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CRYSTAL CHEMISTRY

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BY

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AUTHOR'S PREFACE

CHEMICAL crystallography in the nineteenth century had as its goal the discovery of a correlation between crystal form and chemical constitution, and this work attracted the interest of so many chemists and crystallographers of the time that by the close of the century much important information on the crystal form of different kinds of chemical compound had been collected. If, however, this information was neither sufficiently extensive nor sufficiently fundamental to justify for itself the title of Crystal Chemistry, it was nothing more than a consequence of the fact that at the time the experimental means were not available for the investigation of the internal structure of crystals. The discovery of X-ray interference by von Laue and the pioneer structure determinations of W. H. and W. L. Bragg revealed the possibility of investigating the internal architecture of crystals.

Thanks largely to the efforts of the Goldschmidt and Bragg schools and to the work of Pauling and the Stockholm Institute of Metallography, the first two decades of X-ray work have seen not only the accumulation of an enormous amount of material on the structures of the crystals investigated, which has of itself already led to results of immediate importance, but also the formulation of many fundamental principles of a general nature. In this way it has been possible to clarify our ideas of the constitution of certain classes of compounds, our knowledge of which some ten years ago was based on conceptions borrowed from the chemistry of simple compounds and was frequently gravely in error. And so it is now possible to speak of a science of Crystal Chemistry, a science which in its first stage, like chemistry itself, is of an experimental character, but which day by day establishes itself on a firmer theoretical basis.

In such a brief account of the developments of Crystal Chemistry as that given in this book a detailed discussion of much work, which will no doubt be of the greatest importance in the future development of the subject, has had to be omitted. Thus no account is given of the extensive researches of Niggli and his co-workers on the 'stereochemistry of crystalline compounds,' or of the important work of Born and Mayer, in which the

influence of van der Waal forces on the stability of simple ionic lattices has been investigated. Still less has space permitted a complete description of the many simple and complex structures mentioned in the text, and readers who wish to find within a single cover an account of the known structures are referred to the admirable 'Structurbericht' of the Zeitschrift für Kristallographie compiled by Ewald and Hermann.

Within these limits the author has attempted to review all the more important researches in Crystal Chemistry which have appeared up to the time of publication.

O. HASSEL.

OSLO,
October, 1933.

TRANSLATOR'S PREFACE

THE great mass of experimental material which has accumulated during the last decade, following the application of X-ray methods to the investigation of crystal structures, includes much that is of the greatest importance to the physicist, the chemist, the metallurgist and the geologist, but the almost complete absence of any reference to such work in the majority of standard text-books is sufficient evidence that the significance of these results has not always been fully appreciated, and that a simple and readily accessible account of some of the work in this field should fill a very real need. In collecting together much of this material, Dr. Hassel has rendered a valuable service, and it is in the confidence that English readers will find in it much of interest that I have undertaken the translation of his 'Kristallchemie.' I hope that the book will be of value to the academic student, but I hope, too, that it will fulfil a wider mission in revealing the power and versatility of the tool which X-ray methods provide for the investigation of the solid state. The chapters on Metallic Systems, to give but one example, suggest many directions in which this tool is likely to find wide application in the near future.

I have not hesitated to translate freely. I have made frequent reference to original papers, and where the sense has seemed obscure or the argument condensed, I have expanded a few lines into a paragraph or even a page. Only in Chapter XIII have I departed from this principle: in attempting to reproduce in a few pages the substance of a theory originally published in several lengthy papers, the author has undertaken a very difficult task, and yet it hardly seems that the physical importance of Weissenberg's ideas is sufficient to warrant treatment at greater length in a book of this kind. In this chapter I can only claim to have made a faithful translation of the original.

Within the compass of a book of this size the treatment of many branches of the subject must necessarily be brief, but it is hoped that the generous provision of references to original papers will enable those who are especially interested in any particular field to pursue their interests further. Certain branches of the

subject are not treated at all. Thus there is no account of the work of Bernal and others on the structures of many complex bodies of biological interest, nor does a discussion of liquid crystals find a place in the book; the reader interested in the latter subject may well refer to the report of the Faraday Society discussion of 1933.[1] I give in the Appendix a brief bibliography of works on the application of the methods of visible and infra-red spectroscopy to problems of crystal chemistry, another important field of which no account is given here. For the benefit of those readers who are not familiar with the common structure types I have added a set of illustrations of those of most frequent occurrence (pp. x–xi).

