *KL* region. It is very little and wants much supplementing.

As to the *LM* region the evidence is scantier still. Table I. contains a few values for Pt and Au; Bragg and Peirce give one or two for the same metals which are in fair agreement with those of the same table. No other figures appear to be available. Nothing whatever is known of the transformation coefficient beyond the *M* boundary. The positions of the *M* boundaries are well known however (p. 66) in the case of the heavy elements.

The most remarkable feature in these results is their purely arithmetical nature. The transformation coefficient is known, at any rate approximately, as soon as *N* and λ are given. These quantitative relations must have some close relation to the nature of radiation and to the construction of the atom; but we have no explanation of them as yet.

The *scattering* coefficient differs materially in all its characteristics from the transformation coefficients. Its magnitude was first calculated by J. J. Thomson, who assumed that it was due to the radiation from the electrons over which the primary radiation passed. He showed that

$$\sigma = n\frac{8\pi}{3}\cdot\frac{e^4}{m^2},$$

where o is the fraction of the primary energy which is **lost in** crossing a distance of one centimetre in a space containing *n* electrons to the unit volume; *e* is the charge on the electron in electromagnetic units, and *m* the mass of the

electron. It is assumed that the charge on the electron is confined within a space whose dimensions are small compared to the wave length of the radiation, and that the action of each electron is not affected by the presence of other electrons: there is no combined action.

In order to realise the consequences of breaking these two conditions let us imagine two electrons to occupy the space of one. The scattering effect due to the two is twice as great as if they were well removed from each other, because e^4/m^2 is increased four times by doubling both e and m. Combination between the two is at its maximum. If the two are now gradually separated, the combined scattering effect in general quickly declines. The rate at which it falls off depends upon the orientation of the line of separation to the direction in which the radiation is travelling, and upon the ratio of the distance of separation to the wave length, the latter quantity now being of influence for the first time. For certain movements in certain directions the effect of combination may be negative ; but if an average is taken for all orientations, and the effect of combination is found in terms of the distance of separation only, the effect is always positive. If n electrons are scattered at random through a given volume, the whole scattering is always more than n times the scattering due to a single electron, though the excess is generally negligible. In other words, Thomson's formula gives a minimum value for the scattering effect.

Thomson's formula was used by Barkla to determine the number of electrons in the atom ; his result being that the number was approximately half the atomic weight. It was found by Barkla and Sadler *(Phil. Mag.,* 17, p. 739, 1909), that σ/ϱ was equal to .2 for a wide range of "materials and wave lengths ; and that so it was independent of the wave lengths as Thomson's theory predicted.

Further experiments over wider ranges have shown that the value of σ/ϱ is not so constant as was at first supposed. Barkla and Sadler, Crowther, and others have shown that

when **the** scattering substance is composed of heavy elements it increases rapidly with the atomic weight. On the other hand, the value for Al has been found by several observers to be about .15 ; and generally for light elements and short waves the value is less than .2. Indeed, in the case of *y* rays, the whole absorption coefficient, including both scattering and transformation coefficients, is only about .04.

These variations from the value given by the formula can be explained as due to non-fulfilment of the original conditions. In the heavy atoms the electrons are more crowded together than in the light atom, and there is effective combination : consequently there is increased scattering. If the scattering is less than expected when the wave lengths are very small, it must be supposed that the electron charges are not confined within areas whose dimensions are small compared with the wave length : as we have already seen, any opening out of the charges brings the coefficient down at once. A. H. Compton has studied the effect *(Physical Review,* Sept. 1919), and has arrived at the conclusion that the diameter of the electron must be as great as 2×10^{-10} cm. approximately.

If we remove the condition that the electrons are scattered indiscriminately it is possible for combination to be exceedingly effective, when spacings and mutual orientation are duly related to the length and direction of the incident wave. This is in fact the effect on which is based all the work that is described in this book.

CHAPTER VI

X-RAY SPECTRA

THE earliest observations of the reflection of X-rays by crystals * showed that the X-rays could be differentiated in respect to wave length and displayed in a spectrum containing lines. Since that time, X-ray spectra have been studied with great care by many observers, who have been attracted both by the precision with which experiments can be made and by the importance of the results. It would be out of place here to give more than a summary of the work that has been done. With this limitation we shall proceed to discuss various points in turn.

In the first place it has been found that the spectra of all elements are strikingly alike ; in all of them the relative positions and intensities of the lines are very much the same, it is only the absolute positions that change methodically from element to element. Something of this kind might have been anticipated from the previous work of Barkla, Kaye and other observers.

In two papers published in the *Philosophical Magazine* † Moseley described a series of experiments from which he deduced the highly important rule that the frequencies of corresponding rays in the spectra of the elements advanced steadily with the number which indicated the, place of each element in the periodic table. He showed at once that there was a. regularity in the succession of the elements which had been obscured by the irregularities in the differences

* W. H. and W. L. Bragg, *Proc. Roy. Soc*, 88, p. 428.

†Dec. 1913, p. 1024, and April 1914, p. 703,

between their weights, and thus brought into atomic theory an order and a possibility of advancement of which full advantage has since been taken; unfortunately not by Moseley himself.*

The greatest advances in X-ray spectrometry are due to Siegbahn, Stenstrom and other workers at the University

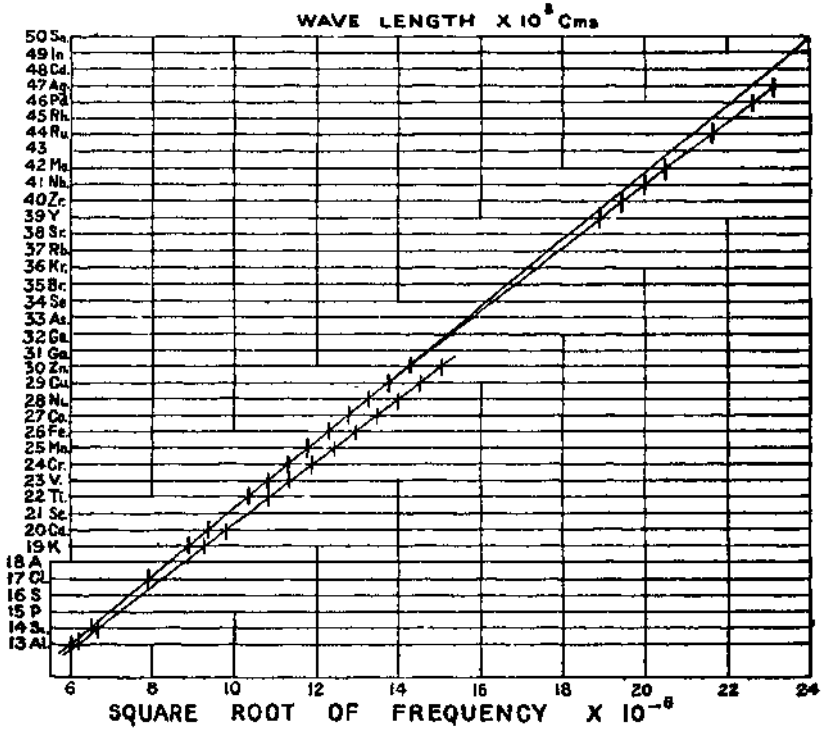


FIG. 16.—*K* Series.

of Lund, to de Broglie in Paris, to Wagner in Germany, and to Duane, Patterson, Overn, Dershem and others in America.

The lines of an X-ray spectrum are conveniently divisible into series *K, L, M,* and so on ; of these the *K* series contans the lines of highest frequency. Four lines known as a_1,a_2, *ß, y, are* shown by all elements; and, in addition, some fainter lines are found in the same region of the spectrum in the case of atoms of low atomic number. In the case of

* H. G. J. Moseley was killed in the Gallipoli campaign, 1915.

each of these lines the square root of the frequency plotted against the atomic number gives a line which is nearly straight. 'This is" shown in Figs. 16 and 17, which are drawn from Moseley's observations; the importance of plotting against atomic number rather than atomic weight is shown in Fig. 18.

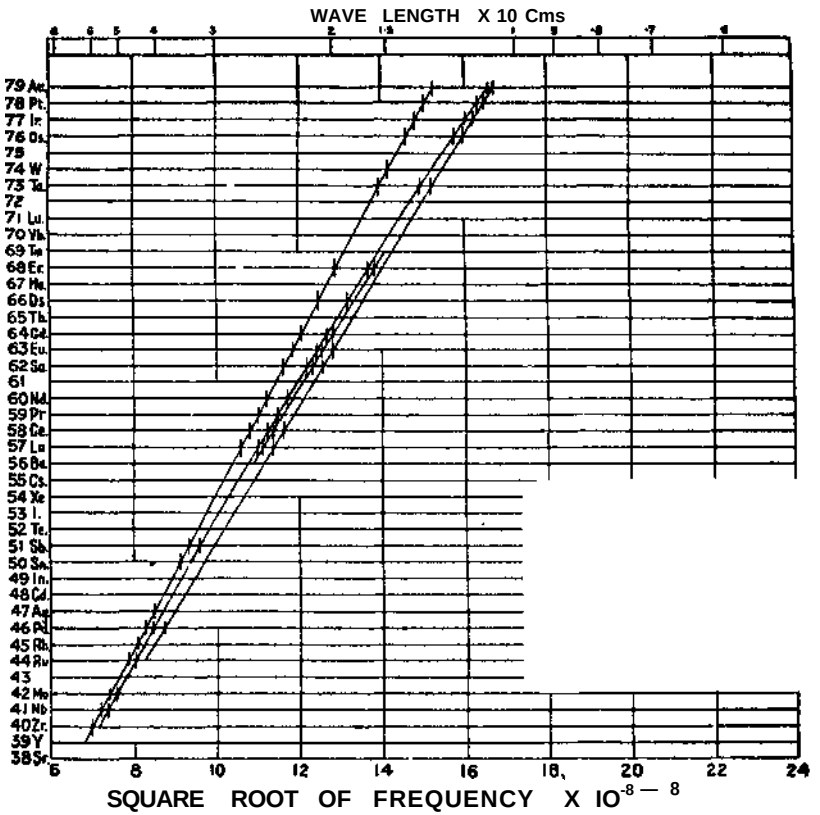


FIG. 17.—*L* Series.

These drawings, which appeared in the first edition of this book, still show the results of observation so far as drawings can do so ; it is necessary to use numbers in order to express the increased accuracy of modern data, since the improvements cannot be shown on a small scale diagram. The wave lengths of the lines in the *K* series of a large number of the elements from sodium to tungsten are given

in Table III., which with most of the other tables in this chapter are reproduced from *Bulletin I.* 6 *of the National Research Council of the National Academy of Sciences,* written by Duane.

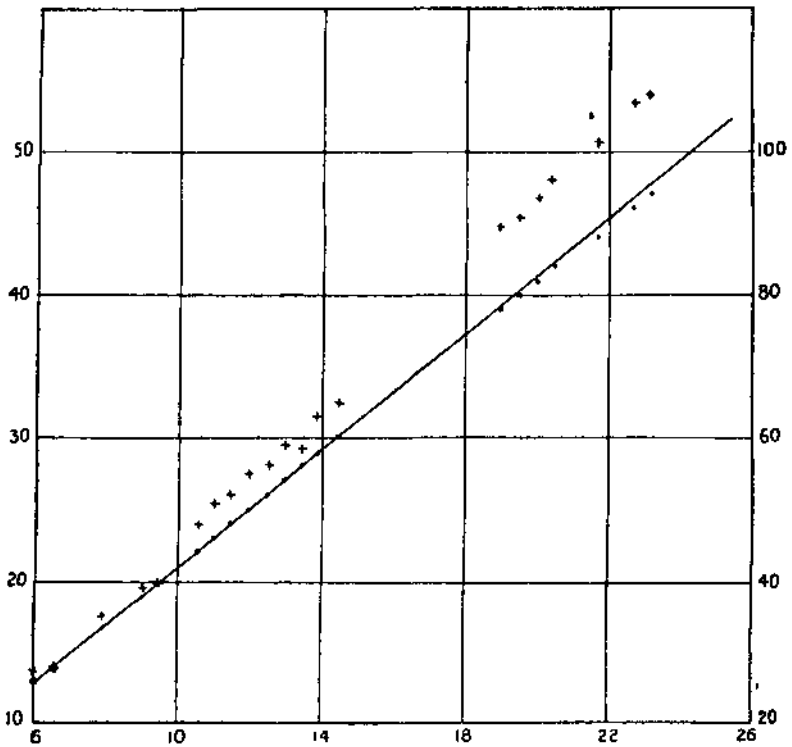


FIG. 18.

Crosses, frequency and atomic weight, figures on the right.
Dots, „ „ „ number, „ „ left.

Most of the figures in this table are due to Siegbahn and his co-workers at Lund. It will be observed that a very high order of accuracy is attempted.

In the *L* series of each element the wave lengths are several times as great as in the *K* series. For most elements the ratio is about seven or eight, but it increases rapidly as the atomic" number becomes small. For oxygen, carbon, and so on, it is about thirty. There are many more lines in the *L* series than in the *K,* and they can be divided into at

TABLE III.

EMISSION WAVE-LENGTHS IN THE *K* SERIES, $\lambda \times 10^8$ cm.

Photographic Methods. For Rock Salt: d=2.814 x 10^{-8} cm.
For Calcite d=3.028 x 10^{-8} cm.

Chemical Element	Atomic Number	α_3	α_2	α_2	α_1	β_1	γ
Sodium	11	—	11.8836	11.8024	11.7814	11.591	—
Magnesium	12	—	9.8675	9.79940	9.78620	9.53450	—
Aluminium	13	—	8.31940	8.26460	8.25300	7.94050	—
Silicon	14	—	7.10917	7.06382	7.05372	6.73933	—
Phosphorus	15	—	6.14171	6.10219	6.09500	5.78513	—
Sulphur	16	—	5.36066	5.32833	5.32175	5.01913	—
Chlorine	17	—	4.71870	4.692		4.39450	—
Potassium	19	3.738	3.73386	3.724		3.44638	—
Calcium	20	3.359	3.35186	3.328		3.08297	3.06740
Scandium	21	3.032	3.02526	3.011		2.77366	2.755(5)
Titanium	22	2.746	2.742	2.729		2.50874	2.49367
Vanadium	23	2.502	2.498	—	—	2.27968	2.26537
Chromium	24	2.288	2.28517	—	—	2.08144	2.069
Manganese	25	2.097	2.093	—	—	1.902	1.892
Iron	26	1.932	1.93239	—	—	1.75397	1.736
Cobalt	27	1.785	1.78524	—	—	1.61715	1.606
Nickel	28	1.657	1.65467	—	—	1.49669	1.48403
Copper	29	1.543	1.53736	—	—	1.38887	1.382
Zinc	30	1.437	1.433	—	—	1.294	1.281
Gallium	31	1.34161	1.33785	—	—	1.20591	—
Germanium	32	1.261	1.257	—	—	1.131	1.121
Arsenic	33	1.174	1.170	—	—	1.052	1.038
Selenium	34	1.109	1.104	—	—	0.993	—
Bromine	35	1.040	1.035	—	—	0.929	0.914
Rubidium	37	0.926	0.922	—	—	0.825	0.813
Strontium	38	0.876	0.871	—	—	0.779	0.767
Yttrium	39	0.840	0.835	—	—	0.746	0.733
Zirconium	40	0.793	0.788	—	—	0.705	—
Niobium	41	0.754	0.749	—	—	0.669	0.657
Molybdenum	42	0.71212	0.70783	—	—	0.63110	0.6197
Ruthenium	44	—	0.645	—	—	0.574	—
Rhodium	45	0.6164	0.6121	—	—	0.5453	0.5342
Palladium	46	0.590	0.586	—	—	0.521	—
Silver	47	0.567	0.562	—	—	0.501	0.491
Cadmium	48	0.543	0.538	—	—	0.479	—
Indium	49	0.515	0.510	—	—	0.453	0.440
Tin	50	0.490	0.487	—	—	0.432	—
Antimony	51	0.472	0.468	—	—	0.416	0.408
Tellurium	52	—	0.456	—	—	0.404	—
Iodine	53	—	0.437	—	—	0.388	—
Caesium	55	0.402	0.398	—	—	0.352	—
Barium	56	0.393	0.388	—	—	0.343	—
Lanthanium	57	0.376	0.372	—	—	0.329	—
Cerium	58	0.360	0.355	—	—	0.314	—
Praseodymium	59	0.347	0.342	—	—	0.301	—
Neodymium	60	0.335	0.330	—	—	0.292	—
Tungsten	74	0.21341	0.20860	—	—	0.18420	0.17901

TABLE IV.

EMISSION WAVE-LENGTHS IN THE *L* SERIES, x10^{8} cm.

Photographic Methods. For Rock Salt d =2.814 x 10^{-8} cm.

For Calcite d=3.028 x 10^{-8} cm.

Chemical Element.	At. No.	l	α_2	α_1	α_3	η	β_4	β_1	β_2	β_3	β_5	γ_1	γ_2	γ_3	γ_4
Zinc	30	—	—	12.346	—	—	—	—	—	—	—	—	—	—	—
Arsenic	33	—	—	9.701	—	—	—	—	—	—	—	—	—	—	—
Bromine	35	—	—	8.391	8.360	—	—	9.449	—	—	—	—	—	—	—
Rubidium	37	—	—	7.335	7.305	—	—	8.141	—	—	—	—	—	—	—
Strontium	38	—	—	6.879	—	—	—	7.091	—	—	—	—	—	—	—
Yttrium	39	—	—	6.464	6.440	—	—	6.639	—	—	—	—	—	—	—
Zirconium	40	—	—	6.083	6.057	—	—	6.227	—	—	—	—	—	—	—
Niobium	41	—	5.731	5.724	5.709	—	—	5.851	—	—	—	5.386	—	—	—
Molybdenum	42	—	5.410	5.403	5.381	—	—	5.493	5.317	—	—	—	—	—	—
Ruthenium	44	—	4.853	4.83567	4.823	—	—	5.175	—	—	—	—	—	—	—
Rhodium	45	—	—	4.587_{78}	4.577	—	—	4.61100	—	—	—	4.17282	—	—	—
Palladium	46	—	4.374	4.358_{50}	4.352	—	—	4.364_{80}	—	—	—	3.935_{70}	—	—	—
Silver	47	—	4.155	4.145_{44}	4.133	—	4.071	4.137_{30}	3.904	4.030	—	3.716_{36}	3.597		
Cadmium	48	—	3.959	3.947_{92}	—	—	3.861	3.926_{64}	3.698	3.823	—	3.514_{85}	—	—	—
Indium	49	—	3.774	3.763_{67}	—	—	3.676	3.730_{95}	3.514	3.639	—	3.328_{00}	—	—	—
Tin	50	—	3.604	3.591_{93}	—	—	—	3.547_{88}	3.354	—	—	3.155_{20}	—	—	—
Antimony	51	—	3.443	3.431_{77}	—	—	3.337	3.377_{62}	3.172	3.300	—	2.994_{60}	2.903	2.889	2.831
Tellurium	52	—	3.299	3.281_{69}	—	—	3.184	3.218_{36}	3.021	3.149	—	2.845_{07}	2.782		
Iodine	53	—	3.155	3.141_{26}	—	—	3.044	3.069_{84}	2.881	3.007	—	2.706_{13}	—	—	—
Caesium	55	—	2.899	2.885_{87}	—	—	2.911	2.930_{86}	2.750	2.873	—	2.577_{12}	—	—	—
Barium	56	—	2.786	2.769_{81}	—	—	2.668	2.677_{50}	2.514	2.629	—	2.359_{50}	2.234		
Lanthanum	57	—	2.674	2.659_{31}	—	—	2.558	2.562_{94}	2.407	2.520	—	2.236_{25}	—	—	—
Cerium	58	—	2.573	2.555_{10}	—	—	2.453	2.452_{96}	2.307	2.414	—	2.136_{80}	—	—	—
							2.357	2.350_{61}	2.212	2.307	—	2.044_{60}	2.003		

TABLE IV. *(Continued).*

EMISSION WAVE-LENGTHS IN THE *L* SERIES, $x10^{8}$cm.

Photographic Methods. For Rock Salt $d = 2.814 \times 10^{-8}$ cm.

For Calcite $d = 3.028 \times 10^{-8}$ cm.

Chemical Element.	At. No.	l	α_2	α_1	α_3	η	β_4	β_1	β_2	β_3	β_5	γ_1	γ_2	γ_3	γ_4
Praseodymium	59	—	2.472	2.457_{35}	—	—	—	2.253_{53}	2.120	2.217	—	1.956_{41}	1.937	1.933	—
Neodymium	60	—	2.379	2.364_{94}	—	—	2.167	2.167	2.036	2.128	—	1.873_{43}	1.803	1.775	—
Samarium	62	—	2.210	2.200	—	—	—	1.993_{17}	1.884	1.965	—	1.725	1.659		—
Europium	63	—	2.131	2.121	—	—	1.923	1.918	1.810	1.888	—	1.662	1.599	1.590	—
Gadolinium	64	—	2.054	2.043	—	—	1.851	1.844	1.744	1.811	—	1.597	(1.562)	(1.558)	—
Terbium	65	—	1.983	1.973	—	1.935	1.784	1.775	1.682	1.745	1.659	1.531	1.477	1.470	1.437
Dysprosium	66	—	1.916	1.907	—	—	1.721	1.709	1.622	1.683	—	1.470	1.422	1.418	—
Holmium	67	—	1.854	1.843	—	—	1.657	1.646	1.568	1.620	—	1.415	1.369	1.365	—
Erbium	68	—	1.794	1.783	—	1.725	1.599	1.586	1.514	1.560	—	1.367	1.323	1.316	—
Aldebaranium	70	1.892	1.681	1.670	—	1.618	1.490	1.474	1.414	1.451	1.422	1.267	1.228	1.223	—
Cassiopeium	71	1.834	1.629	1.619	—	—	1.437	1.421	1.368	1.399	—	1.224	1.188	1.183	—
Tantalum	73	—	1.528	1.518	—	1.435	1.343	1.323	1.280	1.303	—	1.135	1.101	1.097	—
Tungsten	74	1.675_{85}	1.484_{52}	1.473_{48}	—	1.4177	1.298_{74}	1.279_{17}	1.24191	1.260_{00}	1.2031	1.095_{59}	1.06584	1.059_{66}	1.026_{47}
Osmium	76	—	1.398	1.388	—	—	1.214	1.194	1.167	1.176	—	1.021	—	—	—
Iridium	77	1.840	1.360	1.350	—	—	1.176	1.154	1.133	1.138	1.101	.989	.962	.956	.917
Platinum	78	1.499	1.323	1.313	—	1.242	1.142	1.120	1.101	1.098	1.072	.958	.933	.929	.900
Gold	79	1.457	1.283	1.271	—	1.197	1.102	1.080	1.065	1.059	1.035	.922	.898	.894	.869
Mercury	80	—	1.251	1.240	—	—	—	1.049	1.042	—	—	.896	—	—	—
Thallium	81	1.385	1.215	1.205	—	1.124	1.036	1.012	1.006	.998	.977	.864	.844	.840	.808
Lead	82	1.348	1.186	1.175	—	1.091	1.008	.983	.983	.968	—	.842	.820	.816	.792
Bismuth	83	1.317	1.153	1.144	—	1.059	.977	.950	.954	.937	.923	.810	.794	.790	.762
Pollonium	84	—	—	1.101	—	—	—	.920	—	—	—	—	—	—	—
Radium	88	—	—	1.010	—	—	—	—	—	—	—	—	—	—	—
Thorium	90	1.117	.969	.957	—	—	—	.766	.797	.758	—	.654	.635		—
Uranium	92	1.066	.922	.911	—	—	—	.720	.756	.710	—	.615	.596		—

Reference : These wave lengths have been measured by Siegbahn and his co-workers at Lund.

least three distinct groups based on the fact that the manner of increase of frequency from element to element is not quite the same from group to group. For instance, the graphs for the lines /, a_2, a_1, $ß_2$, and $ß_5$ are almost straight; but the graphs for other *lines are curved.* The wave-lengths of the *L* series are shown in Table V, and are also due to the observations at Lund.

TABLE v.

EMISSION WAVE-LENGTHS IN THE *L* SERIES OF TUNGSTEN, $\times 10^8$ cm.

	Photographic Methods. For Rock Salt $d = 2.814 \times 10^{-8}$ cm.				Ionisation Methods. For Calcite $d = 3.028 \times 10^{-8}$ cm.	
Line.	Gorton.	Dersham.	Overn.	Siegbahn.	A. H. Compton.	Duane and Patterson.
l				1.67505		1.6756 ± 10
α_2	1.476	1.4828	1.4839	1.48452	1.4840	1.4839 ± 3
α_1	1.466	1.4722	1.4731	1.47348	1.4728	1.47306 ± 11
η		1.4163		1.4177		1.4176 ± 7
					1.3360	
β_4	1.292	1.2977	1.2984	1.29874	1.2982	1.2985 ± 4
	1.283	1.2868	1.2872	1.2871		
β_1	1.275	1.2784	1.2793	1.27917	1.2787	1.27892 ± 9
β_3	1.256	1.2586	1.2598	1.26000	1.2598	1.2601 ± 3
β_2	1.237	1.2416	1.2434	1.24191	1.2416	1.24193 ± 12
			1.2355	1.2395		
		1.2202	1.2212	1.2205	1.2183	
			1.2132	1.2118		
		1.2098	1.2097			
β_5		1.1773	1.2021	1.2031		1.2040 ± 7
		1.1292	1.1302	1.1284		
γ_1	1.094	1.0953	1.0967	1.09553	1.0961	1.09608 ± 7
			1.0794			
		1.0705	1.0724			
γ_2		1.0648	1.0659	1.06584	1.0650	1.0655 ± 4
γ_3	1.057	1.0587	1.0596	1.05965	1.0580	1.0596 ± 3
		1.0427	1.0446		1.0396	
ι	1.025	1.0253	1.0263	1.02647	1.0247	1.0261 ± 6

References: W. S. Gorton, *Phys. Rev.,* Feb. 1916, p. 203, and March 1916, p. 334. A. H. Compton, *Phys. Rev.,* June 1916, p. 646. E. Dershem, *Phys. Rev.,* June, 1918, p. 461. O. B. Overn, *Phys. Rev.,* Aug. 1919, p. 137. Manne Siegbahn, *Phil. Mag.,* Nov. 1919, p. 639. Duane and Patterson, *Phys. Rev.,* 1920.

In Table V. only Tungsten lines are shown : the comparison of the results by different observers shows the precision which X-ray spectrometry has attained.

The lines of the *M* series have been less fully studied, being much more difficult to observe. The tables here given are due to Stenstrom and to Karcher respectively.

TABLE VI.

EMISSION WAVE-LENGTHS IN THE *M* SERIES, $\lambda \times 10^8$ cm.

Photographic Method.

For Rock Salt $d = 2.814 \times 10^{-8}$ cm.

Chemical Element.	Atomic Number.	α	β	γ	δ	ε
Uranium	92	3.9014	3.7083	3.4714	2.943	2.813
Thorium	90	4.1292	3.9333	3.6565	3.127	3.009
Bismuth	83	5.1072	4.8993	4.5238		
Lead	82	5.2751	5.0648	4.6637		
Thallium	81	5.4499	5.2384	4.802		
Gold	79	5.819	5.601	5.115		
Platinum	78	6.035	5.818	5.295		
Iridium	77	6.245	6.029			
Osmium	76	6.477	6.250			
Tungsten	74	6.976	6.749	6.091		
Tantalum	73	7.237	7.012			
Lutecium	71	7.818	7.593			
Ytterbium	70	8.130	7.898			
Erbium	68	8.770	8.561			
Holmium	67	9.123	8.930			
Dysprosium	66	9.509	9.313			

Reference : Wilhelm Stenstrom, Doctor's Dissertation, Lund, 1919.

TABLE VII.

EMISSION WAVE-LENGTHS IN THE *M* SERIES, $\lambda \times 10^8$ cm.

For Selenite log 2d = 1.18300.

Chemical Element.	Atomic Number.	α_1	β_1	β_3	γ_1	γ_2	γ_3
Bismuth	83	5.124	4.915	4.604	4.534	3.932	3.840
Lead	82	5.290	5.078		4.675	4.073	
Thallium	81	5.468	5.254				
Mercury	80	5.649	5.439				
Gold	79	5.848	5.632	5.446	5.154	4.530	4.439
Platinum	78	6.049	5.831	5.649	5.329	4.733	4.623

Reference : J. C. Karcher, *Phys. Rev.*, April 1920, p. 285.

We now come to a very important feature of these series. At the head of each set of series frequencies stands an absorption known as, la, etc. ; reference has already been made thereto. This critical frequency is in all cases at least as great as the highest frequency In the series to which it belongs. It makes an absolutely sharp division Between tKose frequencies which, as incident radiations, can excite the whole of the rays of the series, and those radiations which cannot excite any of them. At the same time, considering frequencies close to the critical value, those which are greater than that value are many times more highly absorbed by the radiator that emits the series than those which are less; and, if the radiator is a gas, produce in it a correspondingly greater ionisation. There is one critical absorption known as Ka in the *K* series, there are three La_1, La_2, La_3 attached to the *L* series and according to Coster *(Phys. Rev.*, Jan. 1922), there are five in the *M* series, all of these having been directly observed. Reasons are given by Coster (see *Phil. Mag.*, June 1922), for supposing the full number in the *M* series to be five, and in the *N* series to be seven.

Critical absorption frequencies can be measured with great accuracy by taking advantage of any of the three differentiations just described. The following tables show what measurements have been made. The first relates to two substances only, bromine and iodine ; generally, either methyl bromide or methyl iodide is used in the ionisation chamber of the spectrometer. The curve showing the general radiation from an X-ray bulb as measured by ionisation methods shows a sudden break at the critical point of the gas employed. The second table shows the results of measurements by absorption screens. In Fig. 19, due to Duane,t the two sharp breaks in the curve are due,

***According to Duane and Patterson *(Proc. Nat. Ac. Sci.*, Sept. 1920), there are occasional slight departures from this rule, but Coster *(Phys. Rev.*, Sept. 1921, and Jan. 1922) concludes that there are no exceptions.**

† *Phys. Rev.*, Dec. 1917.

TABLE VIII.

CRITICAL lONISATION WAVE-LENGTHS, *K* SERIES, x10^{8} cm.

Ionisation Method. For Calcite d =3.028 x 10^{-8} cm.

Chemical Element.	Atomic Number.	Wave Length.
Bromine	**35**	**•9I79±9**
Iodine -	**53**	**•3737±3**

References : Blake and Duane, *Phys. Rev.*, July, 1917, p. 98, and Dec. 1917, p. 697. Duane and Hu, *Phys. Rev.*, June, 1918, p. 448, and Dec. 1919, **p. 516.**

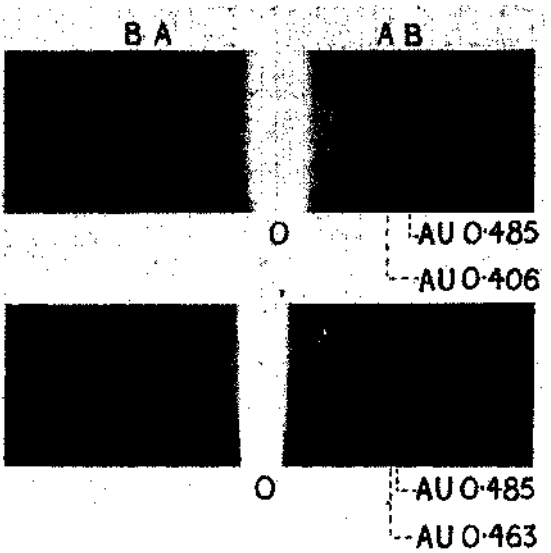
TABLE IX.

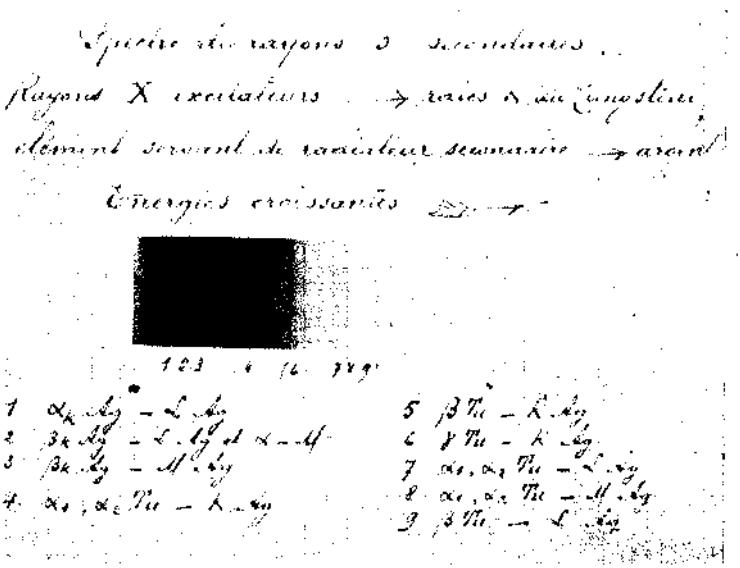
CRITICAL ABSORPTION WAVE LENGTHS, *K* SERIES, x 10^{8} cm.

Chemical Element.	Atomic Number.	Photographic Methods. For Rock Salt d=2.814 × 10^{-8} cm.			Ionisation Method. For Calcite d=3.028 × 10^{-8} cm.
		de Broglie.	Wagner.	Fricke.	Blake, Duane, Hu.
Magnesium -	12			9.5112	
Aluminium -	13			7.9470	
Phosphorus -	15			5.7580	
Sulphur - -	16			5.0123	
Chlorine -	17			4.3844	
Argon - -	18			3.8657	
Potassium -	19			3.4345	
Calcium - -	20			3.0633	
Scandium -	21			2.7517	
Titanium -	22			2.4937	
Vanadium -	23			2.2653	
Chromium -	24			2.0675	
Manganese -	25				1.8892
Iron - -	26		1.740		1.7396
Cobalt - -	27				1.6018
Nickel - -	28		1.485		1.4890
Copper - -	29	1.388	1.375		1.3785

TABLE IX. *(Continued).*

Chemical Element.	Atomic Number.	de Broglie.	Wagner.	Siegbahn-Jonsson.	Blake, Duane, Hu.	
Zinc	30				1.2963	
Gallium	31				1.1902	
Germanium	32				1.1146	
Arsenic	33				1.0435	
Selenium	34	1.003			.9790	
Bromine	35	.916	.917		.9179	
Rubidium	37	.812			.8143	
Strontium	38	.767			.7696	
Yttrium	39				.7255	
Zirconium	40	.684			.6872	
Niobium	41	.648			.6503	
Molybdenum	42	.614			.6184	
Ruthenium	44				.5584	
Rhodium	45				.5330	
Palladium	46	.505	.513		.5075	
Silver	47	.482	.484		.4850	
Cadmium	48	.460	.462	.4629	.4632	
Indium	49				.4434	
Tin	50	.421	.422	.4231	.4242	
Antimony	51	.401	.405		.4065	
Tellurium	52	.385	.383	.3877	.3896	
Iodine	53	.369	.369	.3715	.3737	
Caesium	55	.340		.3436	.3444	
Barium	56	.327	.331	.3306	.3307	
Lanthanum	57	.313		.3186	.3188	
Cerium	58	.300	.298	.3064	.3068	
					Duane, Fricke, Shimizu, Stenström.	
					First Order.	Higher Orders.
Praseodymium	59			.2946		
Neodymium	60		.282	.2835	.2861	
Samarium	62			.2636		
Europium	63			.2543		
Gadolinium	64			.2456		
Terbium	65				.2398	
Dysprosium	66			.2294	.2308	
Holmium	67			.2214		
Thulium	69	.208				
Neo-Ytterbium	70	.2015				
Lutecium	71	.195				
Tungsten	74				.1785	.17806
Osmium	76				.1683	
Platinum	78	.152		.1578	.1582	.1581
Gold	79	.149		.1524	.1537	.1532
Mercury	80	.146		.1479	.1493	.1488
Thallium	81	.142		.1427	.1448	.1449
Lead	82	.138		.1385	.1412	.1409
Bismuth	83	.133		.1346	.1375	.1369
Thorium	90			.1127	.1139	.1124
Uranium	92			.1048	.1075	





MAGNETIC SPECIMEN OF CATHODE RAYS.
(De Broglie.)

Facing page **65.**

one to the sudden change in the ionisation effect on the gas of the ionisation to an analogous change in the absorbing effect of the screen. The same effect is shown photographically in Plate III., Fig. I,

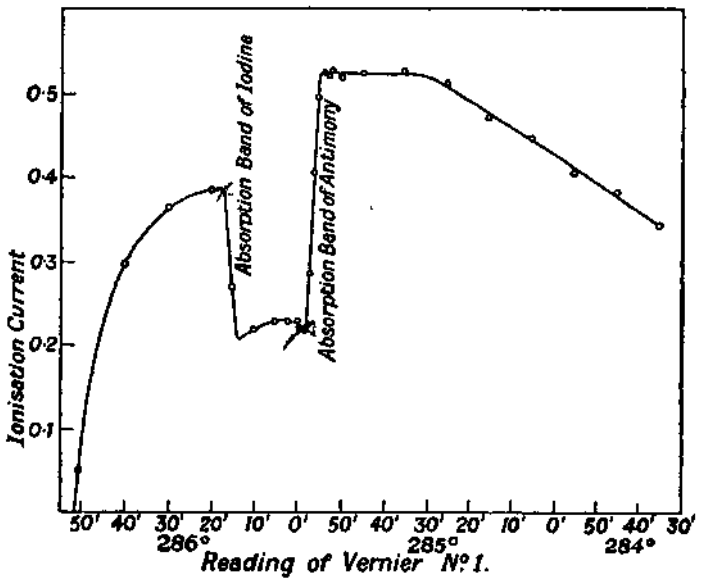


FIG. 19.

(Physical Review, Dec. 1917.)

due to de Broglie, where one edge of the band lies at the critical value of the absorbing screen (Sb 0406, Cd 0463), the other at the critical value of the silver (0485) of the photographic plate.

Critical absorption values in the *L* series are given in Table X., and of the *M* series in Tables *IXa* and XI. The latter is due to Coster, and contains observations by himself and by Stenstrom.

TABLE IXa.

	Ma_1	Ma_2	Ma_3	Ma_4	Ma_5
U - -	3491	3326	2873	2385	2228
Th - -	3721	3552	3058	2571	2388
Bi - -	4762	4569	3894	—	—

TABLE X.

CRITICAL ABSORPTION WAVE-LENGTHS IN THE L SERIES, $\lambda \times 10^8$ cm.

Photographic Methods. For Rock Salt d=2.714X 10^{-8} cm.

Chemical Element.	At. No.	de Broglie. α_1	α_2	α_3	Wagner. α_1	α_2	α_3
Tungsten -	74	1.215	1.083	—	—	—	—
Platinum -	78	1.069	.930	—	1.072	.934	—
Gold - -	79	1.038	.898	.858	1.036	.914	—
Mercury -	80	1.006	—	—	—	—	—
Thallium -	81	.974	.840	—	—	—	—
Lead - -	82	.945	.811	—	—	—	—
Bismuth -	83	.921	.786	.753	—	—	—
Radium - -	88	.802	.668	—	—	—	—
Thorium -	90	.757	.624	.604	—	—	—
Uranium -	92	.718	.588	.564	—	—	—

Ionisation Methods. For Calcite d=3.028x 10^{-8} cm.

	Duane and Patterson. a_1	a_2	a_3
Tungsten - -	1.2136±1	1.0726±5	1.024 ±3
Platinum - -	1.0704±3	.9321±3	.8885±9
Gold - - -	1.0383±3	.8993±3	.8606±8
Mercury - -	1.0067±5	.8700±3	.8335±9
Thallium - -	.9776±3	.8415±3	.8055±14
Lead - - -	.9497±9	.8133±3	.7803±9
Bismuth - -	.9216±3	.7872±3	.7532±9
Radium - -			
Thorium - -	.7596±3	.6286±3	.6044±7
Uranium - -	.7214±3	.5918±3	.5685±7

References : de Broglie, *Journ. de Phys.*, May-June 1916, p. 161, and Jan. 1919, p. 31. Wagner, *Ann. d. Phys.*, March 1915. Duane and Patterson, *Nat. Acad. Proc*, Sept. 1920.

TABLE XI.

CRITICAL ABSORPTION WAVE-LENGTHS IN THE *M* SERIES, $\lambda \times 10^8$ cm.

Chemical Element.	At. No.	Photographic Method. α_1	α_1'	For Rock Salt $d=2.814\times10^{-8}$ cm. α_2	α_3
Thorium - -	90	3.721		3.552	3.058
Uranium - -	92	3.491	3.459	3.326	2.873

Reference: Wilhelm Stenstrom, Doctor's Dissertation, Lund, 1919.

The critical frequencies of an element are naturally fewer in number than the emission frequencies, since a series of emission frequencies has one critical fequency at its head. For this reason, and because it appears that every emission frequency is *the* difference of. two critical frequencies, the latter may be regarded as the more fundamental. Their dependence on atomic number has been carefully examined by several workers, especially Duane, de Broglie and Wagner. The figures given in the above tables may be used to show

TABLE XII.

CRITICAL ABSORPTION WAVE NUMBERS. *L* SERIES OF X-RAYS.

Values of $1/\lambda$ and of $\sqrt{1/\lambda}$.

Chemical Element.	Atomic Number.	$1/\lambda$	$\sqrt{1/\lambda}$ La_1	Differences.
Tungsten	74	.8240±1	.9077	
Platinum	78	.9341±3	.9665	.0147±1
Gold	79	.9631±3	.9814	.0149±3
Mercury	80	.9933±4	.9966	.0152±4
Thallium	81	1.0229±3	1.0114	.0148±4
Lead	82	1.0530±3	1.0262	.0148±3
Bismuth	83	1.0851±3	1.0417	.0155±3
Thorium	90	1.3164±5	1.1473	.0151±1
Uranium	92	1.3862±5	1.1774	.0151±2
			La_2	
Tungsten	74	.9323±5	.9656	
Platinum	78	1.0728±4	1.0358	.0176±1
Gold	79	1.1120±4	1.0545	.0187±4
Mercury	90	1.1494±4	1.0721	.0176±4
Thallium	81	1.1883±5	1.0901	.0180±5
Lead	82	1.2295±5	1.1088	.0187±5
Bismuth	83	1.2703±4	1.1271	.0182±5
Thorium	90	1.5908±8	1.2613	.0192±1
Uranium	92	1.6898±8	1.2999	.0193±3
			Lb_1	
Tungsten	74	.977±3	.988	
Platinum	78	1.1255±12	1.0609	.0182±5
Gold	79	1.162±1	1.0788	.0171±11
Mercury	80	1.200±1	1.0953	.0174±11
Thallium	81	1.242±2	1.1142	.0189±15
Lead	82	1.282±2	1.1320	.0178±16
Bismuth	83	1.328±2	1.1523	.0203±13
Thorium	90	1.655±2	1.2863	.0192±2
Uranium	92	1.759±2	1.3263	.0200±7

how closely the frequencies follow a steady progress from element to element, as for example in Table XII., p. 67, due to Duane and Patterson *(Proc. Nat. Acad. Set.,* Sept. 1920, P. 513).

The longest waves included in all these tables do not exceed 13 A.U. in magnitude. The spacings of the crystal should be of the same order as that of the wave lengths to be measured, and hence there is a limit to the use of the natural diffraction grating. Between these and the shortest waves of the ultra violet is a gap, which narrows continually nevertheless. Millikan, using an artificial grating of special construction, has pushed the investigation of the ultra violet spectrum so far that the two fields of enquiry are now in sight of each other though they do not actually touch. His extreme limit is a line of the *L* series of aluminium lying at 136.6 A.U. Some of his measurements of the L_a lines of elements of low atomic number are collected together in the following table :

L_a (Millikan, *Proc. Nat. Acad. Sci.,* Oct. 1921).

Al	**144.3**	**O**	**834.0**
Mg	**232.2**	**N**	**1085.3**
Na	**372.2**	**C**	**1335.0**
Ne	—	**B**	**2497**
F	**657.2**		

It must be observed that the spectra are complex, and that for the atomic numbers below that of neon there is some uncertainty as to which of the lines are to be taken as analogous to the *L* line of the X-ray spectra. There is, however, very good evidence that the choice has been rightly made : each of the lines enumerated is strong and an important member of the spectrum in which it lies. Moreover, the progression from element to element is what would be expected from an extension of Moseley's principle into these regions. Also, there is a wide gap between the *L* lines of the element and the next set of lines in the ultra violet spectrum, which latter no doubt are analogous to the *M* lines of the X-ray spectra. For instance, there is a blank

between the *L* line of Mg at 232.2 and the first of the *M* lines at 1700.

Relations which are obviously of great theoretical importance are found to exist between emission frequencies and critical frequencies. An emission frequency is very often found to be the difference between two known critical frequencies. The converse does not appear to be true : every difference of critical frequencies does not correspond to an emission. An emission frequency is never the difference of two other emission frequencies, nor a critical frequency of two other critical frequencies. Many of these relations have been very carefully worked out by Duane, to whom the following two tables are due. The first of them shows the frequencies of the *K* series of tungsten as differences of critical frequencies. The numbers are the reciprocals of wave lengths in A.u.

Ka - La_1 4.792 ±0.003	a_1 = 4.7930±0.001
Ka - La_2 = 4.685 ±0.003	a_2 = 4.6858 ±0.007
Ka ~ La_3 = 4.639 ±0.006	a_3 = 4.65 ±0.82
Ka - Ma_3 = 5.433	ß = 5.429

The next table refers to the frequencies of certain *L* lines of uranium and thorium :

U	Th	U	Th	U	Th
$La_1 - Ma_1 = 1.099$	1.047	$La_1 - Ma_2 = 1.085$	1.034	$La_1 - Ma_3 = 1.038$	0.988
$L\alpha_1 = 1.098$	1.045	$L\alpha_2 = 1.085$	1.032	.....	...
$La_2 - Ma_1 = 1.322$	1.322	$La_2 - Ma_2 = 1.389$	1.309	$La_2 - Ma_3 = 1.342$	1.263
.....	...	$L\beta_1 = 1.389$	1.305	.....	...
$La_3 - Ma_1 = 1.472$	1.385	$La_3 - Ma_2 = 1.458$	1.372	$La_3 - Ma_3 = 1.411$	1.326
.....	...	.....	...	$L\beta_3 = 1.408$	1.319

The quantum theory suggests a physical interpretation of these numerical relations. According to the theory as developed by Bohr the frequency of Ka multiplied by *h* is the quantum energy associated with an electron revolving in the innermost ring round the central core of the atom. If sufficient energy is absorbed from a passing radiation to remove an electron from this ring, the potential energy of

the atom is increased by an amount equal to the quantum energy. There are outer rings with less quantum energies ; these are *L* rings, *M* rings, and so on. If an electron moves from an *L* ring to the *K* ring to take the place of an electron which has been removed from the atom, there will be available for radiation an amount of energy equal to the difference between the *K* quantum energy and the *L* quantum energy ; and, according to Bohr's ideas, homogeneous radiation is emitted during the transfer whose frequency is equal to this difference of the quanta divided by *h*. By an extension of this process the whole emission is accounted for : every emission is due to the passing of an electron from one ring to another, and the emission frequency is always the difference of two critical or ring frequencies.

The question at once arises as to what relations exist between the frequency of the original radiation which started the chain of events and the frequencies of the emission lines. The fact that, if the incident frequency exceeds the critical frequency by the smallest amount, the radiation specially absorbed, suggests that an energy quantum of this radiation is spent in the removal of the electron ; the removal cannot take place unless the incident quantum is large enough, and if it is only just large enough the process is already in full working. If the energy of the incident quantum is sensibly larger than is required, what becomes of the balance ? To this question de Broglie has lately given a clear answer. The excess energy is found to be in the possession of an electron which is set in motion simultaneously with the other energy transformation ; and this is in fact the photo-electric effect. By the development of a method first used by Robinson and Rawlinson,* he has obtained magnetic spectra of the electrons emitted from substances on which monochromatic X-rays are allowed to fall. In these spectra are to be found ' lines,' each due to electrons of a certain speed : if the substance is present in a very thin layer the line is quite fine, otherwise it is sharp

* *Phil. Mag.,* Aug. 1914.

on the high velocity side and melts gradually away on the other because some electrons lose speed on the way out from the substance in which they arise. In each case the energy of the electron is equal to the difference between the quantum energy of the incident radiation and the quantum energy of one of the critical frequencies of the substance.

It may serve to make the process clearer if we consider an ideally simple case, that of a hypothetical atom having but one critical frequency v_0, struck by monochromatic rays of frequency v. The quantum energy hv absorbed from the radiation is then divided into two parts, hv_0, which is emitted as radiation of frequency v_0 and $h(v \sim v_Q)$, which is emitted as the energy of a single electron. Actually, there is no case so simple as this. An atom possesses several rings or shells; and there are many possible methods of subdivision of the original quantum, so that the experimental magnetic spectra contain many lines. A number of examples have been given by de Broglie.* One of these is reproduced as Fig. 2, PI. III. In a second case the X-rays from a tungsten anticathode fell upon a rhodium salt, producing a magnetic spectrum which showed three rays or bands whose quantum energies, divided by h, were :

$$408 \times 10^{16}, \quad 472 \times 10^{16}, \quad \text{and} \quad 870 \times 10^{16}.$$

The strong lines of the K series of tungsten have frequencies :

$$1420 \times 10^{16} \quad \text{and} \quad 1629 \times 10^{16}.$$

The K critical frequency of rhodium is 565×10^{16}. The principal L critical frequency is 78×10^{16}.

Rays in the magnetic spectrum might, therefore, occur according to this principle, at $(1420 - 565) \times 10^{16} = 855 \times 10^{16}$, and at $(1629 - 565) \times 10^{16} = 1064 \times 10^{16}$. The former is to be identified with the third of the observed rays, the latter was not observed. But, further, the characteristic rays of rhodium, of frequencies 490×10^{16} and 544×10^{16}, have been excited; and each of them should continue the process.

* *Journal de Physique,* **Sept. 1921, p. 265.**

Accordingly the following rays might be found in the magnetic spectrum :

$(490 - 78) \times 10^{16} = 412 \times 10^{16}$ and $(544 - 78) \times 10^{16} = 466 \times 10^{16}$,

and this is actually the case. No other rays ought to be found in that part of the spectrum which has been photographed, and all those present have been accounted for.

Whiddington has also carried out experiments of this kind. His results are fully described in the *Philosophical Magazine*, July 1922. They are in general agreement with those of de Broglie.

Transformations of energy of similar kind must occur in the target of the bulb. Here the electron strikes the target, and in consequence there is an emission of the rays which are characteristic of the metal of the target. It is necessary here also that the quantum energy of the radiation, *i.e.* of the electron stream, should exceed the critical value for the target; and it might reasonably be expected that the surplus energies would be taken up by some of the electrons of the secondary radiation. No experiments have been made to test this point.

The general radiation which is emitted by a target may be excited in some different way, as has already been observed. It might also be looked on as due to a transformation in which the critical frequency concerned was very small. It is against the latter supposition that transformations for which there is a large difference between the incident and the critical quanta seem to be infrequent, whereas the general radiation may be strong compared to the characteristic.

It is beyond the proposed scope of this book to go further in the discussion of the theory of X-ray spectra. The fine structure of the lines, and the explanation of detail on the basis of the theories of Bohr and Sommerfeld, are given in the published works of these investigators.

CHAPTER VII

CRYSTAL STRUCTURE

THE atoms and molecules of the substance composing a crystal are arranged in a definite pattern. It is this arrangement which distinguishes a crystal from a block of the same substance in the amorphous state. The crystal form, displaying itself as a polyhedron bounded by plane faces, is generally assumed whenever a substance is deposited as a solid from solution or from the molten or vaporous state. The atoms, in assembling together to form the solid, adopt a geometrical disposition of perfect regularity. Each chemical compound has its own crystalline form, by which in most cases it may be identified.

Crystals have hitherto been grouped into systems and classes on the evidence of their external form and symmetry alone. Until quite recently nothing definite has been known concerning their internal constitution, though several theories have been put forward to explain the external forms by assigning various arrangements to the atoms. Nevertheless it has been possible, without exact knowledge of crystalline structure, to lay down certain geometrical laws to which all such structures must conform as regular patterns in space. We can investigate and classify the different ways in which it is possible to make a space patten}. In this way we arrive at a classification which is the same as that to which we are led by observation of crystal symmetry. It is believed that the geometrical theory of crystal structure is now complete, and that further advance must be made by experimental discoveries concerned with actual crystals.

Let us suppose that in a crystalline structure the atoms are grouped into the units of pattern mentioned above. The groups are to contain as few atoms as possible, consistent with the requirements that the whole crystal can be built by packing these groups together, all the groups being similar and similarly oriented. If a point is now chosen in each of the groups in the same way, for example the centre of a particular atom, these points serve to indicate the positions of the groups to which they belong. Thus by neglecting the complicated structure of atoms surrounding each point, and considering the points alone, we arrive at a series of points in space which form the foundation on which the crystal is built. Such a series of points is of the greatest importance in the theory of crystal structure : it is known as a 'Space Lattice.'

In order that a set of points in space may form one of these space lattices, they must satisfy certain conditions. Since the points have been chosen in the same way from each unit of the pattern, it follows that every point must be situated similarly to every other point; each has neighbours in the same directions and at the same distances from it. All ways of drawing points in space which satisfy these conditions reduce in the end to the following method. Space is divided into parallelepiped cells by three sets of parallel planes. The planes belonging to a set are all equidistant and parallel, but the distance between the planes need not be the same for all three sets, and the planes of different sets may make any angle with each other. By taking every point where three planes meet, a lattice is formed which satisfies the conditions stated above.

Suppose now that Fig. 20 represents the space lattice actually underlying a crystal that is being measured. It is clear that the orientation of any face which the crystal may possess is determined by the lattice alone, and not by the pattern unit which is grouped round each point. The faces of the crystal represent possible ways of arranging points of the space lattice in planes (compare p. 9, Fig. 2). For

instance, in Fig. 21 a series of points lie in the plane *ABC*, the parallelepipeds being pictured as blocks packed so as to show this plane, which is known as a ' net plane ' of the structure.

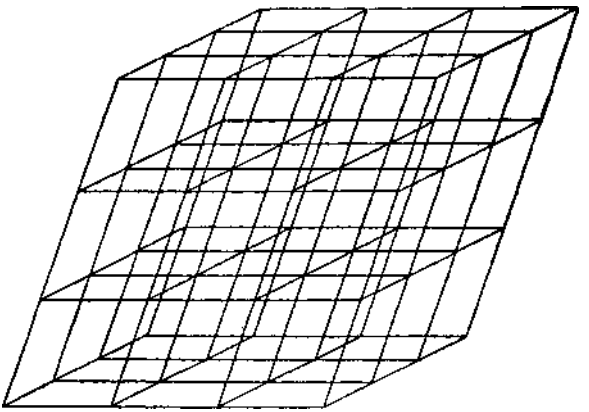


FIG. **20.**

The same points can be arranged in any number of ways on parallelepipeds, those in the figure representing only one possible way of carrying out the arrangement. Let some

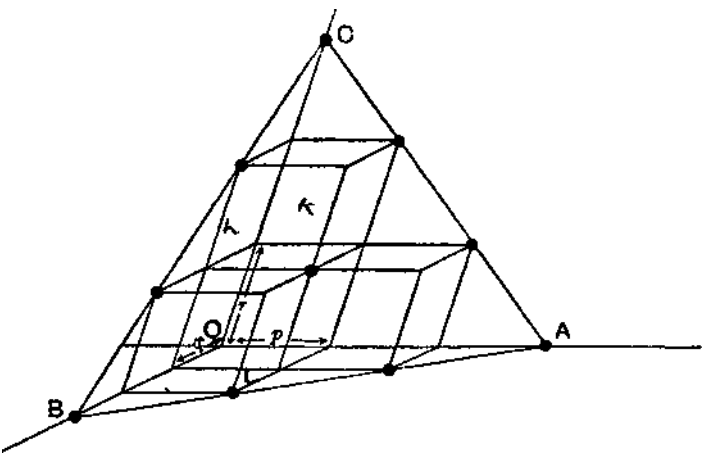


FIG. **21.**

particular way of drawing the parallelepiped be chosen. The three directions to which the edges of the parallelepiped are parallel may then be called the axes of the crystal, and

all its faces can be named with reference to these axes. The way in which the planes are referred to the axes is as follows. In Fig. 21 we have drawn a typical plane *ABC* on which a set of particles lie. Let *0* be the origin at a parallelepiped corner, and *OA, OB, OC* parallel to the axes of the crystal. The plane *ABC* cuts off the intercepts *OA, OB, OC* from the axes, and if the ratio of these intercepts is known the orientation of the plane *ABC* is thereby defined. (It will be evident from Fig. 21 that net planes of all types can be drawn by choosing for *OA, OB, OC* any multiples of the parallelepiped edges.) If these edges are called *p, q, r* respectively, then the ratio $\frac{OA}{p}$ must be a whole number. Similarly, $\frac{OB}{q}$ and $\frac{OC}{r}$ are whole numbers. Therefore

$$\frac{OA}{p} : \frac{OB}{q} : \frac{OC}{r} = N_1 : N_2 : N_3,$$

where N_1 N_2, N_3 are whole numbers. It follows that

$$\frac{p}{OA} : \frac{q}{OB} : \frac{r}{OC} = N_2N_3 : N_3N_1 : N_1N_2,$$

the last three quantities being again whole numbers. These are the ratios which are used by crystallographers when they wish to designate any particular plane of a crystal. The numbers are divided by any common factor, so as to make them as simple as possible, and finally, if

$$\frac{p}{OA} : \frac{q}{OB} : \frac{r}{OC} = h : k : l,$$

the plane in question is defined as the plane *(h, k, I),* the indices being written in brackets.

For the plane drawn in Fig. 22,

$$\frac{OA}{p} = \frac{OB}{q} = \frac{OC}{r},$$

and the plane is represented by indices (in). The intercepts which this plane makes on the axes are proportional to the sides of the elementary parallelepiped. The ratios of these three quantities are then called the *axial ratios* of the crystal.