Throughout the book atomic radii and interatomic distances are expressed in terms of the Ångström unit (A.U.) $= 10^{-8}$ cm. In place of the Schoenflies system of space group notation used by Dr. Hassel I have throughout adopted the Hermann-Mauguin system recommended by the International Abstracts Committee of crystallographers.[2] I have quoted all references in the form recommended in the 2nd Edition of the 'World List of Scientific Periodicals' (Oxford University Press, 1934).

In conclusion, it is a very great pleasure to me to express my thanks to Mr. F. I. G. Rawlins, M.Sc., F.Inst.P.; it was he who first drew my attention to Dr. Hassel's book, and throughout the course of the translation he has taken a real and most helpful interest in its progress. I am also indebted to him for the references which comprise the bibliography contained in the Appendix.

R. C. EVANS.

CAMBRIDGE,
December, 1934.

[1] 'Liquid Crystals and Anisotropic Melts,' *Trans. Faraday Soc.*, 29, 881 (1933).
[2] Report of the Abstracts Committee, *Z. Kristallogr.*, 79, 495 (1931).

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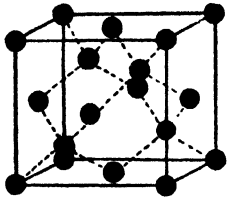
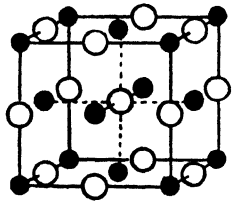
(The numbers indicate the co-ordination in each case.)



Diamond
4



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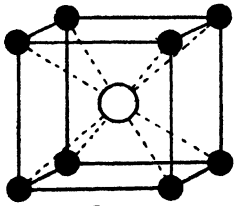

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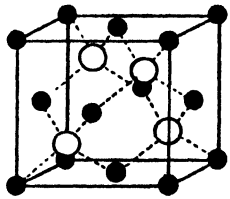

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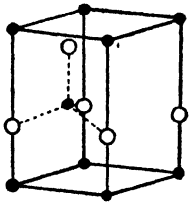

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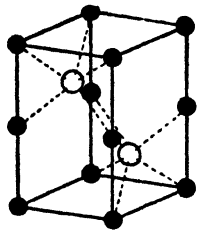
4



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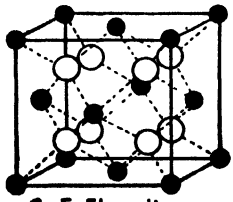
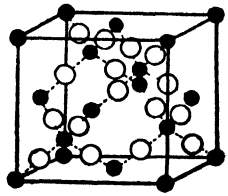
COMMON STRUCTURE TYPES: AX_2 COMPOUNDS.

(The numbers indicate the co-ordination in each case.)



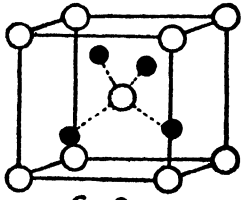
CaF_2 Fluorite

8 4



SiO_2 Cristobalite

4 . 2



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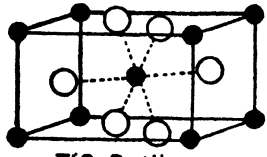

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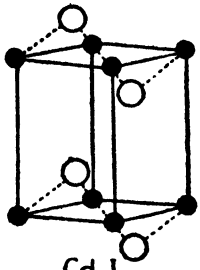

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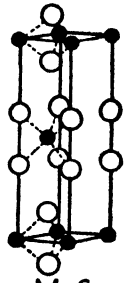


MoS_2

6 3

CRYSTAL CHEMISTRY

INTRODUCTION

Historical Survey. It is the aim of Crystal Chemistry to formulate the relationships which exist between the structure and chemical constitution of crystalline substances. The discovery by Mitscherlich in 1818 that the potassium and ammonium salts of phosphoric and arsenic acids showed a strongly marked correspondence in their crystal morphology may be considered as the first important step in the investigation of the relationship of crystal form and chemical constitution. Soon after this discovery of isomorphism Mitscherlich was able to show that by varying the external conditions a single chemical elemer sulphur, could be made to crystallise in several different syst thus conclusively disproving the assertion of Hauy that al crystal forms of a definite chemical substance could be re to some common fundamental form. In the decade fol Mitscherlich's discovery much important work on the lography of simple and complex substances, and func investigations on mixed crystals, were carried out. In add Mitscherlich himself we may mention in this connectior of Rammelsberg and de Marignac and of the chemi and Bunsen.