The axial ratios are denoted by the symbols *a, b, c,* and since it is merely ratios that we require, *b* is usually put equal to i. We have

$$a:b:c-a:i:c=p:q:r.$$

In the case of an actual crystal the ratios $a : b : c$, and the angles the axes make with each other are determined as the results of measurement of the inclination of the crystal faces to each other. There is, however, a certain freedom of choice, which is so made that the indices of the most

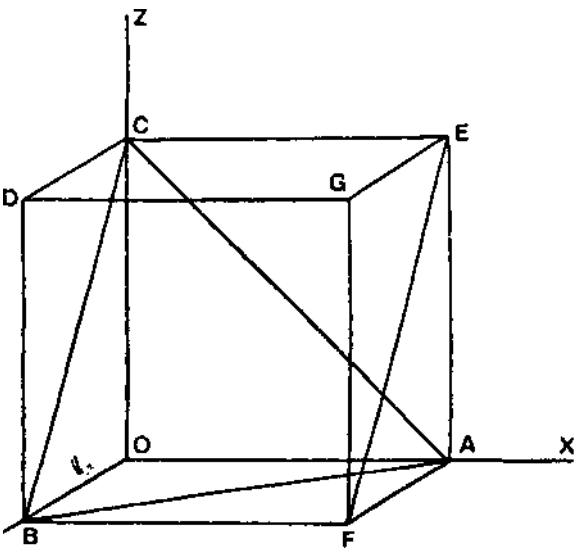


FIG. 22.

important faces have simple values. When suitable directions for the axes have been chosen, and some well marked plane has been selected, to be called the plane (in), the intercepts which this plane makes on the axes then give the ratios $a : b : c$. The indices of all the other plane faces of the crystal may now be determined, and it is not difficult to see, from the above example, that all these faces will have a set of indices *(h, k, I)* which are integers.

Let us take as an example the naming of the faces of a cubic crystal. Such a crystal has three equal axes at right angles, represented by *OX, OY, OZ* in Fig. 22.* If

the crystal were bounded by a face parallel to *EGFA*, this face would be named the face (100). For since the face is parallel to two of the axes, the intercepts it makes on these two are to be regarded as infinite, so that the three intercepts are in the ratio *OA* : : , and the inverse of these numbers gives the indices $h : k : / = \mathrm{I} : \mathrm{o} : \mathrm{o}$. The face *CEFB* is parallel to the *X* axis, and makes equal intercepts on the *Y* and *Z* axes. It has indices (on). The face *ABC* makes equal intercepts on all three axes, and is therefore the face (in). Now the crystal may have two faces on opposite sides parallel to *ABC*. We distinguish these faces from each

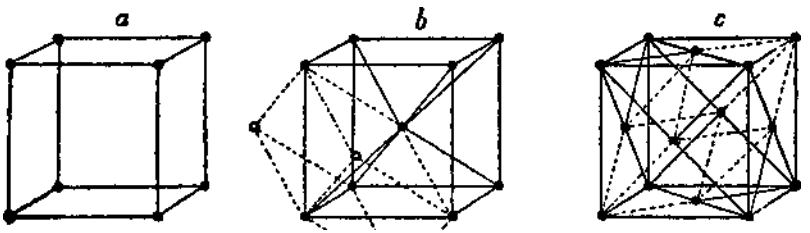


FIG. 23.

other by calling them (111) and (-I, -I, -I) respectively, the latter being written (I I I). If the body of the crystal is on the same side of *ABC* as the origin in Fig. 22, this plane is called (I I I), the opposite face being called (I I I).

To return to the space lattice. In general the sides of the elementary parallelepiped of Fig. 20 may be of any length and be inclined at any angle to each other. As a special case, the three sides might be equal and make right angles with each other. If this were so, the parallelepiped would become a cube as in Fig. 23.

A crystal built up on such a lattice as this will have a cubic character, that is to say, it can be referred to three identical axes at right angles, and therefore belongs to the' cubic system of crystals. On examining all the ways of arranging points on space lattices, we find two more, each of which can be referred to the cubic system of axes,

their forms will display the symmetry of the lattice. For instance, we will now suppose that the cube in Fig. 24 represents, not an element of the structure, but an actual crystal which has grown under ideal conditions into a perfect cube by developing faces {100}. Beside it there is another cubic crystal (Fig. 24), which has developed into an octahedron. It will be seen that the octahedron has the same axes, planes, and centre of symmetry as the cube. Although their forms are so different, both crystals are ' cubic.' Any actual crystal will not form perfectly symmetrical solid figures, for accidents of growth will cause irregularities. Some faces of the octahedron will be larger than others, but because these octahedron faces are a result of the underlying cubic structure of the crystal, they will still make the same angles with each other, and so be recognisable.

The atom being spherical, as assumed, the lattice and the crystal have the same symmetry. A space lattice such as that on which we have supposed the atoms to be arranged has an infinite set of axes, planes, and centres of symmetry all of which are embodied in the structure. For instance, lattice has axes of fourfold symmetry, coinciding with the cube edges in Fig. 23 *(a), (b), (c),* and also parallel a of fourfold symmetry passing through the cube cer The crystal has therefore three axes of fourfold sym at right angles to each other, parallel to the three edges. In the same way it has four threefold axes dicular to the planes {in}, three planes of s parallel to the cube faces {100}, six planes of symme and six twofold axes perpendicular to these pla there is a centre of symmetry at each cube con centre of the lattice, the crystal has also a

ry. Each type of axis in the structure of the crystal.

symmetry

c

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v, cr

by further subdivision into thirty-two classes. A detailed account of the classes would be out of place here, but a list is given of the features which distinguish the six systems. The definitions are based upon those in Miers' *Mineralogy* :

Cubic System. Crystals referable to three equal rectangular axes. All crystals of this system possess four trigonal axes.

Tetragonal System. Crystals referable to three rectangular axes, two of which are equal, the third being a tetragonal axis.

Orthorhombic System. Crystals referable to three unequal rectangular axes, one of which is a digonal axis. This axis has either two planes of symmetry intersecting it, or two digonal axes perpendicular to it, or all these elements of symmetry.-

Hexagonal System. Crystals referable to three equal oblique axes, making equal angles with each other, and possessing one trigonal or hexagonal axis.

fonoclinic System. Crystals referable to three unequal axes, one of which is perpendicular to the other two, and possessing either one digonal axis or one symmetry plane, or both these elements of symmetry.

rthic System. Crystals referable to three unequal oblique axes and possessing at the most a centre of mmetry.

further subdivision, each class has its own characimetry. Now the three space lattices of Fig. 23, • to the cubic system, all have the same elements *i.e.* the full number which the cubic system By themselves they furnish no criterion of the to which the crystal belongs. The round each of these points ration, and

m

A two-dimensional model will serve to show how this comes about.

Fig. 25 *(a)* is supposed to be part of a pattern in two dimensions with tetragonal axis perpendicular to the plane of the* paper. The structure is also symmetrical about such lines as *LL, MM.* The pattern is built up on the lattice *(d),* which possesses the same elements of symmetry, and may be called the typical lattice of the fourfold system in two

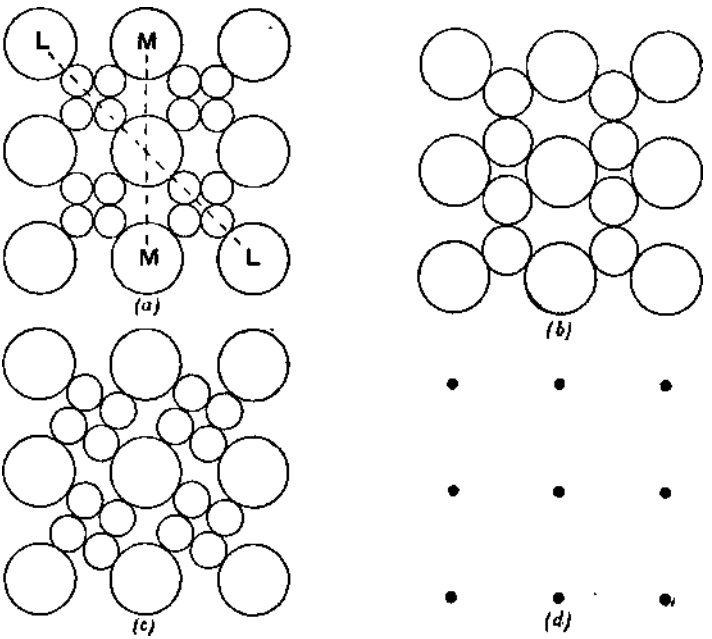


FIG. 25.

dimensions. In Fig. 25 *(c),* we have another pattern built up on the same lattice, and therefore belonging to the same system. Here the groups of four small atom are represented as slewed round. It is obvious that this patten no longer symmetrical about any line ; it has lost ce elements of symmetry which *(a)* possesses. The pat belong to two different classes of the fourfold system class to which *(a)* belongs being characterised by axes and lines of symmetry parallel to *L* and *M,*

(c) belongs has only the fourfold

two dimensional square crystals can in this way be divided into two kinds, those which possess lines of symmetry and those which do not. The fourfold system has been subdivided into two classes, the foundation of the structure in both cases being the same plane lattice. It might be argued that still other classes of crystals could be built up on this same square lattice, Fig. 25 *(b)* being an example. But in this figure the arrangement of the structure makes it clear that if the lattice is a square one, it is so merely by coincidence. It would be natural for the vertical and horizontal dimensions in the figure to be different. In the other cases the structure provides a reason for the equality of the two rectangular axes. Considerations of this kind show that there are only two classes in this category.

These considerations may be carried over to the three-dimensional case. The three cubic space lattices provide a basis, on which crystals are built up which possess some, but not necessarily all, of the elements of symmetry possessed by the space lattices. They are classified according to their symmetry, the cubic system being divided into five classes, just as the fourfold system in two dimensions is divided into two classes. The tetragonal system is divided into seven classes, the hexagonal into twelve classes, and so on, the whole) number of classes being thirty-two.

The results obtained with the X-ray spectrometer enable us to discover both the space lattice on which the atoms are arranged and the way in which they are grouped round each point of the space lattice. Several of the cases which we shall presently discuss provide illustrations of the manner which the symmetry of the group determines the sym- ry of the crystal as a whole. As in Fig. 25 *(c)*, the s of atoms are so arranged as to limit the number of nts of symmetry, while retaining sufficient to cause picture to be cubic. This arrangement of the atoms so long a matter of speculation that it is interesting ual examples which support the theory of crystal

CHAPTER VIII

THE ANALYSIS OF CRYSTAL STRUCTURE, (1)

IF a crystal is mounted on the table of the X-ray spectrometer, and the ionisation chamber is set so as to receive the beam of X-rays reflected by the crystal, the wave lengths of the rays entering the ionisation chamber will be given by the formula

$$n\lambda = 2d \sin \theta,$$

where d is the spacing of the crystal planes, and n is an integer. Fig. 26 shows the results of an examination of the reflection by various faces of potassium chloride and sodium chloride crystals. The crystal is set at a series of angles Θ over a range between 4^0 and 20^0. The ionisation chamber is set in each case at the angle $2d$, so that it receives the reflected beam, and the strength of this beam is measured by observing the ionisation when the X-ray bulb is operated for an interval of about 5 seconds.

The radiation from the bulb consists of a general radiation of all wave lengths over a certain range, with in addition a characteristic radiation of certain definite wave lengths constituting the X-ray spectrum of the material of which the anticathode is made. This is shown by the form of ionization curves. At all angles a measurable effect is r duced corresponding to the reflection of the general radia At certain angles the effect is greatly increased, these the angles at which the crystal reflects one of geneous components of the X-ray spectrum.

The two peaks which are so clearly marke- are produced by the K_a and K_β components spectrum.

The crystals of sodium and potassium chloride belong to the cubic system, and the similarity of their chemical constitution and crystalline form makes it natural to suppose that they possess crystalline structures of the same type

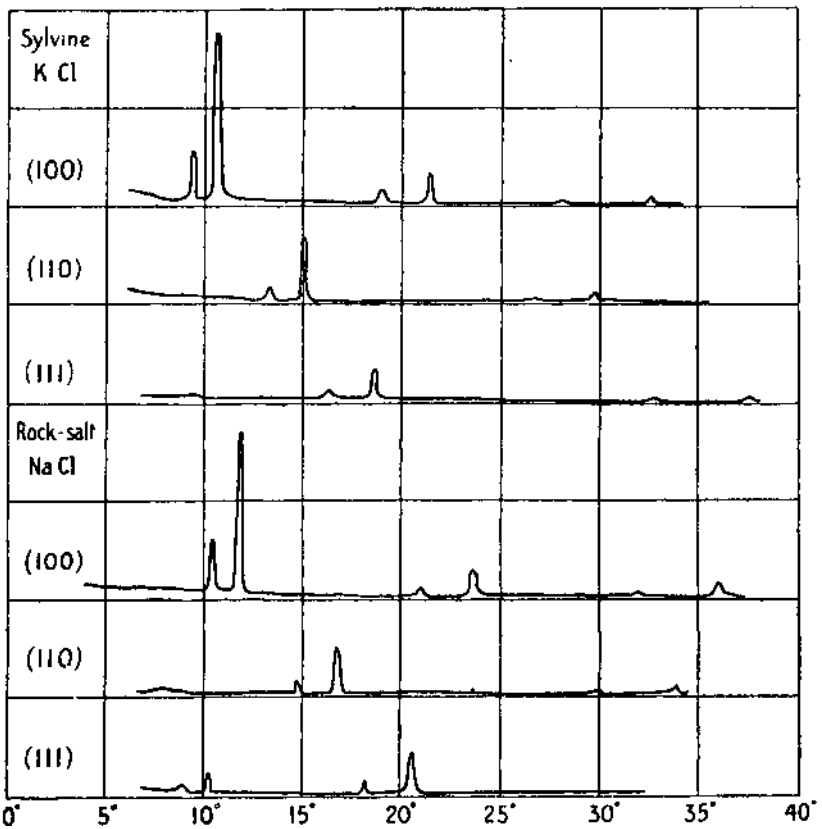


FIG. 26.—Abscissa = angle of setting of the ionisation chamber, 20.

X-ray spectra given by corresponding faces of the two
s strongly resemble each other and support the

a given by potassium chloride are of the simpler
ace gives a series of peaks on the ionization
diminishing regularly as the glancing angle
tance, the larger of the two peaks reflected

from the cube face (100) of KC1 (the K_a line) occurs at glancing angles *

$$5° 23', \quad 10° 49', \quad 16°20'.$$

We notice that

$$\sin 5^0 23' : \sin 10° 49' : \sin 16^0 20' = 0938 : 1875 : 2813$$
$$= 1 : 2 : 3,$$

so that these peaks are reflections of the line in the first, second, and third orders. The same relation holds for the other faces.

The angle at which reflection of the first order takes place depends on the spacing between the planes.

Since $=2d \sin \Theta$, the spacing d is inversely proportional to $\sin \Theta$. In the case of the KC1 crystal, the reflections occur at glancing angles 5° 23', 7° 37', 9° 23' for the faces (100), (no), and (III) respectively. Therefore

$$\frac{1}{d_{(100)}} : \frac{1}{d_{(110)}} : \frac{1}{d_{(111)}} = \sin 5° 23' : \sin 7° 37' : \sin 9° 23'$$
$$= .0938 : 1326 : 1630$$
$$= 1 : 1.413 : 1.738.$$

That is, the ratio is, within the error of measurement,

$$1 : \sqrt{2} : \sqrt{3}.$$

To see what this means, we must consider the three types of space lattice which possess cubic symmetry. These are the simple cubic, the cube-centred, and the face-centre cubic lattices.

Fig. 27 *(a)* represents the unit cube of the simple cubic lattice, having a point at each corner of the cube. The distance between the planes parallel to (100) on which the points lie is equal to the side of the cube, which will be called a. The planes (no) are parallel to *BCEF* in the figure, and the spacing between successive planes is equal to *OP,* this being the perpendicular distance between the neighbouring

* These figures are the measurements made in the original investigat and could now be replaced by others of a far higher order of accu This has not been done, because the accuracy of the original exp was more than sufficient to establish the principles under discus

plane, passing through the points *OA*, and the plane *BCEF*. Similarly, the distance between the planes (III) parallel to *ABC* is equal to *OQ*.

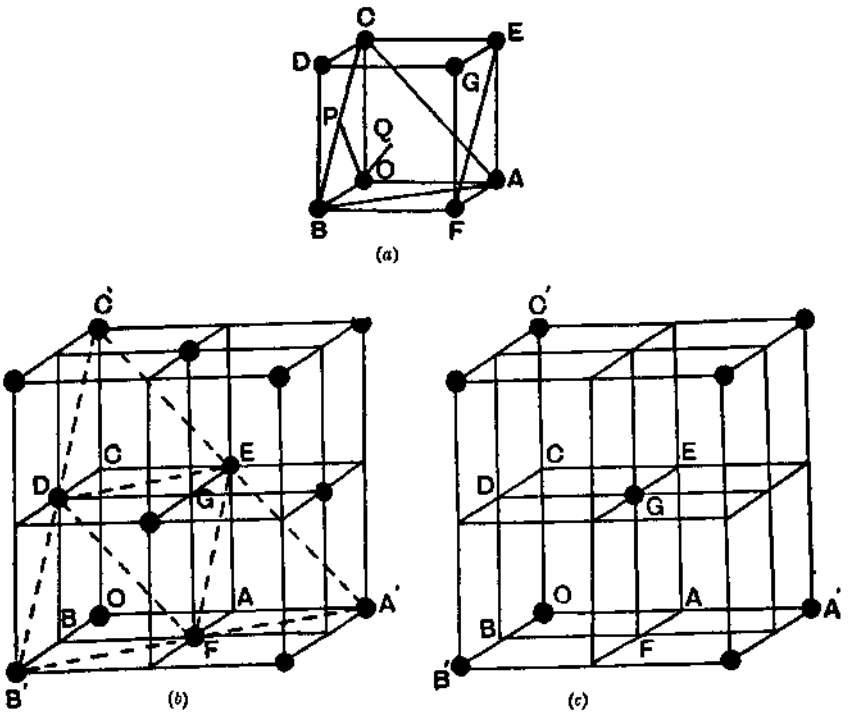


FIG. 27.

Since $$OP = \frac{OD}{2} = \frac{a\sqrt{2}}{2},$$

$$OQ = \frac{OG}{3} = \frac{a\sqrt{3}}{3};$$

we have $$d_{(100)} = a,$$

$$d_{(110)} = OP = \frac{a}{\sqrt{2}},$$

$$d_{(111)} = OQ = \frac{a}{\sqrt{3}}.$$

Therefore $$\frac{1}{d_{(100)}} : \frac{1}{d_{(110)}} : \frac{1}{d_{(111)}} = 1 : \sqrt{2} : \sqrt{3}.$$

27 (6) represents the unit cube of a face-centred cubic The cube is drawn to twice the previous scale, in

order that it may be partitioned into eight smaller cubes, the sides of which are equal to *a* as before, and which have points of the lattice situated at one half of their corners.

It can be seen from the figure that $d_{(100)}$ is equal to a, and that $d_{(110)}$ is equal to $\frac{a}{\sqrt{2}}$, as in the previous case. It is no longer true, however, that $d_{(111)}$ is equal to $\frac{a}{\sqrt{3}}$. In the previous case $d_{(111)}$ was equal to *OQ*, the perpendicular from *0* on the plane through *ABC*. In Fig. 27 *(b)* there are no points of the lattice at *A*, *B*, and C, and if the plane is extended in space it will pass through corners of squares not occupied by atoms. The next (III) plane to that passing through *0* is the plane *A'B'C*, and the distance between successive planes is twice as great as before, being equal to $\frac{2a}{\sqrt{3}}$. We therefore have

$$\frac{1}{d_{(100)}} : \frac{1}{d_{(110)}} : \frac{1}{d_{(111)}} = 1 : \sqrt{2} : \frac{\sqrt{3}}{2},$$

this being characteristic of the face-centred cubic lattice.

It can be shown similarly for a cube centred lattice, as in Fig. 27 (c),

$$\frac{1}{d_{(100)}} : \frac{1}{d_{(110)}} : \frac{1}{d_{(111)}} = 1 : \frac{1}{\sqrt{2}} : \sqrt{3}.$$

The spectra in the case of potassium chloride are those to be expected from a lattice of the first of these three types. The spectra therefore indicate that in the KC1 crystal the units which diffract the X-rays are arranged on a simple cubic lattice.

When the results for KC1 and NaCl are compared, it will be seen that corresponding spectra occur at slightly smaller angles for the first crystal than for the second. For instance the first order reflection from (100) occurs at 5^0 23' for KC at 6° 0' for NaCl. The planes must be more widely space in the first case in the ratio

$$\sin 6° 0' : \sin 5^0 23' + 1.1$$

If the crystals have the same structure, this should correspond to the difference in molecular volumes of the two crystals.

We have

Molecular volume of KC1

$$= \frac{\text{Molecular weight}^*}{\text{Density}} = \frac{38.90 + 35.20}{1.99} = 37.20.$$

$$\text{Molecular volume of NaCl} = \frac{22.80 + 35.20}{2.17} = 26.70.$$

Since the volume occupied by a molecule is proportional to the volume of unit cube of the lattice in each case, the spacing of the (100) planes is proportional to the cube root of the molecular volume. For corresponding planes

$$\frac{d_{(KCl)}}{d_{(NaCl)}} = \sqrt[3]{\frac{37.20}{26.70}} = 1.118,$$

agreeing with that calculated from the angle of reflection.

The spectra given by NaCl differ in one respect from those given by KC1. The face (111) gives a reflection at a glancing angle of 10° 27' corresponding to that at 9^0 23' for the corresponding face of KC1. This is not, however, the reflection of the first order, for a smaller peak occurs at about half this angle. The reflections of the first order correspond, in other words, to those given by a face centred cubic lattice, not a simple cubic lattice, since the spacing $d_{(111)}$ is apparently the largest of the three under consideration.

This dissimilarity between KC1 and NaCl suggests that the diffracting centres, which appear to be arranged on a simple cubic lattice in KC1, are not molecules, for if they were there is no reason why the similar structure NaCl should not also give spectra characteristic of a cube lattice. It is found that of the series of similar crystals NaCl, KC1, KBr, K I , it is only KC1 which gives these simple spectra. When

's remembere that the efficiency of the atom in scattering

hts are expressed in terms of the atomic weight of

X-rays must be supposed to depend on the number and arrangement of the electrons in its structure, a simple reason suggests itself for the special behaviour of the KC1 crystal. The potassium and chlorine atoms contain nearly the same number of electrons and act with approximately equal

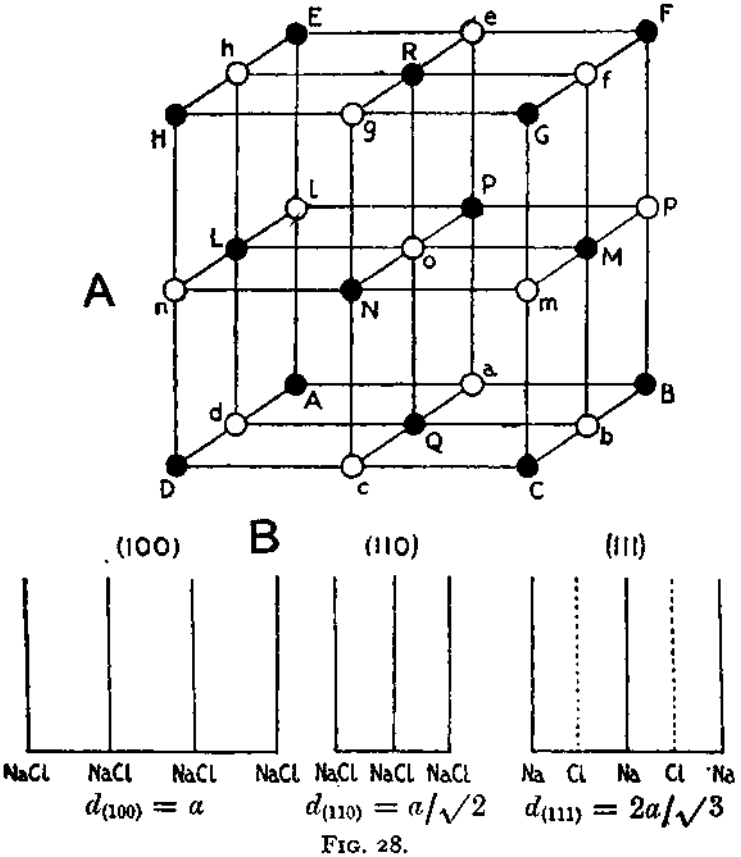


FIG. 28.

efficiency as diffracting centres. In this way we are led to suppose that all these crystals have a structure such as is represented in Fig. 28.

The two kinds of particles represent atoms of metal (K or Na) and halogen (CI, Br, I). Considering the points of one kind alone, the whites for example, it is clear that they lie on a face-centred lattice, such as is hinted at by the spectra of rock salt. If the atoms are identical as regards their

behaviour to X-rays, the structure reduces to a straightforward cubic one.

The arrangement of the atoms in planes is shown diagrammatically by Fig. 28 *B.* The planes (100) contain atoms of both kinds. The constitution of the (100) planes in both crystals is such that they contain metal and halogen atoms. The (no) planes are built up in the same way, but their distance apart is smaller in the ratio 1: *2.* The (III) planes are of a different nature, however. The successive planes contain atoms of the metal alone, and chlorine atoms alone, alternately.

If the X-rays are reflected from the planes (III) in Fig. 28 *B,* the true distance $d_{(111)}$ is that from like plane to like. The angle of the first reflection is given by the equation $=2d_{(III)} \sin 6$. But halfway between the planes containing chlorine atoms are spaced planes containing metal atoms. These reflect waves which are, for the first reflection, just out of step with *(i.e.* in opposite phase to) the waves reflected from the CI planes. Their effect is to tend to destroy the first reflection, and in fact every reflection of the odd order, while they strengthen the reflections of even order. This effect is apparent in the spectrum of (in) NaCl, where the planes containing sodium of atomic weight 23 alternate with the planes containing chlorine of atomic weight 35.5. In the case of KC1 the atomic weights (39 and 35.5) are so close that the spectra of odd order are absolutely cut out. The crystal behaves as if the distance $d_{(111)}$ was that between planes of alternate kinds, and the spacings of the planes (100), (no), and (III) are thus apparently those of a simple cube lattice.

An analogy may be traced between this case and that of a line grating. A line grating gives a series of spectra with monochromatic light, the equation

$$a \sin \theta = n\lambda,$$

determining the positions of the spectra. Here *a* is the distance between line and line of the grating, and *6* the

angle through which the incident rays are diffracted. The angle at which the first spectrum occurs is given by

$$\sin\theta = \frac{\lambda}{a}.$$

Suppose that every odd line of the grating were made a little wider that the even lines, so that it diffracted more light, a spectrum would appear corresponding to the distance *2a* between the widened lines ; its angle would be given by

$$\sin\theta = \frac{\lambda}{2a}.$$

If the widening were small this spectrum would be very faint compared with the others, and it would appear at approximately half the angle of the first bright spectrum. Between the first and second bright spectra would be a faint one corresponding to

$$\sin\theta = \frac{3\lambda}{2a},$$

and so on. The peaks reflected from rock salt (III) are exactly analogous to the alternate bright and faint spectra reflected by such a grating. Parallel to this face the odd and even planes are of a different nature, like wide and narrow lines of the grating.

When the successive planes parallel to a face are identical as regards their action on the X-rays, the reflections diminish regularly in intensity as their order increases. If this regularity is absent it implies that the successive planes are different as regards spacing or constitution.

Having once found the structure of any one crystal, such as sodium chloride, it is possible to determine the absolute dimensions of the space lattice on which it is built up, and so to determine the wave length of the lines in any X-ray spectrum.

The volume of a cubic element, such as LONndQcD in Fig. 28, is equal to $(d_{(100)})^3$. In any given volume of the structure there are an equal number of cubes and cube corners. This can be realised most simply by noting that

each cubic element has eight corners, but that each corner is shared equally between eight cubes, so that there is on the whole a one to one correspondence between corners and cubes. Since one atom is situated at each cube corner, each molecule of NaCl is associated with a volume $2(d_{(100)})^3$ of the structure. In unit volume of the crystal there will be $\frac{1}{2(d_{(100)})^3}$ molecules. If M is the molecular weight of the molecule and m the mass of the hydrogen atom,

$$\frac{M \cdot m}{2(d_{(100)})^3} = \varrho,$$

where ϱ is the density of the crystal.

For sodium chloride

$$M = 58.0,$$

$$m = 1.662 \times 10^{-24},$$

$$\varrho = 2.17,$$

$$(d_{(100)})^3 = \frac{Mm}{2\varrho} = \frac{58.0 \cdot 1.662 \cdot 10^{-24}}{2 \cdot 2.17} = 22.21 \times 10^{-24},$$

$$d_{(100)} = 2.81 \times 10^{-8} \text{ cm.}$$

Since the palladium K_a line is reflected at an angle of $6° 0'$,

$$\lambda = 2 \cdot 2.81 \cdot \sin 6° 0'. \times 10^{-8} \text{ cm.}$$

$$= .587 \times 10^{-8} \text{ cm.}$$

Zincblende, ZnS,* is another binary compound which forms crystals belonging to the cubic system. The spectra of zincblende are shown diagrammatically in Fig. 29.

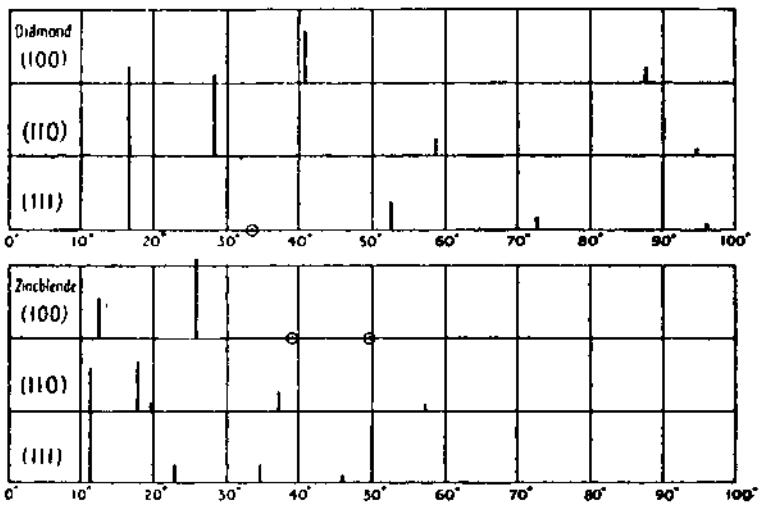
In the case of this crystal the first order spectra have the same relative positions for the three faces as have those of rock salt. The ratio of the sines of the angles approximates closely to the ratio $1: \sqrt{2} : \frac{\sqrt{3}}{2}$. It would appear that it is again the face-centred lattice that is the basis of the structure (Fig. 27 (b)).

* W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc,* A, Vol. 89, pp. 286, 473.

The first order reflection of the palladium K_a line from the face (100) occurs at an angle of 6° 20'.* For this face therefore

$$d_{(100)} = \frac{\lambda}{2 \sin \theta} = 2.78 \times 10^{-8} \text{ cm.}$$

If one molecule of zincblende is associated with each point of the face-centred lattice, we can calculate the spacing



Rh rays. FIG. 29.

$d_{(100)}$ from the known density and molecular weight just as in the case of rock salt. This gives

$$d_{(100)} = \sqrt[3]{\frac{M \cdot m}{2\varrho}} = 2.76 \times 10^{-8} \text{ cm.}$$

in agreement with the spacing given by the reflection. Although there are as many atoms of zinc and sulphur as of sodium and chlorine to a unit cube of each structure, the arrangement of the atoms cannot be the same, as a comparison of the spectra will at once show. Since, firstly, the spectra indicate a face-centred lattice, and secondly, this comparison with rock salt shows that one molecule

* The spectra in the figure were obtained with a rhodium anticathode, and owing to the larger wave length (0.614×10^{-8} cm) appear at slightly greater angles.

is associated with each point of the lattice, it will be assumed that the zinc atoms are on a face-centred cubic lattice. We will then try possible arrangements of the sulphur atoms relatively to the zinc atoms, seeking to explain the observed spectra in this way.

In the zincblende spectra, it is the (110) planes which alone show a normal decrease in the higher orders. These planes have first, second, third order reflections which decrease in intensity in a normal manner. Therefore, the sulphur atoms must lie in the same (110) planes as the zinc atoms. The (100) planes, on the other hand, have a small first spectrum, just as do the (III) planes of rock salt. The sulphur planes must alternate with the zinc planes, and so tend to cut the first spectrum out as compared with the second. If the sulphur atom is to lie in the (110) planes, but halfway between the (100) planes (cf. Fig. 30, *A),* it must be placed at the centre of one of the small cubes, into eight of which the whole cube of that figure is divided.

The structure of rock salt as given in Fig. 28 may be regarded as composed of two intersecting face-centred cubic lattices. The sodium atoms are arranged on one, the chlorine atoms on the other, and the two are relatively placed in such a way as to make up the structure. In this case also the zinc atoms are on one face-centred lattice, the sulphur atoms on another, but these are so placed relatively to each other that the sulphur atoms are at the centres of the small cubes of the zinc lattice. The structure is that shown in Fig. 30.

The structure is such that only four sulphur atoms can be shown in the figure, this being all there are inside the unit cube of the structure. If cubes such as this are placed side by side so as to continue the space lattice, it will be seen that the sulphurs are also on a face-centred lattice, and equal in number the zinc atoms.

In Fig. 30, *B,* the arrangement of the planes parallel to (100), (II0), (III) is shown diagrammatically. The zinc and sulphur atoms lie on the same (110) planes, and the

simple structure of these planes corresponds to the regular set of spectra shown in Fig. 30. The arrangement of the (100) planes is like that of the (111) planes of rock salt (see Fig. 28). It is, again, the case of a grating with the odd

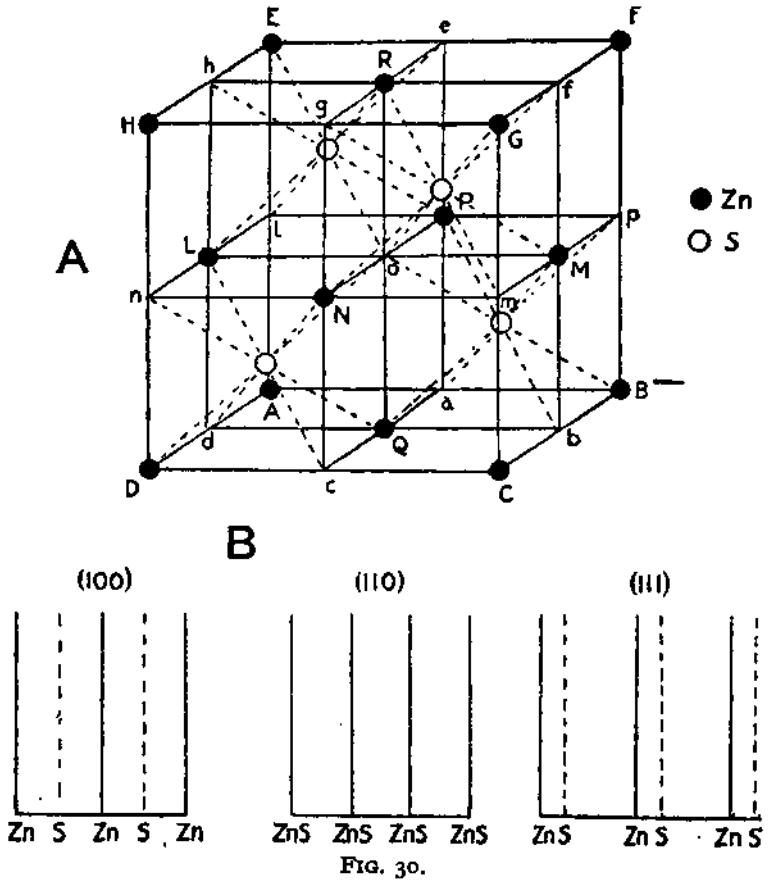


FIG. 30.

lines stronger than the even lines. The first spectrum corresponds to the distance $d_{(111)}$ between the zinc planes, but it is weak compared to the second. The difference between the reflecting power of Zn (65) and S (32) is apparently greater than that between CI (35.5) and Na (23), for the first spectrum of zincblende (100) is stronger comparatively than that of rock salt (111). Otherwise the two cases are similar.

The (111) planes are of a new type, the spacing of the sulphur planes being such that the distance Zn-Zn is four times the distance Zn-S.

It is not hard to see how this will influence the spectra. Although the sulphur planes are between the zinc planes, they slightly increase the resultant intensity of the first order reflection. For the second order reflection, however, the waves from the sulphur planes will be exactly out of phase with the waves from the zinc planes. At this angle the wave train reflected from one zinc plane is two wave lengths behind the train from the next plane, *i.e.* the phase difference of these trains is 4π. The phase difference

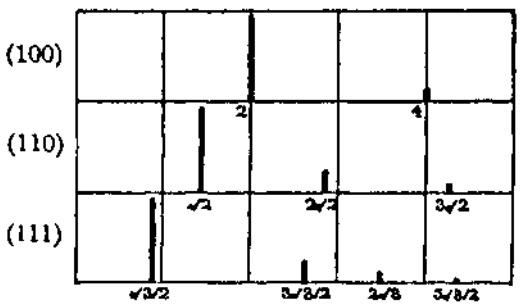


FIG. 31.

between zinc and sulphur is a quarter of this amount, and so the trains are in opposite phase. The second reflection will therefore be weak as compared with the first and third. An inspection of the spectrum actually obtained, Fig. 29, shows that this is so; the third spectrum is if anything stronger than the second, while for a normal set of planes the second spectrum should be twice as strong as the third. This arrangement of zinc and sulphur atoms explains the peculiarities of the spectra reflected from the three principal faces of the crystal.

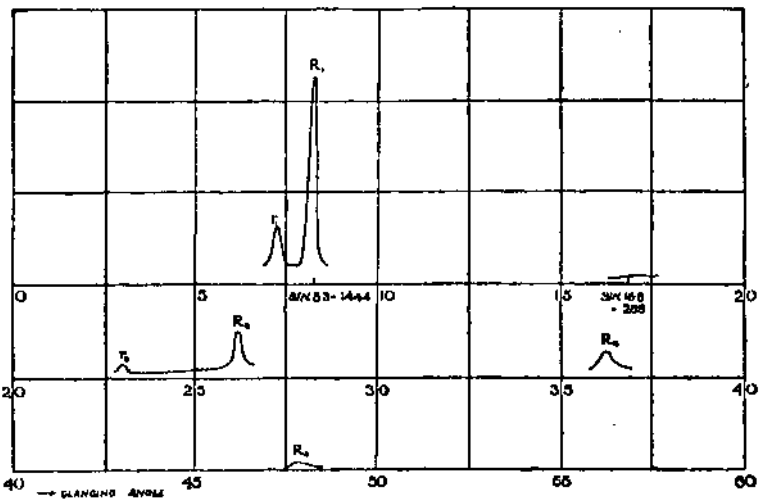
The next crystal considered is a simpler example of the laws governing the X-ray reflection than zincblende. Zincblende has been discussed first here because it shows better the underlying face-centred cube lattice, which is the basis of its structure, and also of the one now to be considered.

Diamond,* one of the forms of carbon, forms crystals belonging to the cubic system. The spectra from faces (100), (110), (111) of diamond are given diagrammatically in Fig. 31, the spectra from the last face being given in detail in Fig. 32.

The first spectra occur at angles whose sines are in the ratio

$$2 : \sqrt{2} : \frac{\sqrt{3}}{2}.$$

This ratio is not characteristic of any space lattice (cf. pp. 88, 89). Moreover, the spectra reflected from the face



Rh **ray.** FIG. 32. Crystal angle.

(111) are peculiar in that no second spectrum can be detected, although the first, third, fourth, and fifth spectra are quite plain. This peculiarity has to be explained by an arrangement of atoms of one kind only. In zinc-blende the second (111) spectrum was small because the sulphur planes divided the distance between the"zinc planes in the ratio 1:3, but the second spectrum was not cut out

* W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc, A,* Vol. 89, p. 277.

† Recently this second spectrum has been detected and measured, although it is very weak indeed compared with the other orders. The carbon atom must be slightly tetrahedral. *Proc. Phys. Soc.* Aug. 1921.

entirely because the sulphur has atomic weight 32, as compared with zinc atomic weight 65. If the planes were to become identical in nature, retaining the same spacing, the second spectrum would entirely disappear. Moreover the

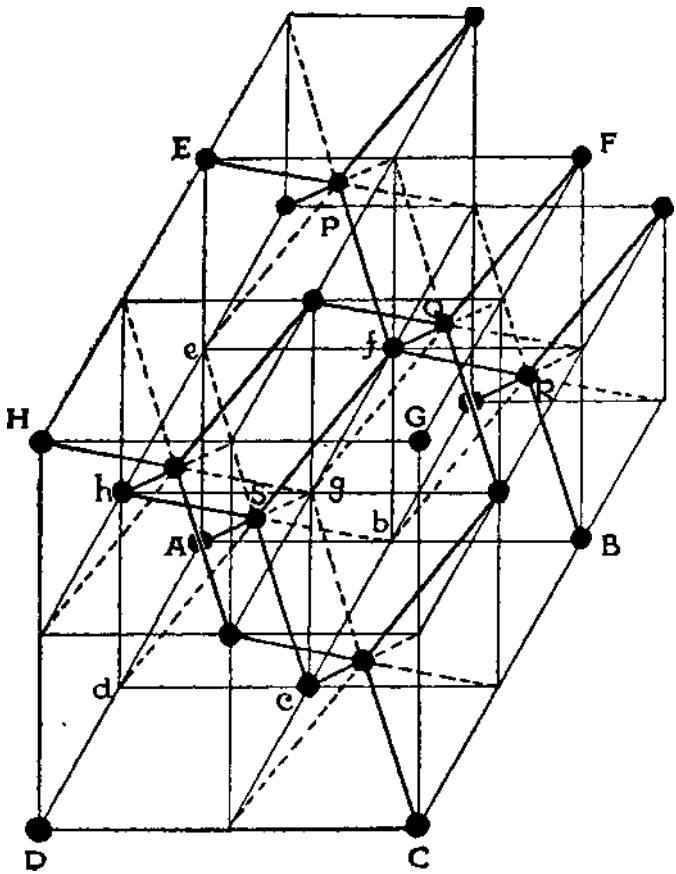
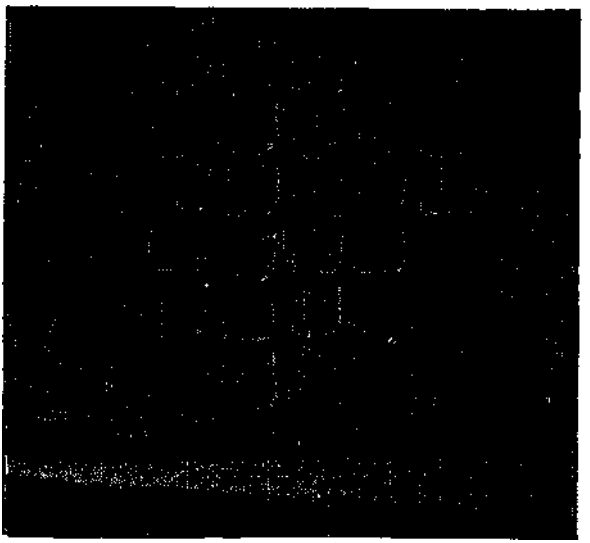


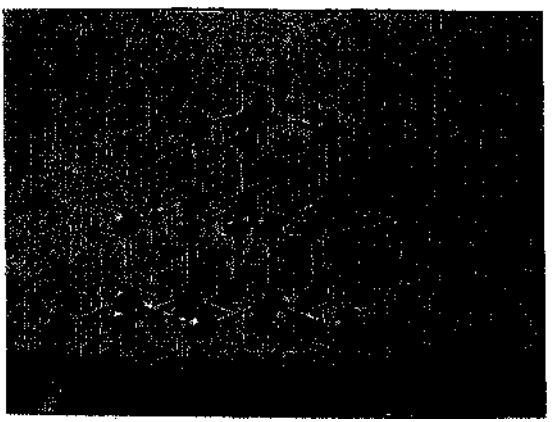
FIG- 33.

first (100) spectrum would disappear since' all the (100) planes would also be identical in their nature. The spectra would then become exactly like those of diamond

We are thus led to substitute carbon atoms for those both of zinc and sulphur in the zincblende structure, so as to get the structure shown in Fig. *33.* The arrangements of planes parallel to the faces (zoo), (100), (111) can be got from the



MODEL OF DIAMOND.
Horizontal and vertical planes perpendicular **to the paper** are **(no)** planes.



MODEL OF DIAMOND.
Horizontal planes perpendicular to the paper are (111) planes.

Facing page 100.

planes of zincblende by considering Zn and S equivalent. The planes parallel to the face (100) are closer together, and therefore throw the first spectrum farther out than either of the other sets of planes.

The planes (no) are $\sqrt{2}$ times, the (111) planes $\frac{4}{\sqrt{3}}$ times, as far apart as the planes (100). The arrangement satisfactorily explains both the positions of the first spectrum from each face, and the fact that the face (111) has no second spectrum.

This arrangement must satisfy a further test if it is correct. The spacing of the planes calculated from the atomic weight and density of the crystal must agree with those given by the spectra.

In the structure one carbon atom is associated with each unit cube, since two carbon atoms replace the molecule of zinc sulphide. The side of the unit cube is given by

$$a = \frac{11.92m}{\varrho} = 1.78 \times 10^{-8} \text{ cm.}$$

The K_a line of palladium is reflected at an angle of $19^0\ 0'$, whence

$$d_{(100)} = .89 \times 10^{-8} \text{ cm.}$$

that is, $d_{(100)}$ is equal to one half the side of the unit cube, as is to be expected from the structure which has been assigned to the crystal.

In the structure of the diamond as given in Fig. 33, the carbon atoms are arranged on two interpenetrating face-centred lattices. Each carbon atom of lattice *B* is surrounded by four carbon atoms belonging to lattice *A*, arranged tetrahedron-wise, and *vice versa*, just as each sulphur is surrounded by four zincs in Fig. 30.* This suggests a more simple way of considering the, structure ; we can draw links from atom to atom in such a way that

* A convenient way of getting the structure is to take a face-centred cubic lattice *(A)* and imagine it translated parallel to itself along a cube diagonal one-quarter of the length of the diagonal. The new position is that of the lattice *B*, and the points of both lattices *(A)* and *(B)* taken together give the positions of the carbon atoms.

each carbon atom is linked up to four carbon atoms surrounding it. The arrangement of cubes shown in Fig. 33 disappears, and we obtain the structure of which a model is shown in Plate IV. In these photographs the balls representing the atoms are built up into a tetrahedron, which rests on one of the faces (111). The arrangement of the planes parallel to this face in pairs, which possess the spacing of Fig- 33, can be traced very well in the photograph.

There remains one simple structure which is very similar to those considered above ; it is that of fluorspar, CaF_2.* The spectra are sufficiently described by saying that, they are identical with those of diamond. The structure which explains these spectra is quite simple. The calcium atoms are arranged in a face-centred cubic lattice, while the fluorines occupy the centres of the small cubes, as do the sulphur atoms in zincblende (Fig. 30). In this case, however, there are twice as many fluorine atoms as calcium atoms; we must therefore place fluorine atoms at the centres of all the small cubes, instead of choosing only one-half of the cubes, as in the zincblende structure. The arrangement of the principal planes is then given by Fig. 34. This arrangement gives the right value for the molecular volume of fluorspar, as in the case of the other crystals.

The spectra of fluor have an especial interest for the following reason. It will be noticed that in this case, as in that of diamond, the first (100) spectrum and second (111) spectrum are absolutely extinguished. In diamond the (100) planes belonging to lattice *A* (see p. 97) are interposed with planes belonging to lattice *B*, of an identical nature, and the first spectrum naturally disappears. In the case of fluorspar the planes containing calcium atoms are interposed with planes containing twice as many fluorine atoms, and the observed disappearance of the first spectrum shows that the calcium planes and fluorine planes are nearly equivalent as regards reflecting power. It has been supposed that the potassium and chlorine atoms have nearly equal

* *Proc. Roy. Soc,* A, Vol. 89, p. 474.

diffracting powers, because they contain approximately the same number of electrons. It would appear that one calcium atom, containing twenty electrons, balances two fluorine atoms, each with nine electrons, for the same reason. In the next chapter further instances will be given which lend support to this hypothesis. It is at any rate approximately true that, for the small glancing angles which come into

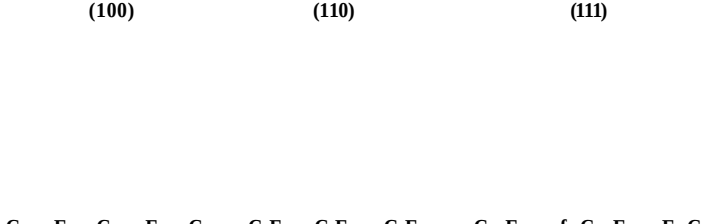


FIG. 34.

consideration here, the atom scatters a wave the amplitude of which is proportional to the number of electrons in its structure.

The structures assigned to these crystals not only explain the spectra in each case, but also explain the relations between the spacings for the different crystals. Whatever the class of symmetry to which a crystal belongs, rays of known wave length can be used to measure the absolute dimensions of the elementary lattice cell, and so to find the number of molecules associated with each cell. This being determined, various arrangements of the atoms can be tried in order to explain the relative positions and intensities of the reflections, and in this way the structure of the crystal may be determined.

CHAPTER IX

THE ANALYSIS OF CRYSTAL STRUCTURE. PT. II.

IT has been seen that the intensities of the spectra given by the faces of crystals may be explained by assuming that the contribution of any atom to the reflected wave is proportional to the number of electrons it contains, or alternatively, to its atomic number. A more complete investigation of the intensities shows that this law, while holding with some accuracy for the reflections of low order where the angle through which the rays are scattered is small, ceases to be even approximately true when the reflections of higher order are considered. The relations between the intensities of spectra, which are of considerable complexity, will be referred to at greater length in Chapter XIII. Nevertheless, this approximate relation is of considerable assistance in unravelling the structure of more complex crystals than those already considered. The intensities of the spectra depend both on the position of the atoms in the crystal and on their relative contributions in scattering the X-rays. In testing various theoretical arrangements, it is found that the intensities vary very greatly for quite small changes in the positions of the atoms. Without having a complete knowledge of the effect of each atom, it is therefore possible to place the atoms with considerable accuracy.

The greater complexity of the crystal structures which will now be considered is due to their possessing fewer elements of symmetry than such crystals as fluor or zincblende. In these latter crystals the atoms are situated at certain definite points of the space lattice, at the corners

or centres of the cubic cells. They cannot be displaced from these precise positions without a degradation of the symmetry of the crystal. In arranging the atoms in various ways in order to explain the spectra, one has to choose between certain definite alternatives, and this simplifies the analysis. In a more complex crystal, a typical atom of one of the components may lie at any point along some axis, or in some plane, of the lattice. As long as all the other atoms occupy corresponding positions, the arrangement will be in accordance with the crystal symmetry. Instead of having to choose between definite alternatives, it is necessary to fix the value of some parameter or parameters which determine the position of the typical atom, and which may have any values over wide limits. The greater the number of these indeterminate parameters, the more difficult it is to analyse the structure.

The series of carbonates $MgC0_3$ (Magnesite), $CaC0_3$ (Calcite or Iceland Spar), $MnC0_3$ (Rhodochrosite), $FeC0_3$ (Chalybite), $ZnC0_3$ (Calamine) occur in nature and form one of the best known series of isomorphous minerals. They belong to a rhombohedral class of the hexagonal system. The crystal in each case has an axis of threefold symmetry, with three symmetry planes intersecting in it, and three axes of twofold symmetry at right angles to it. A rhombohedron of calcite is shown in Fig. 35, and it serves to illustrate the arrangement of these axes and planes of symmetry. The edges of the rhomb are all equal; so are the angles *AOB, BOC, CO A.* The axes of symmetry are marked in the figure, *00'* being the trigonal axis. Digonal axes pass through the middle points of opposite edges, such as *BD* and *EA.* The planes of symmetry pass through *00'* and the edges *OA, OB, OC* respectively.

The crystals cleave parallel to the faces of these rhombs, in a very perfect manner. We may take cells of this shape as being the unit cells of the structure, and suppose the whole crystal built up by stacking together such unit cells. Three edges of the rhomb which meet in the axis of threefold

symmetry, such as *OA, OB, OC,* are taken as the axes of the crystal. They are of equal length, in accordance with the threefold symmetry, and they make the same angle with each other. For calcite this angle is 101° 54'; and it is withiti two degrees of this value for all the crystals of the series. When *OA, OB, OC* are taken as axes, the face *OBC*

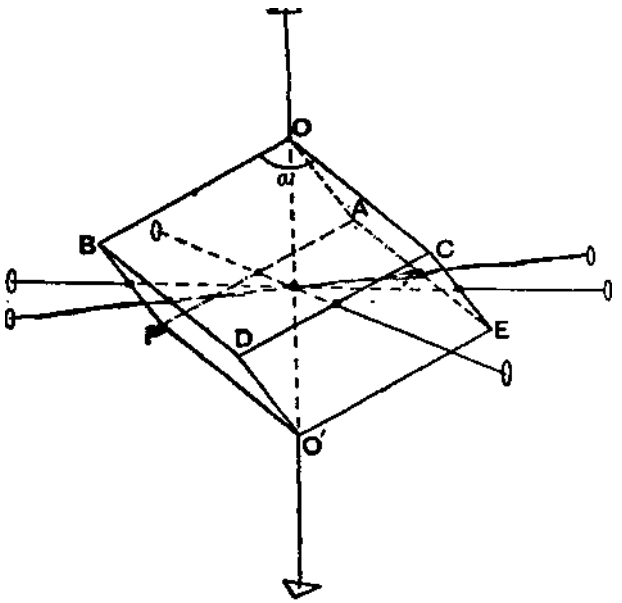


FIG. 35.

becomes the face (100) of the crystal. The face *ABC* has indices (111). The angle *BOC* defines the form of the rhomb.

The angle of reflection of the principal palladium ray from a rhomb face is found to be 5° 21', and, substituting in the usual formula, we find that $d_{(100)}$=3.03 xio~^{8} cm. From the form of the rhomb, the volume of the elementary cell, in which $d_{(loo)}$ is the perpendicular distance between any pair of opposite faces, can be calculated. It is 1.096 x $d_{(loo)}^{3}$. The density of calcite being 2.71, the mass contained in this elementary cell is

$$2.71 \times 1.096 \times (3.03 \times 10^{-8})^3 = 8.24 \times 10^{-23} \text{ grams.}$$

Now the mass of a molecule of $CaCO_3$ is

$$99.38 \times 1.662 \times 10^{-24} = 16.5 \times 10^{-23} \text{ grams.}$$

This shows that one molecule of $CaCO_3$ is associated with two of the elementary cells. It was found in the case of rock salt that each molecule of NaCl was associated with two of the cubic cells. The lattice on which the $CaCO_3$ molecules are arranged may best be visualized by comparing it to the NaCl structure in Fig. 28. If that structure is supposed to be compressed in a direction parallel to one of the trigonal axes such as *EC,* its dimensions perpendicular to that axis remaining the same, it will become a rhomb similar to the rhomb of calcite. The angles *AEH, HEF, AEF* meeting at *E* are to be supposed to be increased by the compression, until from being right angles they become angles of $101^0\ 54'$. The whole structure now has the form of Fig. 36, *A.* The calcium atoms are situated at one half the points of the lattice, represented by the black dots, and the carbon and oxygen atoms form a group about the white dots (or *vice versa).*

Assuming this to represent the marshalling of the $CaCO_3$ molecules, we can calculate the spacings for the various planes and compare with experiments. The following table gives the comparison:

Plane.	Calculated Spacing.	Calculated Angle.	Observed Angle.
100	$d_{(100)} = 3.04.$	5° 26'	5° 21'
110	$d_{(100)} = 2.48.$	6° 40'	6° 36'
no	$d_{(110)} = 1.92.$	8° 38'	8° 42'
111	$d_{(111)} = 2.79.$	5° 55'	5° 46'
211	$d_{(211)} = 1.43.$	11° 35'	11° 39'

Since the calculated angles agree with those observed for the first order reflection in all cases, it is evident that a right choice of lattice has been made.

The peculiar features of the spectra may now be employed to determine the arrangement of the atoms of calcium, carbon, and oxygen associated with each point of the lattice.

The structure which is arrived at is shown in Fig. 36. It is not necessary to enter into the analysis here, but it should be noticed that the structure contains one of the indeterminate parameters referred to above. The calcium and carbon atoms alone are shown in Fig. 36, *A*, for the sake of

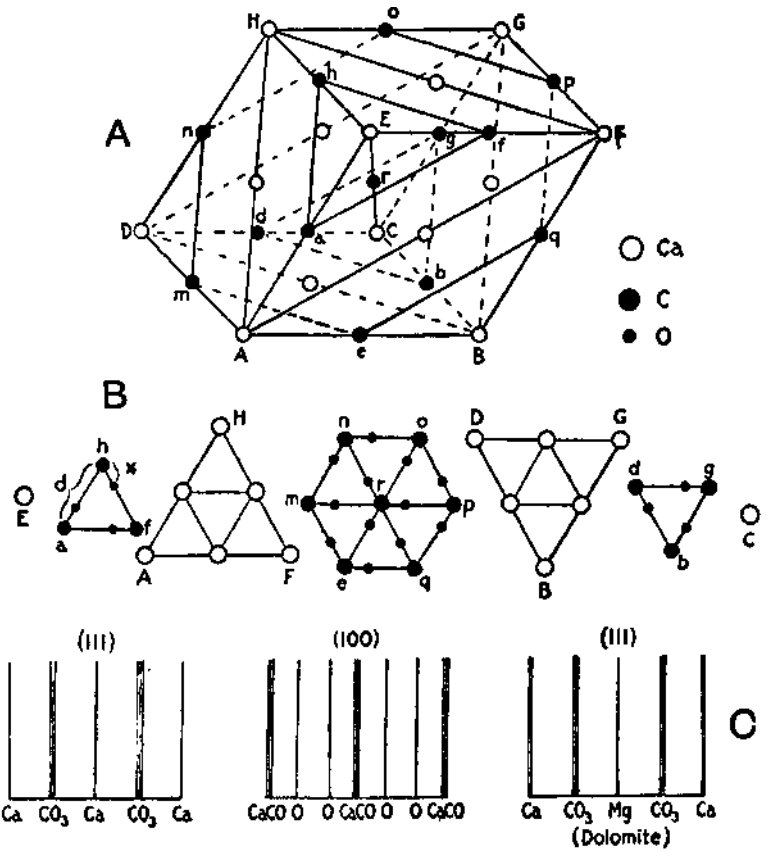


FIG. 36.

simplicity in the representation. They occupy positions of symmetry which are determinate, corresponding in fact to the position of the sodium and chlorine atoms in sodium chloride. The oxygen atoms lie on lines joining the carbon atoms in the (111) planes. In order to show their arrangements, the structure is given as a series of layers perpendicular to the trigonal axis in Fig. 36, *B*. The way in which

these layers are taken from the unit rhomb is sufficiently explained by the lettering of the figures. Their precise position is determined by the ratio *x/d* (Fig. 36, *B),* which may have any value.

Fig- 36, *C,* shows the arrangement of the (in) planes perpendicular to the trigonal axis. The planes are evenly spaced and contain alternately calcium atoms and CO_3 groups.

The structure of each crystal of the calcite series is similar to that of calcite itself; and in particular they all have the same arrangement of planes perpendicular to the trigonal axis. Moreover, there is another crystal which, though of very different composition, imitates the calcite series so closely in its crystalline shape and molecular volume that it has always been supposed to be built up in the same way. This substance is sodium nitrate, $NaNO_3$. An investigation of its reflection spectra shows that this similarity is indeed the result of similarity of composition. As still another crystal of the same structure, we have dolomite, $CaMg(CO_3)_2$. Its similarity to calcite is so great that, although it is of a more complex composition, it is justifiable to treat it as a simple carbonate, the atomic weight of the metal being taken to be the mean of those of calcium and magnesium.

The results of the examination of this series of crystals is shown in Fig. 37, the reflecting surface being in each case the (111) plane.

The spacing $\mathbf{d}_{(111)}$ is, throughout, the distance between two CO_3 planes as in Fig. 36, C. Halfway between these, planes are the metal planes. The effect of the latter is, as in previous similar cases, to decrease the first order reflection and increase that of the second order. If the njetal planes were of negligible effect compared with the CO_3 planes, the first, second, and third spectra would diminish regularly in intensity. If the metal planes had an effect equal to that of the CO_3 planes, we would have to consider the distance $\mathbf{d}_{(111)}$ as being halved. The first spectrum would be entirely

destroyed, for the waves from the CO_3 and metal planes would be equal in amplitude and opposite in phase. If the effect of the metal planes is anywhere between the two extremes, the effect will be that the ratio of the second spectrum to the first is larger than the normal.

In the series of spectra of Fig. 37, the effect of the progressive change of the atomic weight of the metal throughout this series of carbonates is seen. The gradual disappearance

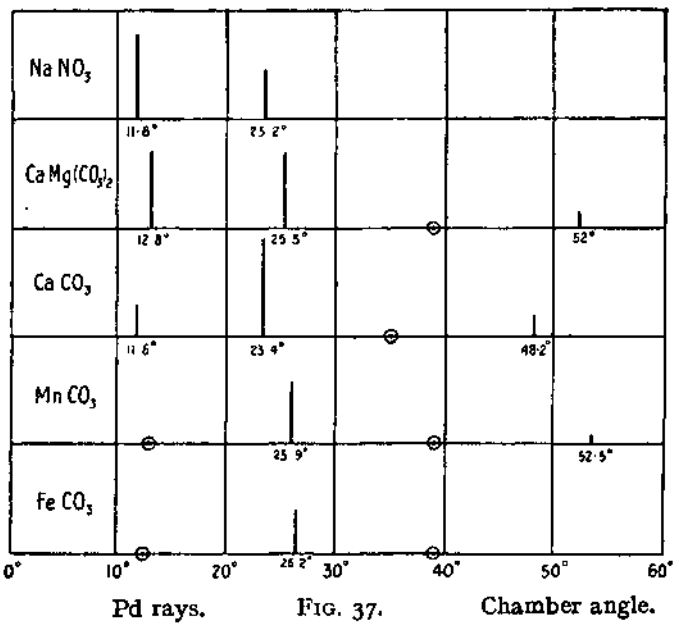


FIG. 37.

of the first spectrum, as the alternate planes approximate in their reflecting effect, can be observed. In $NaNO_3$, the Na planes have little effect compared with the NO_3 planes, and the first spectrum is greater than the second. In $FeC0_3$, the Fe planes must be equal to the CO_3 planes in reflecting power, for the first spectrum is extinguished.

The alternate planes become equal in reflecting power when their masses per unit area are equal. It would be more precise to say that they become equal when the sum of the atomic numbers in equa[1] areas are equal, since the equality must be ascribed to a correspondence of the number of

electrons diffracting the X-rays. The ratios of these sums are:

$$\text{Na} : \text{NO}_3 = 11 : 31,$$

$$\frac{\text{Ca} + \text{Mg}}{2} : \text{CO}_3 = 16 : 30,$$

$$\text{Ca} : \text{CO}_3 = 20 : 30,$$

$$\text{Mn} : \text{CO}_3 = 25 : 30,$$

$$\text{Fe} : \text{CO}_3 = 26 : 30.$$

If, as wouid appear probable, the metals and acid radicles exist in the crystal as ions, the metal will have lost one or more electrons to the radicle, the number lost corresponding to its valency, and the ratio for $NaNO_3$ will be 10 : 32, that for $CaCO_3$ 18 : 32, and so forth.

This signifies that the amplitude of the diffracted wave, when an X-ray passes over an atom, is approximately proportional to the number of electrons contained in the atom, for small angles of scattering. In the case of $FeCO_3$, for example, each Fe atom must balance a CO_3 group. Since the effects of carbon and oxygen must be approximately the same, each must be one quarter as effective as an iron atom in scattering. In fluor, we have seen that the effect of a fluorine atom is half that of calcium. In these cases the law can be directly tested.

When X-rays pass over an atom, the scattering must be ascribed to the electrons, since the enormously greater mass of nucleus will prevent its being set in oscillation by the waves. Now Barkla has shown that the scattered *energy*, at any rate for atoms of low atomic weight, is proportional to the mass of matter present. Since the atomic number, or number of electrons in the atom, is one half the atomic weight for the light elements, this means that the intensity of radiation scattered in all directions by an atom is proportional to its atomic number. As against this, the results from crystals point to the amplitude of the scattered radiation being proportional to the atomic number *N*, and

therefore the intensity being proportional to N^2, in contradiction to Barkla's result.

This contradiction is only apparent, and due to the fact that we are examining the radiation scattered in a direction which makes a small angle with the primary beam. The electrons are arranged throughout a volume of the same order as the accepted atomic volume, and act independently in scattering the X-rays. For small angles of scattering the diffracted waves from the greater proportion of the electrons will be in the same phase, and the total amplitude will be nearly N times that due to a single electron. At greater angles of scattering the wavelets diffracted by the separate electrons give less support to each other, and the effect is greatly reduced.

This will perhaps make it clear how it is possible for the total amount of radiation scattered in all directions by the atom to be N times that scattered by a single electron, whereas at small angles of scattering it is the amplitude of the scattered wave which is proportional to the atomic number N.

Let us suppose that in a crystal there are parallel reflecting planes of two kinds, A and B, whose relative reflecting powers are N_1 and n_2. We wish to find the influence of the spacing of the planes on the form of the X-ray spectra. Let the distance between successive A planes be d, that between an A and a B plane, x.

If x is made zero, the successive planes become identical in character. Such an arrangement of planes gives, as we have seen, a series of spectra which diminish regularly in intensity. Their intensities may be called

$$I_1, \quad I_2, \quad I_3, \quad I_4, \quad \text{etc.}$$

Under these circumstances the planes A and B reflect waves which are in the same phase. Taking a single plane AB, the amplitude of the reflected wave is the sum of the amplitudes due to A and B independently. (See Fig. 38 (upper part).)

Since the amplitude is proportional to the reflecting power of the plane, the intensity is proportional to

$$(N_1 + N_2)^2.$$

When x is not zero, the waves from the A planes and those from the B planes are not in phase with each other.

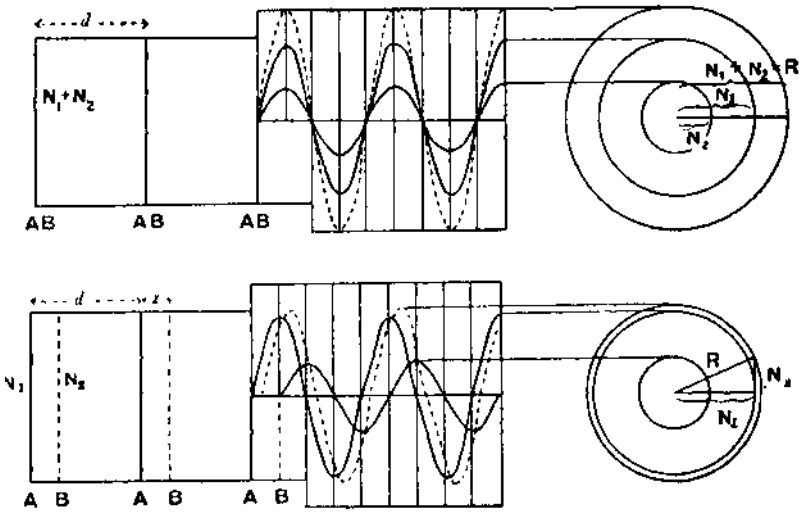


FIG. 38.

Each pair of planes sends off two wave trains of the same length, but differing in phase and amplitude (Fig. 38 (lower part)). The phase difference of the two sets of waves is given by

$$\frac{\theta}{2\pi} = \frac{x}{d} \text{ for the first spectrum}$$

$$= \frac{2x}{d} \text{ for the second spectrum}$$

$$= \frac{3x}{d} \text{ for the third spectrum,}$$

and so forth. The amplitudes are proportional to N_x and N_2. The amplitude of the resultant wave is proportional to R, where R is the resultant of two vectors N_1 and N_2, making an angle θ with each other, so that

$$R^2 = N_1^2 + N_2^2 + 2N_1N_2 \cos\theta.$$

The energy of the reflected wave train is proportional to the square of the amplitude. When the planes are coincident this energy is proportional to $(N_1+N_2)^2$. When they are not it is proportional to $N_1^2 + N_2^2 + 2N_1N_2 \cos 0$.

Comparing then the intensities of the reflections for the two cases:

(1) when $x = 0$ the reflections have intensities

$$I_1,\ I_2,\ I_3,\ I_4,\ I_5,$$

(2) when $x \pm 0$ they have intensities I_1', I_2' I_3', I_4', I_5' where

$$I_1' = I_1 \frac{N_1^2 + N_2^2 + 2N_1N_2 \cos \frac{2\pi x}{d}}{(N_1+N_2)^2},$$

$$I_2' = I_2 \frac{N_1^2 + N_2^2 + 2N_1N_2 \cos \frac{4\pi x}{d}}{(N_1+N_2)^2},$$

and so on.

As an example of the manner in which it is possible to account, at any rate approximately, for the observed variations from a normal decrease of spectra with increasing order in the case of reflection by a complex series of planes, let us take the case of zincblende (100). Here the planes containing zinc and sulphur atoms are equally spaced,

$$N_1 = 30, \quad N_2 = 16, \quad \frac{x}{d} = .50,$$

$$\frac{I_1'}{I_1} = \left(\frac{30-16}{30+16}\right)^2 = .093,$$

$$\frac{I_2'}{I_2} = 1.$$

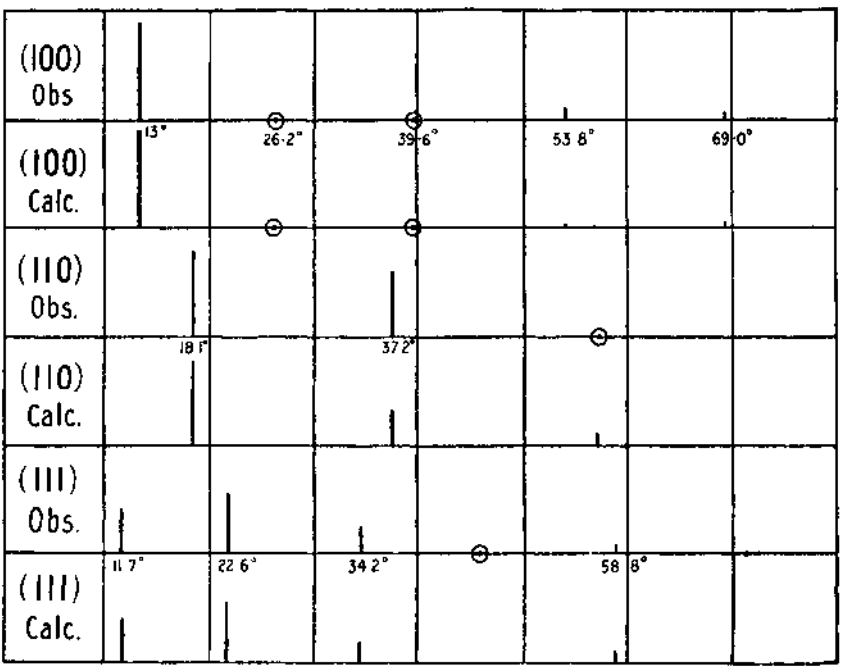
The experimental ratio of first to second order reflection is 52 : 100, the first order being abnormally small. If the zinc and sulphur atoms had been in the same planes, our calculations show that the ratio would have been

$$\frac{52}{.093} : 100 = 100 : 18,$$

this being about the normal ratio of first and second order spectra.

Iron pyrites, another cubic crystal, provides a good instance of the way in which this approximate analysis may be made to determine with considerable accuracy the crystal structure, and as the symmetry of its structure is also of interest it will be described in some detail.

The spectra of iron pyrites are given in Fig. 39. It will be seen that they are a more complicated set of spectra



Rh rays. FIG. 39. Chamber angle.

than any as yet examined. The planes parallel to all three types of faces have a complex arrangement, as shown by the peculiarities of their respective spectra. In no case is there a regular succession of spectra diminishing in intensity towards the higher orders.

The first spectra are in each case very plainly marked. They occur at angles 13^0, 18.1^0, $n.7^0$ (rhodium bulb), and the sines of the glancing angles have the ratio

$$1 : \sqrt{2} : \frac{\sqrt{3}}{2},$$

which is characteristic of the face-centred cubic lattice. This lattice being chosen as characteristic of the crystal structure, calculation shows that one molecule of FeS_2 is associated with each point of the lattice.

Therefore when marshalling the atoms into their positions in the crystal, one iron atom and two sulphur atoms must be associated with each point. The most simple way in which this can be done corresponds to the structure of fluor-spar (see p. 102). The iron atoms would then lie on a face-centred latttice, while the sulphur atoms would occupy the centres of all the small cubes of the figure.* In all the cubic structures so far dealt with, it is at these cube centres and corners that we have found the atoms to be placed. If we limit ourselves to these positions, and wish to build up a structure with one molecule of FeS_2 to each point of a face-centred lattice, this particular arrangement characteristic of fluor-spar is the only way in which it can be done.

Such an arrangement will not explain the observed spectra. Sulphur is approximately of half the atomic weight of iron, as fluorine is of calcium, and therefore we should expect the spectra typical of each face to be more or less the same for the two crystals. This is far from being the case. The (100) spectra, for instance, have a strong first and no second spectra in iron pyrites, no first and a strong second in fluor-spar.

The sulphur and iron atoms in FeS_2 cannot be in these very symmetrical positions, viz. at cube corners and centres. Some of the elements of symmetry must be sacrificed in order to explain the spectra observed.

In Fig. 40 *(a)* represents a small cube of the fluor-spar structure of p. 102. It has a fluorine atom at its centre and calcium atoms at four of its corners.

The four diagonals which are drawn intersecting in the centre of the cube are axes of threefold symmetry of the whole structure, and are, of course, continuous through a row of cubes. Four such axes pass through each corner of the cube, of which only one appears in the figure.

* Compare Fig. 30, where *four* of the centres are occupied.

If the atom at the centre of the cube is to be displaced from its position, it is impossible to retain the four axes of symmetry passing through it. One at most can be retained, the atom sliding along a diagonal as in Fig. 40 *(b)*. If it left the axis every trigonal axis would be destroyed and the crystal would be no longer cubic. In pyrites the displaced atom is the sulphur atom, the iron atoms being at the corners. Each sulphur atom has only one trigonal axis passing through it, while the fluorine had four. Similarly, each iron atom lies on only one trigonal axis.

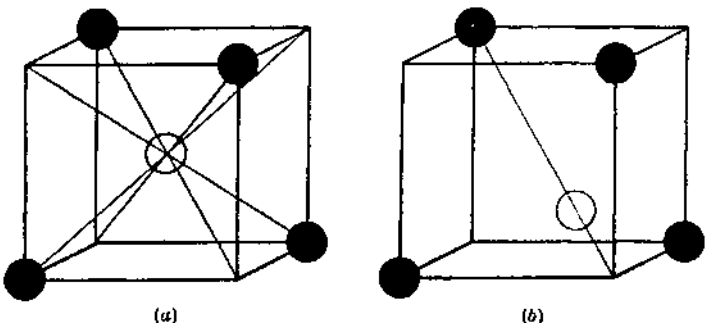


FIG. 40.

In Fig. 40 *(b)*, one axis going through one of the atoms is shown ; the axes which pass through the other three iron atoms lie in neighbouring cubes. This arrangement, which is rather difficult to visualise, may be made more clear by Fig. 41, which shows eight of the cubes stacked together in two sets of four, the sets being separated so as to make the construction more obvious. In each cube one diagonal is drawn, and none of these diagonals intersect each other. Each diagonal making a trigonal axis is continued in both directions and is common to a whole string of cubes.

We may think of the sulphur atom as initially in a symmetrical position at the cube centre. It lies on one of these chosen diagonals, the diagonal having an iron atom at one end and an empty corner at the other. To arrive at the actual crystal structure the sulphur atoms are now displaced by equal amounts along the diagonals, and it remains to be

found by how much. So long as the typical sulphur atom lies on the chosen diagonal symmetry alone gives no criterion as to its precise position. This must be found by *quantitative* measurements of the strengths of the spectra. Placing the sulphur atom at different points along the diagonal, it is possible to calculate theoretically the relative intensities of the spectra, in the way employed above in the case of rock salt and zincblende. These theoretical values are then

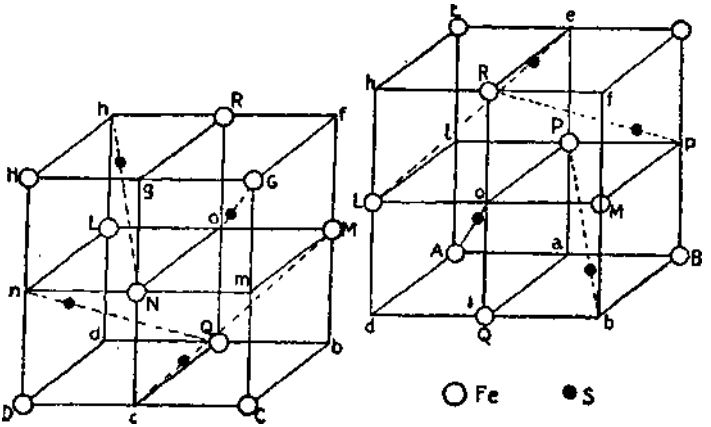


FIG. 41.

compared with the actual spectra obtained, and it appears that there is only one position for the sulphur atoms which explains the facts.

A first approximation to the position of the sulphur atoms can be got from the (100) spectra. The first spectrum is large, the second and third are too small to detect, and the fourth and fifth easily measurable. The iron atoms lie on (100) planes whose distance apart is that of two opposite sides of the cube in Fig. 40 (6), and the sulphur atoms lie between them. If the distance between sulphur planes and iron planes were $\mathbf{d}_{(100)}/4$, the sulphur planes would tend to destroy the second spectrum (cf. diamond). If this distance were $\mathbf{d}_{(100)}/6$, it would tend to destroy the third spectrum. Since it is actually found that both have become too small to observe, the distance must be about $\mathbf{d}_{(100)}/5$.

In order that it may have this value, the sulphur atom must be displaced along the diagonal until it divides it in the ratio 1: 4. As far as these planes go, the displacement may take place either towards or away from the iron atom along the diagonal without altering the spectra, but consideration of the spectra of the (111) planes shows that the displacement takes place towards the empty corner and away from the iron atom, as in Fig. 40 *(b).*

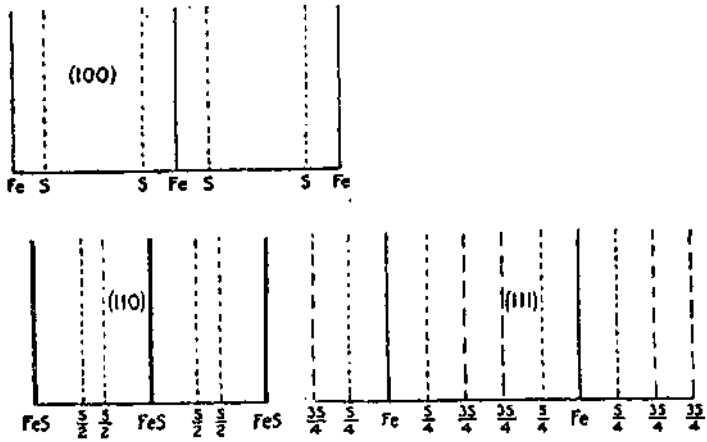


FIG. 42.

Let us sum up the whole structure, now that this displacement has been approximately determined. The iron atoms are arranged on a face-centred cubic lattice. A series of non-intersecting threefold axes are then chosen, one passing through each iron atom, so that each small cube of Fig. 41 has a single diagonal which is a threefold axis. Each cube contains one sulphur atom, which lies on the diagonal near the empty cube corner and divides the diagonal in the ratio 1: 4. The symmetry of this structure is still that of the cubic class ; it will be discussed in the next chapter.

The planes (100), (110), (111) are arranged as in Fig. 42. These planes are of a much more complicated kind than the simple *AB, AB* type arrangement hitherto considered.

The intensities of the spectra are calculated, however, in exactly the same way, except that we must now find the resultant of several vectors instead of that of two only. As an instance, let us take the planes (100), whose arrangement is of a simple type. Each plane containing the iron atoms lies between a pair of planes containing sulphur atoms. The quantity x/d for these planes is equal to 1/5, which means that the wave trains from the pair of sulphur planes differ in phase from that from an iron plane by $2\Pi/5$ for the first spectrum, $4\pi/5$ for its second, $6\pi/5$ for the third, and so forth.

We have therefore

$$I_1' = \frac{\left(26 + 32\cos\frac{2\pi}{5}\right)^2}{(26+32)^2} = 0.38,$$

$$\frac{I_2'}{I_2} = \frac{\left(26 + 32\cos\frac{4\pi}{5}\right)^2}{(26+32)^2} = 0.00,$$

$$\frac{I_3'}{I_3} = \text{etc.} = 0.00,$$

$$\frac{I_4'}{I_4} = \text{etc.} = 0.38,$$

$$\frac{I_5'}{I_5} = \text{etc.} = 1.00.$$

If the sulphur atoms are in this position, we should therefore expect the first and fourth spectra to be present in about their normal ratio, the second and third spectra to be absent, and the fifth spectrum (which is in general very small) to be enhanced. This is in general agreement with the experimental data.

Similar calculations show that for the (no) planes the arrangement of atoms we are testing gives an enhanced second order spectrum, and that for the (111) planes the first and fourth spectra should be small and the fifth enhanced. In both cases this agrees with observation.

The higher the order of the spectrum, the more sensitive the ratio $\frac{I'}{I}$ to small changes in the spacing of the planes. The mere presence or absence of some reflection of high order may often be used to limit the value of the unknown parameter to a very small range.

We have taken the ratio of the distance x of the sulphur atom from a cube corner to be one-fifth of the cube diagonal d. Ewald, by a very careful examination of the Laue diagram given by FeS_2, comes to the conclusion that xfd is equal to .226 instead of .20 as has been assumed here. This will illustrate how accurately the diffraction effects may be used to determine the structure.

The intensities of reflection which have been cited as examples in this chapter have been measured by a method which can only give aproximate results. They represent the maximum effect observed in the electroscope when the crystal is set in each case so as to give the most powerful reflected beam. The errors introduced in this way, and the means which may be employed to eliminate them, will be discussed in the chapter on ' Intensity of Reflection.' The complete investigation of a crystal by accurate methods is laborious, and has only been carried out in a few cases, and for this reason the approximate method has been described in some detail as the crystal structures so worked out are of interest.

CHAPTER X

ANALYSIS BY THE METHOD OF THE POWDERED CRYSTAL

IN order to obtain a diffraction pattern by Laue's method, or to analyse crystal structure by means of the X-ray spectrometer, it is necessary, as has been explained already, that the crystal should be at least a few milligrams in weight, and should be reasonably free from twinning or distortion. The number of crystals which can be examined by these methods is therefore limited.

The powerful method of analysis which has been developed by Debye and Scherrer,* and independently by Hull,* overcomes these limitations, and can be employed to analyse the structure of any crystalline substance. The majority of substances, especially the elements and compounds of simple chemical composition, are difficult to obtain as large crystals, while on the other hand these simple crystalline forms are of the greatest interest, as they lend themselves more readily to an analysis of the inter-atomic forces which determine the crystal structure. The method has, therefore, opened up a new field of the greatest interest and importance.

The method consists in sending a fine beam of monochromatic X-rays through a mass of finely powdered crystalline matter, or of small crystals, the particles of which are arranged at random so that their axes are oriented in all directions. The substance under examination is irradiated

*** P. Debye and P. Scherrer, *Kgl. Ges. d. Wiss.*, Gottingen, Dec. 1915. *Phys. Zeit.* 17. 277, July, 1916.**

† A. W. Hull, *Phys. Rev.* 10, p. 661, Dec. 1917.

by homogeneous X-rays of wave length λ. The rays are reflected in the first order by a set of planes with spacing ' d' when they are incident on them at a glancing angle Θ given by $\sin\theta = \lambda/2d$. Amongst the crystalline particles irradiated by the X-rays, a certain number will be so oriented that the relation for reflection is satisfied, and reflection takes place. The reflected X-ray beam makes an angle of 2Θ with the incident beam. Since the particles may be oriented in any direction, all the beams reflected at this angle will lie on a cone, with the incident beam as axis, whose semi-vertical angle is 20.

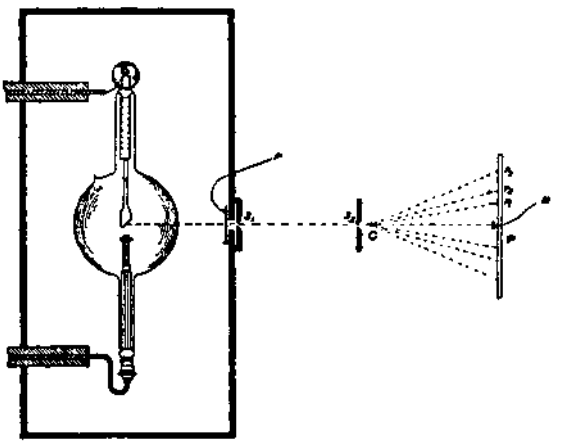


FIG. 43. (Hull.)

The same is true for every type of plane of the crystal structure which is capable of reflecting the X-rays, and for each order of reflection. If a photographic plate is placed as in Fig. 43, so as to intercept the reflected rays, all beams corresponding to any given face and order of reflection fall on the plate at some position on a circle, with the point of incidence of the transmitted beam as centre, and are recorded as a halo surrounding the central image. The figures of Plate V, taken from a paper by Hull, show the patterns given by aluminium and by molybdenum irradiated by rays from a molybdenum anti-cathode.

Friedrich * published in 1913 the results of some experiments in which he had obtained diffraction rings or haloes of this nature when a beam of X-rays was passed through a plate of paraffin wax. There can be no doubt that these

* W. Friedrich, *Phys. Zeit.,* April, 15, 1913.

rings were due to the diffraction of the waves by the crystalline wax, although their significance was not fully realised at the time. In the same year H. B. Keene * described experiments of similar character in which he used rolled metal sheets.

The arrangement of the photographic plate shown in Fig. 43 permits only of the registration of such reflected beams as make a small angle with the transmitted beam. In order to record all reflected beams, Debye and Scherrer made use of a photographic film bent in the form of a cylinder so as to surround completely the crystalline powder placed at its centre. A hole is cut in the film where the incident rays enter, and another hole is made on the far side so that the transmitted beam is not scattered by striking the film, as it is found that the scattered radiation fogs the record.

When the film is unrolled, the diffraction patterns have the form shown in PI. VI. The haloes in the centre are made by rays which have been diffracted through a small angle, those at the sides by rays which have been reflected through nearly 180^0.

The haloes appear on the film as arcs of circles. The radius of curvature of these arcs is smallest for rays reflected through a small angle or an angle which is nearly 180^0, and becomes very large near the centre of the film. Rays deflected through a right angle would lie in a plane at right angles to the incident beam intersecting the film in a straight line at its centre. A reference to the figures in the original paper by Debye and Scherrer, will make clear the formation of these arcs.

Fig. 44, which is taken from an article by Scherrer in Zsigmondy's *Kolloidchemic,*† illustrates a camera of the type used for holding the film. The X-ray beam enters by the brass tube on the left, 9 cm. in length and 1.5 mm. internal diameter. The tube is opened out at its end so that rays scattered or reflected by the crystalline brass may not affect

* *Nature,* Aug. 14, 1913. † P. Scherrer, *Kolloidchemie,* p. 398.

the film. The substance under examination is enclosed in a thin celluloid tube 10 mm. in length and approximately

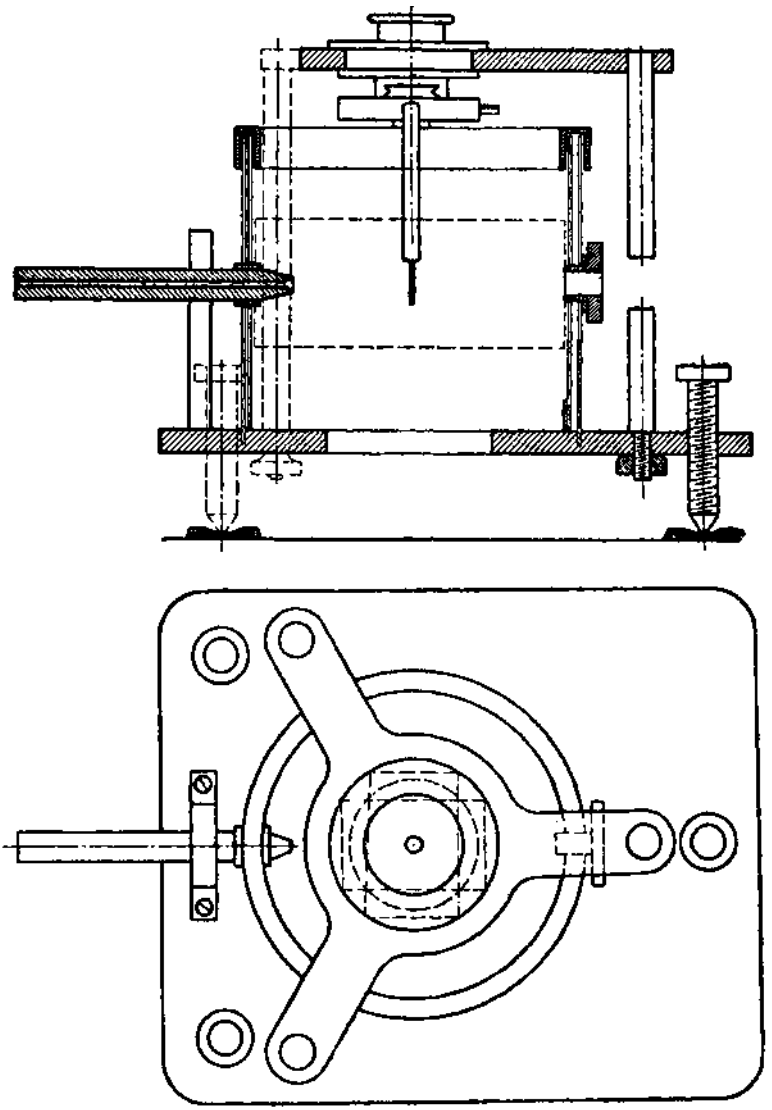


FIG. 44.

Camera for powder photographs. Zsigmondy, *Kolloidchemie,* p. 398.

r mm. in diameter. In some cases it is possible to compress the substance into a rod of these dimensions, when the

enclosing tube may be dispensed with. The tube holder can be adjusted so as to be exactly in the centre of the camera chamber. This consists of a brass cylinder of 57 mm. diameter inside which the film is fastened, and covered with black paper to exclude light. The film is pierced so as to allow the rays to pass out of the chamber on the far side, by the opening shown on the right, without being scattered.

The intensities of the diffraction maxima are measured photometrically. As a source of the X-rays Debye and Scherrer have generally employed a bulb with an anticathode of copper, or some other metal of low atomic weight. The wave lengths of the copper K_α and K_β lines are 1.549×10^{-8} cm. and 1.402×10^{-8} cm. respectively. These soft radiations would be strongly absorbed by the glass walls of an X-ray tube of the ordinary type, and to obviate this an X-ray bulb constructed partly of metal is employed (Fig. 45). The copper anticathode is sealed by means of wax or solder into an outer metal casing. Opposite the anticathode a window is pierced in the metal casing which is covered by a sheet of aluminium $\frac{1}{20}$th millimetre in thickness, through which the X-rays pass without excessive absorption. The rest of the tube consists of a glass bulb, in which an aluminium cathode is mounted in the usual way, and which is sealed by wax to the metal casing. Both the seal and the anticathode are water cooled.

As an example of the analysis of a structure by the powder method, we may take the case of lithium fluoride, described by Debye and Scherrer in their original paper. This salt crystallises in the cubic system, like rock-salt.

In a simple cubic space lattice, the representative points are arranged at the corners of a series of cubes. If the cube edge is of length a, it can be shown that the distance d between successive planes in the structure, parallel to a face whose indices are (h, k, l), is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}.$$

For instance,

$$d_{(100)} = a,$$

$$d_{(110)} = \frac{a}{\sqrt{2}},$$

$$d_{(111)} = \frac{a}{\sqrt{3}}.$$

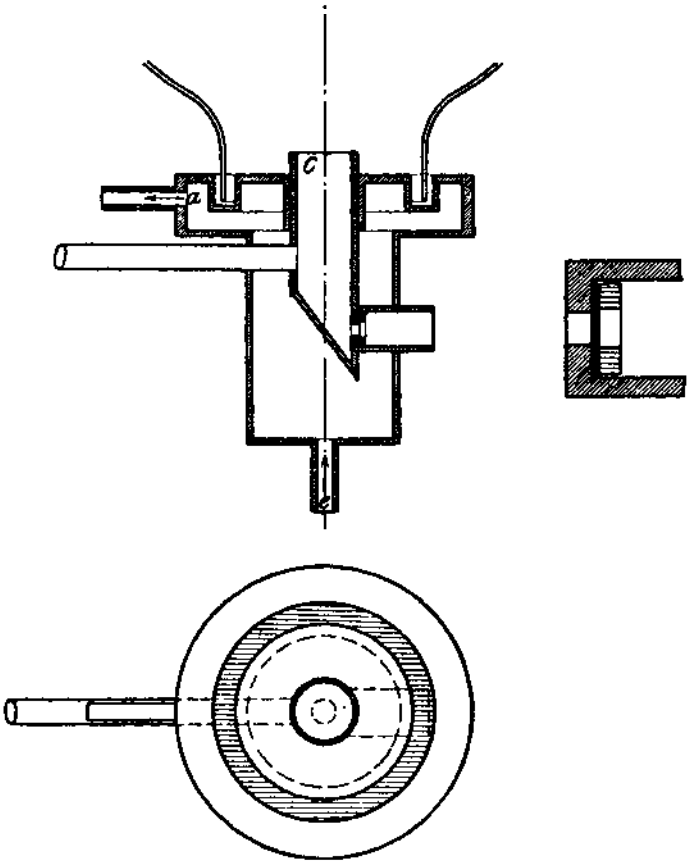


FIG. 45.

X-ray bulb for powder photographs. Zsigmondy, *Kolloidchemie*, p. 396.

The formula for reflection states that,

$$n\lambda = 2d \sin\theta,$$

whence

$$\lambda = 2 \sin\theta \frac{a}{\sqrt{n^2h^2 + n^2k^2 + n^2l^2}}.$$

If we put $nh = h_1$, $nk = h_2$, $nl = h_3$, this equation becomes

$$\frac{\lambda}{2a} = \frac{\sin\theta}{\sqrt{h_1^2 + h_2^2 + h_3^2}},$$

where the indices $(h_1\ h_2,\ h_3)$ express both the orientation of the plane and the order of reflection. For instance, if the indices are (2, o, 0) the equation gives the glancing angle θ for the true second order reflection from the (100) planes.

The following table, taken from Debye's paper, gives the results for the haloes of finely powdered lithium fluoride. In the first column the blackening of the film is denoted by the indices *w.w.* =very weak, w=weak, m=medium, *s* = strong.

LiF (COPPER RADIATION).

Intensity obs.	20 in degrees.	sin δ.	h_1, h_2, h_3.	$\frac{\sin\theta}{\sqrt{h_1^2+h_2^2+h_3^2}}$	No. of planes.	Intensity calc.
w.w.	*30.0*	*259*	J, J, J	*.150**	*8*	—
w	*33.8*	*290*	*I, I, I*	*.168*	*8*	—
S	37.8	323	I, I, I	.187	8	3.85
S	44.2	377	2, O, O	.189	6	10.2
w	*56.2*	*472*	2, *2. 0*	*.167*	*12*	—
S	63.8	528	2, 2, O	.187	12	10.2
w.w.	*67.4*	*554*	3, 1, 1	*.167*	24	—
w.w.	*71.4*	*583*	2, 2, *2*	*.168*	5	—
m	76.6	620	3. 1, 1	.187	24	3.15
m	80.8	647	2, 2, 2	.187	8	4.51
m	97.8	753	4, 0, 0	.188	6	1.86
w	111.0	824	3, 3, 1	.189	24	1.82
S	116.0	848	4, 2, 0	.190	24	8.10
S	137.[6]	932	4, 2, 2	.190	24	6.75.
w.w.	*153.2*	*973*	*4. 4. 0*	*.172*	*12*	—
S	166.6	993	{3, 3, 3 / 5, I, I}	.191	{8 / 24}	1.71

Since $\frac{\lambda}{2a} = \frac{\sin\theta}{\sqrt{h_1^2+h_2^2+h_3^2}}$, the quantity on the right-hand side should be a constant for each wave length when values of h_1, h_2, h_3 correctly chosen for each angle θ are substituted in the formula. In a simple case such as the one illustrated here, the right values (h_1, h_2, h_3) are quickly found by trial. It will be seen that the expression $\frac{\sin\theta}{\sqrt{h_1^2+h_2^2+h_3^2}}$ in the fifth column approximates to two values .189 and .168.

* Apparently an irregular observation.

These correspond to the two wave lengths in the copper radiation, K_a and K_β respectively, for which

$$\lambda_\alpha = 1.549 \text{ A.U.},$$
$$\lambda_\beta = 1.402 \text{ A.U.}$$

We therefore obtain two equations for the length a of the cube-edge.

$$2a = \frac{1.549}{0.189} \text{ A.U.},$$

$$2a = \frac{1.402}{0.168} \text{ A.U.},$$

giving values for a of 4.11 and 4.17 cm. respectively. Since these values agree within the error of experiment, it is clear that the haloes have been correctly grouped into the two sets corresponding to the K_a and K_β radiations.

It will be noticed that the indices in column (4) are either wholly odd or wholly even, and that reflections corresponding to a set of mixed indices do not appear. This is what we should expect if the cube of side 4.1 A.U. contains four molecules of LiF, arranged like the sodium and chlorine atoms of rock-salt (Fig. 91). In this structure the atoms of any one kind are arranged on a face-centred cubic lattice. The distance $d_{(111)}$ for the face-centred lattice is equal to $4.1/\sqrt{3}$, which is the same as it would be if the atoms were arranged at the corners alone. The distance $d_{(100)}$ is, however, equal to 4.1/2, so that the corresponding indices h_1, h_2, h_3 must be set equal to 2, o, o. The same is true for planes parallel to any face whose indices are mixed. The form of the indices in the third column indicates that the atoms are based on a face-centred cubic lattice.

This resemblance between the structures of LiF and NaCl is confirmed by the fact that the reflection (111) is much weaker than (200). The reflection (111) occurs from a set of planes containing Li and F atoms alternately, so that the (111) reflection is weakened as in the case of rock-salt.

Finally, this structure of LiF may be checked by testing whether it accords with the density of the salt. The mass in Angstrom units of 10^{-24} grams, of four molecules of

LiF =4 x (6.89+18.84) x 1.66 =158. The density of the crystal is 2.29, so that the mass associated with a cube of side 4.14 cm. is given by

$$a^3\varrho = (4.14)^3 \times 2.29 = 162,$$

which shows that we are correct in assigning four molecules to the cube.

In the fifth column is given the number of co-operating planes corresponding to each reflection. Let us consider any one crystalline fragment in the powder, and assign to it cubic axes having certain definite positive directions. We may take it that there is a certain probability that the plane *(h, k, I)* may be set so as to reflect the rays. Five other planes with positive indices, making six in all, will reflect the rays through the same angle, their indices being obtained by permutation of *h, k, L* Since any of these indices may also be negative, we must multiply this by 2^3 in order to obtain the total number 48 of possible permutations, and so the number of co-operating planes. In the general case, the probability that some plane will reflect the rays in this particular direction is 48 times as great as the probability that the plane *(h, k, I)* will be set so as to do so. In other cases, the total number of planes is not so great. Debye gives the following rules for the number of planes.

General case	=48.
Two indices equal, 48/2	==24.
Three indices equal, 48/(2 x 3)	-= 8.
One index zero, 48/2	= 24.

For instance, in the case of the plane (100) we divide by two because two indices are equal, and by four because two indices are zero, so that the total number of planes is 6 (corresponding to the six faces of the cube).. In estimating the intensity of the lines, we must allow for the fact that, other things being equal, a larger number of co-operating planes will correspond to a stronger diffraction of the rays

by the powder. The theoretical intensities in the last column are calculated by the formula :

$$I = (A_F + A_{Li})^2 \cdot \frac{N}{h_1^2 + h_2^2 + h_3^2}$$

or

$$I = (A_F - A_{Li})^2 \cdot \frac{N}{h_1^2 + h_2^2 + h_3^2},$$

the first expression being used when the indices of the planes are even so that waves diffracted by the lithium and fluorine atoms are in phase, the second expression when the indices are odd and these waves are in opposite phase. A_{Li} and A_F are the atomic numbers of lithium and fluorine, and it is assumed that the intensity falls off inversely as the square of sin θ, or as $\frac{1}{h_1^2 + h_2^2 + h_3^2}$. The intensities so calculated show a parallelism with the observed intensities of the haloes as indicated in the first column.

The structure of graphite is of great interest, for many reasons, and it has been examined independently by Debye and Scherrer and by Hull. Graphite forms very imperfect crystals ; so that it is practically impossible to complete its analysis by the single crystal method. The cleavage plane gives, however, a very strong reflection, since the graphite flakes are roughly arranged in a parallel order. In the first edition of this book it was stated that the spacing of the (111) plane had been determined, by the single crystal method, to be 3.42.

The powder method must eventually provide the materials for a definite solution. At present, however, there is some uncertainty because Debye and Scherrer differ considerably from Hull, both in the measurement and in the interpretation of the photographic results. Both analyses give the same value as the single crystal method for the (111) spacing ; and both agree in supposing that the projection of the atoms grouped about a in plane, upon that plane, is hexagonal, and is very nearly the same as that of diamond. But, whereas Hull imagines that the (111) layer is of the same

puckered character as in diamond (see Fig. 33, p. 100), Debye and Scherrer flatten out the layer, so that the three linkages of a carbon atom to its nearest neighbours lie in one plane. The point is of great interest because in the one case the three bonds make the same angles with each other as they do in diamond ; whereas on the alternative hypothesis they have changed their relative orientations.

Debye and Scherrer have examined also various samples of amorphous carbon, and have obtained the very interesting result that however the carbon is prepared it shows diffraction maxima, and that these occur at the same angles of reflection as for graphite. The bands are, however, far broader and more diffuse. The explanation which Debye and Scherrer give of this is very ingenious. It is ascribed to the fact that the homogeneous fragments of crystal in the 'amorphous carbon' are very minute. The number of regularly spaced planes in each crystal which reflect the X-rays is small, and in consequence the diffraction maxima lack sharpness. The effect may be compared to the diffraction of light by a grating with only a few lines. Such a grating has a low resolving power, since the diffraction maxima corresponding to homogeneous light of any wave length are broad, and it is impossible to resolve two lines which are close together in the spectrum. In the same way the crystalline fragment, in which there is only a small number of planes, will reflect X-rays over a wide range of angles on either side of the angles given by $n\lambda = 2d \sin\theta$, and the maxima on the curve will be broadened in consequence.

Scherrer has used this effect to make an interesting series of measurements on the size of individual particles of metals in a finely divided form. He has examined, for instance, colloidal gold which has been prepared in various ways.

Particles of gold, which have been precipitated chemically, give sharp interference maxima, or haloes. This is shown by PI. VI. (1), a Debye photograph taken with precipitated gold. Here the breadth of the haloes can be completely accounted for by the dimensions of the column of powder

on which the rays fall, and the breadth of the X-ray beam. Although the gold is in a very finely divided state, the individual crystals of gold are sufficiently large to give a sharp reflection of the rays. PI. VI., Fig. 2, is taken with colloidal gold. It will be seen that in this case the haloes, while occurring in exactly the same positions, are far broader and more diffuse, due to the smallness of the individual gold crystals.

From the breadth of the haloes it is possible to compute the average size of the crystalline particles. In the case of a crystal where the diffracting atoms are arranged on a cubic lattice, and where the average thickness of the crystal parallel to a cubic axis is *D*, it may be calculated that:

$$B = 2\sqrt{\frac{\log_e 2}{\pi}} \cdot \frac{\lambda}{D} \cdot \frac{1}{\cos\frac{\theta}{2}} + b,$$

where the symbols have the following significance.

B = The angular breadth of the halo measured between points at which the intensity has fallen to half its maximum value.

0 = Angle through which the rays are diffracted.

λ = Wave length of rays.

b = Minimum breadth of halo determined by the dimensions of the X-ray beam and column of powder.

By measuring *B* photometrically, and plotting it against $\frac{1}{\cos\frac{\theta}{2}}$, Scherrer derives a value for the constant $2\sqrt{\frac{\log_e 2}{\pi}} \cdot \frac{\lambda}{D}$, and so deduces a value for *D*.

In the case of the preparation of precipitated gold, which gives the haloes shown in PI. VI., Fig. 1, the breadth of the crystals is large in comparison with the edge of the unit cell. The second preparation, which gives the broader haloes shown in PI. VI., Fig. 2, consists of much finer particles. The

breadth of the haloes indicates that the dimensions of the crystals in any one direction do not exceed 18.6 Au. Since the elementary face-centred cube, which forms the unit of the lattice on which the gold atoms are arranged, has a side of length 4.07, it follows that in any direction in the crystal there are not more than four or five of these cubes.

The fact that the haloes occur in exactly the same positions in these two photographs is very remarkable. Moreover, the dimensions of the crystal structure deduced from the positions of the haloes agree exactly with those deduced by Vegard in his determination of the structure of the reflection from large gold crystals. It would appear that the atoms take up exactly the same relative positions in these minute crystals as they do in large crystals. The forces which govern their positions of equilibrium must be extremely local since, in the case of the minute crystals of colloidal gold, we *get* no distortion of the structure in spite of the fact that no atom in the crystal has more than two or three other atoms between it and the exterior surface.

A number of substances have been examined by the powder method of analysis. In many cases, substances thought to be amorphous have proved to be crystalline in nature. Even such substances as cellulose show a regular pattern when submitted to this method of analysis. Glass, on the other hand, proves to be a truly amorphous substance, there being no trace of any haloes when it is irradiated by X-rays.

The subject is further discussed in Chap. XVI.

CHAPTER XI

CRYSTAL ANALYSIS AND CRYSTAL SYMMETRY

IN the preceding chapters the structure of a series of cubic crystals has been described. Though all these crystals belong to the cubic system, they belong to different classes of the system. For instance, rock salt, fluor and diamond are assigned to the holohedral or ditesseral central class of the cubic system. Zincblende belongs to the ditesseral polar, pyrites to the tesseral central class, each class being defined by its peculiar elements of symmetry. It is interesting to trace the connection between the symmetry as displayed by the crystal as a whole and the arrangement of atoms revealed by the spectrometer analysis.

A diagram of the NaCl structure is given on p. 91. Among the axes, planes, and centres of symmetry are the following:

Every cube edge is a rotation * axis of fourfold symmetry.

Every cube diagonal is a rotation axis of threefold symmetry.

The diagonals of the cube faces are rotation axes of twofold symmetry.

A plane of symmetry coincides with each cube face.

A plane of symmetry passes through opposite parallel edges of each cube.

A centre of symmetry lies at each cube corner.

*** A rotation axis of n-fold symmetry is such that a simple rotation of $2\frac{\pi}{n}$ around this axis brings the structure into self-coincidence. It is called a rotation axis to distinguish it from a screw axis, which is such that a rotation of $2\frac{\pi}{n}$ round it and a movement along it are necessary to bring the structure to self-coincidence.**

If the structure on which the molecules are built possesses these elements of symmetry, they will also be possessed by the crystal as a whole. That is to say, the crystal of rock salt has as symmetry elements :

Three fourfold axes	(100).
Four threefold axes	(111).
Six twofold axes	(110).
Three symmetry planes	(100).
Six symmetry planes	(100).
A centre of symmetry.	

This is the full complement which a cubic crystal can possess. A crystal which has these elements of symmetry is said to belong to the holohedral class.

Reference to the structure of fluor-spar, described on p. 102, will show that this crystal has the same elements of symmetry as rock salt. They coincide in every respect with regard to their symmetry axes and planes, these being in fact the axes and planes of the face-centred cubic lattice. In both these cases the structures assigned to them would indicate that the crystals belonged to the holohedral class, and this is also the class to which they have been assigned by crystallographic evidence.

Compare with this the structure of zincblende, which is repeated in Fig. 46, this time in plan. The black and white zinc atoms of that plan are situated in different planes of the crystal structure, the whole plan representing two layers of cubes. It is the same with the sulphur atoms ; the black atoms are at the centres of the upper layers. This plan will make it clear that there are planes of symmetry perpendicular to the plane of the paper and cutting it in *AC, BD.* The crystal has therefore planes of symmetry parallel to (no).

However, there are no planes of symmetry parallel to (100). Such planes would cut the plane of the paper in lines parallel to *AB* and *AD,* and it is evident in the plan that this line and others parallel to it do *not* represent planes of symmetry.

Moreover, there are no axes of fourfold symmetry perpendicular to the plane of the paper in Fig. 46. Axes of twofold symmetry alone pass through cube centres and cube corners.

Considering the diagram in Fig. 30, p. 97, which represents the arrangement of the (111) planes in zincblende,

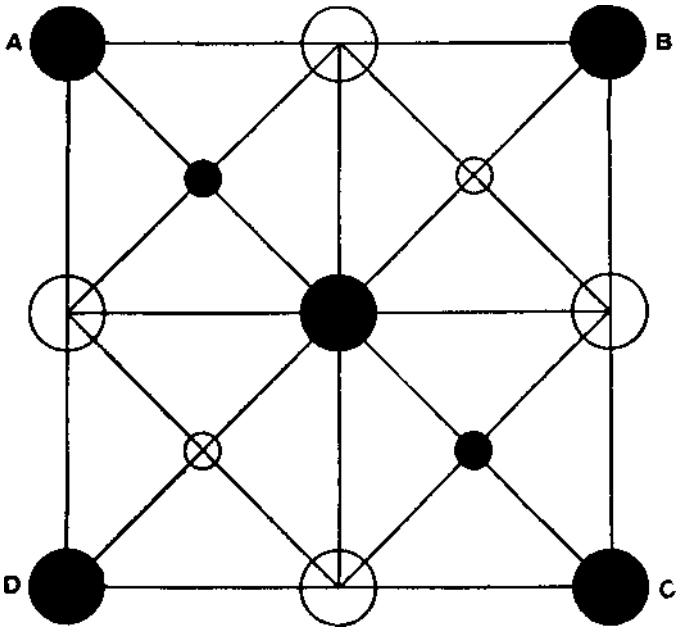


FIG. 46.

The large circles represent zinc atoms, the small circles sulphur atoms. Blacks and whites of each size are in different planes.

there is another feature characteristic of its peculiar symmetry. The zinc and sulphur planes occur in pairs, an arrangement which gives ' polarity ' to the axis of threefold symmetry perpendicular to these planes. Passing in one direction along the axis the zinc plane of each pair occurs first; proceeding in the opposite direction, the sulphur plane. Suppose that the crystal were being developed as an octahedron, with (111) planes as faces, and that the ZnS molecules were being deposited on the growing faces in these pairs of planes. Two opposite faces of the

octahedron would be different, one having a last layer of zinc atoms and the other of sulphur atoms. Half the faces of the octahedron would be of one kind, and the other half of another.

This corresponds to what is observed in the case of a crystal of zincblende; it is the phenomenon known as 'hemihedrism.' If a crystal of zincblende has octahedron faces, they are in general unequally developed. Half of them, which alone would make up a tetrahedron, are large, and the other half small. They are further to be distinguished by the action of solvents on them, which attack them in different ways. In some cases the faces of one kind alone are developed, so that, instead of a complete octahedron, the crystal has the shape of a tetrahedron. Further, if an insulated plate cut perpendicular to a threefold axis is touched with a heated njetal rod, positive or negative electrification results according as a face of one kind or the other is touched.

Though the structure cannot explain the reason why one octahedron face develops more rapidly than the other, it explains why a difference between the faces is to be expected. The crystal structure is in accordance with the symmetry exhibited by the crystal as a whole.

Consider now the case of diamond, which is derived from the zincblende structure by substituting carbon atoms for both zinc and sulphur atoms. Its plan is represented in Fig. 47.

This structure at first sight appears to occupy a somewhat anomalous position. It possesses, of course, at least all the elements of symmetry of the zincblende structure. In this case, however, the (in) axes are no longer polar, since the two planes of each pair are now alike. This polarity, which causes ZnS to be hemihedral, is now absent, and diamond must belong to the holohedral cubic class. The crystal must have elements of symmetry which zincblende does not possess, namely, symmetry planes parallel to (100), fourfold axes of symmetry, and a centre of symmetry.

A consideration of the structure in Fig. 47 shows that there are no reflection planes of symmetry or ' rotation ' axes of symmetry which could give rise to the holohedral symmetry of the crystal as a whole. Their places are taken by ' glide ' planes of symmetry and ' screw ' axes of symmetry. Two of the fourfold screw axes are marked in the figure; it

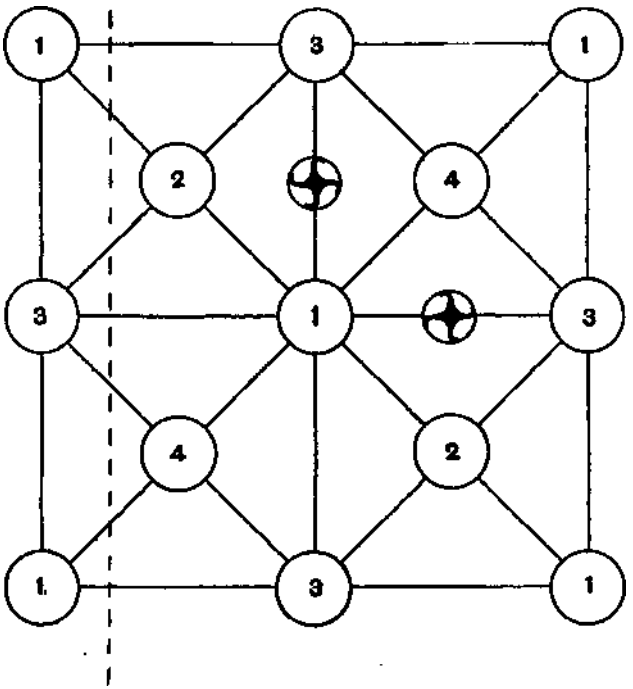


FIG. 47.

will be seen that the points 1 2 3 4 are arranged in a spiral round the axis. The dotted line represents a plane of ' gliding reflection.' By its operation 1 turns into 2, and 3 into 4. 1 is to be imagined reflected in the plane, at the same time receiving a translation which brings it to 2.

If the structure has as elements of symmetry these screw axes and gliding planes, the crystal must have corresponding rotation axes and planes of symmetry. A rotation axis is, of course, the only kind which can be possessed by a crystal,

for when the crystal is imagined turned round this axis through $2\frac{\pi}{n}$ into self-coincidence, its centre must remain fixed. The diamond crystal, according to the structure here put forward, is holohedral. There has been a great deal of controversy among crystallographers as to the class to which diamond should be assigned ; on the whole the evidence has seemed to be in favour of the holohedral class, the alternative being the class to which zincblende belongs. However, even

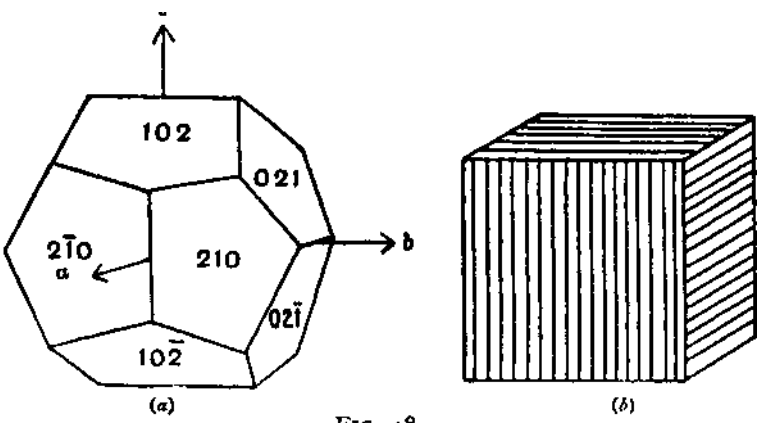


FIG. 48.

Iron Pyrites.

if the crystal really belongs to this latter class, the fact that the evidence for assigning it to this class is so doubtful, shows that its departure from holohedral symmetry must be very slight indeed.' More will be said on this point in connection with cuprite and sylvine.