The conception of isomorphous series was of r in inorganic chemistry, but it gradually becar many cases an unambiguous application of th phism was attended by many difficulties. T appeared that a correspondence of atomi between two atoms or atom groups importance in producing was any chemical Kopp who firs morphism sh

A furth Pasteur ir

tion, a discovery which was later confirmed for the acid itself and for many other similarly constituted substances, and which has found a simple explanation in the theory of the asymmetric carbon atom put forward by van't Hoff and Le Bel in 1874. The work of Mitscherlich on organic substances was of less importance, but in this field the experiments of Hiortdahl in 1865 on the crystal form of the members of an homologous series led to interesting results, and he was able to show that in many cases there was a correspondence in the angles in certain definite zones. A little later Groth investigated a number of problems in the crystallography of organic compounds, and thanks to his inspiration many other researches were initiated on the properties of numerous important chemical compounds in relation to their crystal form. The correlation of the experimental material available emphasised the value of the concept of 'topic parameters' put forward by Muthmann, and in fact these topic parameters were able to express in part the information which we now obtain from measurements of the unit cell of a crystal structure. From the wealth of experimental material collected ·ᵐportant new aspects of the subject appeared, and gradually ᵒ grew up from the borderland of chemistry and crystal- ıphy a new science of chemical crystallography. Only after had shown, in 1912, that in simple cases X-rays could be ɔ determine exactly the positions of the individual atoms ˈstal was the necessary experimental material available ɔre complete understanding of the laws of crystal structure relation to chemical constitution, and of the individual ᵊs of the constituents of a crystal lattice.

CHAPTER I

THE RADII OF ATOMS AND IONS IN CRYSTALS

Earlier Work. Laue's discovery of X-ray interference, and the subsequent pioneer researches of W. H. and W. L. Bragg on structure analysis, provided an entirely new foundation for chemical crystallography. Not only did the early investigations of the structures of simply constituted crystals give a brilliant confirmation of the predictions of classical geometrical structure theory, but they also threw unexpected light on the forces within the crystal lattice. In the case of diamond, for example, in which every carbon atom is surrounded by four neighbours symmetrically disposed at the corners of a regular tetrahedron, we see the physical realisation of the predictions of organic chemistry concerning the spatial distribution of the carbon valencies. In the sodium chloride structure every sodium ion is surrounded by six chlorine ions arranged at the corners of a regular octahedron, and every chlorine ion is surrounded by six sodium ions similarly situated, an arrangement which may be accounted for in terms of the electrostatic forces between the ions. Most of the alkali halides crystallise with the sodium chloride structure, and it is possible to recognise regularities in the lattice spacings of these structures. Thus, for example, the difference between the interatomic distances in two halides with the same cation is very nearly the same whichever of the alkali metals that cation may be, while conversely, for the halides of a given pair of alkali metals, this difference is nearly independent of the particular halogen in combination, as may be seen from Table I. In such cases we can say that to a first approximation the atoms in the crystal have constant effective radii whose sum is equal to the interatomic distance, so that we are led to the picture of a crystal structure as based on a packing of spheres. It is clear, however, that such a picture must not be pressed too far, for in polymorphous substances the molecular volumes of the various forms are in general different. Nevertheless, in 1920 W. L. Bragg published a table of effective radii based on obtained structures at that time investigated. These values all have the

TABLE I

	Li	Δ	Na	Δ	K.	Δ	Rb.	Δ	Cs.
F	2·01	0·30	2·31	0·35	2·66	0·16	2·82	0·18	3·00
Δ	0·56		0·50		0·48		0·45		(0·57)
Cl	2·57	0·24	2·81	0·33	3·14	0·13	3·27	(0·30)	(3·57)
Δ	0·18		0·17		0·15		0·16		(0·14)
Br	2·75	0·23	2·98	0·31	3·29	0·14	3·43	(0·28)	(3·71)
Δ	0·25		0·25		0·24		0·23		(0·24)
I	3·00	0·23	3·23	0·30	3·53	0·13	3·66	(0·29)	(3·95)

radii proved themselves of great value in the investigation of new structures, but in many cases they led to contradictions due to the fact that they took no account of the different kinds of interatomic binding forces.

If, however, we compare only those compounds in which the forces are of the same kind, as, for example, the series of alkali halides, where they are of a purely electrostatic nature and where striking regularities in interatomic distances can be clearly seen, it is naturally easier to deduce atomic sizes. From the measured interatomic distances, however, it is clearly possible to obtain only the sum of two atomic radii, and for an absolute determination of the individual radii an independent measurement of the radius of some one atom is required. In 1921 Davey published a set of atomic radii derived from a consideration of the alkali halides on the assumption that the K^+ and Cl^- ions were of the same size, since they have the same extranuclear electron distribution. Such an assumption, however, can hardly be justified, for since the nuclear charge on the K^+ ion is two units greater than that on the Cl^- ion we should expect the former ion to have a smaller radius than the latter, and, indeed, Davey's results led to the very improbable conclusion that the radius of the Na^+ ion was some 10 per cent. greater than that of the F^- ion.