Iron pyrites, like zincblende, has a ' hemihedral' crystalline form. This hemihedrism is, however, of a different nature; pyrites belongs to the class known as ' tesseral central.' A cube of iron pyrites has striations on its faces, and those on each face are parallel to a cube edge and perpendicular to those of the neighbouring faces (see Fig. 48). This shows that the crystal does not possess a fourfold axis of symmetry perpendicular to the face, but merely a twofold axis. The cube has a centre of symmetry, however, which

distinguishes it from zincblende. It has planes of symmetry parallel to (100), whereas in zincblende the planes of symmetry are parallel to (no). The crystals possess, in fact, all the elements of symmetry possessed by the cube in Fig. 48, taking into account the markings on the face of that cube.

Fig. 41, p. 118, represents the structure of iron pyrites as assigned to it by our analysis. In Fig. 49 all the atoms of a unit cube are projected on one of the cube faces. It

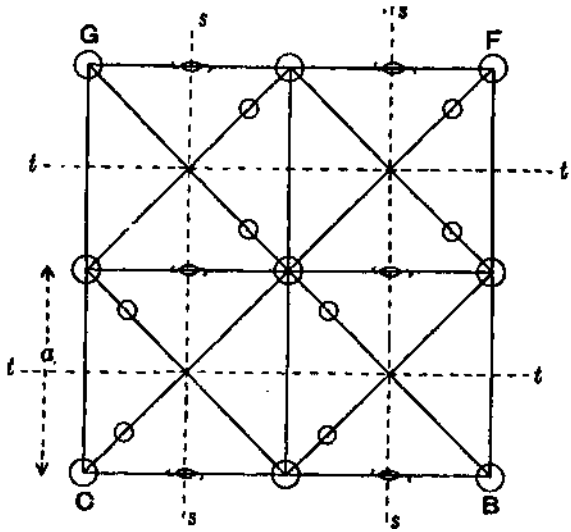


FIG. 49.

will be evident that there is a reason why markings on the corresponding cube face of the crystal should be vertical, rather than horizontal, or *vice versa.* The sulphur atoms of the structure appear in pairs arranged vertically. This is only another way of saying that the structure, like the crystal, has twofold axes where a holohedral crystal would have fourfold axes. The twofold screw axes are marked in position in Fig. 49.

The dotted lines represent glide planes of symmetry. Every cube corner is a centre of symmetry. The non-intersecting threefold axes of symmetry have already been explained.

The structure of the crystal as revealed by the spectrometer is again in accordance with the symmetry exhibited by the crystal as a whole, so that the structure explains why the crystal develops a hemihedral form. The hemihedrism of pyrites betrays itself by forms such as that in Fig. 48. The cubic axes of the crystal are here drawn in position. It is perhaps clear that a holohedral crystal would have four faces surrounding each axis where it emerges from the crystal, for example (210), (210), (201), (201). Instead of this the faces (210), (210) alone appear, meeting in a line which is parallel to the scratches on the cube face.

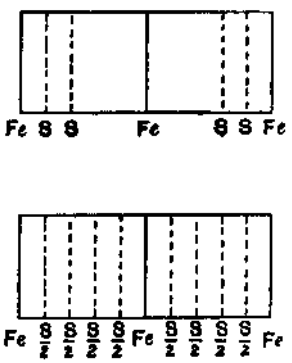


FIG. 50.

Upper diagram 210 planes.
Lower diagram 120 planes.

This figure is a common form of iron pyrites, it is known as the pyritohedron in consequence.

The explanation of the difference between the faces (210) and (120) cannot in this case be similar to the explanation of the hemihedrism of zincblende. There are no polar axes, for the crystal structure has centres of symmetry. But if we take the plan of the crystal structure as given in Fig. 49, and find the arrangement of the planes parallel to the faces (120) and (210), the difference of these faces is accounted for. The arrangement of the planes is shown in Fig. 50.

The planes (210) and (120) have a different arrangement. In the one case the arrangement repeats itself at twice as great an interval as in the other case, so that $d_{(210)}$ is twice as great as $d_{(120)}$.

This conclusion can be tested by cutting the two faces (120) and (210) on a cube of pyrites, and reflecting the X-rays from them. The results of this measurement are given in Fig. 51. The first reflection from the face (210) occurs at about 14^0, that from the face (120) at about 28°, This measurement brings out an interesting fact, namely, that

the face (210), which is commonly developed in pyrites crystals, is the face with the larger spacing $d_{(210)}$. The face (120) is much more rarely developed. One can remember how the structure of Fig. 49, and an actual cube of pyrites,

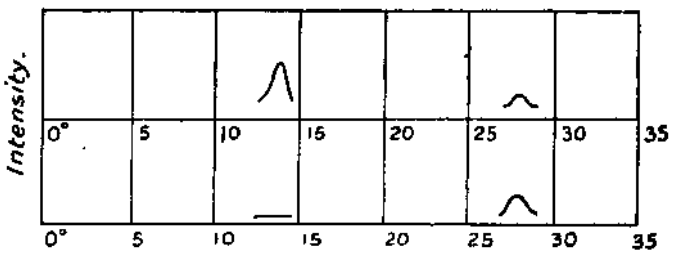


FIG. 51.

must be placed so as to be similarly situated, by noting that the scratches on a pyrites face are parallel to the pairs of sulphur atoms observed when looking at the parallel face of the structure.

Fig. 52 gives the spectra for the faces (111) and (111) of a crystal of zincblende. These are two opposite faces of

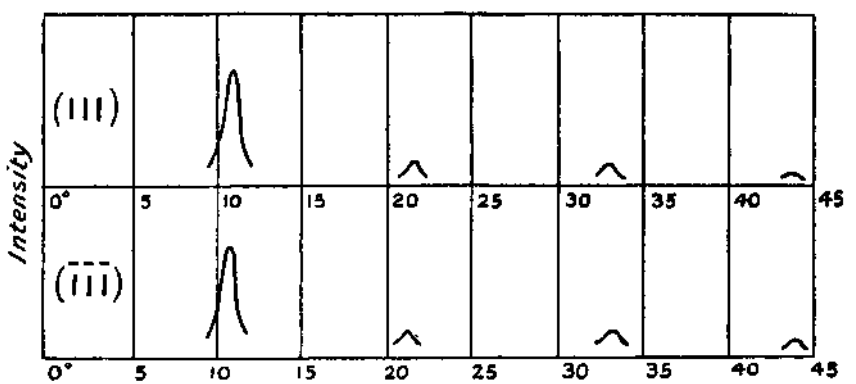


FIG. 52.

an octahedron, one at each end of the polar axis of the crystal. As has been explained, such a pair of faces show the greatest difference in their development, etch-figures, and pyro-electric properties, and on this account zincblende is

referred to a hemihedral class of the cubic system. The X-ray spectra, on the other hand, do not distinguish between these two faces.

A pair of faces (hkl) a n $(\bar{h}\bar{k}\bar{l})$i l l always yield identical spectra when the X-rays are reflected on each face in turn. To put this in another way : when examining by the X-rays the faces of a crystal to find differences which might be due to the hemihedral nature of the crystal, all crystals will behave as if they had a centre of symmetry. If a centre of symmetry were added to the elements of symmetry already possessed by zincblende, it would raise that crystal to the holohedral class. Therefore all Laue-photographs taken with zincblende will indicate a holohedral symmetry of the crystal, and in particular a photograph in which the incident rays are parallel to a cubic axis of the crystal will show a fourfold, as against a twofold, symmetry. On the other hand, the hemihedral iron pyrites already has a centre of symmetry. Adding a centre of symmetry does not raise it to the holohedral class, and we can therefore understand the fact that Laue-photographs of iron pyrites give unmistakable indications of its hemihedral nature.*

Very similar spectra are yielded by two crystals which belong to the same class as pyrites, namely Hauerite, MnS_2, and Cobaltite, CoAsS. It is not easy to get such large crystals of these substances as those of iron pyrites, so that the reflections are very much weaker. They suffice to show, however, that all three crystals are built up in a similar way.

The case of cobaltite is rather interesting. Cobalt replaces the iron, and arsenic atoms replace one-half the sulphur atoms in the pyrites structure. If this is carried out in a symmetrical way the structure loses some of its elements of symmetry, for the trigonal axes become polar. The centres of symmetry at the cube corners of Fig. 41 are destroyed, for each has now an arsenic atom on one side and

*** This point has been dealt with very fully by G. Friedel *(Comptes Rendus*, Dec. 1913, p. 1533. See also W. L. Bragg, *Phys. Zeit.*, 15 Jahr, 1914, Seite 77-79).**

a sulphur atom on the other. The structure belongs to a still lower class of the cubic system, namely, the tesseral polar class. The typical crystal of the class is the mineral Ullmannite, NiSbS. This crystal has not yet been examined, but it is natural to suppose that NiSbS and CoAsS belong to the same class.

There remains but one class of the cubic system of which we have not given a corresponding example in crystalline

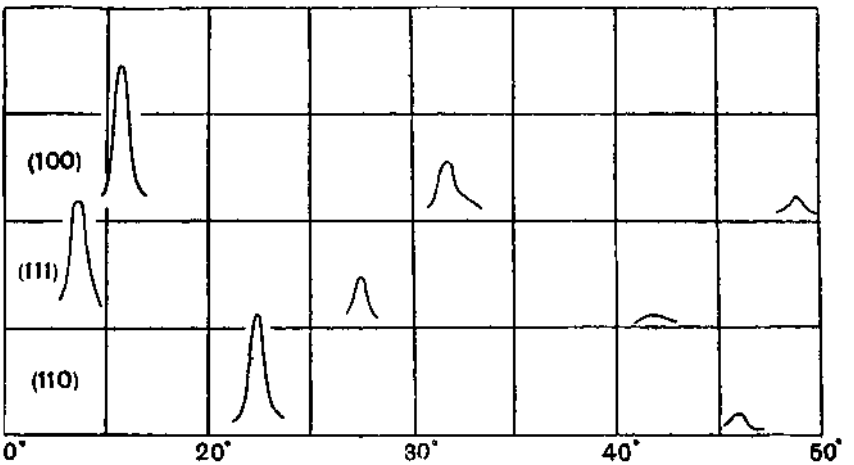


FIG. 53.

Cuprite spectra.

structure. This class is typified by Cuprite, Cu_20. The crystals have no planes of symmetry and no centre of symmetry, but they possess the complete number of axes of symmetry of the cubic system. The class is known as the holoaxial class, and crystals belonging to it have two enantiomorphous forms. They are either right or left-handed.

The spectra and supposed structure of cuprite are shown in Figs. 53 and 54. The spectra are typical of the face-centred cubic lattice. There can be little doubt that the heavy copper atoms are arranged in a face-centred cubic lattice, the oxygen atoms being so light that they make comparatively little difference to the intensities of the

spectra. The absolute dimensions of the structure confirm this supposition. Taking the copper atoms to be on a face-centred lattice, the oxygen atoms must now be allotted to the structure in such a way that there are two atoms of copper to one of oxygen. The most simple way of doing this leads to the construction shown in Fig. 54. The oxygen atoms lie on a cube-centred lattice, the copper atoms on a face-centred lattice, and the two intersect as shown.

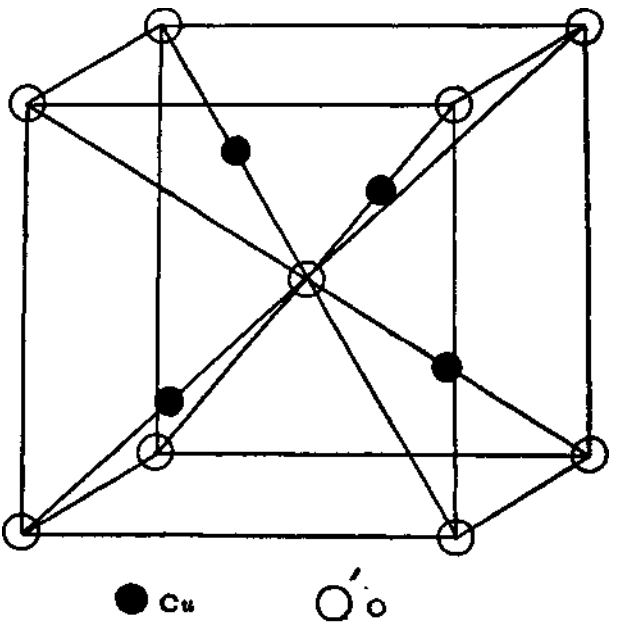


FIG. 54.

This structure has holohedral symmetry. If the copper and oxygen atoms have these exact geometrical positions, the crystal of cuprite ought to exhibit holohedral symmetry. Instead of this, certain uncommon forms of the crystal show that its symmetry is in reality holoaxial. If this holoaxial symmetry corresponded to a large distortion like that in the case of iron pyrites, which involves a large displacement of the sulphur atoms, it is probable that the spectra would show the influence of this distortion. They would not be as straightforward as they are. The spectra alone indicate the

holosymmetric structure given in Fig. 54. A very slight distortion of the structure would not affect the spectra, but might have sufficient influence on the growth of the crystal to account for the rare forms of cuprite which show holoaxial symmetry. Correspondingly, the crystallographic evidence would seem to show that the distortion of the structure is slight. The etch-figures of cuprite indicate a holosymmetric crystal, and the crystal does not rotate the plane of polarisation of light. It is only on account of the existence of crystals which show a holoaxial hemihedrism that cuprite is assigned to the holoaxial class.

These observations apply equally to the case of potassium chloride, which was the first example worked out in this book. Potassium chloride is assigned by crystallographers to the holoaxial class of the cubic system. We have seen that the examination by means of the X-ray spectrometer indicates the structure given in Fig. 28, which has perfect cubic symmetry. Any distortion of this structure must be slight, or the spectra would give evidence of it. When a potassium chloride crystal is etched with water, it displays facets (931) in accordance with holoaxial symmetry, and on this evidence is assigned to the cuprite class. Again, however, there is no trace of rotatory polarisation.

Ammonium chloride is assigned to the holoaxial class on similar evidence, while the spectra give to this crystal a structure with holohedral symmetry. The chlorine atoms are arranged on a simple cubic lattice, the nitrogen atoms are at the centres of the cubes at the corners of which the chlorine atoms are situated. The arrangement of the hydrogen atoms is doubtful, as they are so light that they do not appreciably affect the X-rays. It is interesting to notice that ammonium chloride is not isomorphous with the other alkaline halides, although it also crystallises in the cubic system. Each unit cube of the structure contains in the one case half a molecule of KCl, in the other case a whole molecule of NH_4C1.

This division of crystals into those in which the distortion

from perfect symmetry is large, and those in which it is small, is interesting. On the one hand, we have zincblende, pyrites, hauerite, cobaltite, etc., in which the symmetry of the crystal is obviously related to the symmetry of the structure. The distortion from holohedral symmetry is so large as to change completely the character of the spectra. On the other hand, we have cuprite, potassium chloride, and possibly diamond also, in which the spectrometer gives a structure which is of higher symmetry than that assigned to the crystal by crystallographic evidence. The departure of the first set of crystals from holohedral symmetry is very obvious, while it is on very slight evidence that the second set is believed to depart from the class of higher symmetry.

CHAPTER XII

CRYSTAL ANALYSIS AND THE ATOMIC FORCES

THE unit of crystal structure is the smallest portion of a crystal which, repeated through space without change in character or orientation, makes up the crystal. It contains within itself every kind of atom, and every kind of bond, every feature, and every property which the crystal possesses as a whole. If we investigate the physical properties of the crystal we investigate the physical properties of the crystal unit. If we can discover the number and the arrangement of the atoms within the unit we may hope to discover also the part played by each atom in forming the characteristics of the unit or crystal. The methods of X-ray analysis tell us very readily the number of atoms in the unit and are throwing more and more light on their arrangement.

This mode of progress has its analogies in the previous history of physics and chemistry. Some of the properties which substances possess are also possessed by the individual atoms or molecules of which the substances are composed. In the main, the properties are those which are displayed when the substance is gaseous or liquid ; when, in fact, the atoms and molecules are not linked together into crystalline form. Progress has been founded on the discovery of the constitution of the smallest portion,—that is to say, molecule or even atom—which displays in full the properties referred to. The part played by each of the atoms forming the molecule is then examined. The further this analysis is carried the more does it become possible to carry out **the**

reverse process of synthesis, and to design, even to construct a substance having any desired properties.

The general limitation to the properties of substances in the gaseous or liquid state is really severe. We remove it when by the aid of X-ray analysis we examine the structure of the crystal unit, because it displays all the properties of the solid. A crystal has elasticities, thermal expansions, thermal and electric conductivities, dielectric capacities, optical activities ; and all these not only as scalars but as vectors also. Quartz, to take a simple example, has many properties as a crystal, some of them most remarkable, which are possessed to the full by the crystal unit of quartz. We now know that the unit consists of three molecules of SiO_2: and are well advanced towards a knowledge of the relative positions of the nine atoms in the unit. The power of rotating the plane of polarisation of light, to take one physical property as an example, is a property of the single unit, just as much as of the whole crystal, and is derived from the arrangement of the atoms within the unit. It is not a property of the molecule, still less of the separate atoms. We are in a position to consider this and all the physical properties of the crystal as dependent on the structure of the unit, and, ultimately, on the forces exerted by each atom; in other words, on the structure of the atom. The crystal unit ranks in its uses and very possibly in importance with the atom and the molecule.

So far as X-ray analysis of the crystal unit has progressed in the few years since its inception it has followed the same course as the investigation of the molecule, in that the properties of the whole have been considered, in turn, in relation to the unit. The previous chapter contains a brief description of the method and results of this procedure in regard to form and symmetry. We can transfer to the crystal unit all that has been learnt concerning crystal symmetry. It has been shown that considerations of pure geometric symmetry are of the greatest value in helping to fix the positions of the atoms in the unit, particularly in the

case of simple structures. The present chapter contains some account of the application of other physical properties in the same manner ; and particularly of the linear relations as contrasted with the angular relations which enter into questions of symmetry. The chapter contains also a few notes relating to other physical properties, elasticities, thermal expansions, and conductivities ; but they are so few that they can be considered only as pointing the way to further research.

It is, of course, one of the main objects of science to discover the mode of action of atomic forces, in which enquiry the crystal unit will give assistance that is important and unique. Whatever it has to tell must be considered with reference to such information as has already been obtained in other ways. For this reason it is convenient to give here a brief account of the atomic structure, as it has been held to be established by other lines of research.

It is generally believed that the atom consists of a nucleus surrounded by electrons. Each electron bears a negative charge of 4.77×10^{-10} electrostatic units, this being the natural unit of electricity. The nucleus is positively charged, its total charge being an integral multiple of the same electrical unit. The positive charge on the nucleus of the atom is therefore Ne, where e is the electronic charge with a positive sign, N an integer which is termed the ' Atomic Number/ In an uncharged atom the nucleus is surrounded by N electrons each with its charge $-e$. The nucleus is in itself a complex structure, the dimensions of which are, however, very small compared with those of the electron system surrounding it. The whole of the mass, except for a very small fraction due to the electrons, is associated with the nucleus.

Apart from the mass of the atoms, and such properties as are influenced by mass, it would appear that the physical and chemical properties of the atom depend solely on the magnitude of the nuclear charge. For instance, all atoms with a nuclear charge of 790 are, in both chemical and

physical properties, atoms of lead, though these isotopes may have atomic weights ranging from 206 to 214. Each place in the periodic table corresponds to an element with a definite nuclear charge. Hydrogen has a nuclear charge of one unit, helium of two units, and so forth through the list of elements up to uranium with atomic number 92. When atoms take part in a chemical transformation the electron systems surrounding the nuclei are modified, but the nuclei themselves remain unaltered, and the identities of the atoms are preserved. It is only in the case of a radioactive transformation, where the charge on the nucleus is altered by the emission of an a or ^ particle, that transmutation of one element to another takes place.

As to the arrangement of the electrons around the nucleus, and the nature of the forces which hold them in place or in their orbits, very little indeed is known. Bohr's theory and its development by Sommerfeld have predicted spectra with marvellous accuracy, and Bohr has recently extended his original theory so as to suggest an explanation of the grouping of the elements in the periodic table: but as yet no precise application of the theory can be made except in the case of the simplest atomic systems. However, in the absence of any complete theory of atomic structure, it is still possible to give a partial explanation of valency, an explanation which is of considerable interest in relation to the structure of crystals.

Various electronic hypotheses of chemical combination and valency have been put forward from time to time, and the discovery of the relation between atomic number, and the place occupied by an element in the periodic table, has greatly strengthened these hypotheses. This may be illustrated by considering the case of a series of successive elements in the periodic table, such as sulphur, chlorine, argon, potassium, calcium. The atomic numbers, or numbers of electrons surrounding the nucleus, are 16, 17, 18, 19, 20 for these five elements. The argon atom **enters into no** chemical combinations with other atoms, **and its**

valency must be taken to be zero. We must suppose that the eighteen electrons surrounding the argon nucleus are in some way arranged in a highly stable system with a weak external field of force. The next atom in the series, that of potassium, has a nuclear charge of nineteen units, and the neutral atom is surrounded by nineteen electrons. Potassium is a characteristic univalent electropositive element. In solutions of its salts the atom appears as an ion with a single positive charge, indicating that one of its electrons has been given up. This distinction between the properties of argon and potassium is explained by supposing that in potassium, as in argon, eighteen electrons form a very stable system around the nucleus, but that in the potassium atom an additional electron, the nuclear charge being now *ige*, forms no part of this stable system, and so is easily detached from the atom. On this view, the potassium ion resembles closely the argon atom, differing from it only in possessing a nuclear charge of 19 instead of 18 units. Superimposed on the weak field characteristic of the 18 electron system, then, there is an electrostatic field about the ion corresponding to a charge of $+e$ on the atom as a whole. This tendency to lose an electron and become a positive ion is held to be the basis of the chemical properties of the potassium atom. In the calcium atom the removal of *two* electrons causes the reversion of the electron configuration to the argon type. Chlorine, on the other hand, has one electron less than argon, and an electron must be absorbed into its system in order that the argon configuration may be realized. The charges on the electrons then exceed the charge on the nucleus by one unit, so that the chlorine ion is univalent and electronegative. Similarly, sulphur is electronegative and divalent.

This view has been largely developed by Kossel,* to whom the diagram in Fig. 55 is due. In this figure the number of electrons in the atom of each element is plotted against its atomic number. Since, in the uncharged atom, these

*** Kossel, *Uber Molekulbindung als Frage des Atombaus* ; *Ann. der Phys.* 49. 230, 1916.**

two numbers are equal, the points (circles) representing these neutral atoms lie on a straight line inclined at 45 °. When the atom has become an ion, and has lost or gained electrons in doing so, the number of electrons it contains is

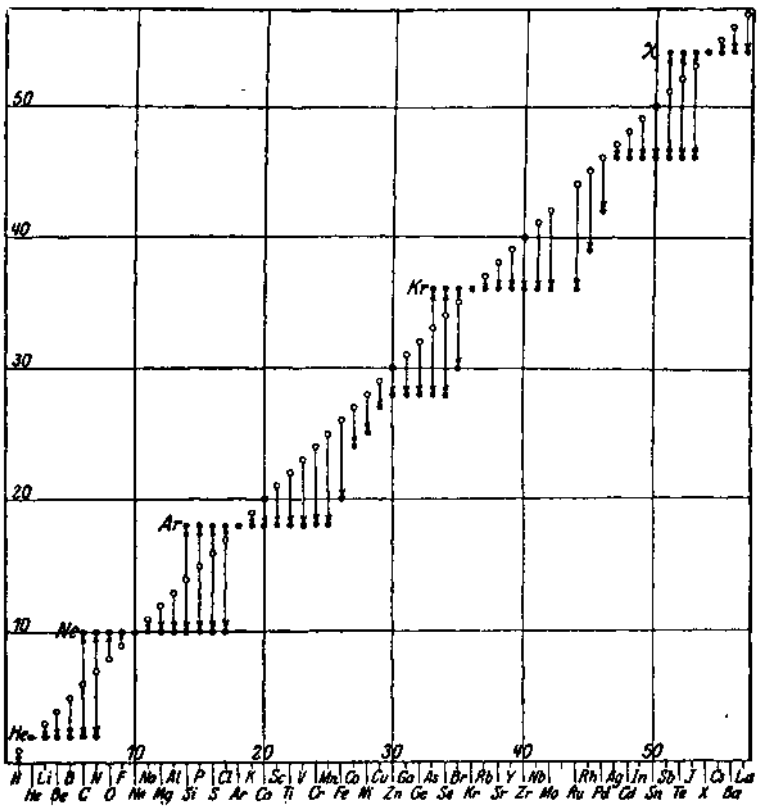


FIG. 55.

represented as a dot. The diagram illustrates the conclusion stated by Kossel as follows,' The elements of strongly polar character, which lie in the neighbourhood of the inert gases, possess when ionised exactly the same number of electrons as these inert gases.' At the level of each inert gas there exists a horizontal row of dots representing ionised atoms which have the same number of electrons when functioning with full valency. This regularity is evident in the neighbourhood of the inert gases, where a very stable

system can be reached with a small alteration in the total number of electrons. Irregularities occur in the middle of the long periods where this is not the case, presumably due to a tendency to revert to some intermediate stable system.

The views of the nature of atomic structure which have been set out above may now be compared with the results of X-ray analysis. It appears at once that their probability is greatly strengthened by the new knowledge of the structure of polar compounds such, for example, as potassium chloride. In the structure (Fig. 28) each potassium atom is surrounded by six chlorine atoms situated symmetrically with regard to it, and each chlorine atom by six potassium atoms similarly arranged. The potassium atom is not bound to one chlorine atom so as to form a molecule, but exerts its attraction on several neighbours. This becomes comprehensible if the crystal be regarded as a pattern of potassium and chlorine ions, of opposite sign, held together by electrostatic forces, for these forces correspond to a valency bond which can be subdivided to any extent. The equality of the numbers of atoms of either kind, in solid potassium chloride, is not a result of the pairing of the atoms into potassium chloride molecules, but of the necessity of there being an equal number of oppositely charged ions so that the resulting structure should be electrically neutral. The same holds in the case of a more complex structure, such as that of calcite (Fig. 36). The ions in this case consist of calcium with a double positive charge, and the group $C0_3$ with a double negative charge, these ions being again arranged so that they alternate in a structure very similar to that of potassium chloride.

A large number of crystals are of this type. In calcium fluoride we have an example of a crystal where there are two negative ions to every positive ion. Each doubly charged calcium ion is surrounded by eight singly charged fluorine ions and each fluorine by four calcium ions. The structure of fluor-spar represents the most symmetrical way in which this arrangement can be realised. In zinc sulphide

the ions of one kind are surrounded by four of the opposite sign. We do not know what causes this structure to differ in type from that of rock-salt, but we see the same absence of any indication of grouping into molecules. In NH_4C1 the NH_4 ion is surrounded by eight chlorine ions, and *vice versa.* The number of complex salts which have been analysed completely is small, but it is probable that most of them conform to one of these ionic groupings, although the substitution of a complex ion for a simple atom may distort the crystal structure so that the symmetry is degraded from the cubic or hexagonal to the rhombohedral, or orthorhombic, or an even lower type.

There is, again, a large class of compounds in which the binding forces between the atoms cannot be regarded as due to the attraction of oppositely charged ions. The bonds in these non-polar compounds must differ in their nature from those of polar compounds. The molecules of such gases as chlorine, oxygen, and nitrogen afford the best instance of this binding. When two chlorine atoms combine to form the chlorine molecule we cannot assign an opposite polarity to the members of the pair. We do not know enough about atomic structure to understand the nature of the bond in this case, but the evidence of crystal structure points clearly to its being physically of a different kind to the polar bond, although it is quite possible that there may be a number of intermediate types of bonding which bridge the gap between the two extremes. In order to explain the formation of these non-polar compounds, a way of regarding them as composed of ' electron sharing ' atoms has been developed by Lewis,* and by Langmuir.† This theory cannot be regarded as being in any way a physical explanation of the combination, but it marks a definite advance on the formal way of representing the bonds in the structural formulae of the chemist. It is supposed that when two atoms combine, their structures intermingle in such a way

* G. N. Lewis, *Journ. Amer. Chem. Soc,* XXXVIII., p. 762 (1916).

† I. Langmuir, *Journ. Amer. Chem. Soc,* XLL, p. 868 (1919)

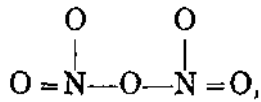
that some of the electrons play a double role. For instance, in the formation of a chlorine molecule, two atoms combine, which, when separate, have one electron less than the stable argon system. When in combination each atom is surrounded by eighteen electrons, two of which it holds in common with the other atom. The chlorine molecule may be regarded as two interlocked argon groups, and, as we shall see later, this appears to be more than a merely formal way of representing the molecule.

The justification for this view lies in the explanation of valency in non-polar compounds which it affords. Such compounds as Cl_2, 0_2, N_20, $C0_2$, and the organic molecules containing carbon, oxygen, nitrogen, and hydrogen, can be explained as due to the tendency of atoms to complete stable electron systems by holding electrons in common In this case the valency force is not an electrostatic attraction which can be exerted on a number of surrounding ions of opposite sign, but it corresponds to a definite valency bond linking up two individual atoms.

The diamond is an instance in which the binding forces throughout the whole crystal structure are of a non-polar type. Every carbon atom in the structure is surrounded by four other atoms. There is here again no assemblage of molecules, but, whereas in the polar compounds there is complete dissociation into charged ions, here there are no ions and the whole crystal must be regarded as a single molecule. The diamond structure is the best example of a structure in which all the bonds are of the kind we have agreed to call ' electron sharing,' and its properties are characteristic of structures in which such bonds exist.

We have contrasted above the two types of bond, polar and non-polar, which hold atoms together in molecules and in crystals. In such cases as the alkaline halides on the one hand, and the molecules of chlorine, oxygen, or nitrogen, on the other hand, the class to which the compound must be assigned is clearly indicated. There are a number of compounds, however, of which the interpretation is not so clear.

According to Kossel's interpretation, the molecule of N_2O_5 is one in which the outer electrons of the two nitrogen atoms, ten in all, have passed over to the oxygen atoms to complete their sets of eight electrons in the L group, each oxygen then resembling neon * in external arrangement. The molecule consists of two nitrogen structures with a positive charge of 5*e* bound by electrostatic forces to five oxygens with a negative charge *-2e*. Langmuir supposes the same molecule to be one in which electron sharing takes place. His picture of the N_2O_6 molecule may be illustrated as below:



where the single bond represents one pair of electrons held in common by two atoms, and the double bond represents two pairs of electrons held in common.

In many cases the distinction between the two interpretations is a formal rather than a real one. For instance, Kossel represents the molecule $CC1_4$ as below :

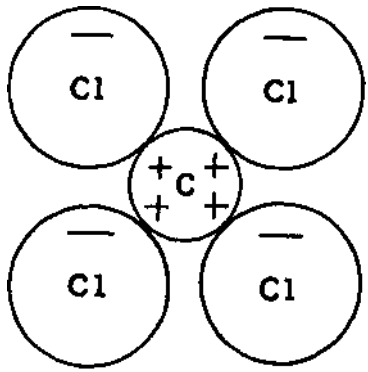


FIG. 56.

*** The atom of the first inert gas in the periodic table, helium, has two K electrons. The next stable structure is realised in neon, of atomic number ten, when the eight additional electrons form a new L group which is completed at that point in the periodic table. For the other inert gases the groups are as follows, according to Bohr:**

Argon 2K, 8L, 8M.
Kryton 2K, 8L, 18M, 8N.
Xenon 2K, 8L, 18M, 18N, 80.
Niton 2K, 8L, 18M, 32N, 18O, 8P.

Here the carbon has a fourfold positive charge and the negatively charged chlorines are held by electrostatic attraction. In the model proposed by Langmuir, a pair of electrons are held in common by the carbon and each chlorine atom, so that the carbon has an outer 'shell' of eight electrons like the stable argon structure. It does not seem very material whether we regard these electrons as part of the chlorine structures alone, or as also forming the outer shell of the carbon atom. There are cases, however, in which there appears to be a real physical difference between the two models. The CO_3 group in calcite is an instance of this. It is an ion with a double negative charge. Kossel regards the three oxygen atoms as having deprived the carbon of its four *L* electrons, and as having taken up an additional two electrons, so that three oxygens with a double negative charge are grouped around a carbon with a fourfold positive charge. According to Langmuir the ion has the structure of Fig. 57.

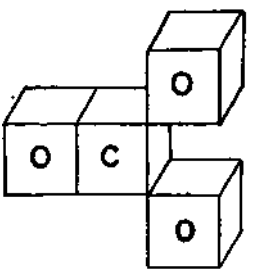


FIG. 57.

In the calcite structure the carbon is surrounded by three oxygens symmetrically grouped around it. There is no evidence of a differentiation between one of the oxygen atoms and the other two, as Langmuir's formula would suggest; and the actual crystal structure is more in accordance with Kossel's interpretation.

There is a further type of interatomic forces which has not been referred to above. Most organic substances are composed of molecules in which the atoms are linked together by electron sharing bonds. Now, these organic substances form well-defined crystals, the units of the pattern being molecules each of which is electrically neutral. Some type of residual forces must bind together these molecules. The bonds do not depend on electron sharing nor on the attraction of ions, though they may be partly electrostatic in character owing to a polar distribution of electric

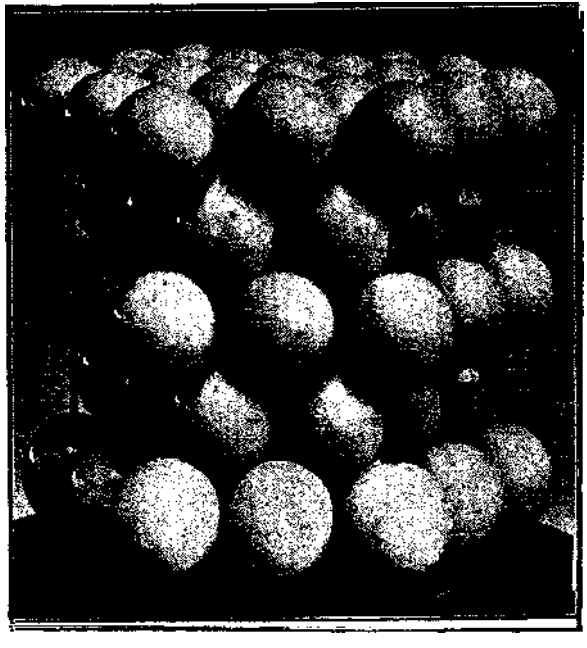
charge in the molecule. Examples of this will be discussed in the chapter on Organic Crystals.

Lastly, there is the problem of the interatomic forces in metals. The forces may possibly be like those in polar compounds, the electrons playing the part of the negative ions.

In order to see the influence of the types of atomic linking upon crystal structure, we will make a survey of the crystals which have been analysed by X-rays. At the same time, another feature of the structure will be examined ; this being the distances which exist between the centres of the atoms. It will be seen that the comparison of inter-atomic distances leads us to make certain empirical generalisations in regard to the contribution made by each atom to the distance separating it from its neighbours. While these generalisations are only approximate, they are of great assistance to analysis. Geometrical considerations alone would allow the atoms to have any position, over a wide range, in most crystal structures. Actually, however, each atom must appropriate a certain volume to itself, and other atoms cannot encroach on this domain. We may attempt to get a measure of the distances within which atomic centres approach each other.

In Fig. 58 is reproduced the well-known Lothar Meyer's curve, which forms such a good illustration of the periodic character of atomic properties. The atomic volume of each element, in cubic centimetres per gram-atom, is plotted against the atomic number. The alkali metal which commences each period of the periodic table is placed at a peak of the curve. Succeeding elements occupy positions on a regular curve, which has a minimum for the elements in the middle of the period, and rises again to the peak occupied by the next alkali metal.

The knowledge of crystalline structure which we now possess enables us to plot this curve in a new way. The structures of a large number of elements are known, the greater proportion of these having been analysed by Hull by the powder method.



1. CUBIC PACKING. 2. HEXAGONAL PACKING.

From Pope's *Modern Aspects of the Molecular Theory.*

Facing page **160.**

Fifteen of these elements, all ductile metals, crystallise with a face-centred cubic structure. This is one of the ways in which a number of equal spheres must be packed in order to occupy the least possible volume. A cubic close-packed structure is illustrated in Fig. 1. PL VII.; each sphere touches twelve neighbouring spheres.

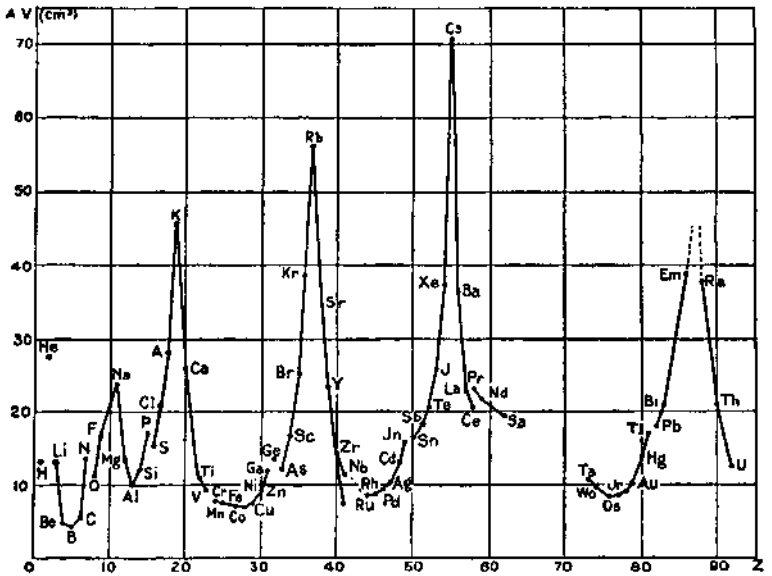


FIG. 58.

There is an alternative way of packing the spheres together into a close-packed structure. The spheres in the (in) planes of PL VII. are placed so that their centres are at the corners of a network of equilateral triangles. Successive (111) layers are packed on top of each other so that the spheres of one layer fit into the hollows between three spheres of the layers above and below. In the structure of Fig. 1. a line starting from the centre of one sphere and perpendicular to the (111) plane, passes through the centre of another sphere three layers distant from the first. We can, alternatively, so pack these layers that every second layer, and not every third, is arrived at from the one we start with by a movement of translation perpendicular to the layers. The resulting structure has hexagonal symmetry and is illus-

trated in Fig. 2. The degree of close-packing is absolutely the same in both cases. Five of the elements crystallise in this way, with an axial ratio which agrees very closely with the ideal ratio for close-packing. Zinc and cadmium have a similar structure, with a larger axial ratio. Cobalt and cerium are interesting as examples of a metal crystallising with both the hexagonal and cubic close-packed structure.

Lithium, sodium, vanadium, chromium, iron, molybdenum, tantalum, and tungsten have their atomic centres arranged on a body-centred cubic lattice. Iron is interesting in that its a, β, and δ modifications appear to have a body-centred arrangement, whereas γ ion between the temperatures of about 900^0 C. and 1700^0 C. has a face-centred cubic arrangement.*

Silicon, and one modification of tin, crystallise with a structure like that of diamond. Antimony and bismuth have a more complex structure, which will be referred to later in this chapter. Aminoff f has analysed mercury, and found that it forms hexagonal crystals. The structure which he assigns to it may be described as a hexagonal modification of the atomic arrangement of the diamond lattice. The hexagonal, approximately close-packed, lattices so intersect that each mercury atom is surrounded by four others.

The following table, due to Hull,‡ summarises the information which has been obtained ; a few additions have been made. References in last column are as follows:

1. Phys. Rev., 10. p. 661, 1917.
2. Proc. Roy. Soc., 89. p. 277,1914.
3. Phys. Zeit., 18. p. 291, 1917.
4. Phys. Zeit., 19. p. 23, 1918.
5. Phys. Zeit., 17. p. 277, 1916.
6. Phys. Rev., 17. p. 12, 1921.
7. Phys. Rev., 18. p. 88, 1921.
8. Journ. Franklin Inst., 1. p. 93, 1922.
9. Phys. Rev., 17. p. 571, 1921.
10. Z. f. Phys. Chem., 98. p. 182, *1921.*
11. Ann. d. Phys., 61. p. 421, 1920.
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13. Phil. Mag., 31. p. 86, 1916.
14. Proc. Roy. Ak., Amsterdam, 21. p. 501, 1919.
15. Phil. Mag., 40. p. 233, 1920.
16. Phys. Zeit., 18. 483, 1917.
17. Phil. Mag., 32. p. 65, 1916.
18. Phil. Mag., 40. p. 233, 1920.
19. Chem. Met. Eng., 25. p. 657, 1921.
20. Phil. Mag., 42. p. 163, 1921.

* Westgren and Phragmen, *Geol. Foren, Forhand.,* Vol. 44, Jan, 1922.

† Aminoff, *Geol. Foren. Forhand.,* Vol. 44, Jan. 1922.

‡ *Journal of the Franklin Institute,* Vol. I., 93, Feb. 1922.

CRYSTAL STRUCTURE OF ELEMENTS.

Substance.	Crystal Structure.		Lattice Constant Side of Elementary Cube or Hexagon.	Closest Approach of Atoms.	Authority.
	Type of Lattice.	Axial Radio.			
Lithium - -	Body-centred cubic		3.50	3.03	Hull[1]
Carbon—					
Diamond -	Tetrahedral cubic		3.56	1.54	Bragg[2]
Graphite -	Hexagonal	2.75	2.47	1.50	Debye[3] Hull[1]
Sodium - -	Body-centred cubic		4.30	3.72	Hull[1]
Magnesium -	Hexagonal	1.624	3.22	3.22	Hull[1]
Aluminium -	Face-centred cubic		4.05	2.86	Hull[1] Scherrer[4]
Silicon - -	Tetrahedral cubic		5.43	2.35	Debye[5] Hull[1]
Potassium -	Body-centred cubic		5.20	4.50	M'Keehan
Calcium - -	Face-centred cubic		5.56	3.93	Hull[6]
Titanium -	Hexagonal close-packed	1.59	2.97	2.90 2.96	Hull[7]
Vanadium	Body-centred cubic		3.04	2.64	Hull[8]
Chromium	Body-centred cubic		2.895	2.508	Hull[9]
Iron - -	Body-centred cubic		2.86	2.48	Hull[1]
	Face-centred cubic		3.60	2.54	Westgren[10] Bain[19]
Cobalt - -	Face-centred cubic		3.554	2.514	Hull[9]
	Hexagonal close-packed	1.633	2.514	2.514	Hull[9]
Nickel - -	Face-centred cubic		3.540	2.505	Hull[1, 9] Bohlin[11]
Copper - -	Face-centred cubic		3.60	2.54	Bragg[12]
Zinc - -	Hexagonal close-packed	1.860	2.670	2.920 2.670	Hull[9]
Germanium -	Tetrahedral cubic		5.61	2.43	Kolkmeyer
Zirconium -	Hexagonal close-packed	1.59	3.23	3.18 3.24	Hull[7]
Molybdenum	Body-centred cubic		3.143	2.720	Hull[9]
Ruthenium -	Hexagonal close-packed	1.59	2.686	2.640 2.686	Hull[9]
Rhodium -	Face-centred cubic		3.820	2.700	Hull[9]
Palladium -	Face-centred cubic		3.950	2.795	Hull[9]
Silver - -	Face-centred cubic		4.060	2.876	Vegard[13]
Cadmium -	Hexagonal close-packed	1.89	2.960	3.28 2.96	Hull[9]
Indium - -	Face-centred tetragonal	1.06	4.58	3.33 3.24	Hull[9]
Tin (grey) -	Tetrahedral cubic		6.46	2.80	Bijl[14]
Antimony -	Rhombohedral hexagonal	2.647	4.28	2.87 3.37	James[15] Ogg[20]

[Continued over

CRYSTAL STRUCTURE OF ELEMENTS—*Continued,*

Substance.	Crystal Structure.		Lattice Constant Side of Elementary Cube or Hexagon.	Closest Approach of Atoms.	Authority.
	Type of Lattice.	Axial Radio.			
Cerium -	Hexagonal close-packed	I.62	3.65	3.64	Hull[7]
	Face-centred cubic		5-12	3.64	
Tantalum	Body-centred cubic		3.272	2.833	Hull[9]
Tungsten	Body-centred cubic		3150	2.726	Debye[16] Hull[9]
Osmium	Hexagonal close-packed	1.59	2.714	2.66 / 2.72	Hull[7]
Iridium	Face-centred cubic		3.805	2.690	Hull[9]
Platinum	Face-centred cubic		3.930	2.780	Hull[9]
Gold	Face centred cubic		4.08	2.88	Vegard[17]
Mercury -	Tetrahedral hexagonal	1.88	3.84		Aminoff
Lead	Face-centred cubic		4.92		Vegard[17]
Bismuth	Rhombohedral hexagonal		4.54	3.11 / 3.47	James[18] Ogg[20]
Thorium	Face-centred cubic		5.04		Bohlin[11] Hull[7]
				3.54	

If we plot the distance of closest approach of the atoms against the atomic number, instead of the atomic volume, we obtain a curve which shows the same periodic character and an even greater regularity than Lothar Meyer's curve.

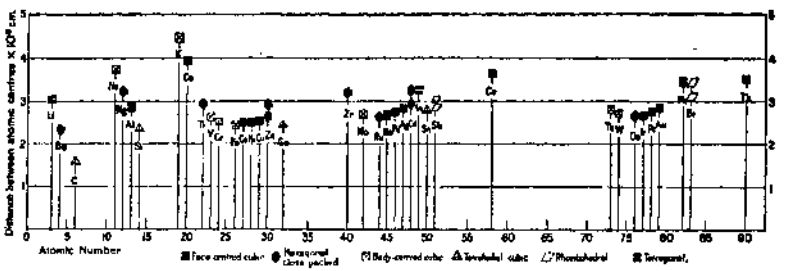


FIG. 59. Elements.

In certain cases the structure of the element is such that there are two different distances of nearest approach between neighbouring atoms ; in these cases two ordinates have been plotted.

The large class of polar compounds, in which the binding forces consist in electrostatic attraction between oppositely

charged ions, will now be considered. These may for convenience be divided into certain groups with characteristic structures, examples of most of which have already been given in this book.

Type 7. *The ion has six neighbours.* The structure of rock-salt is typical of this class. The ions are arranged on two interpenetrating face-centred lattices, in such a way that every point of a simple cubic lattice is occupied by an ion of one sign or the other. This is the form assumed by the compounds of lithium, sodium, potassium, and rubidium with fluorine, chlorine, bromine, and iodine, with the exception of RbF. Ammonium iodide has this form at ordinary temperatures, and its chloride and bromide at 250^0 C.* Other examples are AgCl and AgBr.†

It is also the form assumed by many simple salts of divalent ions. The compounds of magnesium, calcium, strontium, and barium with oxygen and sulphur are probably all of this type. This has been verified in the case of MgO, CaO, CaS, and BaS. Since the selenides and telliirides of these metals are also cubic it appears very probable that we have here another complete series of simple cubic crystals.

Other examples of divalent ions forming simple cubic crystals are the compounds CdO and PbS.

The dimensions of the lattice, in this case the length of the side of the elementary face-centred cube in Angstrom units, are as follows:

SALTS OF MONOVALENT IONS.

	Lithium.	Sodium.	Potassium.	Rubidium.	Ammonium.	Silver.
Fluoride	4.02	4.68	5.38			
Chloride	5.11	5.63	6.26	*6-57*	6.53J	5-56
Bromide	5.47	6.02	6.60	6.93	6.90 +	5-78
Iodide	5-99	6.50	7.IO	7.32	7.20	

* Bartlett and Langmuir, J. *Am. Chem. Soc,* 43, *85,* 1921.

† R. B. Wilsey, *Phil. Mag.,* 42, 262, 1921. J At 250^0 C.

SALTS OF DIVALENT IONS.*

	Magnesium.	Calcium.	Strontium.	Barium.	Cadmium.	Lead.
Oxide -	4.22	4.84	*5.26*	*5.62*	4.61	
Sulphide	*5.08*	5.64	*5-98*	6.40		5.80

Type II. The ion has eight neighbours. The structure of ammonium chloride is typical of this class. The ions of one sign are at the corners of a simple cubic lattice, and the ions of the opposite sign at the centres of these cubes, so that each ion is surrounded by eight of the opposite sign.

Ammonium chloride and bromide at ordinary temperatures, caesium chloride, bromide, and iodide, and thallium chloride, have been found to crystallise in this way. The following table gives the length of the edge of the cube in each case:

	Ammonium.	Caesium.	Thallium.
Chloride	3.86	4.16	385
Bromide -	399	4-33	
Iodide		4.57	

Type Illa. The ion has four neighbours. Zinc-blende is an example. The ions of each kind lie on a face-centred cubic lattice, but the two lattices interpenetrate in such a way that each ion is surrounded by four of the opposite sign. All points occupied by ions form a pattern like that characteristic of the diamond arrangement. Wyckoff has shown that CuCl, CuBr, and Cul are crystals of this type. The following are the dimensions of the lengths of the side of the unit cube :

CuCl -	5.36
CuBr - - - -	5.74
Cul	6.07

This structure has a lower symmetry than that of the first two groups of crystals. The trigonal axes are polar and the crystals hemihedral. It is interesting to note that, while the

* The figures in italics have not been verified by X-ray analysis.

crystals of the first two groups cleave parallel to the cube faces, the crystals of ZnS, CuCl, CuBr, and CuI cleave parallel to the planes (no).

Type IIIb. We have seen that there are two ways of packing equal spheres into the smallest possible volume, and that these have cubic and hexagonal symmetry. In the crystals of the zincblende type the metallic ions are arranged on a cubic close-packed lattice and the ions of the electronegative element are situated between four metallic ions. There is another type of crystal, very similar in structure, in which the ions of each sign are on a hexagonal close-packed lattice, the lattices interpenetrating in exactly the same way, so that each ion is situated between four of the opposite sign. ZnO and CdS are of this type, and so is probably the hexagonal form of ZnS, Wurtzite. Aminoff * has recently shown that AgI at ordinary temperatures has this structure.

The hexagonal close-packed structure has an axial ratio $c : a = 1.633 : 1$. The axial ratios for ZnO. ZnS, CdS, and AgI are as follows :

ZnO -	1.607
ZnS (Wurtzite) - -	1.635
CdS	1.621
AgI	1.639

Aminoff has also examined the compound form of Miersite, 4AgI . CuI. This he has shown to have the same structure as CuI, that of the zincblende type. The structure of AgI is especially interesting in view of the fact that above the temperature of 146^0 C. the hexagonal modification is replaced by a cubic modification. Since the hexagonal modification has the same structure as ZnO and CdS, and in view of the structure of Miersite, it is natural to expect that this cubic modification would prove to be of the zincblende type. This is not the case, however, according to Aminoff. The structure is far more complex, the elementary cube containing at least two molecules.

*** *Geolog. Fdren. Forhand.*, Vol. 44, March 1922.**

Type IV. The structure of fluor-spar CaF_2, has already been discussed. SrF_2 and BaF_2 * crystallise in the same way. The lattice constants are :

CaF_2 -	549
SrF_2 - - - -	5.77
BaF_2 -	6.20

A very large proportion of the simpler chemical compounds crystallise in one or other of the above ways. Examples of more complex crystals, in which there are a large number of atoms in the molecule, will be given later in this chapter.

In a series of compounds, such as the alkaline halides, we can study the effect of replacing one atom by another. When chlorine replaces fluorine, or bromine replaces chlorine, the dimensions of the lattice are increased. In the following table are given the distances between atomic centres for a number of halogen compounds, and the differences of these quantities, which represent the effect on this distance of substituting one halogen for another.

	Li.	Na.	K	Rb	Cs	NH_4	Cu	Ag
F -	2.01	2.34						
	•55	•47						
Cl -	2.56	2.81	313	3.28	3.54	3.26	2.32	2.78
	.17	.20	•17	.18	.21	.19	.17	.11
Br -	2.73	3.01	3.30	3.46	3.75	3.45	2.49	2.89
	.26	.24	.24	.20	.21	.15	•14	
I -	2.99	325	3.54	3.66	3.96	3.60	2.63	

The substitution of one halogen for another causes very nearly the same increase, whatever the metal with which they are both combined, except in the case of the silver and copper compounds. This involves as a corollary that the same holds true for the substitution of one metal for another. If this were rigorously true, it would be possible to express the interatomic distance for any one of these compounds as the sum of two constants $R_A + R_B$, where R_A is a constant

* Davey, *Amer. Phys. Soc*, Nov. 1921.

for each metal and R_B for each halogen. The actual values of these constants are indeterminate, since we only know their sum.

Some of the interatomic distances in the above list have been obtained by X-ray measurement, others have been deduced from the molecular volumes of the crystals. It may be that many of the irregularities in the above table will disappear when all the crystal structures have been analysed. Davey * has recently made accurate measurements on a series of alkaline halides NaF, NaCl, NaBr, KF, KG, KBr, KI, RbBr, CsCl, Csl, and has shown that the additive law is obeyed very accurately indeed for these compounds.

The same appears to be true in the case of the compounds of divalent ions, though in this case only a few structures have been analysed. The substitution of sulphur for oxygen causes a characteristic increase in the interatomic distance.

Metal.	Mg	Ca	Sr	Ba	Zn
Substitution of S for O	.43	.37	.36	.39	.38 A

Similar relationships exist in the other series of crystals.

It is an exceedingly difficult matter to summarise these relationships and to express them in a form which will be useful in analysis, partly because there are many cases which do not fall into line, partly because our knowledge of crystal structure is so limited as yet.

One method of expressing the relationships is to assign to each atom a definite constant which we will call the ' radius of combination ' ; it represents the contribution of the atom to the interatomic distance in any compound. If the constants for two atoms which are nearest neighbours are R_A and R_B, then the distance between them should be $R_A + R_B$. If we consider polar compounds alone, in which R_A is always associated with a metal, and R_B with an electronegative element, the constants are indeterminate since any other set $R_A + x$, $R_B - x$ will serve as well. To fix R_A and R_B some other principle must be involved. Perhaps the best way in which to get an idea of the general relationship

* W. P. Davey, *Proc. Am. Phys. Soc,* August 1921.

between interatomic distances is to see how far a consistent series of constants may be drawn up, and then to discuss the exceptions.

An attempt along these lines was made by one of the authors as follows.* It was found that a series of constants could be drawn up for the polar compounds of the monovalent and divalent elements, which was consistent in itself. As explained above, this still leaves the actual constants indeterminate. In order to fix the constants they were so adjusted as to represent, not only the distances in polar

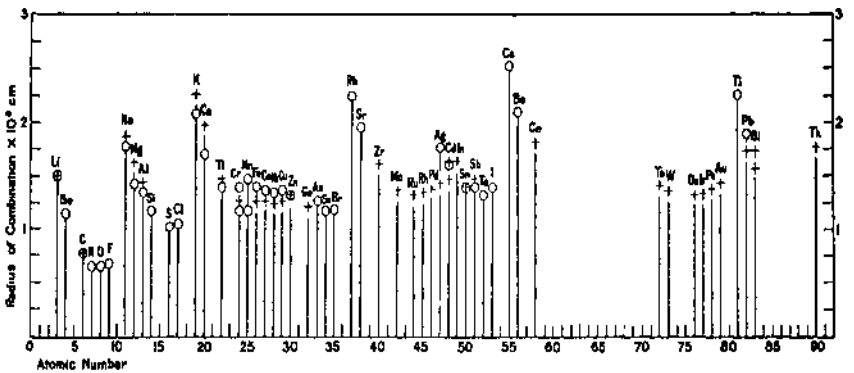


FIG. 60. Compounds.

compounds, but also those when two electronegative elements are in combination. The resulting figures are represented in Fig. 60, where the radii of combination are represented as ordinates (circles) plotted against the atomic numbers, as abscissae.

It is to be emphasised, as was done in the paper referred to above, that these radii of combination are only a set of empirical constants intended to be of use in computing the dimensions of the molecule which is built into the unit of crystal structure. It is only by making further assumptions that we can regard them as having any bearing on the actual dimensions of atomic structure. We know so little about the structure of the atom that no unique meaning can be assigned to what is usually called the ' atomic diameter' of

* *Phil Mag.*, S. 6, Vol. 40, No. 236, Aug. 1920.

an element. In the original paper the quantities which have here been called radii of combination were, for the sake of brevity, called the atomic radii, but as the latter term is misleading it has been replaced by the former in this chapter.

With some exceptions, which will be referred to below, the distance between two atoms, in any polar compound, agrees with that obtained by adding together the corresponding ordinates in this graph to within one-tenth of an Angstrom unit. Since the polar compounds alone cannot be used to fix the absolute values of the constants, these were decided by the closeness of approach of the electronegative atoms, in which cases the interatomic distance is small because of the interlocking of structure which we have called electron sharing. By doing this, a consistent set of constants is obtained which can be applied to compounds in which either type of combination exists.

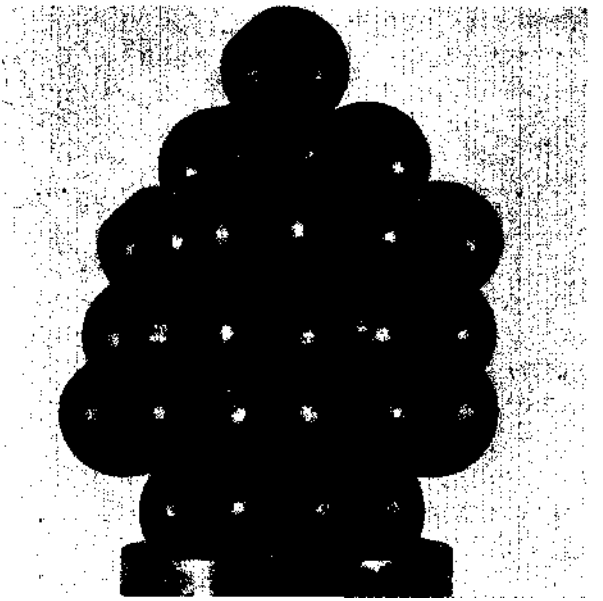
The data for the distance between centres of electronegative atoms in combination is very meagre. We know the distance from carbon to oxygen, and nitrogen to oxygen, in the carbonates and sodium nitrate. We know the distance between the two sulphur atoms in FeS_2, when apparently the S_2 group plays the part of an electronegative ion. Further, we know the crystal structure of a few electronegative elements such as carbon and silicon, where the atoms are bound by electron sharing, and where it is justifiable to halve the interatomic distance in order to deduce the radius of combination. The constants for N, 0, S were arrived at along these lines. The distance between sodium and oxygen centres in $NaN0_3$ is almost identical with that between sodium and fluorine centres in NaF. Similarly, the distance between Ca and O in CaO is the same as that between Ca and F in CaF_2. We must therefore assign to fluorine the same constant as that assigned to oxygen. The values for the other halogens follow from the increases in interatomic distances when they are substituted for each other. This leads to the radii of combination given in the graph.

In each period the constants approach a lower limit for the electronegative elements. These limits have been set in the graph at .65, 1.02, 1.17, 1.35 in the second, third, fourth, and fifth periods respectively.

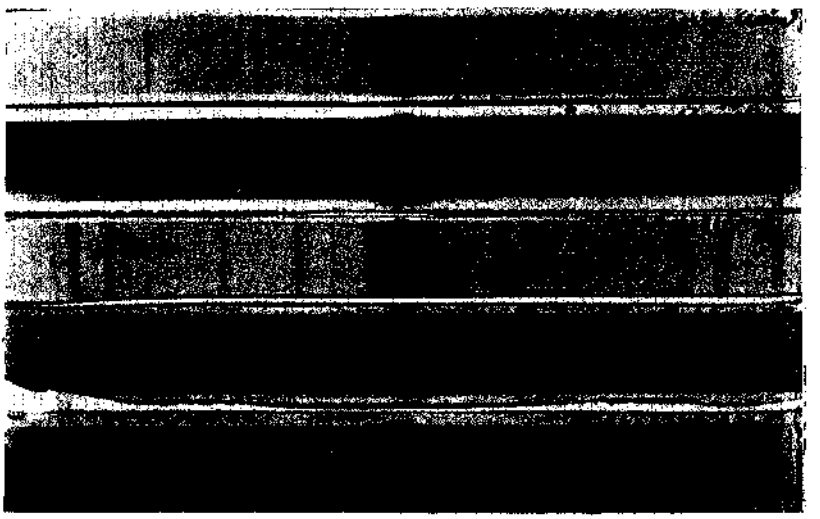
The crosses in the graph represent one half of the interatomic distance for crystals of the elements. In the case of those metals which occur in the middle of the periods (iron, cobalt, nickel, copper, zinc in the third period, for example), it will be seen that the closest distance of approach is not much greater than that which we have deduced for the electronegative elements in the same period. The elements lithium, sodium, magnesium, calcium, on the other hand, have a very large atomic volume and a correspondingly great interatomic distance. We may compare metallic calcium with its compounds in illustration of this. The atoms in the element calcium lie on a face-centred lattice, just as they do in CaF_2 and CaO. However, in CaF_2 the centres of calcium atoms are closer together than they are in the metal itself, in spite of the interposition of the fluorine ions, and in CaO they are still closer again. For these elements the radii of combination in crystals of the element and in compounds cannot possibly be reconciled, and the crosses lie well above the circles in the graph.

In some cases we must assume that there are at least two radii of combination. In AgCl and AgBr, for example, silver must be assigned a constant equal to 1.72, nearly the same as that for sodium. Correspondingly, many silver and sodium salts are isomorphous and have nearly the same molecular volumes. In Ag_20 and Agl,* on the other hand, silver must be given a radius of combination of 1.42, corresponding to one-half the interatomic distance in metallic silver (1.43). In Fe_30_4 and $FeC0_3$ the distance between Fe and O centres gives $R_{Fe}=1.35$. In FeS_2 $R_{Fe}=1.25$, corresponding to $2R_{Fe}=2.52$ in metallic iron. In antimony and bismuth we have a case where, in the crystal of the element, there are two different interatomic distances.

* Cf. Aminoff, *loc. cit.*



MODEL OF BISMUTH CRYSTAL.
Showing that the atom possesses two radii of combination.



X-RAY SPECTRA OF CERTAIN FATTY ACIDS.
(See Muller: *Transactions Chemical Society,* Vol. 123, p. 2043.)

***Facing page* 172.**

For antimony these are 2.87 and 3.37, for bismuth 3.11 and 3.47. The atoms seem to be connected to three neighbours on one side by electron sharing like those of an electronegative element, and to three on the other in the same way that atoms are linked up in metals. The structure of bismuth is illustrated in PL VIII. (See also list on p. 163.)

The existence of two values for the radius of combination of these two elements and of bismuth is further illustrated in the structures of their oxides.

Arsenolite (As_2O_3), senarmontite (Sb_2O_3) and cubic bismuth sesquioxide are isomorphous. An X-ray examination of the two former has been made by Bozorth.* The structure is based on that of the diamond, a group As_4O_6 or Sb_4O_6 replacing each atom of carbon. The molecule is a regular tetrahedron, like the carbon atom : and, as in the diamond, there are two orientations of the tetrahedron, one being the reflection of the other in any plane parallel to a cube face. These deductions follow from the experimental result that a plane *(Imn)* gives a reflection only if *Imn* are all odd or all even, with the further condition that if any of the three, *l*, *m* or *n*, is equal to zero, the sum of the rest is a multiple of four. A full explanation of the validity of this test is given in a discussion of the crystal of basic beryllium acetate which has the same structure.† Since the molecule Sb_4O_6 is a regular tetrahedron the four Sb atoms must lie on the four lines joining the centre of the tetrahedron to its corners, and the six oxygen atoms on the six perpendiculars from the centre on the six sides. The distances of the antimony and the oxygen from the centre are two parameters which cannot be determined from the nature of the structure, but may be estimated from a comparison of reflection intensities. Having thus found values for the parameters, Bozorth concludes that the shortest distances between an antimony and an oxygen within the

* R. M. Bozorth, *Journal of the American Chemical Society,* **July 1923, p. 1621.**

† W. H, Bragg and *G.* T. Morgan, *Proc. Roy. Soc.,* 104, p. **437, Oct. 1923.**

same group or molecule Sb_4O_6 is 2.22 A: if the two atoms belong to neighbouring groups, the shortest distance is 2.61 A. Allowing 0.65 A for the contribution of the oxygen atom to the distance between the centres of oxygen and antimony, the two contributions of the antimony atom are 1.57 A and 1.93 A respectively, which are a little larger than the values found in the antimony crystal itself.

There is a monoclinic variety of As_2O_3 called claudetite, and an orthorhombic variety of Sb_2O_3, valentinite. The unit cell of claudetite contains two groups As_2O_3 and its dimensions are :

$$a=5.35, \quad b=6.5, \quad c=4.45, \quad \beta=94°.$$

If one molecule is placed at each corner of the cell, the other is approximately at the centre. It is possible that in the molecule we now have two arsenic atoms joined together by the closer bond, and that the symmetry of the crystal is lowered in consequence. In the arsenolite group As_4O_6 the arsenic atoms form a regular tetrahedron : in the group As_2O_3 the two atoms of arsenic may have a dumb-bell arrangement.

As an example of another way of regarding these relationships, Davey's paper, which is referred to above, may be quoted. In such a crystal as potassium chloride, for instance, we suppose that both potassium and chlorine atoms are in the form of ions, with a structure approximating to that of argon, so that presumably these ions have very nearly the same dimensions. With this in view, Davey has calculated a set of constants by assigning one half of the interatomic distance to each ion. His results are as follows :

$$R_{Na}=1.25, \quad R_F=1.13,$$
$$RK=RCI=I.56,$$
$$R_{Rb}=R_{Br}=1.73,$$
$$R_{cs}=R_1=1.98.$$

To assign equal radii of combination to these pairs of elements asserts the fact that each ion contributes the same amount to the interatomic distance. On the other hand, the large radius^assigned to potassium and the small radius

assigned to chlorine in the graph do not bring out this equality. In reality, however, we are only dealing with the additive law from two different points of view.

According to the principle of the radius of combination, an atom which is surrounded by neighbours all of one kind, and all linked to it in similar fashion, must also be equidistant from them. It is sometimes possible to go far towards the solution of a structure by the aid of this idea alone, without knowledge of the actual distance between centres.

If, for example, it had been required to determine the structure of rock-salt from the premises that each chlorine atom was to be surrounded by as many sodium atoms, as a sodium by chlorines, and that the relations, including the distance from centre to centre, between neighbours of opposite kinds was always to be the same, and also that the structure was to be cubic, the number of possible solutions would have been limited to three. Each ion of one kind might have had four neighbours of the opposite sign as in zinc-blende, or six as in the actual case, or eight as in the case of ammonium chloride. The decision between the three might be supposed to be made either by X-ray examination or by a knowledge of the actual distance between centres combined with a knowledge of the density of the crystal.

So also, in calcium fluoride, each calcium is to be surrounded by twice as many fluorines as each fluorine by calciums : and with premises similar to those of the rock-salt problem, the number of possible solutions is very limited. The final decision may also be supposed to be made in the same way.

As a matter of fact, these two crystal structures were not solved in this way, but by a more direct use of X-ray methods of analysis. The solutions were useful in establishing the principle of the radius of combination ; they were not obtained by the aid of the principle.

On the other hand, the determination of the structure of ice * may be quoted correctly as an instance in which a

* W, H. Bragg, *Phys. Soc.,* London, XXXIV., p. 98.

suggestion based on an application of the principle was afterwards verified by comparison with the results of X-ray analysis. As in fluor-spar the ratio of the two kinds of ions is two to one. A limited number of solutions of the arrangement of oxygen and hydrogen atoms can be found, each of which satisfies the equal distance principle and gives the two to one ratio. For example, there is the fluor-spar structure itself, which is, however, ruled out at once, because it is cubic, whereas ice is a hexagonal crystal. It is still worthy of note that if oxygen were substituted for calcium and hydrogen for fluorine, so that each oxygen had eight hydrogens as neighbours (see p. 102), and each hydrogen had four oxygens as neighbours, and if the dimensions of the structure were adjusted to give the right density, the distance between the centres of neighbouring oxygens and hydrogens would be far larger than can possibly be the case. For we should then have $„916a^3 = 4(16+2) \times 1.662$, where a is the side of the cube : whence a=5.07. The distance between the centres of adjacent oxygen and hydrogen atoms is a quarter of the cube diagonal, and is therefore

$$5.07 \times \sqrt{3}/4 = 2.2.$$

The oxygen radius is about .65 ; the hydrogen radius cannot be as much as 1.55. A more open structure must be looked for : the number of neighbours must be reduced so that the mutual distance can be reduced also. This suggests that the lightest of all structures, that of the diamond, is to be used as model. Each carbon atom of the diamond is surrounded symmetrically by four others. If an oxygen atom is substituted for each carbon atom, and a hydrogen atom placed between each pair of oxygens, each oxygen has then four hydrogen neighbours, and each hydrogen has two oxygen neighbours. The diamond is cubic, but there is a companion arrangement which is hexagonal. Just as the diamond structure is derived from the close-packed cubic structure (Fig. 33) by adding to the cubic lattice a second lattice derived from the first by a shift along the cube diagonal equal to a quarter of the diagonal or three-quarters

of the (111) spacing, so the ice structure is derived from the close-packed hexagonal structure by a similar shift of three-quarters of the (0001) spacing along the axis. This, then, is the most open, hexagonal, two to one structure that can be suggested. The nearest distance between the centres of two oxygen atoms can readily be found in the following way by comparison with the corresponding distance in the diamond, 1.54 A.u. The densities of diamond and ice are respectively 3.52 and .916 : the weights associated with points on the lattice are as 12 to 18. Consequently if the distance in question is called *d*, we have

$$\left(\frac{d}{1.54}\right)^3 = \frac{3.52}{.916} \times \frac{18}{12},$$

whence d=2.76: the distance between the centres of an oxygen and a neighbouring hydrogen is half this quantity, or 1.38.

The structure is shown in the figure in which a certain number of the atoms are drawn in full, so as to show the general construction. The shortest distance between two oxygens (there is a hydrogen between them)

$$= DP = PE = PQ = \ldots = 2.76.$$

The value of *DF* is calculated to be 4.52 : and of *DA* to be 7.34. These are the values *a* and *c* of the hexagonal lattice.

Analyses of the structure by means of X-rays have been made by Ancel St. John * and by D. M. Dennison † : the latter finds that *a* and *c* are 4.52 and 7.32 respectively. He also finds that if two molecules are associated with each corner of a right prism having a height 7.32 and an equilateral triangle of side 4.52 as base, then the centre of this prism is associated with two more molecules. This partial solution, obtained by X-ray analysis, is in agreement with the complete solution of Fig. 61.

In a diagram such as that of the figure it is necessary to give dimensions to the separate atoms of oxygen and

* *Proc. Nat. Acad. Sci.*, p. 193, July 1918.

† *Science*, Sept. 24, 1920; *Phys. Rev.*, Jan. 1921.

hydrogen ; but it is to be observed that the only linear distance actually determined by analysis is the distance 2.76, which is equal to the sum of the oxygen and hydrogen diameters. The separate diameters can only be inferred from the evidence of other experimental results. For instance, the value 1.30 has been given as the diameter of

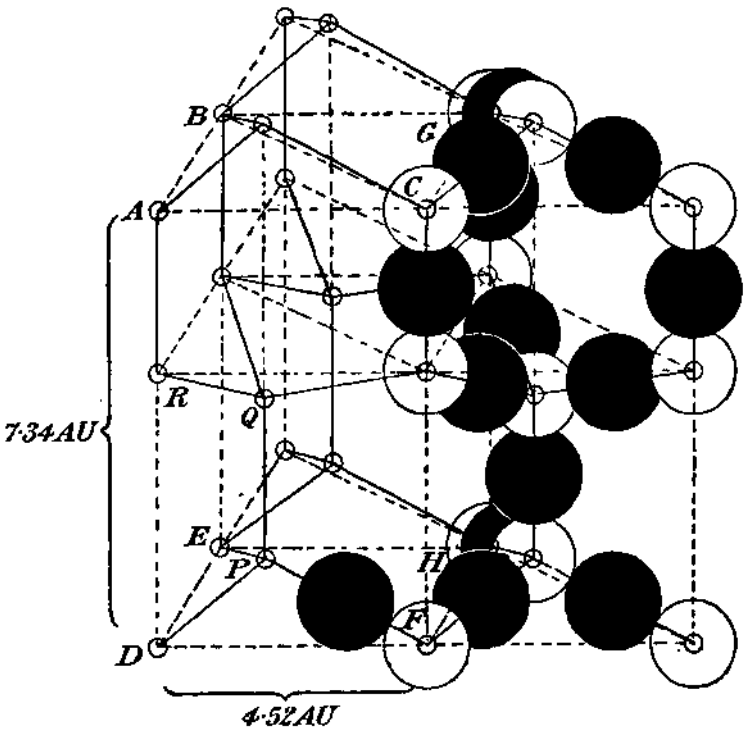


FIG. 61.

Black circles represent Hydrogen Atoms ; white circles represent Oxygen Atoms.

oxygen on a certain definition of this quantity. If this is the diameter of oxygen in the ice structure, the corresponding diameter of hydrogen is 1.46.

We may now proceed to compare the intensities of the lines obtained by Dennison by the Debye-Hull photographic method with the intensities calculated from a knowledge of the structure. These are set out in the following table in which the figures of the last column are taken from Dennison's

paper, while the figures of the last column but one are calculated on the basis of the structure we have derived from the application of the principles of symmetry and of the combination radius:

Plane.	Phase Factor. F.	Number of Co-operating Planes. N.	Spacing Observed.	Factor Proportional to $F.\ N/\sin^2\Theta$.	Observed Intensities (Dennison).
0001	0	1		0	0
0002	8	1	3.67	100	100
0003	0	1		0	0
0004	0	1		0	0
1010	4	3	3.92	177	10
2020	4	3	(1.96)	44	0
3030	16	3	1.30	78	2.5
1011	1.76	6	3 4 4	136	20
1012	2.00	6	2.68	83	15
1013	10.24	6	2.065	243	50
1014	0	6		0	0
1015	10.24	6	1.368	110	20
1120	16.0	3	2.26	236	10
1121	0	6		0	0
1122	8.0	6	1.92	170	10
1123	0	6		0	0
1124	0	6		0	0
2023	10.24	6	1.53	143	15
2025	10.24	6	1.167	80.0	5.0

In comparing the calculated and observed values, it is to be observed:

1. That the relative intensities vary very sharply with slight changes in structure and that a general agreement extending over such a large number of different planes as are given in the table is very strong evidence that the structure is correct.

2. That the calculation of intensities is not yet on a perfectly sound basis, and that discrepancies between different sets of planes are more likely to occur in consequence than between planes in the same set. Thus there is a much better agreement between members contained within the

various groups of the table than between members of different groups.

3. The largest discrepancy in the table lies in the great strength of the observed reflection 0002 as compared with reflections from other planes. The calculations do not give such a prominence to this plane, but the plane is that of cleavage, and this is the principal reflection from that plane. Various explanations can be suggested without effort, as, for example, that the cleavage plane may have been specially favoured in the arrangement of the experiment.

4. The reflection from 2020 may well be obscured by that from 1122.

Mr. F. J. Whipple has drawn our attention to a paper by Dr. E. D. Clarke written a century ago (Jan. 3, 1821) in which he describes an observation of some exceptionally brilliant icicles, which, from his measurement, must have possessed the diamond structure itself, not the alternative hexagonal structure which we have been considering.

A further illustration may be drawn from the determination of the structure of corundum, which is specially interesting as a 3 : 2 arrangement.

Corundum, ruby or sapphire $A1_20_3$ is a trigonal crystal of the calcite class. According to Groth $a : c = 1 : 1.3652$. Density = 3.99.

The volume of a rhomb possessing trigonal symmetry is $a^2c/2\sqrt{3}$. Putting one molecule into the rhomb, we have

$$(2 \times 27 + 3 \times 16) \times 1.662 = a^3 \times 1.3652 \times 3.99/2\sqrt{3},$$

whence

$$a = 4.75,$$
$$c = 6.49.$$

It can be shown that in a trigonal crystal the spacing of the *(Itnri)* plane is given by

$$d_{lmn} = \frac{ac\sqrt{3}}{\sqrt{\{4c^2(l^2+m^2+n^2-lm-mn-nl)+3a^2(l+m+n)^2\}}}$$

Hence

$$d_{100} = ac\sqrt{3}/\sqrt{(4c^2+3a^2)} = 3.48,$$
$$d_{11\bar{2}0} = a/2 = 2.375,$$
$$d_{001} = c/3 = 2.163.$$

The experimental results are 3.49, 2.36, and 2.17 respectively : so that the right number of molecules, viz. one, has been put into the cell.

As will be shown presently, the *c* axis ought to be doubled, so that the unit cell includes two molecules, one being the image of the other across any of the three planes of symmetry which the crystal possesses. But the point is for the moment unimportant, and we may proceed with the consideration of the cell defined above.

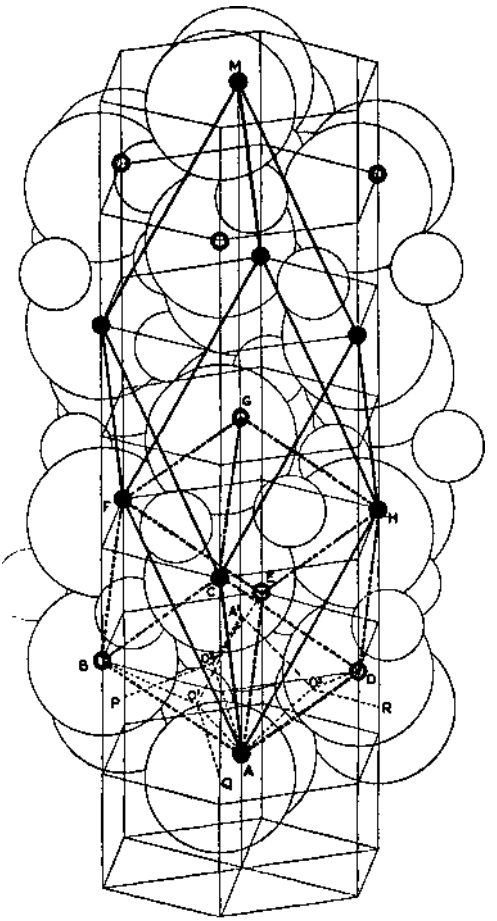


FIG. 62.

Placing an aluminium atom at each corner of the rhomb *ABCDEFGH* (Fig. 62) we have to find the positions of the second aluminium and of three oxygens. For reasons of symmetry, the second aluminium is on the axis and the oxygens must be arranged symmetrically around it. It would be a severe strain on our present power of interpreting X-ray spectra to rely upon that alone to complete the determination of the atomic positions. The problem is greatly simplified by the use of the principle of combination radii. We draw from this the expectation that each aluminium must be at equal distances from six oxygens, and each oxygen

from four aluminiums. Other numbers, such as 3 : 2 or 9 : 6 are conceivable, but are' immediately abandoned on trial. Supposing that the position of the second aluminium is fixed provisionally, it is found that the positions of the oxygens are obvious (see Fig. 63), if the above principle is to be satisfied, and that no uncertainty as to position remains.

NOTE DESCRIBING FIGS. 62 AND 63.

An aluminium atom is placed with its centre at each of the points *A, B, C, D, E, F, G, H,* being the corners of the smaller rhomb shown in dotted lines. The rhomb is drawn in accordance with the crystallographic data as ordinarily given. The second aluminium atom, from symmetry, must lie on the trigonal axis *AG.* Let its centre be at *A'.* The three oxygens belonging to *AA'* must each touch both *A* and *A'* and two other aluminium atoms. Looking down along the axis, as in Fig. 63, on the atoms at the bottom of the rhomb, it is to be observed that *A* is at the lowest level; *B, C, D* are at a level higher than that of *A* by c/3 = 2.16. There are also three aluminiums *P, Q* and *R,* being the upper atoms of aluminium pairs ; they are on a level 2.16 below *A'.* An oxygen atom 0_1 goes into place if it touches *A, Q, B* and *A' :* it is higher in level than the first two and lower than the second two. The other two atoms of the trio will then fit in at 0_2 and O_3 as shown. Alternatively, the trio could have been turned round the trigonal axis through 6o°.

It can be shown that AO_1 bisects the angle *BAQ,* and that if *A A',* the distance between the centres of a pair of aluminium atoms, be denoted by *v,* and AO_1 by *r,* then

$$r = \frac{a}{3} + \frac{c^2}{9a} - \frac{cv}{3a}.$$

This is the condition that O_1 is at equal distances from *A, A', B* and *Q.* The distance is $\sqrt{(r^2 + v^2/4)}$.

The distance *v* is determined by considering the intensities of the in spectra which depend on the relative phases of the oxygen and aluminium layers, and these, in turn, depend on the value of *v.* It appears that v = 2.73 nearly, and, therefore, that r=1.33, and the distance between centres of aluminium and oxygen is 1.90.

If all the molecules at the corners of the small rhomb, which is equivalent to saying all the molecules in the crystal, were similar to the molecule represented by *A,* there would be no plane of symmetry. The crystal has three planes of symmetry (110) ; such as, for example, a plane through *APD* in either figure. The crystal unit really contains two molecules, one being the reflection of the other across a symmetry plane : and is represented by the full-line rhomb in

Fig. 62. In this figure a full black circle is placed at the centre of the lower of each like pair of aluminiums : each pair of the other kind is similarly represented by a ring. In order to bring to self-coincidence after reflection, across the plane through *APD,* for example, the whole must be shifted along the axis through a distance equal to half the axis of the long rhomb. This brings a full circle to a ring and *vice versa.*

No position for the oxygens, other than that chosen, is possible. It might be supposed, for example, that an oxygen could be placed

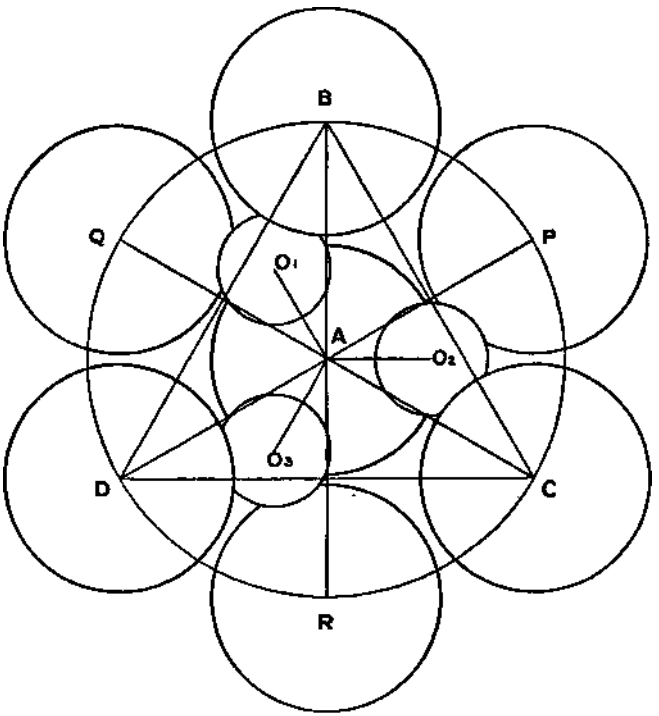


FIG. 63.

so as to lie (Fig. 63) in the plane *AP.* Many conditions would be satisfied by this arrangement, but the plane of symmetry would now contain the dyad axis, which would be wrong. The three dyad axes of the class of crystal to which corundum belongs bisect the angles between the planes of symmetry.

The molecule, as built into the crystal, has a trigonal axis, and three digonal axes, but has no plane of symmetry.

The actual value of the common distance between centres of adjoining aluminium and oxygen atoms has not been assumed; it has been supposed only that there is such a distance. If

the distance is supposed to be known, as the result of an examination of other crystals where Al and 0 are neighbouring ions, the determination is finished. As a matter of fact, it is much safer to use the relative intensities of the in spectra ; it happens that they make a very sensitive indicator. It appears that the distance between the centres of the second Al atom and the centre of the nearest Al atom along the *c* axis is 2.7 : and as this is known to be nearly the diameter of the Al atom, there is a strong presumption that the two Al atoms are, in a sense, in contact. They are doubtless driven together against their own mutual repulsion by greater forces due to the mutual repulsions of the oxygens. The distance from the centre of an Al atom to the centre of an oxygen is 1.90.

It is highly interesting to compare the evidence as to molecular dimensions afforded by crystal structures with that from a very different source, the behaviour of gases. This has been the purpose of a number of recent papers by Rankine.* The theoretical expression for the viscosity of a gas, which is deduced by means of the Kinetic Theory, depends on the free path of the atom or molecule in the gas. The experimental data may be explained by supposing, for purposes of mathematical treatment, that the molecules are bodies of definite size and shape, which rebound on collision, and which exert an attractive force when in close proximity to each other. Taking first the most simple case, that of a monatomic gas where the atoms may be considered as spheres of radius σ, and supposing the attractive force to be non-existent, the average length of the free path is inversely proportional to the area $\pi\sigma^2$ of the target which each atom presents to another atom. The viscosity n, free path A, and radius *a* are connected by the equations

$$\eta = .491\varrho\lambda\sqrt{\frac{3p}{\varrho}},$$

$$\lambda = \frac{1}{4\sqrt{2}N\pi\sigma^2},$$

* *Proc. Roy. Soc,* A. Vol. 98, p. 360, 1921.

where 'p' is the pressure of the gas, 'Q' its density, and N the number of atoms in 1 c.c. of the gas.

The attractive force of the atoms increases the number of collisions by bringing atoms into collision which would otherwise pass each other. It can be allowed for by means of the Sutherland correction, which may be expressed in the form

$$\sigma = \sigma_0\left(1 + \frac{S}{T}\right)^{\frac{1}{2}},$$

where σ_0 is the true radius of the spheres, and a the apparent radius as calculated from the viscosity at a temperature T. The constant S can be calculated from the variation of viscosity with temperature. From these equations we can calculate the effective value of $\pi\sigma_0^2$ by measuring the viscosity n of a gas and its temperature coefficient.

In this case the quantity which has been called the 'radius of the atom is one half of the distance between atomic centres when they approach most closely in a collision.

The values of σ_0 for the inert gases, calculated in this way, are as follows :

Gas.	$\pi\sigma^2$ cm^2. x 10^{-15}	σ cm. x 10- 8.
Neon -	•435	1.17
Argon	.648	1.43
Krypton -	•797	1.58
Xenon	.970	1.75

In the case of a molecule containing several atoms, the viscosity formula gives a means of calculating, not the atomic radius σ directly, but the quantity A ($\pi\sigma^2$ in the case of a single atom) which is the area of the target presented by a molecule to other molecules approaching it from all directions. Rankine compares the area A for the diatomic molecules of the halogens with the area $\pi\sigma^2$ of the inert gases in the following way.

The relation between chlorine and argon will serve as an example. Rankine takes as his model of the chlorine molecule two spheres whose radii are those calculated for the

argon atom, but which interpenetrate at the point where they are linked together (Fig. 64). The distance between the centres of these spheres is set equal to 2.05 following the indications of crystal measurements, and the radii of either 143, so that the extent of interpenetration is considerable. In other words, he supposes that each chlorine atom of the molecule so resembles the argon atom, except at the point where they are linked together, that it behaves in collisions as a sphere of the same size as the atom of argon.

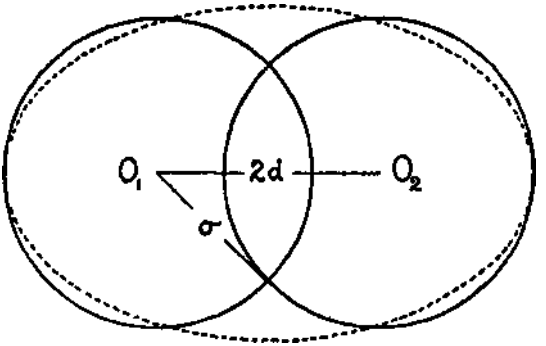


Fig. 64.

He then calculates the mean area of the target which is presented by such a sphere with all possible orientations. In this way Cl_2 may be compared with A, Br_2 with Kr, and I_2 with Xe. Since the data for F_2 are not obtainable, he compares 0_2 with Ne.

In the following table a comparison is made between the mean area *A* of the model and the area S of the diatomic molecule deduced from viscosity measurements.

ALL AREAS IN cm^2, x 10^{-15}

A (calculated).	Gas. .	S (observed).
.67 **1.06** **1.31** **1.61**	Cl_2 I_2	.69 **1.07** **1.28** **1.56**

The correspondence is very striking. Without stressing the

physical interpretation of the correspondence, it appears that the estimate of molecular dimensions deduced from crystal measurements and from the kinetic theory of gases are consistent.

Other interesting relationships which Rankine obtains may be briefly summed up as follows.

$C0_2$ and N_20 are regarded as three spheres in line, with a radius of 1.17 corresponding to neon, and a distance between their centres of 1.30. The mean area *A* of such a model is .895 x 10^{-15} cm^2. *'S'* for $C0_2$ and N_20 is .870 x 10^{-15} cm^2., and .867 x 10^{-15} cm^2., respectively.

The nitrogen molecule N_2 has a mean area 5 = .78 x 10^{-15} cm^2. This is very nearly the same as that of krypton *(S* =.797 x 10^{-15} cm^2.). We might expect a similar identity in structural dimensions to hold between the ions CN~ and Br-, as holds between the neutral units N_2 and Kr. The evidence is in favour of this view.* Two cyanogen ions unite to form C_2N_2 just as bromine forms a molecule Br_2. The mean areas for these gases are :

C_2N_2 S =1.31 x 10^{-15} cm^2.

Br_2 S = 1.28 x 10^{-15} cm^2.

Further, in crystals some cyanides are isomorphous with corresponding halides. In particular KBr and KCN have very nearly the same molecular volumes, 43.1 and 42.8 respectively, and although a complete X-ray examination of KCN has not been made, data obtained by Cooper † indicate that they have the same structure. J It appears that the CN radical behaves in some respects like the simple bromine ion.

We can trace a similar relationship between the ammonium ion NH_4 and the molecule CH_4.§ Ammonium forms salts isomorphous with those of the alkalis, and of very nearly the same molecular volumes as those of rubidium, which

*** Rankine,** ***Proc. Roy. Soc,*** **Vol. 99, p. 330, 1921.**

† P. A. Cooper, ***Nature,*** **1921, 107, 745.**

See also R. M. Bozorth, ***Jour. Am. Chem. Soc,*** **Vol. XLIV., Feb. 1922.**

§ Rankine, ***Trans. Far. Soc,*** **Vol. XVII., Part 3, 1922.**

follows krypton in the periodic table. In accordance with this, we find the molecule CH_4 has an effective area very nearly the same as that of the krypton atom.

$$CH_4 \quad 5 = .772 \times 10^{-15} \text{ cm}^2.$$

$$Kr \quad A = .757 \times 10^{-15} \text{ cm}^2.$$

Langmuir * has drawn attention to a remarkable series of cases of isomorphism which illustrate the part played by the dimensions of the ions in determining crystal structure. The nitrates and carbonates are an example of this. The practical identity in all crystallographic properties and in molecular volume, of sodium nitrate and calcium carbonate, has long been known. Crystals of sodium nitrate when deposited on a freshly cleaved face of calcite form parallel growths. X-ray analysis has shown the structures to be practically identical. We explain this identity of structure by supposing that the singly charged NO_3 ion has the same dimensions as the doubly charged CO_3 ion, and that the greater force, due to the double electric charge, draws the calcium ion into the same proximity with the CO_3 group as the force due to the single charge does in the case of sodium and the NO_3 group. $NaNO_3$, $CaCO_3$, $MgCO_3$, $FeCO_3$, and at high temperatures KNO_3, $RbNO_3$, $SrCO_3$, and $BaCO_3$ form crystals of the calcite type. Similarly KNO_3, $CaCO_3$, $SrCO_3$, $BaCO_3$ are also isomorphous with each other, the typical crystal of this class being the other form of calcium carbonate, the pseudo-hexagonal aragonite. Langmuir cites a number of other cases of isomorphism given by Barker, a few examples of which are quoted here. Just as calcium corresponds most closely to sodium as regards the dimensions of crystalline structure, so strontium corresponds to potassium and barium to rubidium. In agreement with this we find very similar crystalline properties in the case of the following pairs, $KClO_4$-$SrSO_4$; $RbMnO_4$-$BaCrO_4$; $RbClO_4$-$BaSO_4$; $KMnO_4$-$SrCrO_4$; and other more complex crystals.

* *Journ. Amer, Chern. Soc,* Vol. LI., No. 10, Oct. 1919.

The fact that certain crystals form parallel growths on each other is very interesting from the point of view of molecular structure. In 1907 Barker * studied the growth of crystals of the alkaline halides on each other and decided that these crystals must be split up into two groups, having different structures. Crystals of Group A have relatively greater molecular volumes than those of Group B. The members of each group he believed to be iso-structural. Members of Group A form parallel growths on each other, and the same holds for members of group B *inter se* ; while members of group A on group B or *vice versd* yield irregular growths. Barker's table is given below, and it will be seen how fully his conclusions have been confirmed by X-ray analysis.

The figures are the molecular volumes of the crystals.

Group A.—	NaCl,	26.92	(NaCN,	?)	NaBr,	32.21	Nal,	41.06
	KCl,	37.49	KCN,	41.31	KBr,	43.30	KI,	53.06
	RbCl,	43.10	RbCN,	48.60	RbBr,	49.3o	Rbl,	59.62
Group B.—	AmCl,	34-96	(AmCN,	?)	AmBr,	4345	Am1,	58.14
	CsCl,	4215	(CsCN,	?)	CsBr,	47.81	Csl,	57.25

As has been already stated, AmCl and AmBr pass over into group A at high temperatures.

We now add a few notes relating to other physical properties of the crystal unit.

The linear coefficient of expansion of diamond with heat is relatively small: about 1.2×10^{-6} per degree at ordinary temperatures. The corresponding coefficient of expansion of graphite is stated by Fizeau to be 7.9×10^{-6}. But the larger coefficient of graphite is probably due to an enhanced coefficient in the axial direction alone. Backhurst has found an increase of more than 2 per cent, in the 111 spacing of graphite for a rise of 900 ° C. : his results show that the increase with temperature is not linear. Some of Backhurst's curves are reproduced in Figs. 64a and 646. From his results it seems probable that the expansion coefficient

* *Mineralogical Magazine,* Feb. 1907, Vol. XIV., No. 66, pp. 235-257.

perpendicular to the axis is of the same order as in diamond. This suggests that two atoms, when sharing electrons, alter their mutual distance with change of temperature far less than when the bonds are of another type. It is interesting to observe that for bismuth and antimony the coefficient of expansion along the axis is much greater than in the perpendicular direction : in these substances there are atom layers lying perpendicular to the axis in which the atoms are probably joined to each other by electron sharing; but the connection between layer and layer is of a different type, resembling rather the connection between atom and atom in a metal. Also in calcite, for which Benoist found a coefficient of expansion of 25.1 x 10^{-6} along the axis and a negative coefficient -5.6×10^{-6} in the perpendicular direction, it is to be observed that the very strong bonds in the CO_3 group all lie in the 111 plane. The structure of quartz is not yet fully known, but it is not unlikely that the electron sharing bonds in the crystal are on the whole parallel to the axis, since the expansion coefficient along the axis is 7.5 x 10^{-6}, while it is much greater, 13.7 x 10^{-6}, across it.

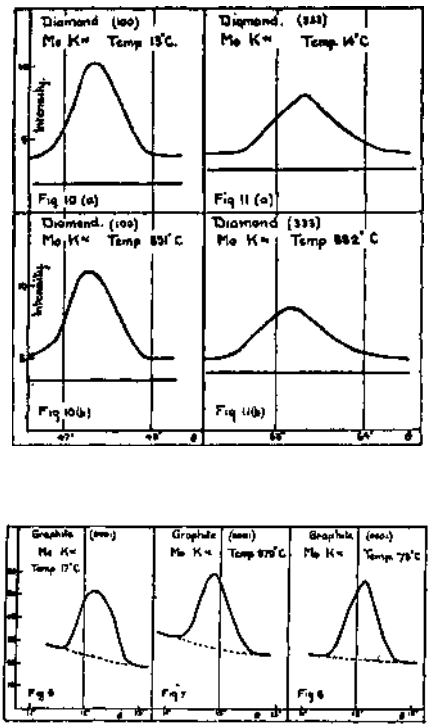


FIG. 64*b*.

These observations are too few to be more than a significant indication of what may be found to hold respecting the relation between expansion coefficients and the nature of the bonds.

The temperatures of melting are also no doubt connected with the nature of the bonds and probably for the same underlying reasons. The very high melting point of carbon, in all forms, may be ascribed to the strength of the electron sharing bond that is to be found both in diamond and graphite, while the very low melting points of the organic substances are, no doubt, due to the weakness of the forces that bind molecule to molecule. Very little is known of these things as yet: the melting point of silicon, which resembles diamond in the nature of its bonds, is high, 1200 approximately; but no explanation can yet be given, in terms of the nature of the bonds, for the fact that this melting point is less than, for example, the melting points of tungsten or rhodium. It is probably safe to say, however, that sulphur has a low melting point because its atoms are bound into molecules, which, as in organic substances, are joined together by a weak form of bond.* In fact, it is impossible to imagine a structure for sulphur which satisfies the condition that

(a) all the atoms are alike ;

(b) each atom has a mass 32 x 1.66 =53.3 A.u. ;

(c) the distance between the centres of two neighbouring atoms in all cases is 2.05 as determined from cases in which there is electron sharing ;

(d) the density of the crystal is only 2, approximately.

The lightest structure that could be made of such atoms, would, being similar to diamond, have a density

$$3.52 \times \frac{32}{12} \times \left(\frac{1.54}{2.05}\right)^3 = 4 \text{ nearly.}$$

The elasticities of the crystal unit are connected very directly with the forces between atom and atom; The type of linking which we have called electron sharing, when the structures of two atoms fuse together to form a complex unit, cannot be explained until the atomic structure is elucidated. In the case of the polar linking, however, we are on surer

* See later, p. 236.

ground, since it is reasonable to assume that the forces which bring the charged ions together are largely those of electrostatic attraction, and these forces can be calculated. The work of Kossel, Born and Lande, Madelung, and Fajans has shown that we can correlate in a quantitative manner these forces of electrostatic attraction with the forces which come into play in chemical combination.

Born and Lande * take the case of the alkaline halides. Here ions of opposite sign are held together in the crystal structure by electrical forces. In addition, a repulsive force must exist which keeps the ions apart, and which counterbalances the electrostatic attraction when the ions are separated by the distance which we measure by means of our X-ray analysis. If it is assumed that the electrostatic forces obey Coulomb's law, we can calculate the amount of potential energy which is lost when N positive ions and N negative ions, originally dispersed in space, come together to form the crystal structure. Madelung f calculates that for a lattice such as that of NaCl it is equal to

$$N \cdot 1.74 \cdot \frac{e^2}{r} \cdot \text{ergs.}$$

This expression must be modified because of the repulsive force which comes into play when the ions approach within a small distance of each other. We cannot calculate this force theoretically, since we do not know the structure of the atom, but we can find its value in the equilibrium positions, since it counterbalances the electrostatic force, and Born and Landè have pointed out that the determination of the compressibility of the crystal enables us to find its rate of variation with the distance. They suppose that the potential energy, set free when the ions come together to form the crystal, is given by the expression :

$$u = N\left(\frac{a}{r} - \frac{b}{r^n}\right)$$

* Born and Land6, *Ber. d. Deut. Phys. Ges.,* 1918, p. 210.

† Madelung, *Phys. Zeitsch.,* 19, 524, 1918.

when $a = 1.74e^2$ as above, and the term $\frac{b}{r^n}$ is due to a repulsive force which decreases rapidly with the distance r, n being greater than unity.

From the condition that $\frac{\partial u}{\partial r}$ =o in the equilibrium position, it follows that

$$b = \frac{ar^{n-1}}{n}.$$

Therefore the expression for u becomes

$$u = \frac{Na}{r}\left(1 - \frac{1}{n}\right).$$

Next, Born and Lande calculate n from the compressibility. They show that if k be the compressibility of the crystal

$$k = 18\frac{9r^4}{(n-1)}a.$$

For a number of the alkaline halides they find a value for n which is approximately equal to 9.

From the above expression for the energy u, we see that, when allowance is made for the forces of repulsion, the potential energy u is eight-ninths of that calculated from the electrostatic forces alone. The alteration made by the additional term is not great, and even though the process by which the term has been calculated may not be completely sound, the correction is probably of the right order. The figures which Born and Lande calculate for the total energy must, therefore, be very nearly the true values. The figures in the following table represent the amount of heat in large calories which is liberated when a gram molecule of the crystal is formed from dispersed ions:

	F	cl	Br	I
Na - -	210.4	170.0	159.7	I46.7
K	192.2	1590	150.6	139.1
Rb	—	154.6	I46.5	135.8

These figures cannot be compared directly with the heats of formation of the corresponding compounds. Starting with solid sodium and gaseous chlorine, the total amount of energy liberated in the formation of NaCl is the difference between the quantity *u* above and the amount of energy absorbed in vaporising the sodium, ionizing the dispersed atoms, dissociating the chlorine molecules into atoms, and ionizing them. We know the latent heat of sodium, the energy necessary to ionize its atoms (measured by the ionization potential of the atom), and the energy necessary to dissociate the chlorine molecules. Since we know experimentally the heat of formation of NaCl from sodium and chlorine, we can calculate the only remaining unknown quantity, the energy required to ionize the chlorine atoms. This proves to be a negative quantity—energy is liberated when the neutral chlorine atom absorbs an electron and becomes an ion. It is found that, for a gram-atom of each element

$$Cl = Cl^- + 119 \text{ calories.}$$
$$Br = Br^- + 84 \text{ calories.}$$
$$I = I^- + 77 \text{ calories.}$$

In other ways a direct check on the estimates of the quantity *u* can be obtained.*

If we take a gram molecule of sodium chloride and of potassium fluoride, and dissolve the crystals in so much water that ionization is complete, the final state is the same as if we had started with equivalent quantities of sodium fluoride and potassium chloride. The sums of the heats of solution will be different in the two cases, however, since we start with different crystal structures. The difference between the total heat of solution for NaCl and KF, and the same total for NaF and KC1, should be equal to the difference between the sums of the structural potential energies given in the above table for the same pairs of structures. This is found to be the case, as the following comparison shows:

* V. Fajans, *Verh, d. Deut, Phys. Ges.*, 21, S. 533, 1919.

							Calculated.	Observed.
KC1	+	LiBr	=	KBr	+	LiCl	+ 4	3.6
KC1	+	Lil	=	KI	+	LiCl	+ 7	7.2
KC1	+	NaBr	=	KBr	+	NaCl	+ 3	2.0
KC1	+	Nal	=	KI	+	NaCl	+ 5	3.4

the energies being in each case expressed in large calories per gram-molecule.

Though the agreement is not in every case good, and though these investigations have not yet progressed very far, there can be no doubt that an advance has been made towards linking up the physical and chemical forces in a quantitative manner.

A few words may be added to this chapter as a summary of its contents.

There is a crystal unit which itself possesses all the properties of the crystal. It contains the substance of a small number of molecules. The chemical molecule may not be found in it: though the unit is divisible into similar atom groups, and a group, as in organic crystals, may be very close indeed to the chemical molecule. It must be the object of research to discover the relation between the structure of the unit and its properties. The researches described in this chapter may be considered as examples of the first experiments in this direction; necessarily fragmentary, and no more, surely, than a preliminary excursion into a very wide field of enquiry.

CHAPTER XIII

THE INTENSITY OF X-RAY REFLEXION

THE efficiency of reflexion of X-rays depends on a number of factors, such as the arrangement of the atoms in the crystal, the amount of radiation diffracted by each atom, the magnitude of the glancing angle, the absorption of the rays in the crystal, and the thermal movements of the atoms. These various factors will be considered in this chapter. The problem is one of great complexity and our knowledge is still very imperfect.

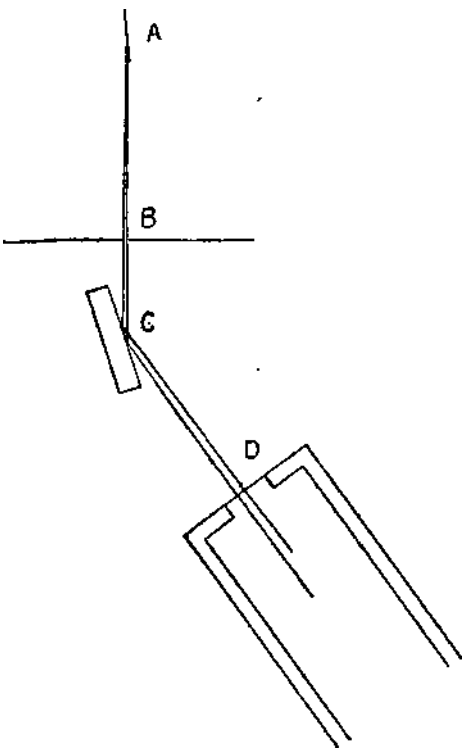


FIG. 65.

In order to make quantitative measurements of the efficiency of reflexion, it is necessary in the first place to give a definite meaning to the term 'Intensity of Reflexion.' Fig. 65 will illustrate the difficulties which present themselves when this is attempted.

A fine pencil of homogeneous rays from a source *A* is

limited by a slit at *B*, and is incident upon a crystal C, so placed that a reflected ray is formed which passes into the ionization chamber *D*. The crystal may be adjusted so as to give the maximum value of the reflected ray and the ionization current may be then measured in *D* during a stated number of seconds. The crystal being removed, the ionization chamber may be turned so that the primary beam enters it directly, and the ionization again measured for a definite time.

An estimate of the intensity of reflexion cannot, however, be based on a comparison of these two quantities. In the first place, the ratio of the two effects will be dependent on the width of the slit at *B*, for the effect of the direct beam is proportional to the width of the slit, whereas this is not the case for the amount of radiation reflected. Reflexion only takes place when the relation

$$n\lambda = 2d \sin \theta$$

holds, and if the slit is sufficiently wide to allow all rays, for which this is true, to fall on the crystal, the reflected radiation will have a maximum value which will not be increased by widening the slit to a greater extent. In the second place, the maximum value of the reflected beam will depend on the degree of perfection of the crystal face. If the crystal is composed of a number of elements very nearly parallel to each other, it may possibly be set so that a large proportion of these elements reflect simultaneously and their combined effect is large. If the crystal is distorted, the elements being oriented in all directions over a range of several degrees as is often the case, then the maximum effect will be smaller since, for any given setting of the crystal, reflexion will only take place over a portion of the crystal face.

These causes of uncertainty can be eliminated by the following procedure. The beam of X-rays is limited by the slit at J5, so that the whole of it falls on the crystal face at *C*. The crystal is turned with uniform angular velocity *co*

throughout the whole range over which reflection takes place, commencing at a setting where no effect is observed, and passing through that for which the effect is a maximum to another position where again the effect is zero. The total amount of radiation entering the chamber while the crystal is thus ' swept ' through the reflecting position is measured by means of the ionisation which it produces. However distorted the crystal may be, every element which lies in the path of the primary beam at some time passefe through the reflecting position, and adds its effect to the total. Further, the total ionization will be proportional to the width of the slit at *B,* since the surface irradiated is increased in proportion when the slit is widened, and reflexion takes place all over the surface.

The total ionization effect *E* is proportional to the power of the incident beam, /, this quantity being measured as the ionization caused by the direct radiation entering the ionization chamber in one second. It is inversely proportional to the angular velocity *co* with which the crystal is turned. The quantity $\frac{E\omega}{I}$ is therefore independent of width of slit and angular velocity, and is a coefficient of zero dimensions which may be taken as a measure of the reflecting power of a crystal face.* Experiment has shown that, with certain reservations which will be discussed later, this quantity is in actual fact a constant for a face of a given type and X-rays of a definite wave length.

The following series of experiments with rock salt was carried out by one of the authors in 1914. More accurate measurements have since been made, but the results will serve to illustrate the striking relationship between the intensities of reflection by various faces and orders. The comparative measurements of the integrated reflexion are given in the following table, where the amount of radiation

*** This quantity $\frac{E\omega}{I}$ is termed by Darwin the ' Integrated Reflexion' from a crystal face. *Vide,* ' The Reflexion of X-rays from Imperfect Crystals,' *Phil. Mag.,* vol. xliii, May, 1922.**

reflected by the face (100) of rock salt in the first order is taken as standard, and the effects given by the other faces are expressed as percentages of this quantity. The same monochromatic radiation (palladium K_α), and the same rate of turning were used throughout.

Face.	1st Order.	2nd Order.	3rd Order.	4th Order.
(100)	100	18.7	6.25	
(110)	41	7.05		
(111)	16.5	24.4	3.1	
				4.2

The first and third orders of reflexion by the face (rn) are abnormally low, since the planes parallel to this face contain alternately sodium atoms alone and chlorine atoms alone, and odd orders are thereby weakened as has already been explained (p. 92). With the exception of these two reflexions, all the values show a regular falling off with

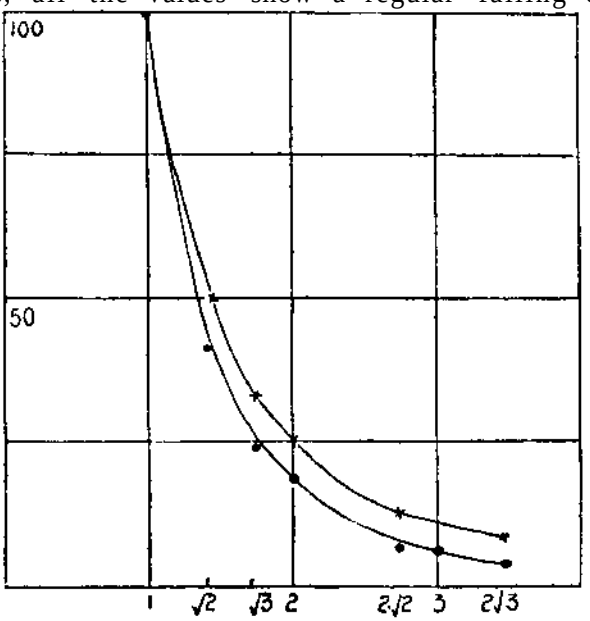


FIG. 66.

increasing glancing angle. In Fig. 66, the integrated reflexion of each order is plotted against the ratio of the sine of its glancing angle to the sine of the glancing angle for the first order reflection from (100). The points, shown by

dots in the figure, all lie on a smooth curve, no matter to which face they belong.

Considering all reflexions in which the effects of the various atoms add together directly, one law of variation with glancing angle holds for all faces. It is of especial interest that the reflexions of even order from the (111) planes, in which the effects of the two kinds of planes add together, fall into line with the rest.

In the figure the upper curve shows how the observed points would have been placed had the intensities varied as the inverse square of the sine of the glancing angle. It will be seen that the points fall off more rapidly than this.

These results are merely comparative. In order to obtain an absolute value for the integrated reflexion by a crystal face, it is necessary to measure the power of the monochromatic radiation incident upon the crystal. If the source of radiation at *A* in Fig. 65 is the anticathode of a bulb, the monochromatic radiation in the incident beam will be accompanied by rays of other wave lengths over a wide range, and so cannot be measured by placing the ionization chamber so as to receive the direct beam. It is, therefore, necessary to single out rays of one wave length by previous reflexion at a crystal face, and then let these monochromatic rays pass through the slit *B*. The power of the incident radiation can then be measured directly, so that we can determine the absolute value of the integrated reflexion $\frac{E\omega}{I}$.

Fig. *6y* shows an arrangement * of the apparatus for making an absolute determination of the coefficient $\frac{E\omega}{I}$. X-rays from the antocathode of a radiator Coolidge tube fall on a crystal C_1. A lead wedge *W* is pressed against the face of the crystal so that the reflected rays must pass around the edge of this wedge. In the particular set of experiments

* A similar disposition of the apparatus was first employed by Compton in order to obtain absolute measurements *(Phys. Rev.*, 10, 95, July, 1917).

referred to below, the crystal was set so as to reflect the K_a line emitted by the rhodium anticathode. The width of the reflected beam depends on the transparency of the crystal to the rays, and in this case it was less than a millimetre where it entered the ionization chamber, a crystal of resorcinol being employed. The beam falls on a second crystal C_2 which is rotated, or falls direct into the ionization chamber when it is desired to measure its intensity.

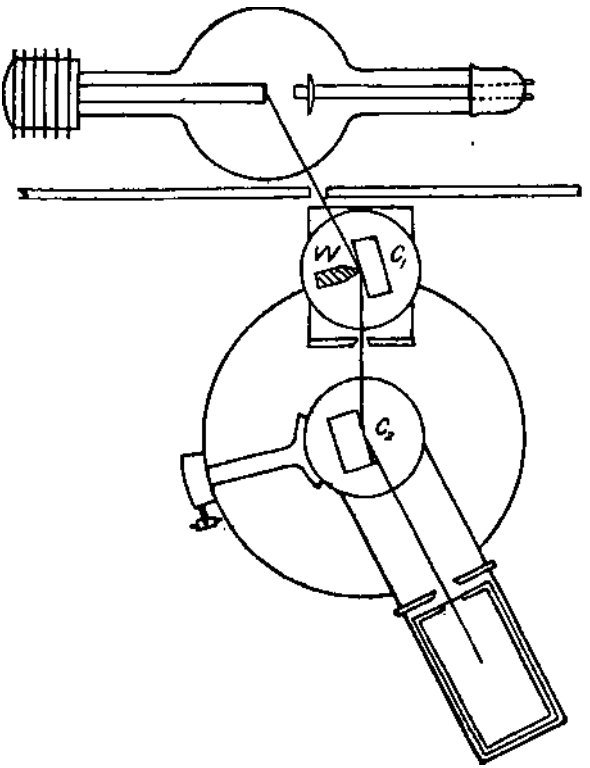


FIG. 67.

The monochromatic beam reflected by the first crystal at C_1 (Fig. 67) is far weaker than that coming direct from the anticathode. In the case of rock salt it is, therefore, necessary to measure the coefficient for high orders by employing a direct beam and comparing the integrated reflexion with that for the face (100) as standard. The

coefficient for this face may be obtained by an absolute measurement such as has been described. In this way the absolute coefficients for a large range of glancing angles can be measured. The integrated reflexions are given in the following table, where the second column gives the values in terms of the reflexion from the face (100), and the fifth column the absolute values of $\frac{E\omega}{I}$.

Plane.	Relative values of coefficient $\frac{E\omega}{I}$.	Cosec Θ.	Absolute values of $\frac{E\omega}{I} \times 10^5$.
100	100	9.21	550
200	19.90	4.60	109
300	**4.87**	307	27.8
400	•79	2.30	435
500	.116	I.84	.64
110	50.4	6.50	2.78
220	6.10	3-25	**334**
330	.71	2.17	3-90
111	9.00	IO.62	**495**
222	33.1	**531**	181
333	.58	**3-54**	3.18
444	2.82	2.65	154
555	•137	2.12	*-75*
311	1.17	*5.56*	6.50
622	2.69	2.78	147
331	.81	4.23	**445**
511	.61	**354**	**335**
711	.302	2.58	1.68

In Fig. 68 the square roots of the integrated reflexions are plotted against the cosecants of the glancing angle. It is convenient to plot them in this way, because the range of values is so large, the fifth order reflected from the plane (100) being, for instance, little more than one-thousandth of the first order effect.

The points plotted in Fig. 68 lie on two smooth curves. Points on the higher curve represent intensities of reflexion where the waves diffracted by both chlorine and sodium

atoms are in phase with each other and so reinforced. Points on the lower curve correspond to reflexions by planes with odd indices in the odd orders, where sodium and chlorine atoms diffract waves opposite in phase.

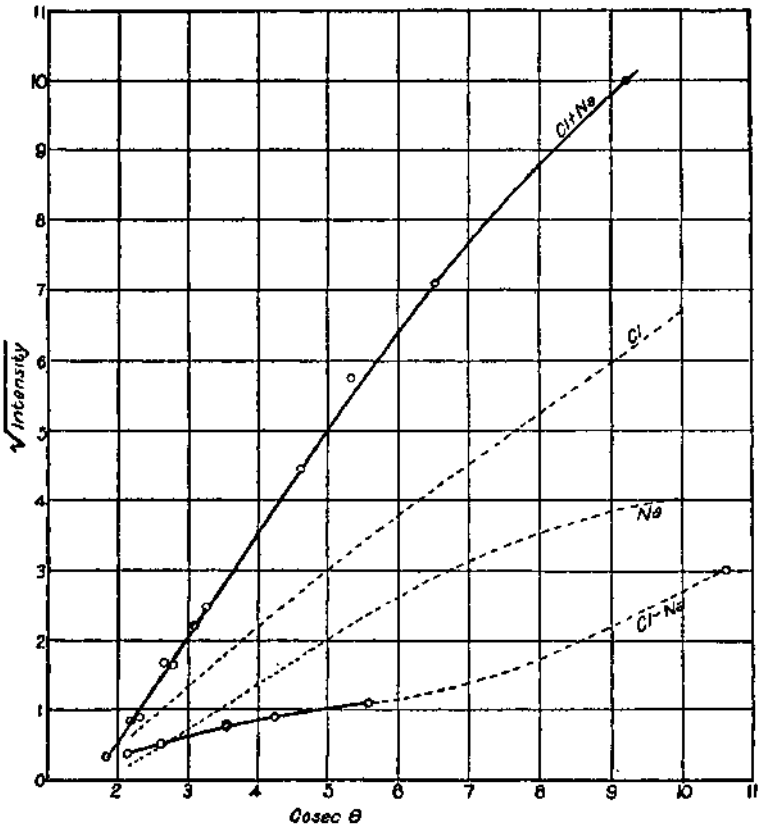


FIG. 68.