Landé's Method. A second method of determining the absolute radii of ions is due to Landé,[1] and is applicable to those structures in which neighbouring ions of the same kind are in contact. If we compare the A—X distance in the following compounds, which all have the sodium chloride structure,

MgO . . .	2·10 A.U.	MnO . .	2·24 A.U.
MgS . . .	2·60 „	MnS . .	2·59 „
MgSe . . .	2·73 „	MnSe . .	2·73 „

[1] Landé, *Z. Phys.* **1**, 191; **2**, 87 (1920).

we see that while MgO and MnO have different interatomic distances, MgS and MnS, and again MgSe and MnSe have almost exactly the same lattice dimensions. This fact leads to the conclusion that here neighbouring atoms are in contact and that the whole structure is to be regarded as a close-packed arrangement of anions with the cations situated in the interstices. In this way we can deduce for the radius of the S^{2-} ion $2{\cdot}60.\sqrt{2}/2$ A.U., and for the Se^{2-} ion $2{\cdot}73.\sqrt{2}/2$ A.U. In Table II. the radii of some anions, obtained in this way, are given. The method of Landé has been extensively applied, and the results

TABLE II. *Anion Radii determined by Landé's Method*

Crystal.	Anion.	Radius.	Crystal.	Anion.	Radius.
MgF_2—MnF_2	F^-	1·25—1·33	TiO_2	O^{2-}	1·32
CdF_2	—	1·35	SiO_2	—	1·27
LiCl	Cl^-	1·81	Al_2O_3	—	1·35
$SrCl_2$	—	1·74	MgS	S^{2-}	1·83
LiBr	Br^-	1·94	MnS	—	1·83
TlBr	—	1·99	MgSe	Se^{2-}	1·93
LiI	I^-	2·14	MnSe	—	1·93
AgI	—	2·16	MgTe	Te^{2-}	2·26
TlI	—	2·10	CaTe	—	2·24
			PbTe	—	2·28

obtained are in very good agreement with those deduced independently by Wasastjerna from the radii of the F^- and O^{2-} ions as described in the next paragraph.

THE WORK OF GOLDSCHMIDT

Wasastjerna's Radii. By means of refractivity measurements Wasastjerna[1] has deduced independently for the radii of the F^- and O^{2-} ions the values 1·33 A.U. and 1·32 A.U. respectively, and it is these values which Goldschmidt,[2] in his systematic study of the crystal chemistry of the simpler compounds, has adopted as his starting point in the derivation of a series of empirical ionic radii. Beginning with the assumption that in crystals of the sodium chloride type the ions are actually in contact, so that the interatomic distance is simply equal to the sum of the corre-

[1] Wasastjerna, *Comment. phys.-math. Helsingf.* (often quoted as *Soc. Sc. Fenn., Comment. physic.-math.*), **1**, 38 (1923).

[2] Goldschmidt, papers on "Geochemische Verteilungsgesetze der Elemente" in the Oslo Academie der Wissenschaften obtain all have t 7 (Oslo, 1926) and 8 (Oslo, 1927).

sponding radii, Goldschmidt has collected a great amount of new experimental material which is of especial value in that he carefully distinguishes the various types of interatomic binding which occur in different structures, a distinction often overlooked in many earlier investigations in which crystals, the binding forces in which were clearly of quite different types, were indiscriminately compared. The radius of an atom [1] depends on the atomic number and on the state of ionisation of that atom, so that one atom will have several radii depending on the degree of ionisation, and we may propound the rule that *the radius of an atom or an ion increases with increasing negative charge, and decreases with increasing positive charge.* It is to be noted, however, that the increase in the effective radius with increasing negative charge is not necessarily accompanied by a corresponding increase in the interatomic distance, since the change of charge gives rise to a corresponding increase in the forces of electrostatic attraction between oppositely charged constituents of the lattice resulting in a partial compensation of the effect. Similarly, the decrease in the atomic radius with increasing positive charge is aggravated by the increase in the forces between the ions. So long as we are dealing with an atom of given atomic number and state of ionisation the radius may be considered to be constant to a first approximation, but the radii of a given atom in different states of ionisation may be very different.