Formulae for the intensity of reflexion of X-rays by a crystal structure were first deduced by Darwin, who treated the whole question from the theoretical point of view very fully in two papers in the *Philosophical Magazine* in 1914.* In Darwin's original treatment the case of a crystal rotating with uniform angular velocity is not considered, but his formulae may readily be extended so as to cover this case.

*C. G. Darwin, 'The Theory of X-ray Reflexion,' *Phil Mag.*, 1914, Pp. 315,675.

Compton, in a later paper,* deduced a formula for the total amount of radiation reflected by a rotating crystal, and obtained results which can be shown to agree with those of Darwin. The full mathematical discussion is too complicated to be entered into here ; a brief summary of the results will alone be given.

The expression for the efficiency of reflexion contains a number of factors, which can be discussed separately.

In the first place, there is the question of the amount of X-rays scattered by each atom of the crystal structure. The X-rays are diffracted by the electrons in the atom, which are set in oscillation when the rays pass over them. The mass of the nucleus is so large that its contribution to the scattered energy is negligible compared with that due to the electron. We will suppose that the forces governing the positions or motions of the electrons in the atom are not sufficiently large to influence appreciably the oscillation set up by the incident rays. If the motions of the electrons were governed by the laws of classical dynamics solely, this would be equivalent to assuming that their free periods are large compared with the period of the incident X-rays. When atoms of low atomic weight, such as sodium and chlorine, are scattering the K_a X-rays from a rhodium anticathode, the rays are of so much shorter wave length than the hardest characteristic rays emitted by sodium and chlorine that it seems justifiable to assume that each electron scatters as if it were a free electron in space.

J. J. Thomson † was the first to give a formula for the amount of radiation scattered by a free electron when electromagnetic waves pass over it. If S is the total amount of energy radiated per second by a single electron, then

$$\frac{S}{P} = \frac{8\pi}{3}\frac{e^4}{m^2c^4},$$

where P is the energy of the incident radiation falling

*A. H. Compton, ' The Intensity of X-ray Reflexion and the Distribution of the Electrons in Atoms/ *Physical Review,* IX. i. p. 29, Jan. 1917.

† J. J. Thomson, *Conduction of Electricity through Gases,* p. 321.

normally on 1 sq. cm. per second, e is the charge on the electron in electrostatic units, m its mass, and c the velocity of light. This expression was used in Barkla's* work on the total amount of radiation scattered by elements of low atomic weight. By finding the total scattering Barkla deduced that the number of electrons in an atom was approximately equal to one-half the atomic weight. This we now know to be the case, so that his work may be taken to confirm the theoretical expression. It will be noticed that the expression is independent of the wave length of the radiation.

When the waves are plane polarized, the oscillations of the free electron are at right angles to the plane of polarization. We will consider first radiation scattered in a direction lying in the plane of polarization, and therefore at right angles to the motion of the electron. The ratio between the amplitude of the electric vector in the incident radiation, and that of the scattered radiation at a distance R from the electron, is given by

$$\frac{A'}{A} = \frac{e^2}{mc^2} \cdot \frac{1}{R}.$$

This expression is independent of the angle through which the waves are diffracted, and of the wave length of the rays. The atom contains a number (Z) of electrons. If these electrons diffract waves which are in phase with each other, as will be the case if the angle of diffraction is small, then the total amplitude will be

$$A' = \frac{A}{R} \cdot Z \cdot \frac{e^2}{mc^2}.$$

When the angle of diffraction is increased, the waves diffracted by the various electrons will be out of phase. The resultant amplitude of the diffracted wave will therefore be less than the sum of the amplitudes contributed by its constituent electrons, owing to interference. The regularity of the curves in Figs. 66 and 68 suggests that the relative

* C. G, Barkla, *Phil- Mag.*, vii. p. 543 (1904), and xxi. p. 648, 1911.

amplitude of this wave varies only with the angle through which the waves are diffracted. We will, therefore, suppose that the average amplitude * diffracted by the atom as a whole is given by

$$A' = \frac{A}{R} \cdot F \frac{e^2}{mc^2},$$

where F is a function of δ which tends to Z when Θ tends to zero.

We will now take the case of a small fragment of crystal which is homogeneous, and so small that the X-rays suffer no appreciable absorption in traversing it. Throughout the fragment the atoms are arranged with perfect regularity. It is irradiated with X-rays of intensity J, J being defined as the amount of energy falling normally on one square centimetre in one second. If it is turned with uniform angular velocity w, the total energy E of the radiation which is reflected is given by

$$\frac{E\omega}{J} = \frac{N^2\lambda^3}{\sin 2\theta} F^2 \frac{e^4}{m^2c^4} \delta V,$$

where δV is the volume of the crystal, N the number of atoms per cubic centimetre,† λ the wave length of the X-rays, 0 the glancing angle at which reflection takes place. For the mathematical analysis the reader is referred to the original papers.

So far the rays have been supposed to be plane polarized. As they are unpolarized, this expression has to be multiplied by a factor

$$\frac{1 + \cos^2 2\theta}{2},$$

since the amplitude of the scattered wave depends on that component of the oscillatory motion imparted to the electron which is at right angles to the direction of scattering.

* For an exact definition of this function see Compton's paper *(loc. cit.* p. 40).

† The atoms are supposed to be of one kind, and arranged on a simple space lattice.

Another factor must be taken into account. The atoms have been supposed at rest in their positions in the crystalline structure. In reality, they will be in movement due to their thermal agitation.

A theoretical discussion of the effect of thermal movement upon the reflexion of X-rays has been given in a series of papers by Debye.* The effect has also been discussed by Darwin.† It is to be expected that temperature will diminish the intensity of reflection, and that the higher the temperature the greater would be the effect. Further, the effect of temperature should be more manifest in the higher orders, where the consequences of the departures of the atoms from their average positions are more serious. These anticipations are borne out by calculation. Debye finds that the influence of temperature may be represented by a factor

$$e^{-\frac{3}{2}\cdot\frac{h^2}{\mu k T_0 a^2}\cdot n^2(h_1^2+h_2^2+h_3^2)\frac{\phi(x)}{x}},$$

in which the symbols have the following meanings :

h_1, h_2, h_3 are the direction cosines of the reflecting planes referred to the axes of the crystal.

a is the length of the cube edge: Debye is considering a crystal of which the atoms are in simple cubic array.

x is equal to T_0/T, where T is the absolute temperature and T_0 the temperature characteristic of the crystal. The latter is used by Debye to denote a temperature at which the substance of the crystal bears a certain standard relation to its specific heat. For sylvine T_0 = 219° absolute, for fluor-spar T_0=474°, and for diamond T_0=1830°. A high value of T_0 implies a small thermal movement and a small capacity for heat.

* *Verh. d. D. Phys-Ges.*, xv. pp. 678, 738, 857 (1913) ; also Ann. *d. Phys.* (1914), p. 49.

† *Phil. Mag.*, Feb, 1914, p. 325.

$\phi(x)$ is a certain function of x which Debye evaluates.

μ is the mass of the atom.

h is Planck's constant $=6.55 \times 10^{-27}$.

k is the gas constant $= 1.35 \times 10^{-16}$.

n is the order of the spectrum.

Since the distance d between consecutive planes is equal to

$$\frac{a}{\sqrt{(h_1^2 + h_2^2 + h_3^2)}},$$

and since $n\lambda = 2d \sin\theta$, where Θ is the angle of reflection, the formula may also be written

$$e^{\frac{-6h^2}{\mu k T_0} \cdot \frac{\phi(x)}{x} \cdot \frac{\sin^2\theta}{\lambda^2}}.$$

Generally, this formula implies that the temperature effect increases with the angle of reflexion and with the temperature, for any given wave length and crystal.

Experiment shows that the numerical values of the Debye factor are at least of the right order.* A crystal may be surrounded, as it stands upon the spectrometer table, by a small electric furnace, in which mica windows are constructed so as to allow of the ingress and egress of the X-rays. The temperature effects are then easy to observe : the results of a certain experiment are shown in Fig. 69, where the

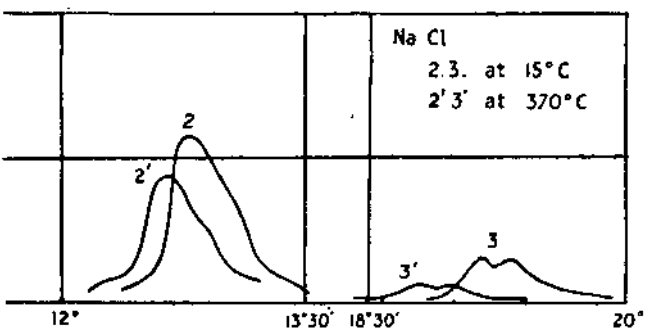


FIG. 69.

curves represent the second and third spectra of the rhodium line at both 15^0 C. and 370^0 C, the crystal face being NaCl

* *Phil. Mag.,* May, 1914.

(100). This line, it will be remembered, is really a close doublet. It is easily seen that the intensity of both orders is diminished by the rise in temperature, and of the third more than the second. The shift of the curves to the left is due to the expansion of the crystal with temperature, causing an increase in the spacing of the planes.

The numerical results of a series of experiments with rock salt are given in the following table, in which the first column gives the designation of the spectrum used, the second the magnitude of the sine of the corresponding glancing angle, the third the ratio of the original intensity to the intensity as affected by temperature, and the last the corresponding value calculated from Debye's formula. The temperatures were 15^0 C. and 370^0 C.

Spectrum.	Sine of Glancing Angle.	Ratio of Intensity at 15^0 C to Intensity at 370^0 C.	
		Observed.	Calculated.
100 1st order	1 x .1097	I.07	1.075
110 „	2X „	I.20	1.16
100 2nd order	2X	I.26	1.35
110 „ „	2 2X „	2.07	I.90
100 3rd order	3x „	I.94	I.92

Though the agreement is far from perfect, there can be no doubt that the effect is a true one, and the calculations are on the right lines.

Some results for sylvine may also be quoted. Calculation from the formula shows that the ratio of the first to the second spectrum should be diminished when the temperature is raised from 17^0 C. to 311^0 C. in the ratio 1.14 to 1 ; and that of the ratio of first to third in the ratio 1.44 to 1. Experiment gives the rather higher values 1.18 and 1.68. On the whole, the experimental results obtained so far seem to give a rather larger change than the formula accounts for.

In the case of fluor-spar the changes are found to be quite small, and this is in agreement with the high value of the characteristic temperature.

These early experiments have recently been supplemented by Backhurst,* who has examined the heat effects in the case of aluminium, diamond, carborundum, graphite and sapphire. The first two of these are cubic crystals to which Debye's formula may be considered to be applicable. Backhurst's results show still an approximate agreement with the formula, but it is clear that the approximation is not very close. Aluminium was examined up to 480^0 C. : the agreement with theory was good for the (222) spectrum, but not for the (200). Carborundum, taken up to 912^0 C, showed a different result for the wave-lengths K_a and K_β of the molybdenum radiator ; according to the formula the result should be independent of wave-length, since $\sin\theta/\lambda$ is a constant so long as the spacing remains the same. Diamond was remarkable, in that it showed no appreciable change with temperature up to 88o° C. ; although according to the formula there should have been a measurable effect.

Graphite and sapphire are in a different category. In each case the structure is far from the simple cubic structure assumed by Debye, and no agreement with his formula is to be expected. Graphite, in a nitrogen atmosphere, was taken up to 850^0 C. Backhurst's curves for diamond and graphite are reproduced in Figs. *64a* and 646, p. 190.

Sapphire is not a cubic crystal, and there is no reason to expect its behaviour to be in accordance with Debye's formula. Backhurst finds results which appear, at first, to be anomalous, in that, for example, the reflection (222) is less affected by temperature than the (111); that is to say, the movement of the electrons appears to affect the high order less than the low order. In the parallel case in optics the indefiniteness of the grating lines has, of course, a greater effect the higher the order. But we have here a new effect, which is to be anticipated, namely, changes in the relative phases of the various atoms in the crystal unit. Sapphire is trigonal, not cubic : its structure has already been discussed (p. 181). When calculating the intensity of **the**

* *Proc. Roy. Soc*, Vol. 102, p. 340, 1923,

reflection from the plane perpendicular to the axis we have to take into account the phases, relative to one of the aluminium atoms, of (1) the second aluminium and (2) the three oxygens, which last are all in one plane. As the crystal expands with the heat, the relative phases alter. Calculation shows, in fact, that the absolute distances, parallel to the axis, between the three planes containing:

(1) The first aluminium,
(2) The second aluminium in contact with the first,
(3) The three oxygens, touching these two aluminiums, do not change appreciably during the expansion.

The whole change occurs in the (111) spacing, which grows 0.5%; this is the distance parallel to the axis between two similar aluminiums. The attempt to examine the relative movements, during expansion with heat, of the atoms in a crystal unit appears to open up a wide field of research.

Before leaving the account of these experiments, it is convenient to refer to certain other of the expansion effects which they show. The method, of course, is capable of showing the expansion of a crystal with temperature in any desired direction ; and the crystal may be very small. The alteration in spacing is always small, so that high accuracy is not easily attainable ; but the method is very direct, and the results cannot under ordinary precautions be affected by any change in the position of the crystal or any distortion of the apparatus. The expansion of graphite is very remarkable, since it appears that there is a very large coefficient of expansion along the axis, far greater than has hitherto been estimated by indirect methods, while the expansion perpendicular to the axis is quite small, perhaps no more than in the case of diamond. This may readily be co-ordinated with the fact that the bonds across the axis are strong as in the case of diamond, and along the axis are quite weak (see later, p. 231).

The Debye factor may be expressed in the form

(where B is a constant for any given temperature), when we are allowing for its effect on the reflexion over a range of glancing angles. The only experimental determinations of the factor for rock salt which have been made are those mentioned above. They lead to the conclusion that the value for B, in the case of rock salt at 288^0 K, is approximately 4.12.

Allowance being made for the polarization factor and the Debye factor, the amount of radiation reflected by a small crystal of volume δV is given by,

$$\frac{E\omega}{J} = \frac{N^2\lambda^3}{\sin 2\theta} \cdot \frac{1+\cos^2 2\theta}{2} e^{-B\sin^2\theta} F^2 \frac{e^4}{m^2c^4} \delta V$$
$$= Q\,\delta V,$$

where Q is a function of 0, and has dimensions (length)$^{-1}$[1].

We have so far supposed the crystal to be composed of atoms of one kind, arranged on a simple space lattice, so that we are always dealing with reflection by a series of equally spaced planes identical in all respects. If the crystal has a complex structure, an extension of the formulae is required, which is not large, however, because the structure is necessarily based on a simple space lattice. The above expression will still hold for the reflecting power, if we substitute for

$$e^{-B\sin^2\theta} F^2,$$

the corresponding expression for a complex group of several atoms, allowing for the different thermal agitations of different atoms. This expression will depend on the scattering function for each atom, the Debye factor for each atom, and on the phase difference introduced by the relative positions of the atomic centres. N will now signify the number of points on the space lattice per unit volume.

We may now consider the case of reflexion by a large crystal in which absorption of the rays takes place. This crystal will be assumed to consist of a number of homogeneous crystalline particles in each pf which the crystalline arrangement is perfect, but which are only approximately parallel to each other owing to distortion of the crystal.

In two cases the total reflecting power of the crystal can be calculated simply. The first of these is the case of reflexion from a crystal face. If a beam of X-rays, whose total power is J, falls on a crystal face cut parallel to the reflecting planes, then it can be shown that the total amount *E* reflected when the crystal is turned with velocity *co,* is given by

$$\frac{E\omega}{I} = \frac{Q}{2\mu},$$

where μ is the linear absorption coefficient of the rays in the crystal.

In the second case a thin slip of the crystal is taken, cut so that the reflecting planes are perpendicular to the crystal face. The total path traversed by the rays before and after reflexion is now $t_0 \sec 0$, where t_0 is the thickness of the crystal slip. For this case

$$\frac{E\omega}{I} = Q \cdot t_0 \sec\theta \, e^{-\mu t_0 \sec\theta}.$$

By measuring the integrated reflexion in either of these cases, we can determine the absolute value of *Q,* and from this the value of *F* in absolute units.

There remains one other effect which has to be taken into consideration. In these formulae μ stands for the linear absorption coefficient of the X-rays. The normal absorption coefficient can be measured directly by placing slips of various thickness in the path of the rays. However, if we place such a slip in the path of a monochromatic beam, and turn it slowly round while measuring the intensity of the transmitted radiation for each position, it is found that when the crystal is so set as to reflect the radiation, the transmitted beam is weakened. The absorption coefficient for X-rays passing through the crystal at the correct angle for reflexion is greater than that for other directions. The following experiment will illustrate this.

In the figure a pencil of rays *AB* emitted by a rhodium anticathode *A* is represented as passing through a slit at *B* and meeting a diamond slip at C, which is mounted upon

the revolving table of the spectroscope. The rays can in part pass through the diamond, and the transmitted beam meets a crystal of rock salt C. The latter is adjusted until it reflects the principal rhodium ray. The ionization chamber can be placed to receive either a reflexion from the diamond or a reflexion from the rock salt. In the former case if the diamond is gradually turned so as to pass through

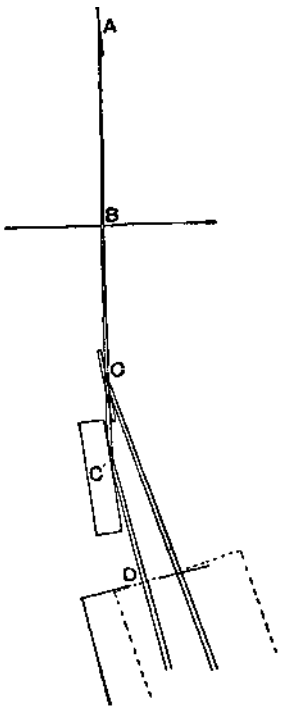


FIG. 70.

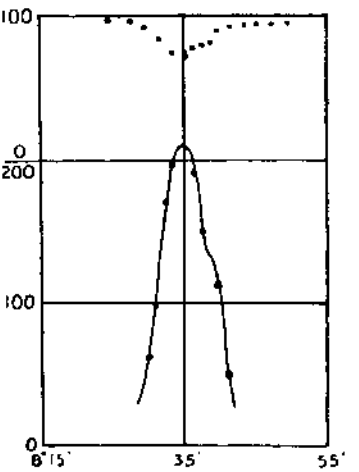


FIG. 71.

the angles 8° 35' and 8° 39', it gives an ionization curve represented by the lower curve, in Fig. 71. If now the ionization chamber is placed so as to receive the reflexion from the rock salt, and the turning of the diamond is repeated, that part of the primary beam which passes through the diamond and is reflected by the rock salt shows diminutions just when the diamond is itself able to reflect. In other words, the reflexion is a diversion of energy from the primary beam to the reflected beam. The readings of the rock-salt

reflexion are given in the upper curve of the figure ; and the absorption bands are seen to correspond exactly to the peaks of the lower curve.

The same effect is very well shown by an experiment of Rutherford and Andrade. A quantity of radium emanation in an extremely fine glass tube is placed at 5 (Fig. 72), the tube lying along a normal to a rock salt crystal *RR*. The *y* rays from the radioactive products find their own reflecting planes at *A A'* in the crystal (the angle *ASA'* being about 3^0) and meet a photographic plate at *BB*. The reflecting planes *cast shadows* at *DD'*. Reflexion takes place

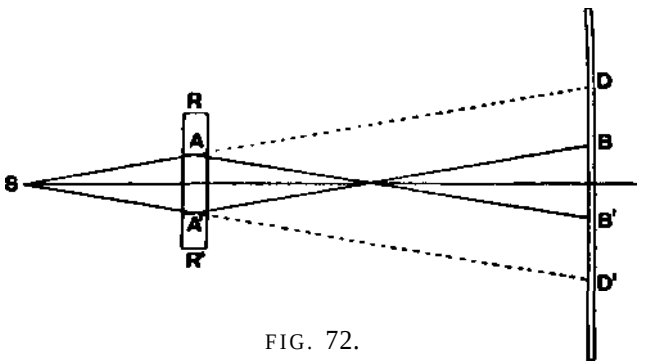


FIG. 72.

also at two planes parallel to the plane of the paper, and the photographic plate shows a pattern of both light and dark lines arranged in a square pattern (see *Phil. Mag.*, 28. p. 263, 1914). This experiment, it may be observed, gives an exceedingly neat and accurate method of measuring the fine angle of reflexion of the *y* rays.

The theory of this increased absorption, when reflexion is taking place, has been discussed very fully by Darwin. When the X-rays traverse a homogeneous crystal, and are reflected, the reflected beam will suffer a further reflexion, after which it will be parallel to the incident beam. . The beam which has been twice reflected is exactly opposite in phase to the incident beam, and so diminishes its intensity. If we had a sufficiently large fragment of perfectly homogeneous crystal, and X-rays were incident upon it at exactly the reflecting angle, Darwin shows that the ' extinction' of

the beam due to this effect is far greater than the normal absorption due to scattering and to the conversion of X-ray into cathode ray energy. Long before the ordinary absorption plays an appreciable part, the X-rays will be totally reflected by the crystal with an inappreciable loss of intensity. In an actual crystal such as rock salt it would appear that the homogeneous fragments are too small for this to take place. They are sufficiently large, however, to give an extinction coefficient comparable with the ordinary absorption coefficient. Rays traversing the crystal at the reflecting angle pass through a number of fragments so set as to absorp them abnormally highly, and therefore the average absorption coefficient is increased.

We will suppose that in this case the effective absorption coefficient μ is a constant, which may be regarded as the sum of the normal absorption coefficient μ_0, and the extinction coefficient e,

$$\mu = \mu_0 + \varepsilon.$$

In the formula for the reflecting power, the correct absorption coefficient to take will be μ, and not μ_0. It is therefore necessary to measure μ in order to deduce the true value of Q from the determinations of the reflecting power.

The value of the effective absorption coefficient μ cannot be determined from a curve such as that of Fig. 71. The beam falling on the crystal is not parallel, and it is not possible to set the crystal so that all the rays of the beam pass through at that angle for which absorption is a maximum.

An attempt has been made to measure μ directly in the following way.* A large number of thin slips of rock salt are prepared cut parallel to a cube face. Mounting such a slip on the spectrometer it is possible to reflect rays on the planes 100 or no which are perpendicular to the face of the slip. The slips are of all thicknesses between .2 and 2.5 mm. For reflexion from such a slip, the formula

$$\frac{E\omega}{I} = Qt\, e^{-\mu t}$$

holds good, where $t = t_0 \sec\theta$.

•Bragg, James and Bosanquet, *Phil. Mag.*, Vol. XLL, March, 1921, and Vol. XLII., Tuly, 1921.

In this equation μ is the effective absorption coefficient since all rays traverse the crystal at the reflecting angle.

By measuring the reflecting power for a series of such slips, we can determine both Q and μ. From the above equation

$$\log \frac{E\omega}{It} = \log Q . - \mu t ;$$

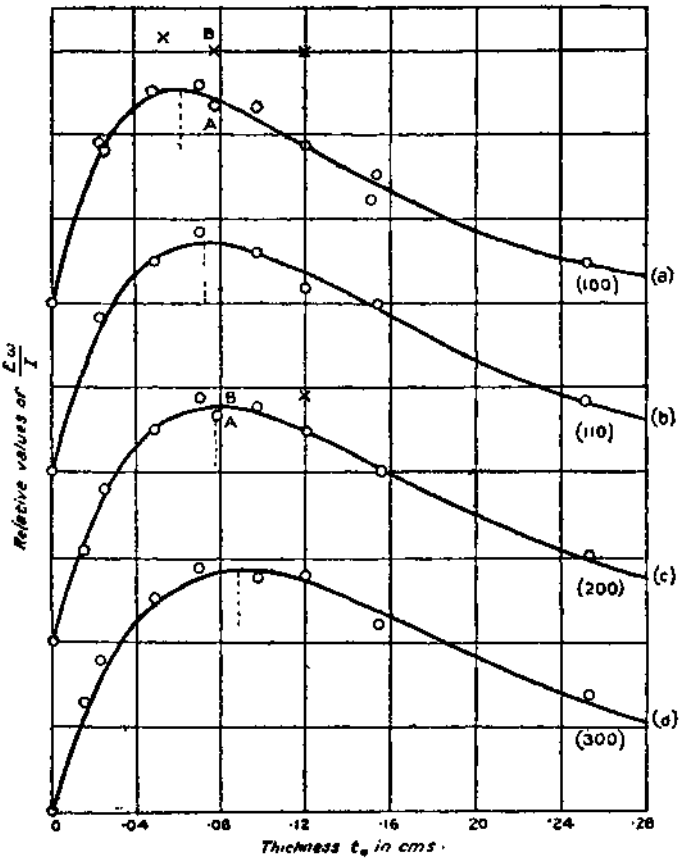


FIG. 73.

if we plot $\log \frac{E\omega}{It}$ against t we ought to get a straight line which cuts the axis t=o at $\log Q$. The slope of the line gives the absorption coefficient of μ.

Figs. 73 and 74 show the results of a series of measurements made with rock salt slips, the X-rays being reflected

in the 1st, 2nd, and 3rd orders from the plane 100, and in the ist order from the plane no. In Fig. 73 the integrated reflexion $\frac{E\omega}{I}$ is plotted against t_0, the thickness of the slip. The curve $y = te^{-\mu t}$ has a maximum when $t = \frac{1}{\mu}$. The greater μ is the smaller will be the thickness t which ,gives a maxi-

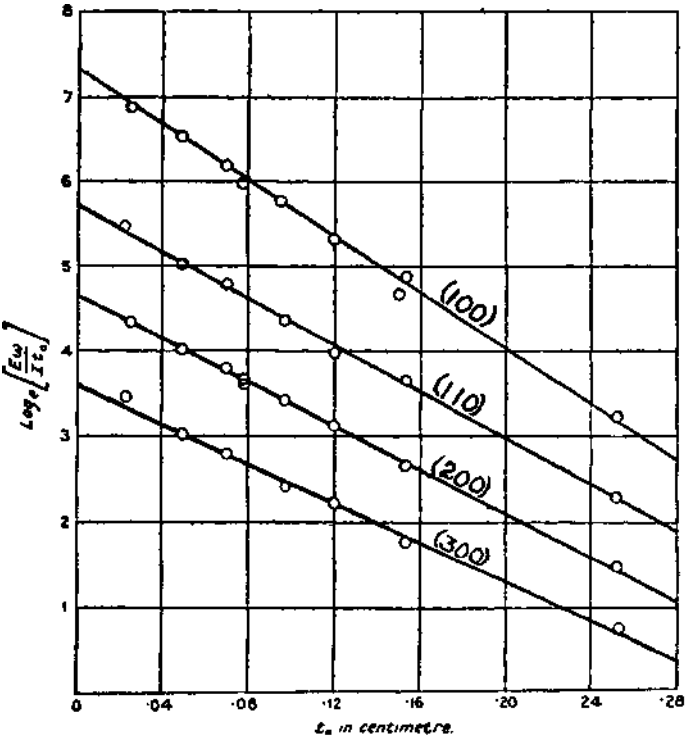


FIG. 74.

mum reflecting power. The maxima occur at values of t_0 equal to .61 mm., .74 mm., .79 mm., and .93 mm. respectively. The normal coefficient of absorption in rock salt is 10.70, corresponding to a maximum at .933 mm., so that we can see how large is the effect of extinction for the (100) reflexion. In Fig. 74, $\log \frac{E\omega}{It_0}$ is plotted against t. The effective coefficient of absorption can, in this case, be deduced from the slope of the curve, which is proportional to μ. The

effective coefficients of absorption μ, the extinction coefficients, and the intensities of reflexion are tabulated below :

Reflexion.	Effective Coefficient,	Extinction Coefficient,	Integrated Reflexion in Arbitrary Units.
(100)	16.30	5.60	IOO
(110)	13.60	2.90	50.5
(200)	12.66	I.96	19.90
(300)	10.72	.02	4.87

Normal coefficient of absorption, 10.70.

In the case of the reflexion from 300 the extinction effect is practically zero.

The increase in the effective absorption coefficient, when rays are traversing the crystal at the reflecting angle, must be due to a very marked extinction taking place in those fragments which are exactly set so as to reflect the rays. The more homogeneous the crystal, the greater we should expect to be the extinction of rays in the crystal as a whole when they are being reflected. Experiment indicates that this is actually the case. We have observed that an untouched surface of a quartz crystal gives a more feeble reflexion than one which has been ground, and it was remarked by Compton that the reflexion of a freshly cleaved surface could be improved by the same treatment. Rock salt shows the effect strongly. For example, a cleaved surface (100) was found to give a reflecting power only 12.9 per cent, of that from a surface which had been ground. Since in this case

$$\frac{E\omega}{I} = \frac{Q}{2\mu},$$

this indicates a very high extinction coefficient. The grinding appears to break up the surface into smaller fragments, and reduce the absorption to something approximately more closely to its normal value. A description of the effect of grinding on the reflexion from a crystal slip will be found in one of the papers referred to *(Phil. Mag.,* **vol. 43, July, 1921).**

In Darwin's papers the question of extinction is discussed very fully from a theoretical point of view. The results given here will show how exceedingly complex is this effect, and what care must be exercised in interpreting the intensities of reflexion from crystals. The existence of this extinction coefficient is very well illustrated by the following experiments with small crystals of diamond.* The crystal

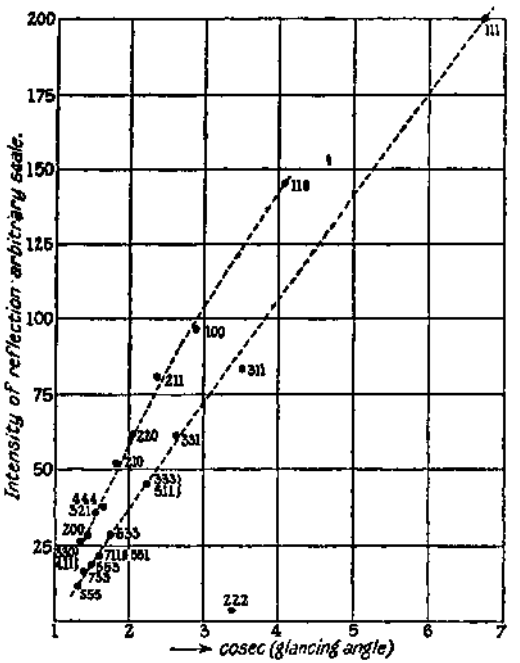


FIG. 75.

under examination was mounted in the X-ray spectrometer on a stand similar to that of a goniometer, and adjusted by means of the X-ray reflexions until a zonal axis coincided with that of the spectrometer. The slit in front of the bulb was opened so wide that the crystal was entirely bathed in the X-rays. The slit of the ionization chamber was also opened wide, the dimensions of the reflected pencil being determined by the size of the crystal. As the crystal is

* **W. H. Bragg,** ***Proc. Phys. Soc.,*** **London, Vol. 33, Part V., August, 1921.**

swept through the reflecting angle, reflexion takes place throughout its whole volume, and the total amount so reflected is measured.

In the figure the intensity of reflexion, measured on an arbitrary scale, is plotted against the cosecant of the glancing angle for a number of planes and orders all belonging to the same zone. The diamond crystal weighed 9.8 milligrams.

The points lie on two smooth curves. Those on the upper curve correspond to reflexions at planes containing equal numbers of carbon atoms, spaced at equal distances apart. The points on the lower curve, such as (111), (311), (331). correspond to reflexions at planes spaced in pairs, the distance between corresponding planes being four times the distance between two planes in a pair (see page 99).

The influence of this arrangement in the planes of either kind should cause the ordinates of the upper curve to be twice those of the lower at the same glancing angle. At an angle Θ all factors in the theoretical expression for the intensity of reflexion are the same, except that for planes of the second class two atoms of a pair scatter waves which differ in phase by $\frac{\pi}{2}$, whereas they are in phase for planes of the first class. The resultant amplitude should be in the ratio $2 : 2$, or $1 : 2$, and so the intensities in the ratio $1 : 2$.

This is approximately true on the left-hand side of the diagram when the points correspond to weak reflexions, but it is far from being the case on the right-hand side. The extinction factor is coming into play, and the strong reflexions are being cut down by extinction to a far greater extent than the weak reflexions.

That this is taking place can be shown by comparing the intensities for diamonds of different sizes: The normal coefficient of absorption of rhodium rays in a corresponding mass of amorphous carbon is inappreciable. If no absorption of the rays were taking place, the formula

$$\frac{E\omega}{J_0} = Q\,\delta V$$

should hold good, δV being the volume of the small diamond crystal. Comparing different crystals, the intensity of reflexion should be proportional to the mass of the crystal. The following table shows how far this is from being the case:

Weight of Diamond in Milligrams.	Comparative Intensities (Integrated Reflexions). (111)	(333).	(444).
61.8	100	33.5	26
9.8	45	IO.4	8.5
4.55.	**34**	**7.0**	**5.4**

The largest diamond weighs more than thirteen times the smallest, but the (111) reflexion is only three times larger, and the (444) reflexion only five times larger than the corresponding reflexion for the small diamond.

Very similar results for reflexion from a crystal face have been obtained for calcite.* The stronger reflexions do not bear the same ratio to the weaker reflexions as consideration of the crystal structure would lead us to expect, this ratio being found experimentally to be smaller than its calculated value.

In the case of reck salt, it has been found that the coefficient of extinction is very nearly zero for the reflexion (300), and it will be still less for reflexion at greater glancing angles. In the case of reflexion from a crystal face, when the formula

$$\frac{E\omega}{I} = \frac{Q}{2\mu}$$

holds good, we can put $\mu = \mu_0 = 10.70$ for all reflexions of high order, and so calculate Q from the results given on page 202. The value of Q for reflexions such as (100), (no), etc., where e is appreciable, can be got from the curves on page 218. We are therefore able to measure Q for a large range of angles, and so deduce the values of F for the chlorine and sodium atoms. What we actually measure are the

* W. H. Bragg, Bakerian Lecture, *Trans. Roy. Soc, A,* Vol. 215, p. 264, 19I5.

quantities $F_{Cl} + F_{Na}$, for reflexions such as (100) and (110), and $F_{Cl} - F_{Na}$ for reflexions such as (111). From these the values for the atoms follow.

The following table gives the values of these quantities:

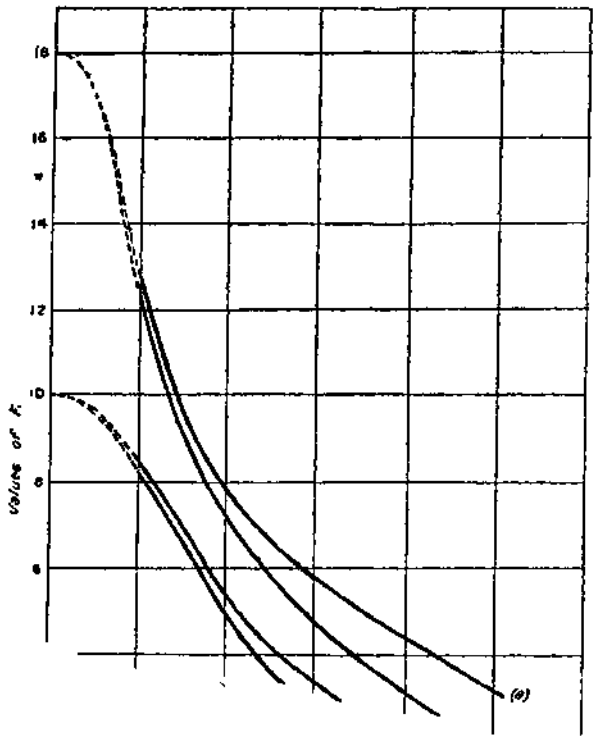
$\sin\Theta$	(Corr. fore).	$F_{Cl} - F_{Na}$	F_{Cl}	F_{Na}	20
.IOOO	21.05	4.4O	12.72	8.32	11°24'
.1305	I8.2I	2.98	10.59	7.6I	15°
•1736	14.89	2.32	8.60	6.23	20°
.2164	12.35	2.53	7.44	4.9I	25°
.2588	IO.51	2.49	6.50	4.OI	30°
.3007	9.II	2.46	578	3.37	35°
.3420	7.90	2.4O	5.15	2.75	40°
.3827	6.83	2.39	4.61	2.22	45°
.4226	5.91	2.39	4.15	1.76	50°
.4617	5.07	2.33	3.70	1.37	55°
.5000	3.92	2.4O	3.16	.76	6o°

In Fig. 76 the values of F for sodium and chlorine are plotted against sin θ. F represents the ratio between the amplitude of the wave scattered by the atom, and that scattered by a single electron. If it were possible to measure F at $\theta = 0$, its value should be equal to the number of electrons in the atom. There are strong reasons for supposing that in rock salt the atoms are ionized, so that the chlorine ion contains eighteen electrons and the sodium

maxima of the curves in

8 AND - -

Let us suppose that the space occupied by an atom is divided into spherical shells, with the nucleus as centre, and that the number of electrons which are located in the shell, whose inner and outer radii are r and $r + dr$, is equal



very large number of atoms is considered. Since the curves for the intensity of reflection show no influence of the orientation of the atom on its diffracting power, we can only deduce the radial distribution of the electrons from the experimental results.

The contribution of the electrons in this shell, to the total amplitude at a distance R diffracted through an angle 20, is given by

$$P\,dr\,\frac{e^2}{mc^2R}\cdot\frac{\sin\varphi}{\varphi},$$

where

$$\varphi=\frac{4\pi r}{\lambda}\cdot\sin\theta.$$

Therefore, at an angle 0,

$$F=\int_0^{r_0}P\frac{\sin\varphi}{\varphi}\,dr.$$

The present problem is to find a form for P which gives results agreeing with the experimentally determined values of F.

It is not difficult to obtain some idea of the average electron distribution by a process of trial and error.* Two forms of solution are given below,† In the first of these the electrons have been assumed to be grouped on spherical shells. The number of electrons on each shell, and the radii of the shells, have been chosen so as to give the best possible fit of the calculated to the experimental values of F_{C1} and F_{Na}. In the second form of solution it has been supposed that the electron distribution from the centre outwards may be represented by a smooth curve, and the general form of the curve has been adjusted so as to give the best fit, the total area of the curve being so chosen that

$$\int_0^{r_0}P\,dr=Z.$$

*** Compton *(loc. cit.)* and Debye *(Phys. Zeit.*, p. 474, July, 1918) have attempted solutions on these lines, the latter using the relative intensities of the lines given by the powder method.**

† W. L. Bragg, James, and Bosanquet, *Phil. Mag.*, Vol. 44, Sept. 1922,

The distribution of electrons on shells is as follows :

Sodium.	Seven electrons on a shell of radius	.29 A^0.
	Three electrons on a shell of radius	.76 A^0.
Chlorine.	Ten electrons on a shell of radius	.25 A^0.
	Five electrons on a shell of radius	.86 A^0.
	Three electrons on a shell of radius	1.76 A^0.

The continuous distribution of electrons which gives the best agreement with the experimental curves is shown in Figs. 77 and 78.

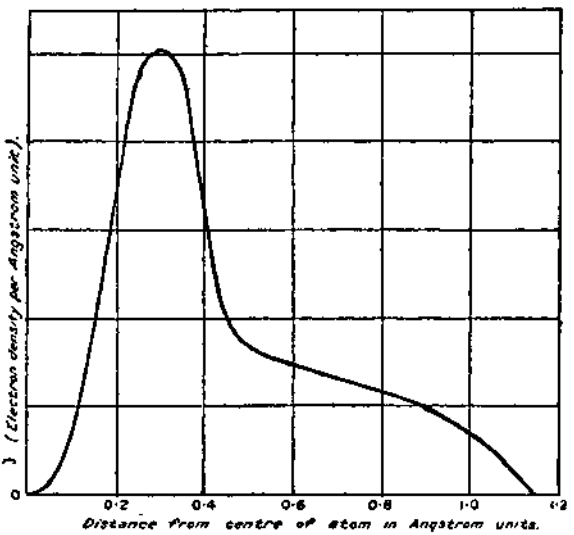


FIG. 77.—SODIUM.

In obtaining these results, it is not certain that full allowance for extinction has been made, and they cannot be regarded as well founded until the question has been properly cleared up.

The intensity of X-ray reflexion has been discussed at some length because it has such an important bearing on the problem of atomic structure. There are very many difficulties in the interpretation of the experimental results. In a recent paper, Darwin * has analysed and criticised some of the results referred to in this chapter. Nevertheless, the

* *Phil, Mag.*, Vol. xliii., May, 1922.

examination of the intensity of reflexion appears to offer a valuable means of testing structures proposed for the atom, since any such structure must explain the way in which the atom diffracts X-rays in various directions. We are actually looking into the atom, using very short wave lengths as a source of illumination.

The most serious difficulty in the way of deducing the scattering factor from the experimental results is the existence of the extinction factor referred to above. It may well be that the powder method, since it employs

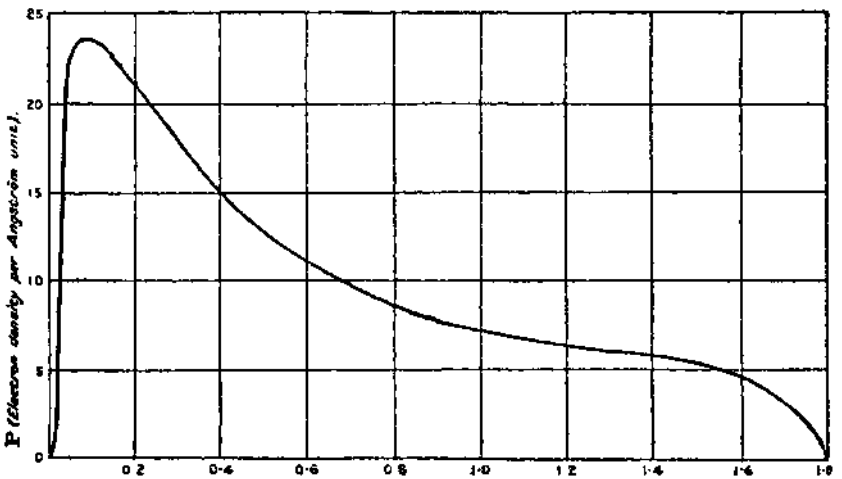


FIG. 78.—CHLORINE.

minute crystals in which perhaps extinction is inappreciable, will prove to be the best way of attacking the problem. Darwin has shown, however, that the homogeneous crystal must be exceedingly minute in order that what he calls 'primary extinction' in each individual may be inappreciable, so that even here there may be some difficulty in analysing the results.

It might at first sight appear paradoxical that, although we are so ignorant of the laws governing the relative intensities, we can yet determine with such accuracy the positions of the atoms in the crystal by considering these intensities. The explanation of this lies in the very great influence on

intensity which the relative positions of the atoms have. Quite a small change of the parameter, which defines the position of one atom with respect to the space lattice, may alter by a hundredfold the ratio between two spectra of high order. The intensities of spectra, therefore, give a most delicate and accurate indication of the relative positions of the atoms.

CHAPTER XIV

ORGANIC CRYSTALS

THE structure of organic crystals offers a very inviting field of research by the methods of X-ray analysis. To the organic chemist the relative positions of the atoms in the molecule, as also of the molecules in the crystal, are of fundamental importance ; and it is with these relations that the X-rays deal in a manner which is new and unique. The complexity of the molecule would seem at first sight to throw great difficulties in the way of arriving at any solution. There seems to be good reason, however, for supposing that the benzene ring or napthalene double ring of carbon atoms has definite form and size preserved with little or perhaps no alteration from crystal to crystal. If this principle is accepted the problem, as regards the aromatic compounds, is simplified at once. For example, naphthalene is then to be regarded as a structure in which there is but one element, the naphthalene double ring, and no longer as an aggregate of ten carbon atoms and eight hydrogen atoms of unknown mutual arrangement. A more complex molecule such as either of the naphthols is not to be regarded as an addition of one oxygen atom to these eighteen, an idea on which nothing can be built, but as a naphthalene double ring of the same size and form as before, except that one particular hydrogen has been replaced by a hydroxyl group. It is then possible to think what changes in the disposition of the molecules might be caused by such a substitution, and to compare conceivable solutions with observations on the dimensions of the new crystal. Such a method of procedure

deviously in good agreement with the ideas of organic chemistry.

There are certain *a priori* reasons for assuming the concrete existence of the benzene and naphthalene rings. If we examine the structure of the diamond we find that the atoms of carbon are tied together so that each is at the centre of gravity of four others. The distance from centre to centre is 1.54 A.u. The rigidity of the diamond and the

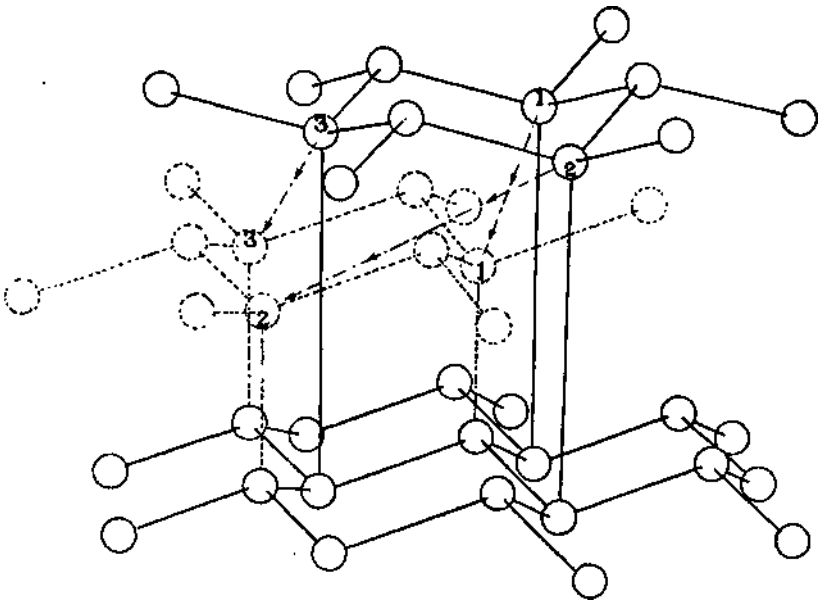


FIG. 79.—THE FIRM LINES OF THE DIAGRAM SHOW THE STRUCTURE OF GRAPHITE. BY MOVING THE TOP LAYER TO THE POSITION SHOWN BY THE BROKEN LINES THE DIAMOND STRUCTURE IS OBTAINED.

open character of its structure, imply that great force is required to alter the orientation of any coupling with respect to the other three belonging to the same atom.* Were it otherwise, all atoms would seek to be surrounded by as many neighbours as possible ; the substance would be close packed, and its density would be more than double what it is. The structure of the diamond may also be looked on as consisting of a series of puckered layers parallel to a given tetrahedral plane (*see* Fig. 79). A sharp blow may

*** W. H. Bragg, *Proc. Phys. Soc,* Vol. XXXIII, Part 5, August 15 (1921).**

cleave the diamond along one of these layers. If we take a model showing two layers as in graphite, lay hold of the upper layer, and move it to the new position shown in the figure, the structure is now that of diamond. This is Hull's determination ; * Debye and Scherrer † would flatten out the puckers in the planes of graphite. The point is not perhaps important for our present purpose, because the molecular dimensions that really matter in what follows are very nearly the same on both hypotheses ; but it is necessary for descriptive purposes at least to choose one form. According to Hull's measurements, the shortest distance between each pair of atoms lying in the same layer is shortened from 1.54 A.u.—the diamond spacing—to 1.50 A.u. The distance between two successive layers has been increased from 2.05 to 3.40. ‡ A carbon atom in one layer is now at equal distances from its three nearest neighbours in the next layer, the distance being 3.25 A.u.

The bonds between one layer and the next are now greatly weakened; the substance cleaves readily in thin flakes. One layer slides with great ease over the other, though the bonds between the atoms in any layer are at least as strong as before. When all the bonds were of the strong kind, the substance, as diamond, was the hardest thing known. When the one set of bonds has been weakened, the substance, as graphite, is used as a lubricant. Probably its efficiency as such depends both on the weakness of the one set of bonds and the strength of the other. Yet these new bonds are perfectly definite, and the distance between two layers and, therefore, the 3.25 distance between atomic centres is a perfectly constant and determinate quantity.

If the strong bonds between the atoms in a layer remain, and are even drawn a little tighter when the graphite form

*** *Physical Review,* X., p. 692, December (1917).**

† *Phys. Zeit.,* 13, p. 297 (1917)-

‡ According to Debye and Scherrer the new spacing is 3.41 : according to the early measurements described in the first edition of this book it is 3.42.

replaces that of diamond, it seems very reasonable to suppose that the single ring or multiple rings which are so clearly to be distinguished in the network may be separated out as such without loosening the bonds between their component atoms. In fact, these latter bonds might be expected to tighten even a little more. Let us assume that a single ring is a benzene ring, a double ring a naphthalene ring, and so on. Taking the spacings as given by Hull for graphite, the dimensions of the benzene and naphthalene frameworks are as shown in Fig. 81. The figure is constructed to show the arrangement of atoms in the naphthalene crystal, but it will also serve to illustrate the point under discussion. The carbon atoms *A to F* form a benzene ring, those from *A to J* the double ring of naphthalene.

The atom centres *A,* and *G,* are 0.71 A.u. above, and the centres *D* and J the same distance below the plane of the diagram which is supposed to contain all the remaining centres. It should be observed that circles are used to represent the atoms as a convenient method of designation, not as implying that the diameter (1.50) may *always* be used in calculating the distance between the centre of any one atom, and the centre of any other atom.

We now proceed to consider the naphthalene crystal. The crystallographic description is (Groth, *Chemische Krystallographie,* Vol. 5, p. 363) :

Monoclinic prismatic, $a:b : c = 1.377 : 1 : 1.4364$, $\beta = 122° 49'$.

The X-ray analysis shows, as we shall see presently, that there are two molecules in the unit cell. The specific gravity of the crystal is 1.152, and the weight of a molecule 128 x1.662 =213 A.u. (It is convenient in this work to extend the Angstrom system of units so that an A.U. of area $=10^{-16}$ cm^2, of volume 10^{-24} cm^3, and of mass 10^{-24} gr.)

We have therefore :

$$b^3 \times 1.3777 \times 1.4364 \times \sin 122^0\, 49' \times 1.152 = 426 ;$$

b=6.05.

The linear dimensions of the cell are then:

$$a = 8.34, \quad 6 = 6.05, \quad c = 8.69.$$

The form of the unit cell is shown in Fig. 80. We suppose each corner of the cell to represent the position of one molecule, all the molecules so represented having the same orientation. The relative position and orientation of the second molecule is still to be found.

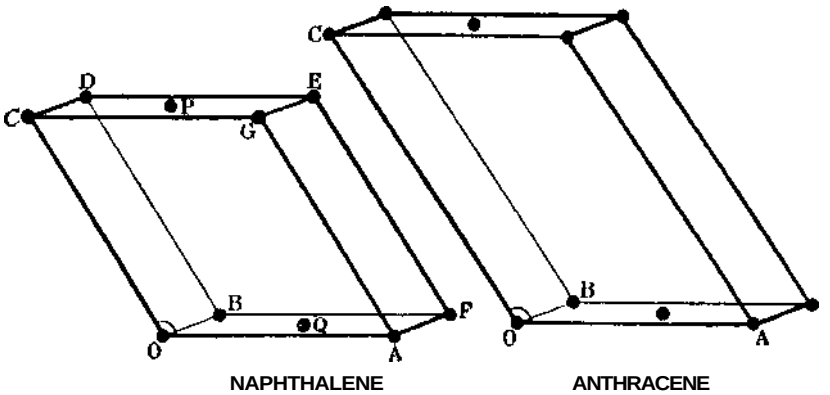


FIG. 80.—UNIT CELLS OF NAPHTHALENE AND ANTHRACENE DRAWN TO THE SAME SCALE.

	OA=a	*OB=b*	*OC=c*
Naphthalene - -	8.34	6.05	8.69
Anthracene -	8.58	6.02	11.18

Naphthalene a = *BOC* =90°, ß=*COA* =122° 49', *y* =*AOB* =90°
Anthracene *a* =*BOC* =90°, ß=*COA* =125° o', *y=AOB=90*^{0}

We now calculate the spacings of the lattice, on the assumption that there is a molecule at each corner only, in order that by comparing the calculated figures with the observed we may be able not only to check the assumptions on which the linear dimensions have been calculated, but also to find the position of the second molecule. The calculated spacings are shown in the second column of Table XIII. The third and fourth columns show respectively the observed spacings and rough estimates of the relative intensities.

TABLE XIII.

Plane.	Calculated Spacing.	Observed Spacing.	Nature of Reflection.
100	7.00	3.46	Strong.
010	6.05	2.95	Very weak.
001 (Cleavage)	7.30	7.30	Very strong : also higher orders.
no (Natural)	4-59	4.55	Strong.
i l l (Natural)	4.70	4.63	Moderate.
20T (Natural)	4.17	4.12	Strong.
021	2.79	2.76	Very weak.
101	7.51	3.71	Very weak.
210	304	2.99	Strong.
211	3.44	3.39	Strong.

The next table shows certain values of the angles between important planes. The observed values were found during the examinations of the crystals, and served as useful guides in the identification of the planes. They are of little use in determining the structure, but are inserted here in order to show how the X-ray method gives angular as well as linear measurements, even when the planes are not shown by the crystal. Much greater accuracy might have been obtained in these measurements, but for the purpose in view the labour would have been wasted.

TABLE XIV.

Angles between.	Calculated.	Found.
100 : 001	57° 11'	57° 16'
110 : 111	36° 32'	36° 34'
201 : 001	85° 45'	85° 48'
021 : 001	67° 47'	67° 35'
201 : 101	30° 21'	30° 23'
210 : 211	24° 12'	24° 24'

The table shows that the 100 and 010 spacings are only half what they should be if there were molecules at cell corners only. But the 001 spacing is right. We conclude that there is a molecule at or very near to each of the points *P* and *Q* (see Fig. 80). Molecules placed at *P* and *Q* can, if they

are like the corner molecules in certain respects, interleave the planes 100, 010, and also 101 by other planes of equal density which halve the corresponding spacings. Other planes are unaffected for reasons which will be considered later.

Although so much information is given in these tables, some of which we have used and some of which we cannot fully use for lack of knowledge, yet it would be hopeless to try to arrange the eighteen atoms of naphthalene on the basis of what has been learnt, without some helpful hypothesis. But we now take the naphthalene double ring as described. Its dimensions are such that it seems quite possible to fit two of them into the cell, if we had some indication as to their orientation thereto.

As to this we get a strong hint from a comparison of naphthalene with anthracene ($C_{14}H_{10}$), whose construction shows three rings in a line, as against the two of naphthalene. The crystallographic data of anthracene are given by Groth :

$$a:b : c = 1.4220 : 1 : 1.8781, \quad ß = 124° 24'.$$

A measurement by the X-ray method *(Proc. Phys. Soc,* 35, p. 167), using a small but perfect crystal, gave the following results:

$$a : b : 0 = 1.423 : 1 : 1.857, \quad ß = 125° 0'.$$

The analysis shows that there are two molecules in the cell, and that the actual linear dimensions are:

$$a = 8.58, \quad 6 = 6.02, \quad c = 11.18.$$

The specific gravity as calculated from these results is 1.255, and as determined directly is 1.250.

If these dimensions are compared with those of naphthalene (see Fig. 80), it will be seen that while *a, b,* and *ft* remain nearly the same, the *c* axis has lengthened considerably, the difference amounting to 2.5 A.u. nearly. Now the extra ring, if of the benzene dimensions, should be responsible for an addition of 2.5 A.u. to the molecule.

It is reasonable to conclude that the molecules in both crystals lie end to end along the *c* axis, and that the structures are similar.

The over-all lengths of the two molecules, without allowance for the hydrogen atoms at their ends, that is to say, *in* the ß-positions, are 6.41 and *8.86* respectively : these figures are obtained from measurement of the lengths of double and treble rings in graphite. There is, therefore, a vacant space between the ends of two molecules of rather more than 2 A.u. into which two hydrogen atoms have to be fitted. This agrees very well with what might be expected ; only it must be remembered that we have no definite indication from studies of crystal structure as to the actual distance between the centres of a carbon and a hydrogen when united by a valency bond, nor between two hydrogen atoms not so united.

We have still to decide in what plane, passing through the *c* axis, the molecule is to be placed, and we have less clear indications with respect to this point than those that have guided us hitherto. On making up a model, however, it is seen that it is much more likely that the plane of the molecule lies nearer to the *ac* plane than the *be* plane. The molecules lock together much better if that is so. Moreover, if the molecules lay in the *be* plane, they would be close neighbours in that plane, and at the same time there would be wide gaps between consecutive planes. The plane 100 should, therefore, be prominent, most probably a natural face, perhaps even a cleavage plane : whereas it is neither of these things. But if the molecules lie in the 010 plane the form of the crystal seems much easier to understand, as we shall see later. The ß-hydrogens of each molecule lie up against the corresponding hydrogens of the next and the 001 plane passes through all the contacts. It would appear to be the weakest junction in the crystal, and therefore the 001 plane is the cleavage plane.

It must be observed that in the junctions between molecule and molecule there are forces far weaker than the valency

forces, which latter unite the atoms of the same molecule. It is the former which bind the molecules into the crystal, nevertheless.

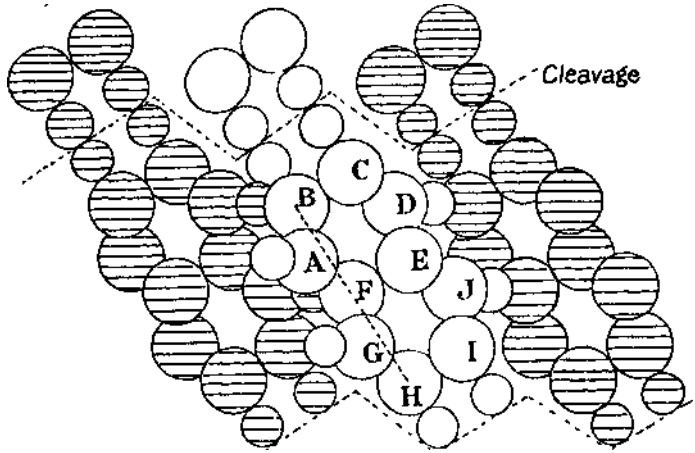


FIG. 81.—SHOWING MUTUAL RELATIONS OF THREE NAPHTHALENE MOLECULES AND PARTS OF OTHERS.

The unshaded circles between the two cleavage planes represent a molecule as at *Q* (Fig. 80). The shaded represent molecules *B* and *F* in the same figure. The small circles represent hydrogen atoms, but their size is uncertain.

Diameter of carbon atom = 1.50. *BH* =4.92. Projection of *AD* on the plane of the diagram =2.50.

When the model is put together in the way now indicated it is found that all the a-hydrogens, those that are attached to the sides of the molecule, lie up against carbon atoms of the next molecule, and that there is an appropriate space waiting for each, of magnitude about 1 A.u., the actual value depending on the orientation of the molecule. The forces exerted at these junctions, though far weaker than valency forces, are stronger than the forces between two ß-hydrogens ; and therefore if the crystal is ruptured it is the latter which give way first. The forces exerted by the a-hydrogens do so across the 110 and 110 planes, and it is not surprising to find that the latter make natural faces of the crystal and give a strong reflection. The structure now found is a very empty one; it is like lace-work in space. That must be

expected, since the specific gravity is so low. The structure is shown in Figs. 81 and 82.

Before proceeding to consider other examples of organic crystals, it will be convenient to state a few principles relating to symmetry which are useful in the analysis of the X-ray results.* A very large proportion of the crystals are monoclinic, or belong to one of the less symmetrical classes of the orthorhombic system. For the sake of brevity we shall limit our consideration to these simpler cases.

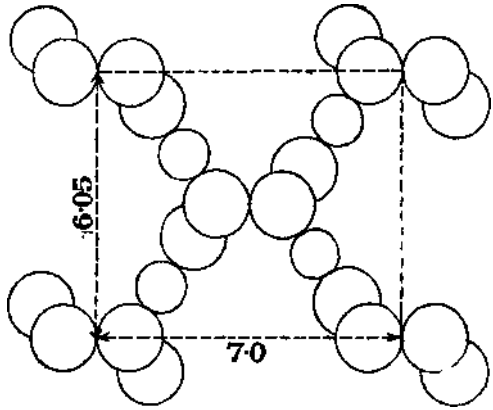


FIG. 82.—SECTION OF NAPHTHALENE CELL PERPENDICULAR TO THE Axis OF *C*, SHOWING α-HYDROGENS CONNECTING THE MOLECULES SIDE TO SIDE.

If a molecule has no symmetry whatever and there is only one molecule in the crystal unit, the crystal itself is necessarily without symmetry and belongs to the lowest class of crystal structure called triclinic asymmetric. If the cell contains more than one molecule the symmetry is of a higher order, because the arrangement is always such as to introduce a symmetry which the molecule did not possess in itself. If for example, there are two molecules in the unit cell, they are so arranged that they have either a common centre of symmetry, the crystal then belonging to the triclinic pinakoidal class, or they are arranged to be the reflections of each other across a plane, which puts the

* Shearer, *Proc. Phys. Soc. of London,* Vol. 35, p. 81,

crystal into the monoclinic domal class, or one is derived from the other by a rotation round a digonal axis, the crystal then belonging to the monoclinic sphenoidal class. The name is, in each case, descriptive of the form which the crystal assumes : and the form is a consequence of the particular arrangement of the two molecules.

If the unit contains four molecules, higher degrees of symmetry are attained. The monoclinic prismatic class is reached if the unsymmetric molecule is first reflected across a plane, and the pair are subsequently rotated through 180^0 about a digonal axis perpendicular to the plane. In the rhombic bisphenoidal class a second molecule is derived from the first by rotation through 180^0 round an axis; the third and fourth are derived from the first and second by rotation round a second axis which is perpendicular to the first. The rhombic pyramidal class is obtained by reflecting a molecule across a plane, and then reflecting the pair across a second plane at right angles to the first plane.

If a crystal belongs to the orthorhombic bipyramidal class and is built up of molecules without symmetry there must be eight of them : if any one of the eight is reflected across any one of a set of three rectangular co-ordinate planes it becomes coincident with another of the eight.

The diagram shows the classification in various ways ; by class number (which is not always the same according to different writers), by name, by diagram according to crystallographic custom, and by co-ordinates of reference to three planes.

It is next to be observed that the operations of reflection and digonal rotation are to be taken as including, it may be, certain parallel shifts, as may be shown in the following way: Let us imagine one half of the molecules to be the reflections of the other half across a certain plane, which we take as the plane of *xz*. It is necessarily a plane of symmetry of the crystal, so that the axis of *y* is now perpendicular to the plane *xz*. The position of a molecule of one kind, which we may call an *A* molecule, can be defined by a set of co-ordinates

of which we take *xyz* as type. If *abc* are the axes of the unit cell, the representative co-ordinates of all *A* molecules are

$$x+pa, \quad y+qb, \quad z+rc,$$

where *p*, *q* and *r* are integers.

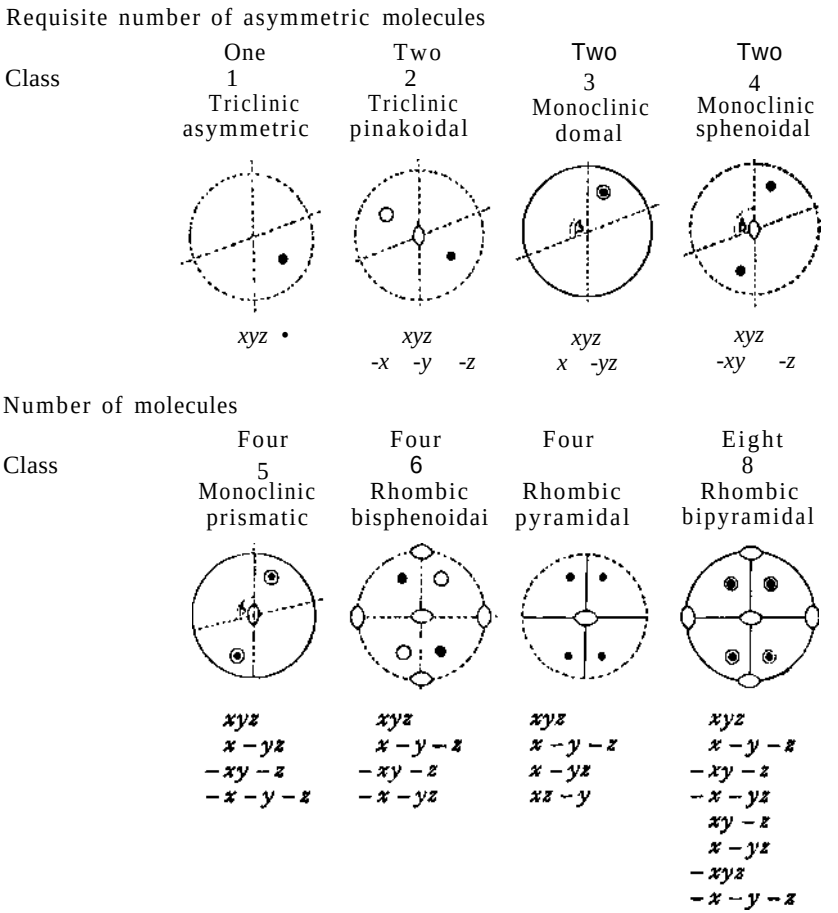


FIG. 83.

The position of a molecule of the other kind, which we may call a *B* molecule, is such that if the whole structure is reflected across the plane of reflection, then, with or without a shift parallel to that plane, the new structure is coincident with the old. Every reflected *A* coincides with a *B*, and every reflected *B* with an *A*.

The co-ordinates of the reflection of any point $x + pa_t$ $y + qb$ $z + re$ in the plane of xz are

$$x+pa, \qquad -y \ -qb, \qquad z+rc.$$

Let the reflected A molecule become coincident with a B molecule, after a parallel shift expressed by adding $(aa, ßb, yc)$ to this and every set of co-ordinates that is required to express the position of the reflected A molecule. The co-ordinates of a B molecule are then :

$$x+pa+aa \qquad -y-qb+fib, \qquad z+rc+yc, \quad \text{etc.}$$

Now, the operations that bring an A molecule to coincidence with a B molecule must, at the same time, bring every B to coincidence with an A. The co-ordinates of the reflection of the point representative of the B molecule are

$$x+pa+aa, \qquad y+qb-ßb, \qquad z+rc+yc.$$

The shift turns these into

$$x \ +pa \ +2aa, \quad y \ +qb, \quad z \ +rc \ + 2yc.$$

Since this is to be representative of an A molecule we have the necessary condition

$$a = o \text{ or } 1/2, \quad y = o \text{ or } 1/2.$$

There is no condition as to ß: obviously there could not be, because the reflecting plane can be conceived as having any required position with respect to the A molecule. In other words if points representing A molecules lie at the corners of the unit cell, the corresponding points representing B molecules must lie on one of the parallels to the b axis drawn through the centres of the faces of the cell, or through the corners of the cell.

Similarly, in the case of digonal rotations, the co-ordinates

$$x+pa, \qquad y+qb, \qquad z+rc$$

become after a rotation of 180^0 round the axis' of y (which is again perpendicular to the plane of xz),

$$-x-pa, \qquad y+qb, \qquad -z-rc.$$

With a parallel shift these become

$$-x \ -pa+aa, \qquad y+qb+ßb, \qquad -z-rc+yc.$$

Again rotating, these become

$$x+pa-aa, \qquad y+qb+ßb, \qquad z+rc-yc,$$

which are converted by the shift into

$$x+pa, \qquad y+qb+2pb, \qquad z+rc.$$

In this case it is ß that must be either o or ½. There are no conditions governing the values of α or *y*. In other words, if points representing *A* molecules are placed at the corners of the unit cell, the corresponding points representative of what we may call the *C* molecules lie either in the same planes, perpendicular to the axis of rotation, as the *A* points: or in planes exactly midway between *A* planes. These rules may readily be found geometrically. For instance, in Fig. 84, an *A*- point, viz. A_1, reflects to *B'* and then shifts to *B*. By the same operation *B* reflects to *A'* and shifts to A_2, which must be an *A* point. Hence *BA'* bisects the line joining two *A* points.

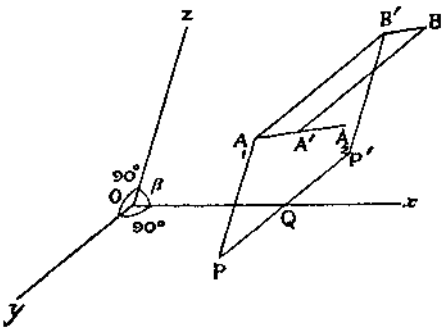


FIG. 84.

The contribution of a molecule to the reflection of the X-rays by any plane is in general different from the contribution of a second molecule derived from the first either by reflection or digonal rotation. If a plane contains one sort only, the true spacing is the distance between any such plane and the next containing the same sort: it is this spacing which is found from X-ray measurements, and which gives the true dimensions of the unit cell. But the two sorts will be effectively alike for certain planes, and the spacing should then be halved. We find this to be the case, and are able in consequence to draw conclusions as to the relative positions of the various molecules in the cell,

If, for example, the crystal unit contains two molecules *A* and C, one derived from the other by a rotation of 180^0 round the *b* axis, a plane drawn through *C* perpendicular to the axis of rotation will either pass through *A* molecules, or exactly interleave planes of *A* molecules, in which case spacing of the (010) plane is halved. This is actually the case with tartaric acid (p. 257). But if we consider planes which pass through the 010 axis the *A* and *C* molecules will not in general produce this result, because the two molecules present different aspects to any such plane.

As an illustration of a case where there are reflected as well as rotated molecules we may take benzoic acid, a monoclinic prismatic crystal whose unit cell contains four molecules. If we denote one of the four by *A*, we may suppose that another *B* is derived from *A* by reflection with or without a shift, and that *C* and *D* are derived from *A* and *B* respectively by digonal rotation. The relations of the four to one another may be expressed by the diagrams:

A	reflects into	*B*
rotates into	centre of symmetry	rotates into
C	reflects into	*D*.

A and *D* are inversions of each other through a centre of symmetry, so also are *B* and *C*.

This statement expresses in fuller terms what is indicated in the diagram of the monoclinic prismatic class on p. 240 : provided that each point or circle on the diagram represents a molecule.

On the supposition that there are four molecules in the cell we have, by calculation from the crystallographic data in the usual way:

a =5.44, 6=5.18, c=21.6, ß=97° 5'.

As the X-ray analysis gives values for the spacings of all the planes agreeing exactly with the values calculated from these

figures, the assumption of four molecules must be correct. We proceed to examine indications as to the relative positions of the four molecules. Consider first the results in Table XV., which shows the approximate intensities of reflec-

TABLE XV.

BENZOIC ACID—C_6H_5 (COOH).

ZONE ABOUT no AXIS.

Plane.	Intensity.		Spacing.	Plane.	Intensity.	Spacing.
	1st Order.	2nd Order.				
118	170	—	—	111	15	3.74
117	33	—	2.30	112	15	363
116	20	—	2.50	113	?	3.42
115	320	—	2.72	114	50	3.21
114	380	—	2.97	115	35	2.97
113	440	80	3.21	116	10?	2.72
112	40	—	3.42	117	50	2.50
111	40	—	3.63	118	0	2.30
no	70		374	—	—	

tion from a long series of planes through the no zone, that is the line in the figure. Since these planes neither contain the crystal axis nor are perpendicular to it, all the four molecules are different with respect to it. Consequently, each point on the above lattice represents the four in all but certain special cases. The series of planes in the zone are found to have the calculated spacings, and the intensities as set down are those found at the correct glancing angles. In no case is the spacing of a plane halved because either *B* or *C* resembles *A* in its action on the plane.

But in the case of the series of planes passing through the *b* axis, (see Table XVI., half the planes show no reflection at the calculated glancing angle. The reason is that in this special case the reflected molecules *B* and *D* are equivalent to *A* and *C* respectively. We have already seen that the *B* molecules must lie on a line parallel to the axis, and passing through the centre of one of the faces, it being assumed that *A* molecules lie at the corners. From the table we deduce

the further limitation that the *B* molecule must lie on the line through the centre of the *be* face, that is to say, *PS* and *QR* in Fig. 85 : since in that case the spacings (1on) are halved when *n* is odd and not when *n* is even. The planes

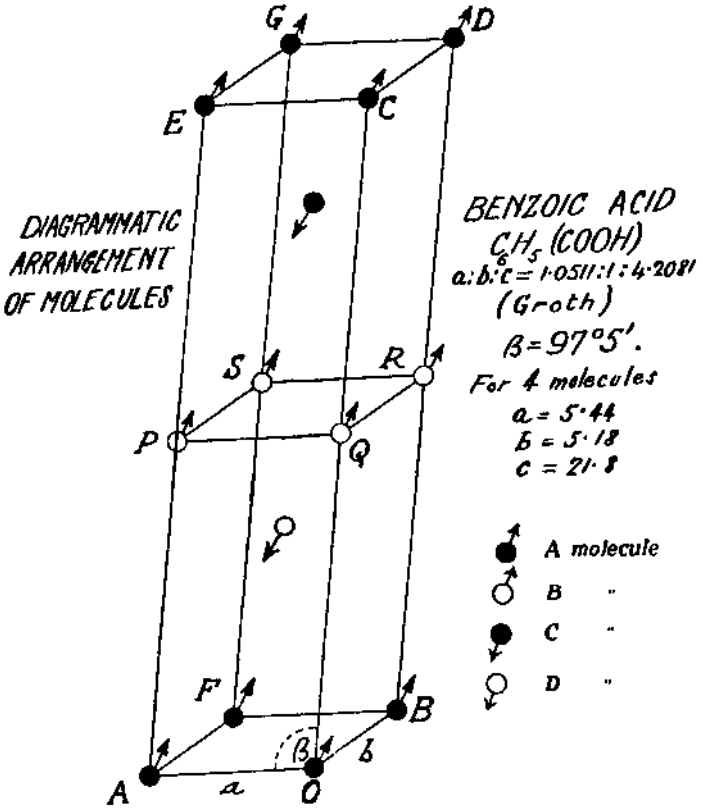


FIG. 85.

(101), (103) are actually found to show some reflection at twice the calculated glancing angle ; that is to say, they show the halved spacing. It is not clear why these reflections are small.

Other results shown in Table XVI. show that the 010 spacing is halved, which implies that the *C* molecules lie in the planes interleaving the (010) planes which are drawn through *A* molecules. The *D* molecules are similarly related to the *B* molecules.

BENZOIC ACID—C_6H_5 (COOH).

TABLE XVI.

ZONE ABOUT "a" Axis.				ZONE ABOUT "b" Axis.			
Plane.	Intensity.		Spacing.	Plane.	Intensity.		Spacing.
	1st Order.	2nd Order.			1st Order.	2nd Order.	
010	0	60	5.16	106	30	0	2.88
011	50	30	4.99	104	90	Trace	365
012	80	90	4.63	102	160	0	4.65
013	100	—	4.19	100	200	0	5.45
014	360	25	3.73	102	380	120	5.16
015	no	—	3.32	104	0	0	—
016	120	—	2.97	106	0	0	—
017	30	—	2.67				
018	80	30	2.40				

The cleavage plane yields a series of spectra of different orders : the intensities are given in Table XVII. This is one

TABLE XVII.

BENZOIC ACID—C_6H_5 (COOH).

REFLECTIONS FROM CLEAVAGE PLANE (001).

SPACING 21.6.

001	0		009	0
002	280		00(10)	30
003	0		00(11)	0
004	220		00(12)	30
005	0		00(13)	0
006	40		00(14)	—
007	0		00(15)	—
008	100		00(16)	Small.

of the planes through the axis whose spacing is halved because the reflected molecule *B* is equivalent to *A*. Consequently there are no odd orders. The comparative strength of the fourth and especially the eighth orders shows that probably the *C* molecule lies not far from the centre of the half-rhomb, either a little above or a little below it. If the *C* molecules were equivalent to the *A* molecule with

respect to this plane, and were exactly in the centre, the 002, 006 ... orders would disappear entirely, leaving only 004, 008, 00(12), etc. The two are not equivalent, for which reason also the position of *C* with respect to *A* in the *ac* plane cannot be simply defined. The (COOH) groups of *A* and *C* face opposite ways, and the effects of the two molecules on the X-rays cannot be calculated as if they were equivalent in magnitude and differed only in phase. Nevertheless, they are sufficiently equivalent to explain in a general way the relative intensities in Table XVII., and the figure has been drawn accordingly. The reflected molecule *B* has been placed at P, S, *Q*, and *R ;* it lies probably at the ends or in the middle of *PS* and *QR*. The *A* and *C* molecules form a double layer, joined together by hydrogen junctions, while the *C* and *B* layers are joined across (COOH) groups, or *vice versa.* Further definitions of position might be based on the relative values of the intensities of the reflections from the different planes, and on the linear measurements of the cell and of the benzene ring in other crystals; but it is doubtful whether it is worth while to go further at present.

It is worth remarking that the cleavage plane has many orders of reflection as in several known cases, and that it can be drawn either through hydrogen junctions only, or COOH junctions only. Probably the former kind of junction is the weaker if we take a precedent from the naphthalene case, and is therefore the cause of cleavage.

Resorcinol is a four molecule crystal belonging to the rhombic pyramidal class (see Fig. 83, p. 240). If one of the four molecules be noted by *A*, the molecule obtained by reflection across the (100) plane may be called A_x, the molecule reflected across (010) by A_y and the fourth, which is the reflection of A_x across (010) or A_y across (100), may be called A_{xy}. There is no digonal molecule: the crystal is polar.

The dimensions of the unit cell are: 0=9.56, 6=10.25, c=5.64. In accordance with the principles laid down above

we may look for the halving of the spacings of half the planes belonging to both the " *a* " or (100) and the " *b* " or (010) zones. The table shows that these effects occur. In both

RESORCINOL (m)$C_6H_4(OH)_2$.

	Observed.	Calculated.	
***a* zone.**			
001 d = 2.84		5.64	
031	2.98	2.98	
051	1.95	1.97	
010	2.55	10.25	
***b* zone.**			
100	2.40	9.56	
501	1.82	1.82	
301	2.78	2.78	
101	4.86	4.87	Strong.
103	1.82	1.85	
001	2.84	5.62	
***c* zone.**			
100	2.40	9.56	
210	4.35	4-35	
110	3.49	7.07	Strong.
120	4.62	4.60	Very strong.
130	1.67	3.29	
140	2.58	2.53	
010	2.55	10.25	

cases, the only planes that give reflections at the calculated angles are those denoted by odd figures only, such as (031), (101). The deduction to be made is that A_x lies on a line parallel to the *a* axis and passing through the centre of the *be* face : and that A_y lies on a line parallel to the *b* axis, and passing through the centre of the *ac* face, lf A_x had been on a line parallel to the *a* axis passing through the centre of the *ac* face, then the planes of the 100 zone which we may denote by *(0, m, n)* would have had halved spacings except when *m* was odd and *n* even : if the line had passed through the centre of the *ab* face, the spacings would have been halved unless *m* was even and *n* odd.

The arrangement of the four molecules, projected upon the *ab* plane must be of the kind shown diagrammatically in Fig. 86 : A_x must lie on *gh,* and A_y on *ef.* The positions of A_x and A_y on these lines must be such as to cause the

apparent quartering of the (100) and (010) spacings which is shown in the table, and roughly indicated in the figure. The molecules A and A_{xy} are coplanar ; so also are A_x and A_y. The one set of planes exactly interleaves the other.

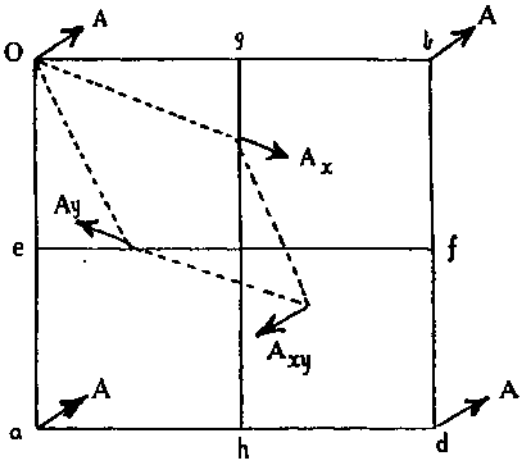


FIG. 86.

A number of other organic crystals have been examined in greater or less detail; some of the results wilt now be considered briefly.

Salicylic acid $C_6H_4(OH)(COOH)$ has two substituted groups instead of one as in benzoic acid. An OH group and a COOH group are substituted for two adjacent hydrogens of the benzene ring. The unit again contains four molecules, and the dimensions are:

$$a = 11.56, \quad b = 11.22, \quad c = 4.93, \quad \beta = 91° \ 22'.$$

The *B* molecule lies on a line parallel to the axis and passing through the centre of the *ab* face.

The phthalic acid unit, $C_6H_4(COOH)_2$ contains four molecules and is again monoclinic prismatic. The dimensions as given by X-ray measurements are :

$$a = 5.06, \quad 6 = 14.32, \quad c = 9.62, \quad \beta = 93° \ 35'.$$

The *B* molecule lies on a line parallel to the axis and

passing through the centre of the *ac* face, as may be inferred from the figures in the following table :

	Calculated.	Observed,	
Zone through *b* axis.			
100	5.06	2.52	Small.
001	9.63	4.82	Orders : 40 : 90 : o : o.
102	3.38	1.72	
103	2.63	2.63	
Zone about 110 axis.			
no	4.76	4.77	Orders 250 : 90 : small: small but > 3rd.
lll	4.18	4.18	Cleavage.
112	3.28	3.31	Very strong : only one order.
112	3.49	3.48	Small.
Zone through axis of a.			
010	1432	7.16	Not observed directly but inferred from
o11	7.98	3.99	other measurements.

Of the planes through the *b* axis 103 shows the full spacing: 101 was not observed. On the other hand, 100 and 102 are halved. The apparent halving of the on spacing is probably accidental. All the planes of the no zone show the full spacing, as was to be expected.

The unit cell of a-naphthol, containing four molecules, has a short *b* axis :

$$a = 13.1,\quad b = 4\text{-}9,\quad c = 13.4,\quad \beta = 117^\circ\ 10'.$$

In this case if the *A* molecules lie at the corners of the cell in the diagram, the other molecules lie nearly at the middle points of the longer edges and the largest face, but the X-ray readings are not yet sufficient to decide more. If we can suppose the length of the molecule to be the same as in naphthalene, the molecules fit well into place if they lie along *OV, QR,* etc., as shown. It seems probable that the molecules at *P* and *R* are the reflections of those at *0* and *W*. Since the molecules in the plane *WZYV* are then the digonal of those in *OAFB* it follows that, as in benzoic acid, the layers lie opposite ways alternately. If the molecules in the *OAFB* plane have all their hydroxyl groups on top of the layer, the hydroxyl groups in the next layer *VWZY* **lie** on the under side. The cleavage plane is the 001 : and no

doubt the break occurs at the ends of the molecules where hydrogens lie against hydrogens as in naphthalene.

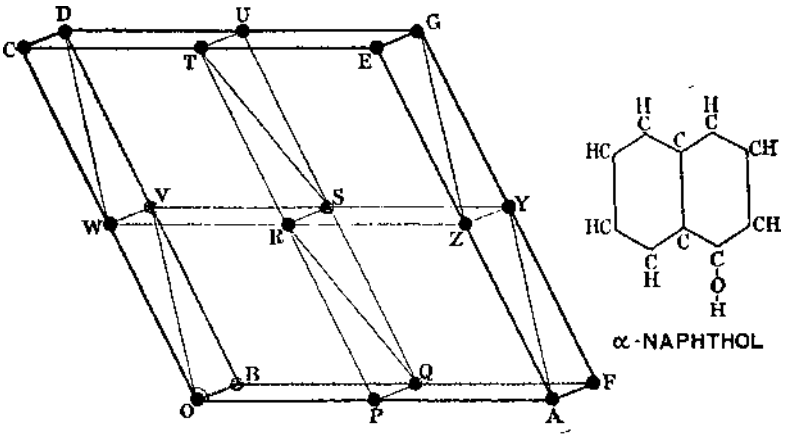


FIG. 87.

The unit cell of ß-naphthol also contains four molecules, the dimensions being:

$$a = 117, \quad 6 = 4.28, \quad 0 = 17.4, \quad ß = 119° \ 48'.$$

The comparison with a-naphthol is very interesting: the *a* and *b* axes are now smaller, and the *c* axis has become longer. This is entirely consistent with our ideas of the structure, because the removal of the hydroxyl group from an a or side position on the molecule to a ß or end position, would naturally cause such changes. In fact, the increase in length of the line *OV,* along which we have supposed the molecule to lie, is from 8.3 to 9.7; the value of the oxygen diameter is known to be about 1.3.

Diphenyl (biphenyl) is a monoclinic prismatic crystal for which

$$a = 8\text{-}10, \ b = 5\text{-}60, \ c = 9\text{-}62, \ ß = 94°46'.$$

It contains two molecules arranged very much as in naphthalene. Dibenzyl ($C_6H_5 . CH_2 . CH_2 . C_6H_5$), stilbene ($C_6H_5 . CH : CH . C_6H_5$), tolane ($C_6H_5 . C ; C . C_6H_5$), azobenzene ($C_6H_5 . NH . NH . C_6H_5$), form a set of four crystals of almost identical structure. In each case the unit cell contains four molecules. There seems to be a strong

resemblance between many of these substances and the monomolecular layers of Langmuir in that they form flaky or tabular crystals consisting of sheets in which the long molecules are packed side by side.

In certain cases, relatively infrequent, the number of molecules is less than the full number required when the molecule has no symmetry of its own. It is convenient to use the term " symmetry number " to denote this full number.

The symmetry number of the monoclinic prismatic class is four: but there are only two molecules in the crystal unit of naphthalene.

As Shearer points out, the naphthalene molecule as built into the crystal must have symmetry of its own. Since it takes the place of two unsymmetrical molecules, its symmetry must be twofold. It has either a plane, an axis, or a centre of symmetry. If it had a plane of symmetry, one molecule would be the digonal of the other, the structure thus providing the digonal symmetry. In that case, the (oio) plane could and probably would be halved : but we should not expect to find any effect on the planes of the (oio) zone. If it had digonal symmetry and the plane of reflection came from the structural arrangement, we might find that the spacings of half the planes in the (oio) zone were halved, but should not expect the (oio) spacing to be halved. As a matter of fact, we find both these effects in naphthalene. We may take this to imply that it has a centre of symmetry, for then the second molecule may be derived from the first either by rotation or reflection. We may denote the molecular symmetry as on p. 240 by *(x, y, z)(-x, -y, -z),* and either operation adds *(x, -y, z)(-x,y, -z)* : the four representing monoclinic prismatic symmetry. In this case, it can be shown that the centre of the *B* molecule must lie halfway between the centres of two *A* molecules, this condition embodying both the two conditions previously laid down, one in relation to digonal symmetry, the other to reflection symmetry. We may find the (010) spacing to be halved *and* half the spacings in the (010) zone. The results set out

in Table XIII. show that this actually happens. We conclude that the molecule, as built into the crystal, possesses a centre of symmetry, and has no plane or axis of symmetry.

Anthracene has not been fully examined : but the molecule may probably be assumed to have a centre of symmetry like naphthalene.

The same can be said of naphthalene tetrachloride ($C_{10}H_8C1_4$). The dimensions of the unit of this crystal are remarkable :

$$a = 8.05, \quad 6 = 10.5, \quad c = 7.35, \quad ß = 112° \ 26'.$$

If these figures are compared with those of the naphthalene unit it will be observed that the *b* axis has been notably increased, and that the increase is 4 A.u., which is nearly

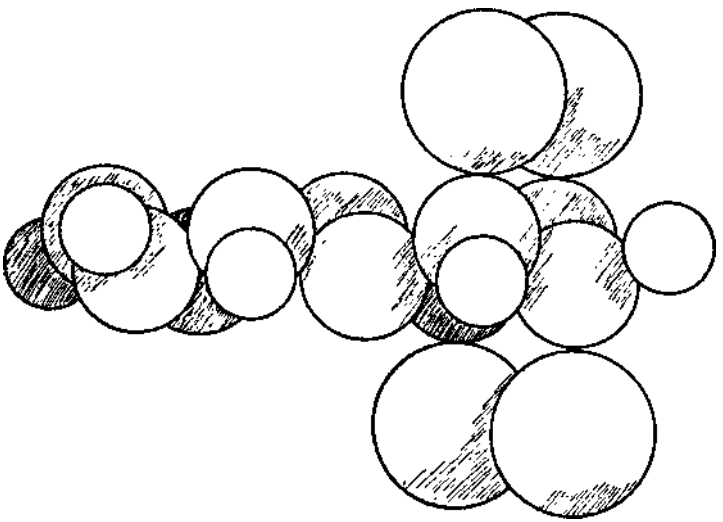


FIG. 88.—NAPHTHALENETETRACHLORIDE, $C_{10}H_8C1_4$

twice the diameter of the chlorine atom. The chlorine atoms are added to the molecules, not substituted for hydrogen atoms. We may suppose the chlorines to be attached to the sides of the naphthalene molecule as in the figure : thus the width of the molecule is increased by 4 A.U. approximately. The molecule may possibly have a centre of symmetry in the crystal even though the nature of its chemical reactions show that the four are all attached at

one end; for, in the crystal each group $C_{10}H_8$ is in contact with eight chlorines.

Dibenzyl is a two molecule crystal, each molecule having a twofold symmetry, the whole being of the monoclinic prismatic class.

Four molecules of acenaphthene make up a cell having the eightfold symmetry of the orthorhombic bipyramidal class : each molecule has, therefore, a twofold symmetry. The cleavage plane cuts across the junctions at the ends of the molecule as in naphthalene.

Finally, two molecules of benzene are contained in the orthorhombic bipyramidal cell:

$$a = 6.45, \quad 6 = 7.24, \quad 0 = 5.8.$$

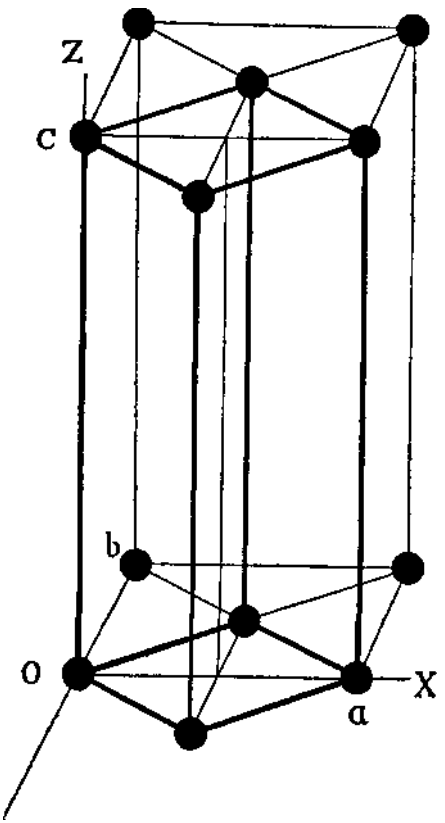
The molecule as built into the crystal must have a fourfold symmetry : but there is no trigonal axis.

The low melting points of organic substances are in general to be ascribed to the weakness of the bonds that bind molecule to molecule. The bonds that bind atom to atom within the molecule are strong, and thus the identity of the molecule is preserved. The low density is no doubt due to the directed nature of the carbon linkages, from which originates the very open structure. The curious and rigid form of the molecule is the cause of the great variety of organic crystals and the close adherence of each to some definite angular form.

It is interesting to consider at this time the application of the same principle of symmetry to one or two inorganic crystals.

Sulphur crystallises in the orthorhombic bipyramidal form (Fig. 89), the symmetry of which, as already explained, can be obtained by employing eight asymmetric atoms. The unit cell has the form of the figure, the dimensions being as shown, and it actually contains eight atoms. But the X-ray analysis also shows that their projection on the axis of *z* are almost equally spaced along that axis, an arrangement which is difficult to explain. For, let us assume

provisionally that the atom has no symmetry. If an atom is placed at each corner as shown, then an atom derived from an *A* by reflection across a plane parallel to *yz,* call it *Ax,* must lie either in an *xy* plane containing A's or in a plane interleaving two such planes: the same is true of *Ay,*



SULPHUR

a= 5 23

***b* = 12 23**

C = 12 23

FIG. 89.

so that both *Ax* and *Ay* lie in planes parallel to the *xy* plane, which either contain *A* molecules or interleave planes containing *A* molecules. By placing them in planes of the latter class we halve the 001 spacing; but no greater subdivision can be obtained from any disposition of *Ax* or *Ay.*

If, further, we obtain a set of *Az* molecules by reflecting across a plane parallel to *xy* and at a distance from it equal to an eighth of the height of the prism, the new set

subdivides the ooi spacing into quarters; approximately only, because the distance between an unsymmetrical atom or molecule and its reflection cannot be definite.

We have now eight atoms in position, but we have not succeeded in obtaining the division of the 001 spacing into eight, which is indicated by the X-ray analysis. There is somewhere an incorrect assumption. It might be that the atom is not to be considered as a point but as two points each carrying eight electrons, separated by a distance equal to one-eighth of the prism height. But this seems very unlikely. More probably there are two sorts or conditions of the sulphur atom, having very nearly the same effect on the X-rays, but making it necessary to suppose that the unit cell contains four sulphur groups, each group containing two atoms, and having a twofold symmetry of its own. By reflection across a plane parallel to *xy* the pair may be doubled so as to make a string of four nearly equidistant sulphur atoms. Reflection of the group of four across the *xz* or the *yz* plane, with a shift parallel to the *Z* axis equal to half the length of *c*, gives a reasonable structure and the nearly eightfold division of the *c* axis which is required.

The difference here indicated might be one of bonding only. If, for example, we imagine four atoms of sulphur arranged by the cubic atom system of Lewis and Langmuir, we might represent the result so (Fig. 90) :

FIG. 90.

Note (added later).—Since this was written a more complete examination has been made by Mark and Wigner *(Zeit. Phys. Chem.* 1924, iii, p. 398). Each of the axes given above should be doubled to obtain the complete unit.

Here the twenty-four outer electrons are so distributed and shared as to give four complete octets.

The grouping resembles that of organic crystals; the close union of certain atoms into a group is accompanied by weak attachments between different groups. In this way we might perhaps account for the low boiling point and the high insulating quality of sulphur.

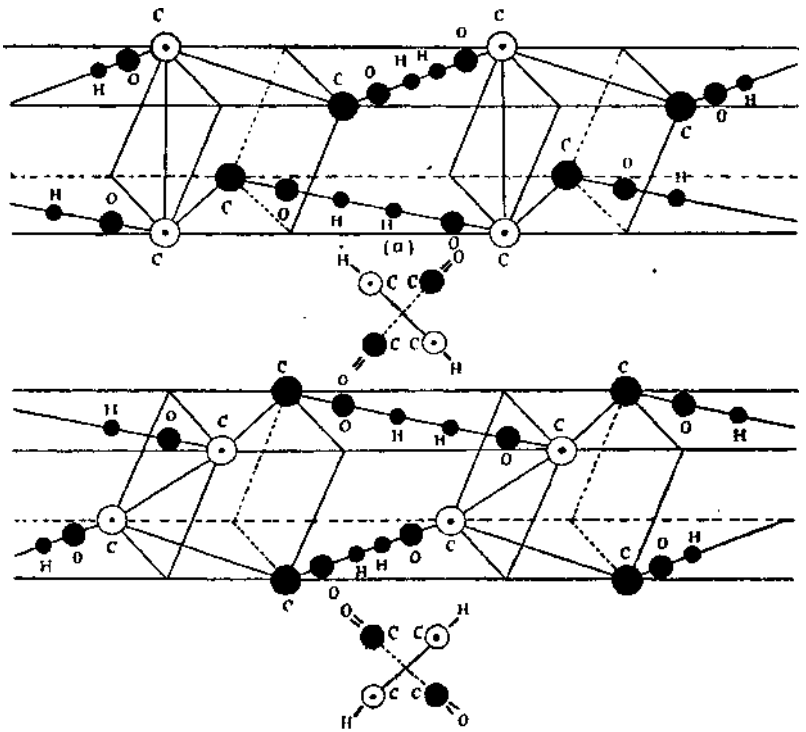


FIG. 91.—TARTARIC ACID: ENANTIOMORPHOUS FORMS, SHOWING IN EACH CASE TWO MOLECULES LYING ALONG THE a-AXIS AND A SECTION CONTAINING THE PROJECTION OF THE CARBON ATOMS ON A PLANE PERPENDICULAR TO THAT AXIS.

Tartaric acid is a crystal of great interest on account of its peculiar optical qualities. Astbury has shown that there are two molecules in the unit cell. The one is obtained from the other by rotation: reflection would indeed be impossible since it converts any right-handed screw into a left-handed screw and the crystal becomes neutral. The

arrangement of *A* and *C* molecules is as shown in Fig. 91 *(Proc. Roy. Soc,* vol. 102, p. 506). The dimensions are :

a-7.70, 6=6.04, *c* =6.195, ß=100° 17'.

Astbury, assuming that the disposition of the atoms in the molecule is actually in close agreement with the chemical formula, finds that the molecules fit very well into position in the unit, the whole having then the structure shown in

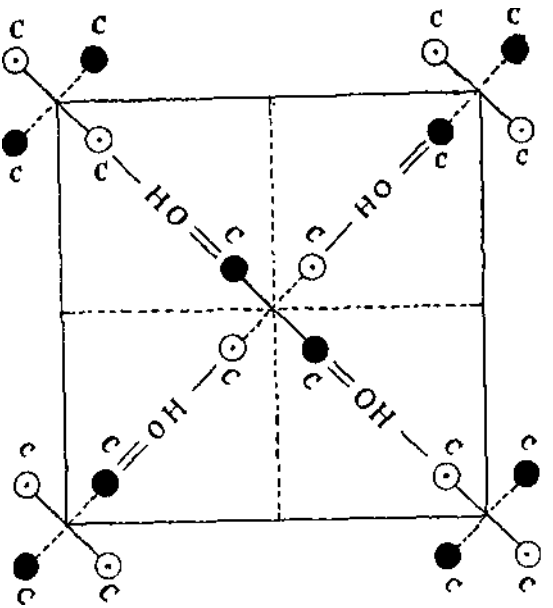


FIG. 92.—TARTARIC ACID, SHOWING ARRANGEMENT OF CARBON ATOMS. LOOKING ALONG AXIS OF *a.*

Fig. 92. The (on) plane gives a far more intense reflection than any other, which is in obvious agreement with the concentration of the atoms in these planes. The cleavage plane cuts across the end-to-end junctions of the molecules as in naphthalene. The structure is in agreement with the essentials of Le Bel and van't Hoff's theory of stereo-isomerism, and shows the connection between the crystal-lographic enantiomorphs and the chemical stereoisomers. It appears that there are two twists in the crystal. One is in the carbon group, the four carbon atoms being arranged

in a **manner** which is at least approximately spiral. There is a second twist in the two strings of oxygens and hydrogens, which join the carbon core of one molecule to that of the next along the *a* axis : it is, in fact, required to counteract the first twist. . As Astbury suggests, the carbon spiral is in all probability a characteristic of the molecule, which remains even when the molecule is put into solution or the outlying portions of the molecule are modified by substitutions. But the second twist, is due to the arrangement of the molecules in the unit, and should disappear in solution, at least when the solution is so dilute that no small groups of molecules are joining up into crystalline form. It has been shown by Lowry that the expression of the optical activity must contain two terms.*

It would be extremely interesting if the connection between optical activity and constitution could be more closely defined. The problem may present no difficulty when more crystals have been examined. So far it would seem that where there is optical activity there must be some approximately spiral arrangement of atoms which are in close combination with each other. Such is at. least the indication of the tartaric acid structure.

We might expect to find the most direct evidence on this point in the structure of quartz, but the structure is not yet known with certainty. In the first edition of this book it was shown that the underlying lattice is of hexagonal form, as shown in Fig. 93. The length of *c* or *Aa* is 5.40 and of *a* or *AB* is 4.84. Three molecules are associated with each point on the lattice, derived from one another successively by rotation through 120^0 accompanied by a shift c/3 or 1.80 along the axis. The manner of derivation is shown in Fig. 94 : there are four unknown parameters, viz. the distance of the silicon from the trigonal axis, and the position, requiring three parameters to express it, of the oxygen relative to the silicon. The analysis was carried up to this point in the first account already referred to.

* Bakerian Lecture, *Phil. Trans. Royal Society*, June, 1921.

Some further consideration may now be given to the question, because it brings in the fundamental question of the directed bonds of carbon and silicon, which is so important in relation to the subject of this chapter.

Let the full black circles in Fig. 95, p. 262, represent a set of silicon atoms lying in a plane perpendicular to the axis

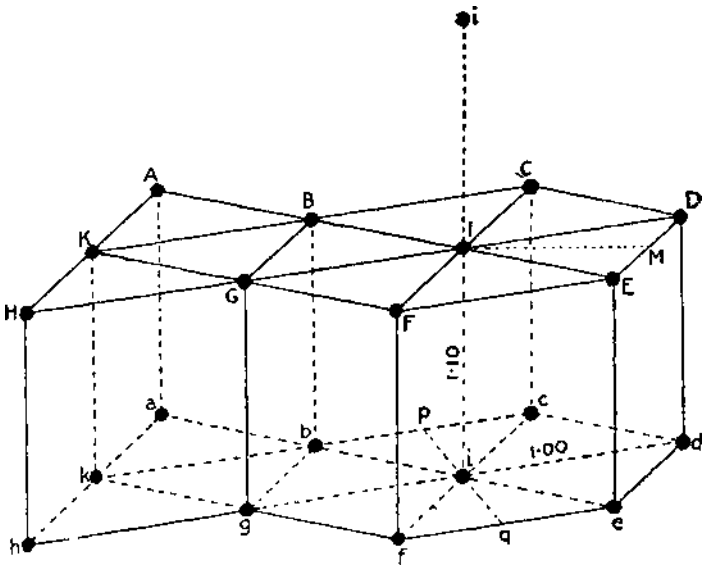


FIG. 93.

of the crystal, and let *aa* be a digonal axis. The molecule to whjich the silicon atom at *A* belongs has a digonal axis coincident with *aa*, and all the other molecules in the plane are oriented in the same direction. They have no other symmetry, if they had it would appear in the crystal. The white "circles are the projections upon the plane of another set of silicon atoms : they all lie in a plane lying 1.80 A.u. below the first plane. The molecule to which, for example, *B* belongs is derived from *A* by a rotation through 120^0 round an axis perpendicular to the paper, and passing through the point *T*, accompanied by a shift of 1.80 A.u. parallel to the axis. The molecule to which the silicon atom at *C* belongs is d\enved from *B* by the same process as that

which brings *A* to coincidence with *B.* A digonal axis *bb* passes through *B,* and a similar axis *cc* passes through *C* : the three projections of the axes meet in *T.* The projection *ABC* is necessarily an equilateral triangle, *aa, bb, cc* being perpendiculars to the three sides, and *B* must lie on *AD,* ***C*** on ***AE.***

The four figures in the diagram represent various positions of *B* and *C* which fulfil the last condition. In the first

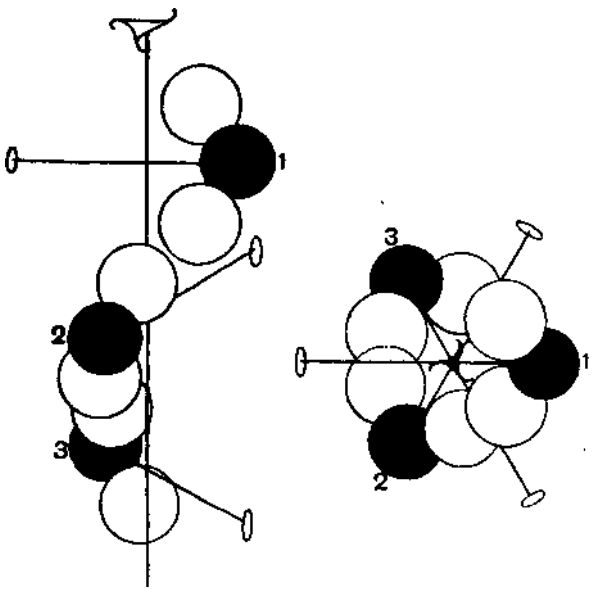


FIG. 94.

figure the projections of *B* and *C* are as close as possible to *A.* The minimum distance is calculated from the condition that the depth of *B* below *A* is 1.80, and the actual distance between the centres of the silicon atoms at *A* and *B* is, if they touch, 2.35 according to Hull's measurement of the silicon diameter. Hence the projection *BC in* Fig. 95 (1) is equal to $V(2\text{-}35^2\text{-}1.80^2) = 1.51$. In the second figure the *B* and *C* molecules are further from *A,* in the third further still, and in the fourth the point *B* has reached the position *N.* If it is taken past *N* there are no new configurations, but merely repetitions of those already obtained : this may

readily be seen if the diagram is extended a little. The projections of the silicons can never be closer together than in the first diagram.

Let us now consider the oxygens. The two associated with *A* are so placed that *aa* is a digonal axis of the molecule.

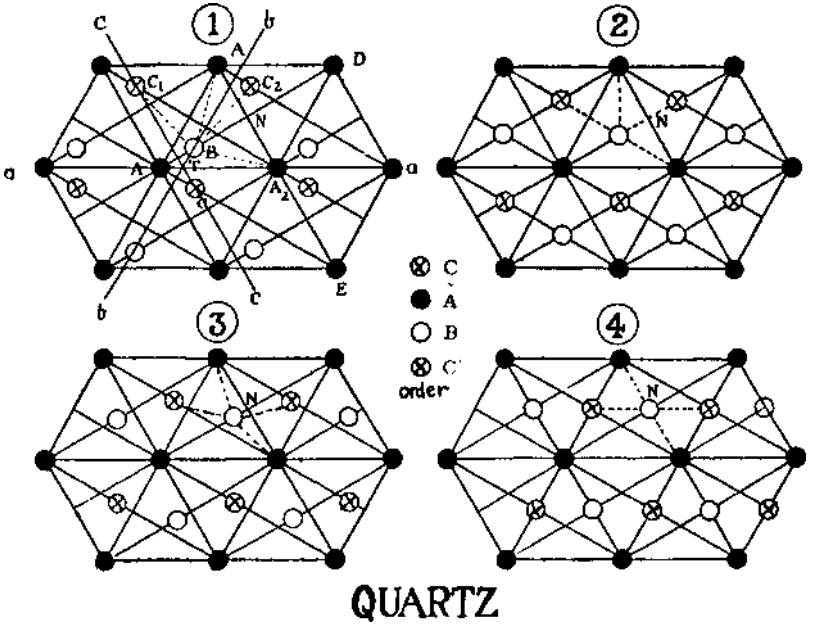


FIG. 95.

There are twice as many oxygens as silicons, and if every oxygen has two silicon neighbours, every silicon has four oxygen neighbours. The crystal has such a low density that it is most unlikely there should be a closer packing, such as, for example, the eight to four of fluorspar. Each oxygen, therefore, connects two silicons, and the two must be in consecutive planes. The distance between two silicons in the same plane is too great to be bridged by an oxygen, and so is the distance between two silicons in planes that are next but one to each other : the closest distance between two such silicons is the distance between *A* and *C* in the first diagram, which is

$$(1.51^2+3.60^2)=3.90.$$

The silicon atom *B* in all four of the diagrams is equidistant from four other silicon atoms, two in the plane above it and two in the plane below, as shown by the dotted lines: we may suppose that the four oxygens which touch *B* form the links represented by these lines. The only alternative is that the two oxygens belonging to *B* in the first diagram join it to *A* and *C* : the oxygens belonging to *A* will then, by symmetry, join it to *B* and to a silicon in the plane above *A,* and so on. Thus each silicon in the spiral of which *ABC* forms part is linked by two oxygens to the silicon atom on either side of it. This is hard to believe, because it leaves nothing to bind the *ABC* spiral to the surrounding spirals, and makes it difficult to account for the hardness of the crystal; moreover, we should have to give a large value to the radius of combination of the silicon in order to bring neighbouring spirals into contact at all. We assume, therefore, that the dotted lines represent the oxygen linkages.

In diagram I the silicons are in contact with one another. There is much to suggest that this hypothesis is correct, and that the silicons are actually sharing electrons. For one thing, the pitch of the spiral of which *A, B, C* form part is equal to the *c* axis, *i.e.* to 5.40 A.u. Now, if the silicons are sharing electrons we may suppose that the angle between the lines joining *B* to *A* and *B* to *C* is the tetrahedral angle $109^0\ 20'$. In such case it can be shown that the diameter of the atom of which the spiral is built $= c/5 = 5.4o/5 = 2.41$: the value found by Hull for silicon in which all bonds are of electron-sharing type and there is no angle in the structure except the tetrahedral angle is 2.35. Moreover, if we follow up this idea we should suppose that the two oxygens attached to the silicon are at the other two tetrahedral points : each silicon now being bonded in tetrahedral fashion to two silicons and two oxygens. It can then be shown (the calculation is omitted as somewhat lengthy) that the oxygen atoms do not lie in the silicon planes perpendicular to the axis, but interleave them, being a little less than one-third of the way across. This agrees with the X-ray

measurements, which show that the intensities of the first, second, and third orders of reflection from the basal plane are as 38 : 40 : 24, and are all small compared to the reflections from other planes, for example, the pyramid planes. Such a result shows that the oxygen atoms cannot lie in the silicon planes, because we should then have a series of intensities decreasing rapidly in the normal way, and the first would be far larger than it is. If their position is calculated from the X-ray results, it is found that they lie on planes which agree with the assumption of a tetrahedral arrangement.

Oxygen atoms, then, form the bridge between spiral and spiral. Since, however, each silicon shares electrons with two other silicons and two oxygens, it cannot share electrons with the oxygens that belong to the next spiral. Each oxygen shares with the silicon to which it belongs, but has no second electron sharing bond. It may be suggested that attraction is still possible between a silicon and the unsaturated oxygens which touch it, and that there may be electrical separations which are the cause of the phenomenon of piezo electricity. If oxygens and silicons are in any way oppositely charged, distortion of the crystal might be able to cause the known electrical effects. Again, it is found that the intensities of reflection from the various planes agree fairly well with those that are observed : a close agreement is not to be expected in the case of so complicated a crystal. The distance between spiral and spiral is rather more than can be bridged by an oxygen of diameter 1.30 ; but we should expect a larger radius of combination at the junction where there is no electron sharing.

If, therefore, we may suppose that the first diagram is correct, we have support for the conception that optical activity is due to a spiral arrangement held together by electron sharing bonds.

If we suppose any other of the four diagrams to be the correct one, we abandon the idea of contact between the

silicons and suppose that each silicon has four oxygen neighbours only. A case of a four-to-two arrangement of this kind is found in ice, and the fact that the simple structure of ice is not adopted is very significant. We have not, obviously, a case of positive and negative ions, which would certainly give a simple structure of the diamond or silicon pattern. But, even if we suppose that the four oxygens must be tetrahedrally round the silicons and share electrons with them, it is difficult to see why the structure is not like that of ice. If we were to place a silicon at the centre of gravity of four silicon neighbours, and interpose an oxygen between each pair of silicons, we should have an electron sharing structure satisfying, it might be supposed, all requirements. If not we must suppose that each oxygen links up with the silicons on each side of it by bonds which cannot be in a line, for otherwise there is no reason for departing from the simple structure.

A structure of this kind has been suggested by Huggins; * but it cannot be correct, since it places each pair of oxygens in the same basal (0001) plane as the silicon to which they belong, and this, as already said, is not in agreement with the X-ray measures of intensities. But apart from this there is no *a priori* reason for ascribing to oxygen such a property. It seems more likely that the first diagram is right. If there is electron sharing between the silicons with directed bonds, we find a good reason for the peculiar structure of quartz. It may be observed that the structure of quartz may on this hypothesis be looked on as due to a tendency of silicons to form long chains analogous to the chain compounds of carbon.

It is known that quartz when raised above 595^0 becomes hexagonal, which might mean that the fourth diagram is then correct: it is the only hexagonal form of the four. The transition ought to be carefully examined on the X-ray spectrometer, for our understanding of the quartz structure cannot be complete until this can be explained.

* *Phys. Rev.*, April, 1922.

Another point which must be cleared up is the exact arrangement of the carbon atoms in the graphite layer. As already said, the structure, given by Debye and Scherrer breaks away from the tetrahedral arrangement, although it is certain that the bonds are still of the electron sharing type, whereas the arrangement is preserved in the structure given by Hull.

CHAPTER XV

THE ANALYSIS OF THE LAUE PHOTOGRAPHS

THE Laue photographs are due to the diffraction by the crystal of the 'white' or general radiation proceeding from an X-ray bulb. All anticathodes give a certain amount this white radiation, in addition to the monochromatic ra which form the line spectrum of the metal of which the are made. A platinum or tungsten anticathode, such as generally used when a Laue photograph is taken, giver most of its X-ray energy in the form of the general rad

Fig. 102 shows the strength of the reflexion in th (100) of rock salt over a large range of glancing an anticathode being composed of platinum. It remembered that at any definite angle, the refle received by the ionisation chamber is in one monochromatic. It consists of all wave lengths the equation

$$n\lambda = 2d \sin \theta,$$

that is to say, it is composed of a series of w $\lambda, \frac{\lambda}{2}, \frac{\lambda}{3}, \frac{\lambda}{4}$, etc. The greater part of it normal the wave length λ, which gives a .first order re angle. The strength of the reflexion at all a sented by a smooth curve (the peaks due to the not being taken into account), and although not give us directly the energy at all points of the rays, it shows that this energy is dis spectrum in a continuous manner.

Each spot in a Laue photograph represents the reflexion of the X-rays by a certain plane *(hkl)* of the crystal structure. It is possible to calculate from the positions of the spots the indices *(hkl)* of the planes, in which reflexion has occurred, and of course also the angle of incidence of the rays on these planes. The efficiency with which each reflexion has taken place is also recorded and roughly indicated by the intensity of the corresponding spot on the plate. The information thus given is very different indeed from that given by the X-ray spectrometer, which examines each plane in detail by itself, the monochromatic radiation which it employs remaining approximately constant in intensity during the xamination of each face. In the Laue photograph every ot represents the action of waves of a different wave length, r *d* and vary from spot to spot. When we compare the tensities of two spots, we are comparing the reflexion of different regions of the spectrum, and initially we do ow the relation between the amounts of radiation of and present in the incident X-ray beam. The exact of the spot is fixed by geometry, and yields no useful on.

of the limitations of this method of investigation, le to deduce the structure of crystals from a study tographs.

iple in two dimensions will best explain how this In Fig. 96 the points represent a crystalline which is referred for convenience to the axes *OX,*

a section of a crystal with this structure is e placed at *0,* the incident rays are represented *AO,* and the reflected rays by the pencils $0S_1$, ne rows of the crystal structure, which reflect g these paths, have indices *(hk),* which corre- indices *(hkl)* of a three-dimensional crystal. which are represented as dotted lines in tance, have indices (11), (21), (31), (41), ch of these types of rows in the crystal

arrangement of the atoms in layers parallel to the r lecting planes. A comparison of the intensities of the variot spots therefore yields information about the arrangement f the atoms in the unit cell, of exactly the same kind as that given by a comparison of the intensities of reflexion of monochromatic light, by various planes, in an analysis by the X-ray spectrometer or Debye photograph. The positions of the spots give the axial ratios and the angles between the axes of the crystal structure. Therefore the Laue diagram contains a large amount of information, the analysis of which is a complex matter, but which has been used with great success in the determination of crystal structure.

In order to subject this information to a general review, an ' index diagram,' such as that of Fig. 105, may be used. This figure is taken from a paper by Aminoff on the structure of a hexagonal osmium-iridium crystal. The abscissa and ordinate of each point are given by

$$x=l, \qquad y=h^2+k^2+hk;$$

the millerian indices *h, k, I* are those of with reference to three axes, the hexagon?[1] is) and two perpendicular to it making an [0] with each other.