Ionic and Atomic Lattices. The experimental results of Goldschmidt soon revealed that it was possible by a consideration of the atomic radii to divide crystal structures into a number of different groups, within any one of which the effective radii of the atoms were constant to a considerable degree of accuracy. The ionic lattices of the sodium chloride type form one such group, those of the cæsium chloride type a second, and those of the fluorite type a third. In all these types, which together may be considered as constituting a main group, the interatomic distances are mutually commensurable, a fact which suggests very forcibly that the atoms in all these structures are in the same state of ionisation. A second main group of commensurable lattices comprises structures of the zincblende, wurtzite, and cuprite types, as well as those of many of the elements. The interatomic distances in this latter main group, while ⌐surable among themselves, are not commensurable with

[1] the sake of conciseness of expression, where there is no danger we shall frequently use the word 'atom' to describe a particle well as in its neutral state.

those of the typically ionic lattices, so that we may conclude that in lattices of the zincblende type the constituents are not to be considered as ionised.

The Influence of Co-ordination and Polarisation. In addition to the state of ionisation of the atoms, there are several other factors which have an important influence on the interatomic distances in a crystal lattice. If we first consider only structures of relatively high symmetry, so that we are not concerned with asymmetric polarisation, we find that not only the charge on the ions, but also their co-ordination number must be taken into account. Thus Goldschmidt found that between commensurable lattices, such as those of the fluorite and sodium chloride types, the lattice dimensions showed systematic differences of the order of a few per cent. The ammonium halides are dimorphous and crystallise with the sodium chloride and cæsium chloride structures, so that they afford an opportunity of making a direct comparison of the interatomic distances in six- and eight-fold co-ordinated lattices, and with these salts it is found that the lattice dimensions of the cæsium chloride structures are about 3 per cent. greater than those of the six-fold co-ordinated structures. This observation that an increase in co-ordination number is accompanied by an increase in interatomic distance has since been confirmed in a number of other cases, and, indeed, is a quite general effect to which we shall frequently have occasion to refer later.

The extension of the work to the insoluble halides of univalent thallium and silver showed that the interatomic distances in these compounds are appreciably smaller than those calculated from the known radii of the halogen ions and the radius of the thallous and silver ions deduced from observations on readily soluble compounds. This contraction, which is clearly associated with the low solubility of the salts, is a consequence of the strong polarising power of the Tl^+ and Ag^+ ions, the influence of which is particularly marked in the presence of the readily polarised halide ions. Silver iodide is dimorphous and crystallises with the zincblende and wurtzite structures, while the copper halides, which also have a strongly polarising cation, have the zincblende structure.

Polyvalent Elements. The radii of many divalent ions have been determined by investigations on the oxides starting from Wasastjerna's value of 1·32 A.U. for the radius of the O^{2-} ion. In the case of the alkaline earth metals the values thus obtained can be confirmed by means of the fluorides, which all have the

fluorite structure, and the results indicate that the lattices of the sodium chloride, fluorite, and rutile types are commensurable, but that the interatomic distances in the two last lattices are somewhat smaller than those to be expected from radii determined in structures of the sodium chloride type.

The compounds of the divalent metals of the magnesium subgroup, as well as of the closely related beryllium, with oxygen, sulphur, selenium, and tellurium, are of particular interest. These compounds for the most part crystallise with a zincblende or wurtzite structure with rather small interatomic distances, a fact which once again is to be attributed to the strong polarising power of the cations, and Goldschmidt pointed out that very good agreement with the observations was obtained if these lattices were regarded as commensurable both with those of the cuprite type and with those of the pure metals. From observations on cuprite and Ag_2O, which has the cuprite structure, he deduced for the radius of the unionised oxygen atom the value 0·60 A.U. One surprising result of the work on the divalent metals is the discovery that the radii of cadmium and mercury are almost identical, but this is a consequence of the so-called ' lanthanum contraction ' which we shall have occasion to discuss in more detail later.

The fluorides of the divalent transition elements, manganese to nickel, have the rutile structure, while the oxides have the sodium chloride structure. A comparison of these two series of compounds shows that the ionic sizes in the rutile lattices are a few per cent. smaller than those in the lattices of the sodium chloride type. The values of the radii of the metal ions deduced from these compounds, taken in conjunction with the radii of the atoms deduced from the metals themselves, enable us to determine in the case of other compounds whether we are dealing with ionic or atomic lattices. Thus in the case of MnS, which has a sodium chloride structure, satisfactory agreement with the observed lattice dimensions is obtained only if we assume that the metal is present in the ionic state.

For trivalent metals the investigation of the structure of the oxides A_2O_3 has been of great value since these oxides for the most part have ionic lattices. Arsenic and antimony oxides form exceptions to this rule in that they have molecular lattices built up of highly symmetrical molecules of the composition As_4O_6 and Sb_4O_6. When we pass on to cations of still higher valency the number of compounds which we can safely regard as ionic in type becomes smaller, but in silica, as well as in the

silicates, we are certainly concerned with the silicon ion Si^{4+}, while a number of tetravalent metals form dioxides of the rutile type which are ionic. Attempts to determine the radius of ions of valency five or more often lead to contradictions, as, for example, in the case of nitrogen, where in the NO_3 group the distance N—O is less than the radius of the oxygen ion O^{2-}.

Commensurable and Incommensurable Lattices. When we compare the radii of a given atom determined from different structures we find that we are always concerned with one of three cases :—

(1) The radii in the different structures are very closely the same, as in the zincblende and wurtzite lattices where the difference is less than 1 per cent.

(2) The radii are nearly the same but show significant differences. The sodium chloride and cæsium chloride types of lattice afford an example in which the difference is about 3 per cent.

(3) The radii are entirely different, and we are clearly concerned with the atom in different states of ionisation.

In the first two cases the lattices are said to be commensurable, while in the third case they are incommensurable. We are thus led to classify all lattices as belonging to one of two mutually incommensurable groups. To the first group belong the zincblende, wurtzite, cuprite, and diamond lattices, as well as the body-centred cubic and cubic and hexagonal close-packed lattices of many of the elements. The second group includes the typically ionic lattices, such as those of the sodium chloride, cæsium chloride, and fluorite types. It is important to notice, however, that many lattices which are geometrically the same as the common ionic lattices are really built up of atoms, and as such belong to the first group, so that geometrical considerations alone do not determine the type of binding and state of ionisation in the lattice. Among the lattices of the ionic group those of the cæsium chloride type have the largest interatomic distances ; in lattices of the sodium chloride type these distances are about 3 per cent. smaller, of the fluorite type about 6 per cent. smaller, and of the rutile type about 8 per cent. smaller.

An interesting comparison is afforded by considering the interatomic distances in a group of binary compounds, in all of which the sum of the atomic numbers of the two constituents is the same, and all of which crystallise with commensurable lattices. CdTe, atomic numbers 48 and 52, and AgI, atomic numbers 47 and 53, form an example, while ZnTe and CuI provide another. In

such pairs of compounds, which all belong to the zincblende-wurtzite group of structures, the interatomic distances are in very close agreement, as is shown by the examples given in Table IIIA.

TABLE IIIA. *Commensurable Lattices: Zincblende, Wurtzite and Diamond Types*

Formula.	Atomic Numbers.	Lattice Dimensions.	Interatomic Distance.
SnSn	50 + 50 = 100	6·46 A.U.	2·79 A.U.
InSb	49 + 51 = 100	6·45 „	2·79 „
CdTe	48 + 52 = 100	6 44 „	2·79 „
AgI	47 + 53 = 100	6·49 „	2·81 „
ZnS	30 + 16 = 46	5 42 „	2·35 „
CuCl	29 + 17 = 46	5 41 „	2 34 „

When, however, we compare in a similar way pairs of binary compounds which have ionic lattices we find that the interatomic distances are no longer the same, but decrease with increasing atomic charge, as is shown by the examples given in Table IIIB.

TABLE IIIB

Sum of Atomic Numbers.	Formulæ.		Interatomic Distances.		Δl per cent.
28	KF	CaO	2·66	2·38	12
46	RbF	SrO	2·82	2·59	9
64	CsF	BaO	3 01	2·75	9
28	NaCl	MgS	2·81	2·54	11
44	RbCl	SrS	3·27	2·93	11
72	CsCl	BaS	3 57	3·17	13

The Goldschmidt Radii. Table IV. contains a summary of the radii of atoms and ions as measured by Goldschmidt up to the year 1926. Wherever possible these radii are reduced to those which would obtain in a structure of the sodium chloride type having six-fold co-ordination. The radii of *atoms* are based as far as possible on observations on the structures of elements, confirmed by a consideration of compounds crystallising with the zincblende or other commensurable structure. A consideration of these results enables us to make the following generalisations:—

(1) In a given period the radii decrease as the positive charge on the ion increases, as is shown by the series

TABLE IV. *Atomic and Ionic Radii (after* Goldschmidt,[1] 1926).