If be the wave length reflected order, it may be shown that

$$\lambda = \frac{2cx}{x^2+\frac{4}{3}\cdot\frac{c^2}{a^2}\cdot y}.$$

The curves =constant are drawn in th nearly straight portions of parabolas origin. All the spots in the figure li aries. One of these is the curve high frequency limit to the spectn the right is the limit set by the photograph. Any spot which an distance of the centre must lie to th

All sats of indices which give spots lying between these two undaries should be represented in the Laue photograph and we can at once see which are faint or entirely missing. These are represented by crosses. An explanation of th non-appearance must be sought for, and this leads to a determination of the positions of the atoms in the unit

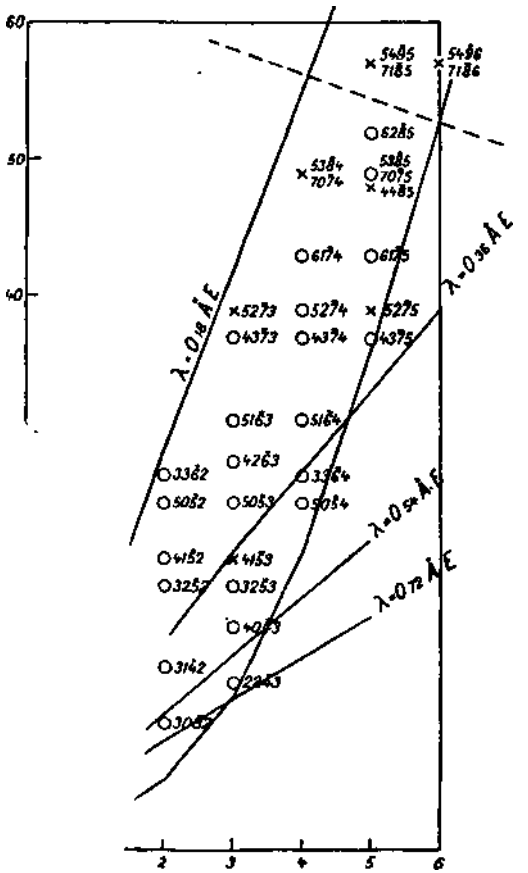


FIG. 105.

of spots are missing, an inconvenient
ably been made, so that the unit
blex. Other sets of axes can then
f simplifying the diagram,
e been used with great success by
noff and others to analyse crystals

of a high degree of complexity. In some cases the method is preferable to that of the Debye photograph, since it is so much easier to assign each spot to the correct plane than to do this for the haloes. Its weakness lies in the fact that exact measurements of the spacings between planes cannot be made with non-monochromatic radiation, so that it has often been found convenient to measure some of the spacings by the spectrometer or Debye method in order to verify the analysis made with the photographs.

CHAPTER XVI

IN this supplementary chapter we shall consider some of the experimental results obtained more recently : and some points already discussed which now seem to require a fuller treatment.

Space groups and molecular arrangement.

In the first place, there is the important point of the relation between the results of X-ray analysis and the proposi-
ons of mathematical crystallography. The latter deals with
tions of symmetry; which is natural, since the manifold
of crystals have been the subject of examination,
er give information concerning the positions of the
from a knowledge of which if sufficient the
y elements can be found immediately. While,
, the two forms of study are dealing with the same
and march together up to a certain point, they
their mode of expression of what they have estab-
ithin this range.

tke a simple example. We will consider the
the benzoic acid crystal by each of the two
the manner in which, in each case, we should
sults obtained.

1 crystallography has proved certain pro-
ing the monoclinic system. Crystals belong-
e described by reference to three axes, one
xis) is at right angles to the other two.
ttices within the system; of which one

called P_m is defined by the statement that there is an equivalent point at each corner of a cell, with parameters *(abcß),* and no other point equivalent to these anywhere else in the cell The other lattice called P^I_m is obtained from P_m by adding equivalent points at the centres of the *ab* or *bc* faces. The system may otherwise be divided into three classes each associated with a particular combination of elements of symmetry. These are designated *(e.g.* in Hilton's *Mathematical Crystallography,* p. 239) as C_8 Hemihedry, C_2 Hemimorphy, C_{2k} Holohedry. The three classes are the contribution of the monoclinic system to the total number of thirty-two classes. Each class may be further subdivided into what are called space groups. In the class C_{24} there are four space groups which have the P_m lattice and two which have the P^1_m lattice. The four belonging to P_m are known as C^1_{2h}, C^2_{2h}, C^3_{2h}, C^4_{2h}. They all have a digonal axis and a plane of symmetry at right angles to it, but differ from one another because the digonal axis may or may not be a screw axis, and the plane of symmetry may or may not be a gliding plane. These six space groups are the contribution of the class C_{24} to the total number of 230 space groups.

The examination of the form of the benzoic acid crystal shows that it belongs to the class C_{2h}; but it is impossible to determine its space group ; it may be any one of the four space groups in P_m or of the two in P^1_m. This method of analysis has come to an end when the class has been determined.

We now turn to the examination of the result that are obtained by the X-ray methods. Without assuming any of the propositions of mathematical crystallography, or any of the indications of the outside form, we may find in the first place that the crystal has a digonal axis and a plane of symmetry at right angles to it. This takes us as far as the other method was able to do. But we do not stop there. We find not only the ratios *a:b: c* but also the actual values of *abc,* and hence by a simple calculation the number of molecules, four, in the cell. We find that if one of these is

placed at each of the corners of the cell *(abcß),* then there is no other within the cell which has the same orientation. Hence we know that the lattice is P_m. In the next place, we find that a second molecule which, in orientation, is the reflection of the first in the *ac* plane requires a shift c/2 in addition to the reflection to bring it to coincidence with the first, and that a third molecule requires a shift *b/2* in addition to a digonal rotation to bring it to coincidence with the first. The position of the fourth molecule depends entirely on the positions of the second and third.

Since both the reflection and the digonal rotation are accompanied by shifts we have actually placed the crystal in the space group $C4_{2h,}$ which is defined by the possession of both these shifts. Because, however, all that is known about C^4_{2h} is that it may exist and is so defined, we are no better off than if we had left the expression of the results in terms of the relative positions of the four molecules as stated above.

The interpretation of the X-ray results proceeds still further; for we may gather from the relative intensities of the different orders of reflection information respecting the relative positions of the atoms in the molecules. We may not. know enough of the reflection laws to make much progress in this direction but we can do something, and we expect that in the future we may do very much more.

In this case, the X-ray analysis has discovered all that, and more than, was found in the observations of form by the older methods. There is however an ambiguity which can occur in certain cases, because the analysis cannot distinguish between the two ends of a polar axis and cannot, therefore, give a direct indication of polarity ; or in other words, may fail to decide as to the presence or absence of a centre of symmetry. On the other hand, the question can be easily answered by observation of the geometrical form.

Resorcinol may be taken as an example of the cases in which ambiguity occurs. Observation of its external form shows that it belongs to the rhombic hemimorphic class of

the orthorhombic system, denoted by the symbol C_{2v} (Hilton) : but cannot determine its space group, out of the twenty-two that are found in that class. On the other hand, the X-ray methods, unaided, can show that it belongs either to the space group C^{10}_{20} of this class or else to Q^{12}_{h} of the holohedral class. The latter class is derived from the former by the addition of a centre of symmetry. If we may assume that resorcinol has no centre of symmetry, either from observation of the form of the crystal, or from knowledge of the form of the molecule, the ambiguity disappears. The X-ray methods have given the linear dimensions of the cell, the number of molecules within it, and certain information about their relative positions, all of which was out of the range of deduction from the outside form.

As regards the mode of expression of the results we do equally well if we use the space group terminology and mention a space group or if we describe the relative positions of the molecules as we find them from our interpretation of the X-ray results. There are 230 possible arrangements just as there are 230 space groups: each arrangement corresponds to one space group. We may define in terms of space groups or in terms of arrangements, as we please. The latter is more natural ro the X-ray methods ; and, moreover, it tells us more simply and directly what is necessary for the further study of the structure of the crystal.

The Refraction and Total Reflexion of X-Rays.

It was predicted by Darwin * in 1914 that an X-ray beam would travel through a substance with a velocity slightly different from that in vacuo. Darwin calculated the magnitude of this effect, and estimated that the ' refractive index ' would differ from unity by an amount of the order of one part in a million. The existence of this refractive index causes a slight departure from the law $n\lambda = 2d \sin\theta$, which gives the positions of the various orders of reflexion ; this law holds exactly for the glancing angle 0' of the rays inside

* C. G. Darwin, *Phil. Mag.*, xxvii., p. 320, I914.

a crystal, but not for the angle *6* which the same rays make before incidence and on emergence. The early measurements of glancing angles were not sufficiently precise to establish the existence of the effect, but the very accurate determinations which have resulted from improved methods of X-ray spectroscopy have clearly demonstrated it. The deviations from the reflexion law were first observed by Stenstrom,* who examined the different orders of reflexion of long wave lengths (2.5 A.) in a sugar crystal. Siegbahn † later showed that the same effect was observable in the *K* lines of copper reflected in calcite. He showed, for instance, that the glancing angle for the first order reflexion of the Ka_2 line was 14^0 42' 0.6", while the same angle as calculated from the second and third order reflexions would be 14^0 41' 55" and 14^0 41' 54.2" respectively. Ewald ‡ in 1920 discussed the departures from the law observed by Stenstrom, and showed that they were of the right order to be explained by Darwin's refractive index.

If this question, like that of the reflexion of X-rays, be treated by the same methods which have been applied to the theory of optical refraction and dispersion, it will be seen that the refractive index exists for both crystalline and amorphous bodies, and depends merely on the wave length of the X-rays and the number of electrons per cubic centimetre in the body. Secondary waves are scattered by the electrons, and these build up a wave front which travels in the same direction as the incident wave. There will be a phase difference between the scattered wave and the primary wave train, and the resultant of the two will differ in phase from the primary beam; the rate of propagation through the body will therefore differ from that in vacuo.

The existence of the refractive index has recently been demonstrated in a striking manner by Compton.§ The

* **W. Stenstrom, *Dissertation*, Lund, 1919.**

† **M. Siegbahn, *Comptes Rendus*, p. 1350, 1921.**

‡ **P. P. Ewald, *Physik. Zeitschr.*, xxi., 1920, p. 617.**

§ **A. H. Compton, *Phil. Mag.*, vol. xlv., June, 1923.**

observed departures from the reflexion law indicate that the index of refraction is slightly less than unity. For instance, results obtained by Duane and Patterson with calcite and the Tungsten *L* spectrum give values for I—u which vary between 10^{-5} and 3×10^{-6}. Theoretical considerations also lead to positive values for I — u of the same order as these. As the refractive index is less than unity, rays falling on a surface at a sufficiently small glancing angle will be totally reflected, and it is this effect which Compton has observed. Although I — *u* is so small, the critical glancing angle is quite appreciable. For instance, Compton calculated that it should be eleven minutes of arc for reflexion of the line = 1.279 A iÅ glass, and observed a critical angle very slightly less than this amount.

In Compton's experiment, a very fine beam of X-rays is allowed to fall at a small glancing angle on a glass plate. Rays coming from the glass plate must pass through a fine slit before reaching the ionisation chamber, and this slit could be adjusted so as to admit rays making any given angle with the primary beam. Setting the slit for a given angle and turning the glass plate, Compton was able to show that a sharply defined maximum in the effect existed when the glass plate was so set as to give specular reflexion of the beam of X-rays, and that the reflexion for small glancing angles was almost total. He then analysed the reflected radiation by an X-ray spectrometer, and was able to measure the critical angle for definite wave lengths. The theory of the effect was confirmed in a remarkable way by his results, as the following table, taken from his paper, shows :

Substance.	Density.	Wave length in A.	Critical Angle exp.	$\delta = 1 - \mu$ exp.	$\delta = 1 - \mu$ theory.
Glass	2.52	I.279	10'	4.2×10^{-6}	5.2×10^{-6}
Glass	2.52	.52	4'	0.9×10^{-8}	0.7×10^{-6}
Silver	IO.5	I.279	22'.5	21.5×10^{-6}	9.8×10^{-6}
Lacquer -		I.279	11'.O	5.1×10^{-6}	

The calculated values of *8* are obtained by means of the formula

$$\delta = \frac{ne^2}{2\pi mv^2}$$

where n is the total number of electrons per unit volume, v the radiation frequency, e and m the electronic charge and mass. In applying corrections to the law of reflexion the difference between the true glancing angle of reflexion Θ_0 and the apparent external glancing angle Θ, is given by Darwin's formula

$$\Theta \sin \Theta \cos \Theta$$

The powder method.

The " powder " method has been found useful in several important cases. It seems that there are considerable advantages in using a slit and correspondingly a mass of powder which is extended in a direction parallel to that of the slit. When a point source of reflected rays is employed, the cones of rays form circles on the photographic plate. But when a row of points or slit is used, the lines on the plate are in one part envelopes of circles : they are more intense, and, as Shearer has pointed out, are sharp on the outside edge. In a considerable experience of the examination of organic crystals, the powder method has been much used, sometimes in conjunction with the ionisation spectrometer and sometimes alone. It has its special advantages and disadvantages, as has already been explained. Chief among the latter must always be the fact that it does not give the angles between the planes of reflexion. All the spacings of the crystal are shown without differentiation on the one plate, and are very difficult to assign unless something is already known of the general form of the crystal or unless the form is obviously of high symmetry. Hull has produced graphical methods of analysing the spectrum when it is known that the crystal belongs to one of the simpler systems. Runge has attempted a more general form of solution *(Phys. Zeit.* 18. p. 509, 1917).

The key to the solution is sometimes furnished by a few measurements made with the ionisation spectrometer on the

same or an isomorphous crystal. Conversely, the powder method is often very helpful during an analysis by the spectrometer, when the form of the crystal is incompletely known. The original method of von Laue is also a useful ally : though in the writers' experience its applicability is not so wide, mainly because it gives no direct measurements of linear dimensions.

Analysts by revolution of a single crystal.

The conjunction of a single crystal, in uniform revolution about a zonal axis, with monochromatic rays registering on a photographic plate is often very useful. It was employed by de Broglie in some of his earlier spectroscopic measurements. It has the advantage over the powder method in that it sorts out the spacings belonging to the zone of rotation : though it shows at the same time spacings belonging to planes of neighbouring zones. If the plate is stationary, there is no means of finding the angles between the various planes of the zone ; but the defect is to some extent overcome by giving the plate a uniform movement of some kind, related in a known manner to the movement of the crystal.

This method has lately been applied in a very interesting way by Muller and Shearer. When working with certain hygroscopic crystals Muller spread them on a glass plate and covered them with a thin layer of paraffin. The plate was mounted so as to revolve about a vertical axis in its plane and was disposed to the X-rays in the manner employed in the original experiments described in the book, when large crystal faces were employed. Some very clear lines were found on the plate which could not be assigned to the crystal under investigation, because they remained when there was no crystalline substance on the glass, except the paraffin. It appears that when fatty acids, their esters and other substances are melted on to a glass plate (or a sheet of mica, which gives convenient reference lines) the

molecules arrange themselves side by side as in the monomolecular films of Langmuir, and N. K. Adam. The substance contains a very great number of these layers, lying on one another in regular stratification. The photographs show excellent sharp lines most of which obviously belong to one type of plane, and are the various orders of reflection from that plane. The photographs of some of the fatty acids, obtained by Muller, are shown in Plate VI. The gradual shrinking together of the lines as we pass from lauric to stearic acids shows a corresponding increase in the thickness of the stratum, which should occur on account of the growing length of the chain. If we assume that the length of the molecule is normal to thstratum, then it is found that each addition of a carbon to the chain causes an increase in the thickness of the stratum of 1.94 A.U. As this is larger than the diameter of the carbon atom, it may be assumed that the stratum is double, containing two molecules end to end, their carboxyl terminations in contact. This has been confirmed by Shearer's measurements of some of the esters, which would not be supposed from chemical reasons to form pairs in this way. He finds that the increase in length due to the addition of each carbon to the same chain, viz. that which is measured by Muller, is now half what it was before. He finds also the very interesting result that the addition of each carbon to the new chain, that of the ester, gives an increase in length of 1.22 A.U. We might suppose that one or both of the chains are inclined at an angle to the layers : or again, that both chains are upright but are differently arranged thus :

chain of ester

\ chain of fatty acid

If this proves to be correct, it illustrates the importance of the tetrahedral angle 109^0 28'.

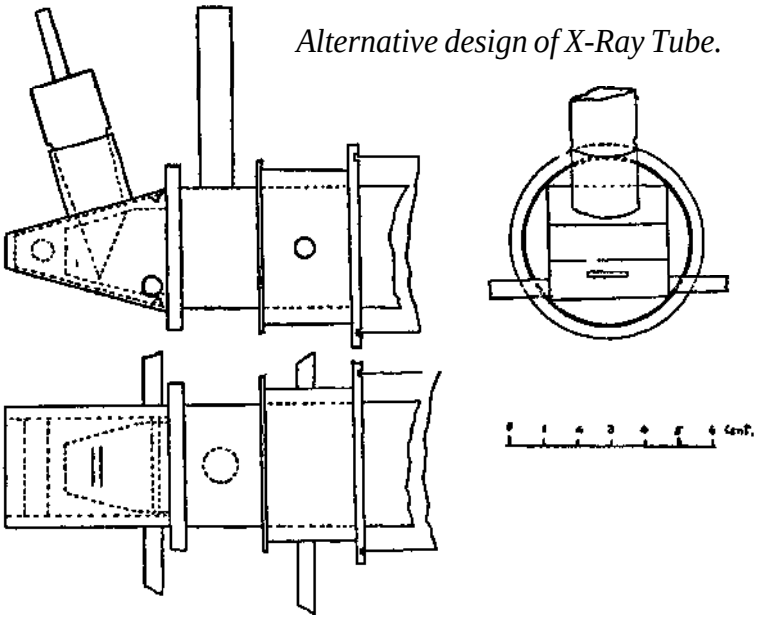


FIG. 106.

The diagrams show an alternative design for the anticathode end of the X-Ray Tube of Fig. 12 (p. 34). By sacrificing one of the two usable slits the other is placed so that it can be easily approached by bulky pieces of apparatus, and the crystal or powder can still be close to the source of the rays.

Metals and Alloys.

Owen and Preston * have shown that the powder method can be successfully applied to the study of the crystallisation of metals and alloys using a plane surface, first made true and afterwards etched to remove irregularly placed surface crystals. They have employed the ionisation method of measuring results. Their observations were made with the object of finding the relative positions of the metals in alloys such as copper aluminium, copper silver and so on. They obtain the very interesting result that the atom of one metal can replace the atom of the other metal in the lattice. The substitution is easy in the case of copper and silver because the sizes of the atoms are approximately the

* ***Proc. Phys. Soc,* 1923.**

same : but difficult otherwise as in the copper aluminium alloy. To these facts can be ascribed both the restrictions on the possible proportions of the latter alloy, and the increase in hardness where the slip planes are, as it were, roughened by the insertion of atoms of larger size.

A very important series of researches on the crystallisation of iron, and the effects due to the addition of carbon is due to Westgren: they are summarised in a paper by Westgren and Phragmen *[Journal of the Iron and Steel Institute,* I., 1922). From their researches it would appear that the carbon atoms do not replace iron atoms in the lattice but are inserted in the interstices of it.

Experiments in this field have also been carried out by E. C. Bain in the United States : a brief account is to be found in *Chemical and Metallurgical Engineering,* Jan. 10, 1923. Bain shows that the substitution of the atoms of one of the ingredients of an alloy in the lattice due to the other can take place in a regular manner. For example, an alloy of gold and copper formed in the proportion of three atoms of the former to one of the latter gives a superposition of the lines due to the simple and the face centred cube lattices respectively. This would happen if the copper atoms were placed at the corners of the cubic cells, and the gold atoms at the centres of the faces : a regular distribution in accordance with the proportion of the mixture. Bain agrees with Westgren in the probable existence of a different state of things in carbon iron alloys, the carbon atoms being attached to but not replacing iron atoms of the lattice: in other words, occupying interstices in the iron lattice.

The slip planes of the aluminium crystal.

The slip planes of aluminium have been examined by G. I. Taylor and Miss Elam *(Proc. Roy. Soc. A.,* vol. 102, p. 643, 1923). They have employed the remarkable crystals prepared by Carpenter and Elam, and observed their crystalline state under strain by the method of the revolving plate

and monochromatic X-rays. This important subject seems likely to attain to great development by the use of such methods : it has been discussed comprehensively by Rosenhain.*

Scattering of X-rays.

In recent papers A. H. Compton† has described experiments which appear to show that a change of wave length occurs when X-rays are scattered by free electrons. It is supposed that a quantum of energy $h\nu$ and momentum $h\nu/c$ strikes an electron, and that the subsequent events may be calculated as if we were dealing with an ordinary mass impact. The electron moves off in one direction, and a new quantum moves off in another direction making an angle ϕ with the direction of motion of the old. The energy of the new quantum is taken to be $h(\nu-S\nu)$ and its momentum $h(\nu-S\nu)/c$ Applying the usual conditions of conservation of momentum and of energy, it can be shown that

$$\delta\lambda = 0.0484 \sin^2\theta/2.$$

Compton using an ionisation spectrometer actually found a change of wave length in agreement with this calculation. Ross ‡ using a photographic method also obtained a very clear confirmation in the case when $\lambda = 0.712$ Å: but failed to find it for the visible wave length of the green mercury line. Muller also, working in the Davy-Faraday Laboratory, has obtained the correct experimental result for the Ka-rays of silver, molybdenum, and copper. As scattering substances Muller used paraffin, glass, and aluminium. There can be no doubt that the effect is clear and easily measurable. The difficulty of its interpretation on a wave theory of X-rays

* Thirteenth May Lecture, Published by The Institute of Metals, London, 1923.

† *Bui. Nat. Res. Coun.*, Washington, No. 20, p. 10, Oct. 1922 ; *Phys. Rev.*, 21, 1923, p. 207 ; *Phil. Mag.*, Nov. 1923, p. 897. See also Gray, *Phil. Mag.*, 26, 1913, p. 611, and *Journ. Frank. Inst.*, Nov. 1920, p. 643, and Florance, *Phil. Mag.*, 27, 1914, p. 225.

‡ *Proc. Nat. Acad. Sci.*, July 1923.

is obvious. A compromise might be sought which would reconcile the quantum theory and the wave theory in respect to this experiment, as it has been sought in previous cases : but the search may well be a waste of time. The ultimate reconciliation depends, it may be argued, on factors which are as yet beyond our powers to appreciate.

APPENDIX I

Many crystals have been analysed by X-rays which have not been described in the preceding pages. The list of crystals given below is far from complete, but may be of service to anyone who wishes to consult the original papers. Brief notes of explanation have been added describing the main features of the structures assigned to the more simple crystals.

Elements.

A description of the crystalline structures of elements, with references, will be found on pp. 161-164.

Carborundum CSi * † ‡ § has been examined by several investigators. The structure is closely related to that of diamond.

Cementite Fe_3C || has been partly analysed by Westgren and Phragmen.

Oxides. Ice, H_2O.

Dennison** and St. John †† have examined the crystalline structure by the powder method. Their results have been analysed by W. H. Bragg ‡‡ and a structure suggested which appears to explain satisfactorily their observations. The symmetry is hexagonal; the arrangement of oxygen atoms resembles that of the carbon atoms in diamond, in

* C. L. Burdick, E. A. Owen, *Journ. Amer. Ghent. Soc,* 40, 1918, 1749.
† A. W. Hull, *Phys. Rev.,* 13, 1919, 292, and 15, 1920, 545.
‡ H. Espig, *Abh. d. Sachs. Akad. d. Wiss.,* 38, 1921.
§ F. von Hever, P. Koller, *Zeit. f. Kristall,* 50, 1915, 260.
|| A. Westgren, G. Phragmen, *Zeit. f. Physik. Chem.,* 102, 1922, 1.
** *Phys. Rev.,* xvii., 1, 1921. †† *Pr. Nat. Acad. Sci.,* vol. 21, 1918.
‡‡ *Pr. Phys. Soc,* London, 34, 1922.

that every atom is surrounded tetrahedrally by four others. The relation between the two structures corresponds to that between cubic and hexagonal close-packed assemblages. A hydrogen atom is situated between every pair of oxygen atoms. The structure is fully described on p. 177.

Cu_20 . Ag_20. The structure of Cu_20 is described on p. 145. The structure there assigned has been confirmed by Niggli * who has found that Ag_20 crystallises in the same way. Wyckoff † has also arrived at the same result for Ag_20. The metal atoms are on a face centred cubic lattice, and the oxygen atoms on a body centred cubic lattice so placed that each is surrounded by four metal atoms. The dimensions of the lattices are

Cu_20 4.26 A.
Ag_20 4.718 A.

CaO,‡ SrO, BaO, MgO,§ *CdO,|| NiO, //* CoO.**

It is probable that all these cubic crystals have the simple rocksalt structure, though only the first and last four have been analysed.

The lattice dimensions are :

CaO. 4.79 A.
MgO. 4.18 Å.
CdO. 4.72 Å.
NiO. 4.20 A.

ZnO †† ‡‡ *BeO* §§. Both compounds form hexagonal crystals, but with a different arrangement. In zinc oxide the zinc

* *Z. fur Kristallographie,* 57, 3, 1922.
† *Am. J. Sci.,* 184, 1922.
‡ W. P. Davey, *Phys. Rev.,* 21, 2, 213 (1923).
§ R. W. G. Wyckoff, *Amer. J. Sci.,* 138, 1921.
|| P. Scherrer, *Z. fur Kristallographie,* 57, 2, 186, 1922.
// W. P. Davey and E. O. Hoffman, *Phys. Rev.,* 15, 2, 333 (1920).
** J. A. Hedvall, *Zeit.f. Anorg. Chem.,* 1922, 120, 327.
†† W. L. Bragg, *Phil. Mag.,* xxxix., June, 1920.
‡‡ G. Aminoff, *Z. fur Kristallographie,* 57, 2, 204, 1922 ; 56, xxiv., 494 (1921).
§§ L. W. M'Keehan, *Proc. Nat. Acad. Soc.,* Sept. 1922.

atoms are arranged as in the hexagonal close-packed assemblage. The oxygen atoms have a similar arrangement, and are so placed that each is at the centre of four zinc atoms. The resulting structure has a polar hexagonal axis.

M'Keehan has shown that in BeO the metal atoms are on a simple hexagonal lattice, the oxygen atoms on a similar lattice, the two interpenetrating so as to form an approximately close-packed assemblage.

Lattice dimensions :

ZnO. a=3.22 A. c = 5.20 A.
BeO. *a* = 2.696 A. c=4.39 A.

CuO. (Tenorite). A solution of the structure of this interesting substance has been attempted by P. Niggli *, in which the copper and oxygen atoms are related in the rocksalt manner, but the whole structure is deformed to triclinic symmetry. The X-ray investigation of this compound led Niggli to suggest an alternative and better setting up of the crystallographic axes.

The unit cell dimensions are:

$$a = 3.74 \text{ A.}$$
$$b = c = 4.67 \text{ A.}$$

and the new angles ;— $\begin{cases} \alpha = 85^\circ\ 21' \\ \beta = 86^\circ\ 25' \\ \gamma = 93^\circ\ 35' \end{cases}$

SiO_2. Quartz.

The structure of quartz has been dealt with in the preceding pages (p. 259 *et seq).*

The silicon atoms are linked together to form a set of spirals, which are linked to each other by oxygen atoms. There are three molecules per unit prism of the hexagonal lattice. This structure is confirmed by M'Keehan †, who considers, however, each pair of oxygen atoms to be placed a little closer to a silicon atom.

* P. Niggli. *Z. fur Kristallographie,* 57, 3, 1922 (Sept.).
† L. W. M'Keehan, *Phys. Rev.,* 21, 5, 503 (1923).

The lattice dimensions are :

$$a = 4.88 \text{ A.} \quad c = 5.37 \text{ A.}$$

The Zircon Group,

Rutile, anatase, zircon, polianite, etc., form an interesting group of minerals all of which possess the Ditetragonal Equatorial type of symmetry. In all except anatase, one form of TiO_2 the structural similarity expresses itself in the axial ratios.*

Rutile, TiO_2	$a : c = 1 : 0.6439.$
Cassiterite, SnO_2	$a : c = 1 : 0.6726.$
Xenotime, Y. P. O_4	$a: c = 1:$ 0.6177.
Zircon, ZrO_2. SiO_2	$a : c = 1 : 0.6391.$
Polianite, MnO_2	$a : c = 1 : 0.6647.$

Anatase is different in that the axial ratios are 1: 1.7771. L. Vegard † ‡ has investigated the structure of rutile, cassiterite, zircon, and xenotime; Williams § has investigated the first two of these substances. These observers do not agree in the relative intensity and even the order of the observed spectra. The structure of rutile has recently been examined by Greenwood *(Phil. Mag.,* Oct. 1924), who agrees with Vegard's determination. St. John || has analysed polianite and obtains results similar to those of Vegard.

The Spinels. ** †† In this group of oxides of the general type R"0 . R"'$_2O_3$, including MgO . Al_2O_3 and FeO . F_2O_3, the bivalent metal atoms are situated upon the " diamond " point system. The alternate octants which have one bivalent atom in the centre, contain also 4 oxygen atoms tetrahedrally placed round this central metal atom. The

*** *Groth. Chem. Kristallographie,* Part I.**

† L. Vegard, *Phil. Mag.,* xxxii., (July) 1916.

‡ L. Vegard, *Phil. Mag.,* xxxii., (Nov.) 1916, also *(ibid.)* May, 1917.

§ C. M. Williams, *Proc. Roy. S o c . , 9 3 ,* 418, 1917.

|| A. St. John, *Phys. Rev.,* 21, 3, 1923 (Proceedings).

**** S. Nishikawa, *Pr. Math. Soc,* Tokyo, 8, 199, 1915.**

†† W. H. Bragg, *Nature, 95,* 561,1915.

remaining octants have 4 oxygens similarly placed and also 4 trivalent metal atoms.

Other Oxides. The Al_2O_3 Group.

The arrangement of atoms in alumina is discussed (p. 180) in this book. Wheeler P. Davey has recently published an abstract * of some measurements he has taken which lead to the same structure.

Davey's measurements are given below:

Al_2O_3. a = 4745 Å.
Fe_2O_3. a = 5-035 A.
Cr_2O_3. a = 4.932 A.

The symmetry of the structure has been discussed at length by G. Shearer †

The trioxides of arsenic and antimony, As_4O_6 and Sb_4O_6, have been examined by R. M. Bozorth, ‡ who assigns to them a structure which has been described on page 173 above. This structure is cubic holohedral, and is essentially a " diamond " arrangement with one As_4O_6 or Sb_4O_6 molecule grouped around each point.

Length of unit cell.

(As_4O_6) a = 11.06 A.
(Sb_4O_6) a = 11.14 A.

The Hydroxides. The only attempt on this type of compound is that of Aminoff,§ who analysed the structure of two similar minerals, brucite, $Mg(OH)_2$ and pyrochroite, $Mn(OH)_2$. The metal atoms are on a simple hexagonal lattice, and the two oxygen atoms are situated at 1/3 and § the height of the unit cell, covering alternate triangles of the lattice. The cell dimensions are :

Pyrochroite.	*Brucite.*
a = 3.34 A.	a = 3.13 A.
c = 4.68 A.	**c = 4.75 A.**

*** W. P. Davey, *Phys. Rev.*, 21, 6, 716 (1923).**
† G. Shearer, *Proc. Phys. Soc*, Lon., 35, 2, 1923 (p. 81).
‡ R. M. Bozorth, J. *Amer. Chem. Soc*, 45, 7, 1621 (1923).
§ G. Aminoff, *Geol. Foren Forhandl.*, Stockholm, May 1919.

Sulphides, Selenides, etc.

Cuprous Selenide Cu_2Se * is based on the CaF_2 (Fluorite) model with a unit cube of length, 5.751 A. Calcium sulphide † and alabandite (MnS) ‡ have a simple "Rocksalt" arrangement of metal and sulphur atoms. The selenides of calcium, strontium and barium † have been dealt with in a paper by Davey. They all conform to the "Rocksalt" arrangement. The unit cube lengths are stated to be as follows:

CaSe. a = 5.914 A
SrSe. a =6.234 A.
BaSe. a =6.616 A.

The structure of cubic zinc sulphide is fully described in a previous chapter (p. 94). There is a hexagonal modification, wurtzite, which has also been solved.§ It is shown to have the dihexagonal polar type of symmetry, as possessed by zinc oxide. Cadmium sulphide, greenockite,|| belongs to the same class. The dimensions for ZnS are :

a=3.855 Å.U.
c=6.31 A.U.

The distance between atom centres in hexagonal ZnS is 2.36 A and in cubic ZnS 2.34 A. Zinc selenide ** has the same structure as cubic zincblende with 0 = 5.651 A. No hexagonal form corresponding to wurtzite has been measured.

Bisulphides. Iron pyrites has been described in detail on p. 115.

Molybdenum disulphide, MoS_2 occurs as the hexagonal mineral, molybdenite. The structure has been worked out by Dickinson and Pauling. †† The metal atoms are on

*** W. P. Davey, *Phys. Rev.*, 21, 2, 380 (1923).**
† W. P. Davey, *Phys. Rev.* 21, 2, 213 (1923).
‡ R. W. G. Wyckoff, *Am. J. Soc*, 184 (1922).
§ G. Aminoff, *Z. fur Kristallographie*, 58, xi., 1923.
|| W. L. Bragg, *Phil. Mag.*, vol. xxxix., June 1920.
**** W. P. Davey, *Phys. Rev.*, 21, 2, 380 (1923).**
††R. G. Dickinson and L. Pauling, *Jour. Amer. Chem. Soc*, 45,1466,1923,

a point system which may be described as a close-packed hexagonal arrangement much elongated along the *c* axis, and there is a sulphur above and below each metal atom.

The side of unit triangle is 3.15 A. and the height 12.30 A. *Chalcopyrite,* $CuFeS_2$*.

The copper and iron atoms in this compound are stated to lie on alternate layers perpendicular to the tetragonal *c* axis. The general marshalling of the structure corresponds to that in zincblende. Half the zinc atoms in the latter crystal must be supposed to be replaced by iron atoms, the other half by copper atoms, the sulphur atoms to retain their positions, and the unit cell to be distorted so that:

$$a = 5.228 \text{ A.}$$
$$c = 5.150 \text{ A.}$$

A reference to cobaltite (CoAsS) and ullmannite (NiSbS) will be found on page 145.

Nickel Arsenide.†

This mineral is usually stated to be ditrigonal polar; Aminoff suggests alternative structures both of which are based on a hexagonal lattice, and the Laue diagrams indicate hexagonal symmetry. The rattice dimensions are :

$$a=3.57 \text{ A.} \qquad c = 5.10 \text{ A.}$$

Hydrides. Lithium hydride,‡ LiH is cubic, with atoms situated as in rocksalt.

Length of unit, $a = 4.10$ A.

The halogen derivatives. Alkali halides.

These have been measured by a number of observers and a summary of the results are given in a paper by Davey.§ || **

* C. L. Burdick and J. H. Ellis, *Jour. Amer. Chem. Soc,* 39, 2518, 1917.
† G. Aminoff, *Z. fur Kristallographie, 58,* xi., 1923.
‡ J. M. Bijvoet and A. Karssen, *K. Akad. Weten.,* Amsterdam, 25, 17, 1922.
§ W. P. Davey, *Phys. Rev.,* 21, 2, 143 (1923).
|| H. Ott, *Phys. Zeit.,* xxiv., 212 (1923).
** P. Debye and P. Scherrer, *Phys. Zeit.,* xvii., 277 (1916).

The arrangement is that of the rocksalt structure for all members of this series with the exception of rubidium fluoride, and the chloride, bromide, and iodide of caesium. The four last mentioned salts are built up on a body centred arrangement, the unit cell having one metal atom at each corner and one halogen in the centre. Davey's measurements of the distance between successive (1oo) planes are given below.

	Fluoride	Chloride	Bromide	Iodide
Li - - -	2.007	2.566	2.745	3.037
Na - - -	2.310	—	2.968	3.231
K - - -	2.664	3.138	3.285	3.525
Rb - - -	3.663	3.267	3.418	3.655
Cs - - -	3.004	4,118	4.287	4.558

Angstrom Units.

Thallium chloride * T1C1 has been found to possess a body centred structure, similar to Caesium chloride, with a=3.85 A. The value of d_{100} for rocksalt is found to be 2.810 Å.† with the greatest accuracy attained. The structure of NaCl has been discussed in a previous chapter.

Potassium Cyanide,‡§ appears to be strictly analogous with the alkali halides. The K atoms and (CN) groups are arranged as in rocksalt, with "a "=6.54 A.U. and with apparently a close approximation of the C and N atoms.

Ammonium Halides.\\ **

The work of G. Bartlett and I. Langmuir || demonstrated the fact that these compounds can exist in two modifications, according to temperature. A modification, the

* W. P. Davey and F. G. Wick, *Phys. Rev.,* xvii., 403, 1921.

† W. P. Davey, *Science,* N.S., vol. liv., No. 1403, 497 (1921).

‡ P. A. Cooper, *Nature,* 107, 745 (1921).

§ R. M. Bozorth, *Jour. Amer. Chem. Soc,* 44, 2, 317 (1922).

|| Bartlett and Langmuir, *Jour. Amer. Chem. Soc,* 43, 2, 86 (1921).

** L. Vegard, *Phil. Mag.,* xxxiii., May 1917.

structure of which resembles that of caesium chloride, exists in each case at lower temperatures, and above a transition point the structure changes to the "rocksalt" arrangement.

Dimensions. Salt.	Arrangement as in caesium chloride.	Transition temperature.	Rocksalt arrangement.
NH_4C1	3.859 A	18_4.3°C	6.533 A
NH_4Br	3.988 A	137.8° C	6.90 A
NH_4I		I7.6°C	5.09 A

In a previous paper, Vegard * worked out the structure of NH_4I and $N(CH_3)_4I$. He shows that in tetragonal tetramethyl ammonium iodide, the *"c"* parameter is the same as the length of unit cube of simple NH_4I. Apparently the methyl radicals are distributed in such a way throughout the structures as to have no influence on the height of the cell.

Phosphonium Iodide † is tetragonal, but resembles in its marshalling cubic NH_4C1. The unit cell dimensions are :

$$a = 6.34 \text{ A.U.}$$
$$c = 4.62 \text{ A.U.}$$

The Cuprous and Silver Haliaes.‡ § II // **

Cuprous chloride, bromide and iodide and one modification of silver iodide are cubic with 4 molecules per unit cell. The arrangement is the same as in zincblende.

Silver chloride and bromide are built up on the rocksalt model, while a second form of silver iodide is hexagonal and has a polar structure, similar to that of zinc oxide.

* L. Vegard, *Phil. Mag.*, xxxiii., May 1917.

† R. G. Dickinson, *Jour. Amer. Chem. Soc*, 44, 7, 1489 (1922).

‡ R. W. G. Wyckoff and E. Posnjak, *Jour. Amer. Chem. Soc*,, 44, 1, 30 (1922).

§ R. B. Wilsey, *Phil. Mag.*, 262 (1921).

|| R. B. Wilsey, *Phil. Mag.*, 46, 487 (1923).

|/ G. Aminoff, *Geol. Fören.*, Stock., April 1922.

** G. Aminoff, *Z.für Kristallog.*, 57, 2, 180 (1922).

Unit cell Dimensions.

Crystal.	Type of Structure.	a.
CuCl - - -	Zincblende	5.49 A.
CuBr -	„	5.82 „
CuI -	„	6.09 „
AgCl -	Rocksalt	5.540 „
AgBr -	„	5.768 „
AgI (cubic) - -	Zincblende	6.493 „
AgI (hexagonal) -	Zinc Oxide (polar)	a =4.593 c=7.53
CuI. 4AgI - -	Zincblende	

Calcium Fluoride has been fully described on p. 102. The calcium fluoride type of crystal grouping is found to be one of common occurrence in more complex chemical compounds belonging to the cubic system.

Cadmium Iodide * CdI_2 has a trigonal structure consisting of three interpenetrating lattices so arranged as to give full trigonal (not rhombohedral) symmetry, *a* =4.24 A, *c*=6.84 A.

Potassium Hydrogen fluoride † is tetragonal, with *a* =5.67 A. and c=6.81 A. The structure is centred tetragonal, and is in some ways similar to that of cubic Ammonium Chloride. It is to be remarked that in this case, as in CdI_2 and MoS_2, there is a comparatively great distance between two adjacent negative radicals.

Stannic Iodide, SnI_4‡ § has been attempted by two authors, both of whom get a structure possessing pyritohedral symmetry, the side of the unit cell containing eight molecules being 12.23 A.

Caesium dichloro-iodide, $CsICl_2$. The introduction || of two CI atoms into the cubic, body centred structure of CsI causes a prolongation of the diagonal on which they are placed, and consequent change of symmetry to trigonal.

An analysis of KI_3, $CsIBr_2$, CsI_3has also been attempted.¶

* R. M. Bozorth, *Jour. Amer. Chem. Soc,* 44, 10, 2232 (1922).

† R. M. Bozorth, *Jour. Amer. Chem. Soc,* 45, 2128 (1923).

‡ H. Mark and K. Weissenberg, *Z. für Physik.,* 16, 1, 1 (1923).

§ R. G. Dickinson, *Jour. Amer. Chem. Soc,* 45, 4, 1923.

|| R. W. G. Wyckoff, *Jour. Amer. Chem. Soc,* 42, 1, 1100 (1920).

¶ G. L. Clark, *Proc, Nat. Ac. Sci.,* 1923, 9, p. 117.

Sodium Chlorate and Bromate. * † ‡ §

Four different attempts have been made to solve these structures. In all cases the unit cube length is the same, viz. 6.56 Å±.02 for $NaC10_3$, 6.73 Å±.02 for $NaBr0_3$. In one solution ‡ the sodium atoms are placed on a face centred lattice and the chlorine atoms make with them a zincblende arrangement. To account for the tetartohedrism the oxygens are placed asymmetrically about the trigonal axes. In the other three solutions the metal and halogen atoms are each close to the corresponding points of a rocksalt structure, but have approached each other along a trigonal axis. The trigonal axes do not intersect. The structures assigned by the various observers vary to some extent in the position of the oxygen atoms.

Other inorganic salts.

*Calcite.*** †† The structure of Calcite has been dealt with at some length in a previous chapter. Other workers have confirmed the structure assigned to it there.

Dolomite ** and *Rhodochrosite* †† have similar structures. The close relationship between Calcite and rhombohedral Sodium Nitrate ‡‡ is further confirmed by a close similarity of lattices.

The *Nitrates* of the bivalent metals,§§ lead and the alkali earths, which crystallise in the cubic (Class 28) type of symmetry, have been shown to possess a tetartohedric structure, in which the metal atoms form a face centred lattice. An $N0_3$ group lies on each of the eight non-intersecting trigonal axes.

*** Kolkmeijer, Bijvoet and Karssen, *K. Akad.*, Weten. Amst., xxiii. No. 4. (1920).**

† Dickinson and Goodhue, *Jour. Amer. Chem. Soc*, 43, 2, 2045 (1921).

‡ G. Wulff, *Z. fur Kristallographie*, 57, 2, 191 (1922).

§ L. Vegard, *Z.für Physik.*, 12, 5, 289 (1922).

**** *Proc. Roy. Soc*, p. 485 (1914).**

†† R. W. G. Wyckoff, *Amer. Jour. Soc*, L. 318 (1920).

‡‡ R. W. G. Wyckoff, *Pkys. Rev.*, xvi., *2*, 149 (1920).

§§ L. Vegard, *Videnskapsselskapets, Skrifter*, 1 ; *Mat. Naturv. Kl.*, 1922, No. 3.

The unit cell dimensions are as follows :

$Pb(NO_3)_2$ a = 7.84 A units

$Ba(NO_3)_2$ a = 8.11 A „

$Sr(NO_3)_2$ *a* = 7.81 Å „

$Ca(NO_3)_2$ *a* = 7.60 A „

*Potassium Sulphate** The fundamental spacings of the rhombic crystals of this type have been measured by Ogg and Hopwood, but no complete analysis of the structure has yet been made.

Unit cell dimensions.

Salt.	a.	*a.*	*b.*	*c.*
K_2SO_4 - -	5.731 A.Å.	5.731 A.Å.	10.008 A.	7.424 A.
$(NH_4)SO_4$ - -	5.951 A.Å.	5.951 A.Å.	10.560 A.	7.729 A.
Rb_2SO_4 - -	5.949 A.Å.	5.949 A.Å.	10.394 A.	7.780 A.
Cs_2SO_4 - -	6.218 A.Å.	6.218 A.Å.	10.884 A.	8.198 A.

Silver Molybdate,† Ag_2MoO_4, is cubic, with *a* = 9.26 A. The Molybdenum atoms are strung upon a diamond point system and the whole arrangement is that of the *Spinel* Group, *i.e.* MoO, Ag_2O_3.

Scheelite, $CaWO_4$, forms crystals of Tetragonal equatorial symmetry, and Wulfenite, $PbMoO_4$, of the Tetragonal Polar type. Dickinson ‡ assigns to both of these compounds the same structure, which has equatorial symmetry. The Pb (or Ca) atoms are built up on a tetragonal point-system of a " diamond " type. The other metal atoms, Mo or W, are on an identical point-system translated half the unit length parallel to the side of the cell. The unit cell dimensions are,

Scheelite a = 5.62 A. c = 8.632 A.

Wulfenite a = 6.00 A. c = 9.462 A.

Alum.

This complex crystal has been attacked by the spectro-

* *Ogg* and Hopwood, *Phil. Mag.*, 518, 1916.

† R. W. G. Wyckoff, *Jour. Amer. Chem. Soc,* 9, 1994 (1922).

‡ R. G. Dickinson, *Jour. Amer. Chem. Soc.,* 42, 1, 85 (1920).

meter * and by the Laue method.† ‡ Vegard and Wyckoff agree in arranging the monovalent and trivalent metal atoms like those of sodium and chlorine in rocksalt, but give a different marshalling to the acid radicals and molecules of water.

The Structure of Complex Salts.

A number of complex chemical compounds which crystallise in the cubic or tetragonal systems have been subjected to investigation. In the majority of cases the crystal is built up of atoms and radicals, marshalled according to some simple cubic arrangement. In the case of the complex cyanides of potassium with zinc, cadmium and mercury, K_2ZnCy_4, etc.,§ the structure corresponds to that of spinel, with the divalent metal atom arranged on a diamond point-system. The compounds enumerated below all conform to a " Calcium Fluoride " structure, modified in each case to accommodate a variety of atoms and radicals.

Compound.	Corresponding to Ca	F_2
||$Zn(Br0_3)_2.6H_20$.	$Zn(6H_20)$	$(Br0_3)_2$
¶ $Ni(N0_3)_2.6NH_3$	$Ni(6NH_3)$	$(N0_3)_2$
**$(NH_4)_2.SiF_6$	$Si(F_6)$	$(NH_4)_2$
ft $NiCl_2.6NH_3$	$Ni(6NH_3)$	Cl_2
ft $NiBr_2.6NH_3$		Br_2
ft $NiI_2.6NH_3$	»	I_2
‡‡ K_2SnCl_6	$SnCl_6$	K_2
‡‡ $(NH_4)_2SnCl_6$		$(NH_4)_2$
§§ $(NH_4)_2PtCl_6$	$PtCl_6$	$(NH_4)_2$

* L. Vegard and H. Schjelderup, *Ann. der Physik.,* Bd. 54, H. 18 (1917).

† R. W. G. Wyckoff, *Z. fur Kristallographie,* 57, 6, 595 (1923).

‡ T. Terada, *Pr. Math. Phys. Soc,* Tokyo, 7, 290 (1914).

§ R. G. Dickinson, *Jour. Amer. Chem. Soc,* 44, 4, 774, 1922.

|| R. W. G. Wyckoff, *Amer. Jour. Science,* iv., 188, 1922.

¶ R. W. G. Wyckoff, *Jour. Amer. Chem. Soc,* 44, 6, 1260, 1922.

** R. M. Bozorth, *Jour. Amer. Chem. Soc,* 44, 5, 1066, 1922.

†† R. W. G. Wyckoff, *Jour. Amer. Chem. Soc,* 44, 6, 1239, 1922.

‡‡ R. G. Dickinson, *Jour. Amer. Chem. Soc,* 44, 2, 276, 1922.

§§ Wyckoff and Posnjak, *Jour. Amer. Chem. Soc,* 43, 2, 2292, 1921.

The chloroplatinites and palladinites * are found to possess a structure analogous to the CaF_2 structure, as do the above compounds, but the vertical axis is shortened so that the symmetry becomes tetragonal. Thus in K_2PtCl_4, the potassium atoms are arranged like the fluorine atoms, and the $PtCl_4$ groups like the calcium atoms, in CaF_2.

Organic Compounds.

Urea -	H. Mark and K. Weissenberg, *Z.fur Physik,* 16, 1, 1, 1923.
Hexamethylene Tetramine	R. G. Dickinson and A. L. Raymont, *Jour. Amer. Chern. Soc,* 45, 1, 22, 1923.
Naphthalene Acenaphthene a Naphthol ß Naphthol	W. H. Bragg, *Proc. Phys. Soc,* London, 34, 1, 33 (1921).
Anthracene	W. H. Bragg, *Proc Phys. Soc,* Lon., 35, 3, 167 (1923).
Tartaric Acid	W. T. Astbury, *Proc. Roy. Soc, A.* 102, 506, 1923.
Racemic Acid	W. T. Astbury, *Proc Roy. Soc,* A. 104, 219, 1923.
Basic beryllium acetate, propionate and acetate-propionate	W. H. Bragg and Morgan, *Proc. Roy. Soc,* Nov., 1923.
Dibenzyl Stilbene Benzil Triphenylmethane Triphenylcarbinol Mannite Cane Sugar	Becker and Rose, *Z. fur Physik,* 369, 1923.
Fatty acids and esters -	A. Muller, *Tr. Chem. Soc,* vol. 123, 1923.

* R. G. Dickinson, *Jour. Amer. Chem. Soc,* 44, 11, 2404, 1922,

For a description of these compounds, some of which have been dealt with in the chapter on Organic Crystals, reference should be made to the original papers.

APPENDIX II

The following investigations are intended to be supplementary to those already mentioned in the text and Appendix I. and will be found to bring the subject fairly **up** to date.

ELEMENTS

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Bismuth : **R.** W. James, *Phil. Mag.,* 1921, 42, 193. L. W. McKeehan, J. Frankl. Inst., 1923, **195,** 59. 0. Hassel and H. Mark, *Z. f. Phys.,* 1924, **23,** 269.

Tungsten : H. C. Burger, *Phystkal Z.,* 1922, 23, 14. A. E. van Arkel, *Physica,* 1923, **3,** 76.

Vanadium : A. W. Hull, *Phys. Rev.,* 1922, **20,** 113.

Germanium : A. W. Hull, *loc. cit.* N. H. Kolkmeijer, *Proc. K. Akad. Wetensch,* 1922, 25, 125 ; *Verslag. Akad. Wetensch,* **31,** 155.

Potassium : L. W. McKeehan, *Proc. Nat. Acad. Sci.,* 1922, **8,** 254.

Beryllium : L. W. McKeehan, *loc. cit.,* 270.

Mercury : L. W. McKeehan and P. P. Cioffi, *Phys. Rev.,* 1922, **19,** 144.

Nickel : F. Wever, *Mitt. Kaiser Wilhelm Inst. Eisenforsch,* 1922, 3,17.

Zinc : H. Mark, M. Polanyi and E. Schmid, *Z. f. Phys.,* 1922, **12,** 58, 78, III.

White Tin : H. Mark and M. Polanyi, *Z. f. Phys.,* 1923, **18,** 75 ; 1924, 22, 200. A. E. van Arkel, *Proc. K. Akad, Wetensch,* 1924, **27,** 97.

Iridium : R. W. G. Wyckoff, *Z. f. Krist,* 1923, **59,** 55.

Tantalum : K. Becker and F. Ebert, *Z.f. Phys.,* 1923, **16,**165.

Thallium : Ditto.

Arsenic : A. **J.** Bradley, *Phil. Mag.* [vi], 1924, **47,** 657.

Selenium and Tellurium : A. **J.** Bradley, *Phil. Mag.* [vi], 1924, **48, 477.** M. K. Slattery, *Phys. Rev.,* 1923, 21, 378.

Argon : F. Simon and C. v. Simson, *Z. f. Phys.*, 1924, **25,** 160.

Rhombic Sulphur : H. Mark and E. Wigner, Z. *Physikal Chem.*, 1924, **111,** 398.

Graphite : O. Hassel and H. Mark, Z. f. *Phys.*, 1924, 25, 317. J. D. Bernal, *Proc. Roy. Soc.* [A], Dec., 1924.

ALLOYS AND INTERMETALLIC COMPOUNDS

Though much of the work on alloys that has been carried out up to the present is fragmentary and ill-defined, the following list will be found useful.

Steel and Cementite.[13]
Cobalt-Iron.[1]
Tungsten-Iron.[10]
Iron-Silicon.[7]
Iron-Nickel.[1,4,9]
Iron-Chromium.[10]
Molybdenum-Iron.[10]
Iron-Manganese.[10]
Copper-Zinc.[1,8, 10,11]
Copper-Aluminium.[2,4,5,8, 10]
Copper-Nickel.[2,10]
Copper-Tin.[8,10]
Copper-Manganese.[10]
Copper-Gold.[10]
Silver-Palladium.[3]
Silver-Gold.[3,10]
Silver-Cadmium.[10]
Silver-Zinc.[10]
Aluminium-Magnesium.[2,8]
Aluminium-Antimony.[6]
Nickel-Aluminium.[8]
Nickel-Tungsten.[8]
Magnesium-Silicon.[6]
Molybdenum-Tungsten.[10]
Iridium-Osmium.[12]
Heusler Alloys.[14]
Palladium-Hydrogen.[15,16]
Amalgams.[17]
Mg_2Sn.[18]

1 M. R. Andrews, *Phys. Rev.*, 1921, 18, 245,
2 E. A. Owen and G. D. Preston, *Proc. Phys. Soc*, 1923, 36,14.
3 L. W. McKeehan, *Phys. Rev.*, 1922, 20, 424.
4 F. Kuchner, *Ann. d. Phys.*, 1922, 69, 59.
5 E. R. Jette, G. Phragmen and A. F. Westgren, *Journ. Inst. of Metals*, 1924, 31, 193.
6 E. A. Owen and G. D. Preston, *Proc. Phys. Soc*, 1924, 36,341.
7 G. Phragmen, *Jernkontorets Ann.*, 1923, 78, 121,
8 K. Becker and F. Ebert, *Z. f. Phys.*, 1923, 16, 165.
9 L. W. McKeehan, *Phys. Rev.*, 1923, 21, 402.
10 E. C. Bain, *Chem. Met. Eng.*, 1923, 28, 21.
11 E. A. Owen and G. D. Preston, *Proc Phys. Soc*, 1923,36, 49.
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14 J. F. T. Young, *Phil. Mag.*, 1923 [vi], 46, 291.
15 M. Yamada, *Phil. Mag.*, 1923 [vi], 45, 241.
16 L. W. McKeehan, *Phys. Rev.*, 1923, 21, 334.
17 C. v. Simson, *Z. Physikal Chem.*, 1924, **109,** 183.
18 L. Pauling,J. *Am. Chem. Soc*, 1923, 45, 2777.

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Strontium Oxide, Barium Oxide : W. Gerlach, *Z. f. Phys.,* 1922, **9,**184.

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Calcium Hydroxide, Magnesium Hydroxide : G. R. Levi, *Giorn. di Chitn. Indust. Applic,* 1924, 6, 333. G. R. Levi and A. Ferrari, *Atti. R. Acad. Linc,* 1924 [v], **33,** i, 397.

Cinnabar : C. Mauguin, *C.R.,* 1923, **176,** 1483.

Sulphides of Magnesium, Calcium, Strontium and Barium : S. Holgersson, Z. *anorg Chem.,* 1923, **126,** 179.

Aluminium Nitride : H. Ott, Z. f. *Phys.,* 1924, **22,** 201.

Solid Hydrogen Chloride : F. Simon and C. v. Simson, Z.f. *Phys.,* 1924, **21,** 168.

Aragonite : W. **L.** Bragg, *Proc. Roy. Soc,* 1924 [A], **105,** 16.

Cobalt Ammonio-Chloride $[Co(NH_3)_6]Cl_2$, **Potassium Chloroplatinate** $[K_2PtCl_6]$, **Rubidium Chloroplatinate** : P. Scherrer and P. Stoll, *Arch. sc. phys. et nat.,* 1922, 4, 232 ; Z. f. *anorg. Chem.,* 1922, **121,** 319.

Hydrazine Dihydrochloride : R. W. G. Wyckoff, *Amer. J. Sci.,* 1923, **5,** 15.

Uranyl Nitrate Hexahydrate $U0_2(N0_3)_2 \cdot 6H_20$: L. Pauling and R. G. Dickinson, J. *Am. Chem. Soc,* 1924, 46, 1615.

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Succinic Acid, Succinic Anhydride and Succinimide : K. Yardley, *Proc. Roy. Soc,* 1924 [A], **105,** 451.

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Acetaldehyde-Ammonia and Metacetaldehyde : O. Hassel and H. Mark, Z. *Physikal Chem.,* 1924, **111,** 357.

Oxalic Acid : H. Hoffmann and H. Mark, Z. *Physikal. Chem.,* 1924, **111,** 321.

Long Chain Compounds : De Broglie and Friedel, *C.R.,* 1923, **176,** 738 ; S. H. Piper and E. N. Grindley, *Proc Phys. Soc,* 1923, **35,** 269; A. Müller, *Trans. Chem. Soc,* 1923, **123,** 2043; G. Shearer, *Trans. Chem. Soc,* 1923, **123,** 3152 ; A. Müller and G. Shearer, *Trans. Chem. Soc,* 1923,**123,** 3156.

Various Compounds : Carbon tetraiodide, Carbon tetrabromide, pentaerythritol, Urea, Monomethyl-urea, Symm.-dimethyl-urea, Metaldehyde, Aldehyde-ammonia, Hexamethylene-tetramine, Hexachlorbenzene, Hexabrombenzene, Benzene : H. Mark, *Bet. d. Deutsch. Chem. Ges.,* 1924, Nov., p. 1820.

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Abnormal Reflection of X-Rays : G. L. Clark and W. Duane, *Proc. Nat. Acad. Sci.,* 1922, 8, 90 ; 1923, 9, 117, 131; J. *Optical Soc. Amer.,* 1923, 7, 455. R. W. G. Wyckoff, *Amer. J. Sci.,* 1923 [v], 6, 277. W. Kossel, *Z. f. Phys.,* 1924, 23, 278. G. L. Clark and W. Duane, *Science,* 1923, **58,** 400.

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INDEX OF SUBJECTS

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