I.	II.	III.	IV.	V.	VI.	VII.	
H^- 1·27							
(H^- 1·54)							
Li 1·56	Be 1·05		C 0·77	N 0·71	O 0·60	F^- 1·33	
Li^+ 0·78	Be^{2+} 0·34				O^{2-} 1·32		
					S^{2-} 1·74		
Na 1·86	Mg 1·62	Al 1·43	Si^{4-} 1·98		S 1·04	Cl^- 1·81	
Na^+ 0·98	Mg^{2+} 0·78	Al^{3+} 0·57	Si 1·13		S^{6+} 0·34	Cl 1·07	
			Si^{4+} 0·39				
					Cr 1·25	Mn 1·29	Fe 1·26 Co 1·26 Ni 1·24
K 2·23	Ca 2·21	Sc 1·51	Ti 1·49	V 1·32	Cr^{3+} 0·65	Mn^{2+} 0·91	Fe^{2+} 0·83 Co^{2+} 0·82 Ni^{2+} 0·78
			(Ti^{3+} 0·69)	(V^{3+} 0·65)	(0·64)	(Mn^{3+} 0·70)	
K^+ 1·33	Ca^{2+} 1·06	Sc^{3+} 0·83	Ti^{4+} 0·64	V^{4+} 0·61	Cr^{6+} 0·3–0·4	Mn^{4+} 0·52	Fe^{3+} 0·67
Cu 1·27	Zn 1·33	Ga 1·33	Ge 1·22	As 1·16	Se^{2-} 1·91	Br^- 1·96	
	Zn^{2+} 0·83	Ga^{3+} 0·62	Ge^{4+} 0·44	As^{3+} 0·69	Se 1·13	Br 1·19	
					Se^{6+} 0·3–0·4		
Rb+ 1·49	Sr^{2+} 1·27	Y^{3+} 1·06	Zr 1·62	Nb 1·43	Mo 1·36		Ru 1·30 Rh 1·34 Pd 1·37
			Zr^{4+} 0·87	Nb^{4+} 0·69	Mo^{4+} 0·68		Ru^{4+} 0·65 Rh^{3+} 0·69
				Nb^{5+} 0·69			(Rh^{3+} 0·68)
Ag 1·44	Cd 1·49	In 1·45	Sn^{4-} 2·15	Sb 1·34	Te^{2-} 2·03	I^- 2·20	
					(Te^{2-} 2·11)		
Ag^+ 1·13	Cd^{2+} 1·03	In^{3+} 0·92	Sn 1·40	Sb^{3+} 0·90	Te 1·33	I 1·36	
			Sn^{4+} 0·74		Te^{4+} 0·89	I^{5+} 0·94	
					W 1·37		
Cs+ 1·65	Ba^{2+} 1·43		Hf 1·66	Ta 1·42	W^{4+} 0·68		Os 1·31 Ir 1·35 Pt 1·38
							Os^{4+} 0·67 Ir^{4+} 0·66
Au 1·44	Hg 1·49	Tl 1·99	Pb^{4-} 2·15	Bi 1·46			
	Hg^{2+} 1·12	Tl^+ 1·49	Pb 1·74				
		Tl^{3+} 1·05	Pb^{2+} 1·32				
			Pb^{4+} 0·84				
			Th 1·82		U^{4+} 1·05		
			Th^{4+} 1·10				
La^{3+} 1·22	Ce 1·83	Pr^{3+} 1·16					
	Ce^{3+} 1·18	Pr^{4+} 1·00	Nd^{3+} 1·15		Sm^{3+} 1·13	Eu^{3+} 1·13	
	Ce^{4+} 1·02						
Gd^{3+} 1·11	Tb^{3+} 1·09						
	Tb^{4+} 0·89	Dy^{3+} 1·07	Ho^{3+} 1·05	Er^{3+} 1·04	Tm^{3+} 1·04	Yb^{3+} 1·00	Lu^{3+} 0·99

[1] The values in brackets are more recent measurements. The value for H^- is taken from Zintl and Harder, *Z. phys. Chem.*, Ser. B, 14, 265 (1931).

(F^-	1·33 A.U.)
Na^+	0·98 „
Mg^{2+}	0·78 „
Al^{3+}	0·57 „
Si^{4+}	0·39 „

(2) For a given element the radius increases with increasing negative charge :—

S^{6+}	0·34 A.U.
S	1·04 „
S^{2-}	1·74 „

(3) In a given period the radii of negative ions in general show no appreciable increase with increasing negative charge, due to the influence of the increased Coulomb forces between the ions (*cf.* p. 6). Thus we have

	F^-	1·33 A.U.
	O^{2-}	1·32 „
or again	Cl^-	1·81 „
	S^{2-}	1·74 „

The Lanthanum Contraction. One other effect which we may mention, and which appears from this table, is the so-called 'lanthanum contraction,' the decrease in molecular volume which takes place in analogous compounds of the rare earth metals as the atomic number increases from lanthanum to lutecium. From the table we see that the corresponding radii of the trivalent ions of the metals themselves decrease continuously from 1·22 A.U. for lanthanum to 0·99 A.U. for lutecium. If now we compare these radii with that of the non-rare earth yttrium, for which Y^{3+} = 1·06 A.U., we see that this value lies in the middle of the range and is in fact very nearly the same as the radius of holmium, 1·05 A.U., so that the increase in ionic radius which takes place with increasing atomic number in passing from yttrium to lanthanum has been completely compensated by the time we reach holmium, while the ions of the rare earths of still higher atomic number are actually smaller than that of yttrium. The influence of the lanthanum contraction is therefore not confined to the rare earth elements, but extends to elements beyond this group of metals, so that, for example, while the atomic radius increases in passing from copper to silver, the radii of the silver and gold atoms are almost exactly the same : the increase in radius to be expected between silver

and gold is exactly compensated by the lanthanum contraction. Since similarities in crystal structure depend so largely on similarities in atomic or ionic sizes, we must attribute to the lanthanum contraction the remarkable chemical resemblance between zirconium and hafnium, and between niobium and tantalum.

CHAPTER II

POLARISATION IN CRYSTAL LATTICES

BEFORE passing on to discuss the later work on the sizes of ions in crystals, we shall in this chapter give a brief account of the more important results of Goldschmidt's work on the influence of polarisation on crystal structure.[1]

The polarising power of an ion increases with increasing charge and with decreasing radius. So long as we are concerned with very symmetrical lattices the influence of polarisation is manifest only in a reduction in the interatomic distances. Cations with shells of eighteen electrons possess particularly strong polarising power, and consequently in the presence of these ions very marked contractions of the lattice are observed; at the same time the lattice energy becomes correspondingly large, and frequently the solubility is very small.

In layer lattices[2] lower symmetry results in the forces of polarisation being asymmetrically exerted, and in these lattices two parallel layers of strongly polarisable anions enclose a layer of strongly polarising cations. These layers extend through the whole crystal and constitute what we may regard as a two-dimensional molecule, within which the forces are essentially ionic in type. Since such groups of layers are always bounded by sheets of anions, the forces between the groups are very much more feeble than those within them, a fact which accounts for the very marked cleavage parallel to the layers which such lattices show. The distance between anion and cation in layer lattices is always very small. Since the forces between neighbouring layers are essentially of the Van der Waal type, these layer lattices may be considered as transitional between ionic and molecular lattices.

Contrapolarisation. We have already mentioned that in many

[1] On the general subject of polarisation and its magnitude in a series of anions, see Born and Heisenberg, *Z. Phys.*, **23**, 388 (1924). On the polarisability of cations see Schrödinger, *Ann. Physik*, **77**, 43 (1925), and on the relation of ionisation potential to polarising power in cations see Goldschmidt, *Norsk geol. Tidsskr.*, **12**, 247 (1931).

[2] Hund, *Z. Phys.*, **34**, 833 (1925).

ionic radicals, such as NO_3^-, SO_4^{2-}, etc., the interatomic distance is smaller than the radius of any of the constituent ions, so that in such radicals we are dealing with cases of very marked polarisation. If we combine with such a radical a cation of very strong polarising power, we may expect this cation to exert a contrary polarising action on the radical, as a result of which it is extended or even completely disrupted. Such an effect is termed 'contrapolarisation.' Particularly strong contrapolarising power is naturally associated with small, highly charged ions, but the geometrical disposition and size of the radical is the most important factor in governing the degree of contrapolarisation observed. The complementary effect, in which a complex cation suffers contrapolarisation due to the influence of a neighbouring anion, is much less common, although one such example has been observed by Goldschmidt in the case of ammonium fluoride, where one of the hydrogen atoms of the NH_4^+ group is slightly displaced towards the fluorine ion.

CHAPTER III

ISOMORPHISM AND MORPHOTROPY

Criteria for Isomorphism. The work of Goldschmidt up to the year 1926 provided sufficient material for important conclusions to be drawn concerning the influence of ionic size and polarisability on isomorphism and morphotropy. The conception of isomorphism has been considerably clarified by the application of X-ray methods to the investigation of crystal structures, since we are now able to determine not only the crystal class and axial ratios but also the space group, unit cell, and in many cases the actual positions of the individual atoms. In order that two substances may be isomorphous not only must their chemical formulæ be analogous, but they must also have similar unit cells containing the same number of positive and negative components in geometrically similar positions. These conditions, however, while necessary, are not sufficient, and it appears from the work of Goldschmidt that isomorphism only occurs when in addition the ionic sizes and their polarisability or polarising powers in the two compounds correspond within certain limits. The combination of a small and strongly polarising cation with a large and readily polarised anion frequently results in the passage of an electron to the cation and the formation of a typically non-ionic structure. In the case of the copper halides this effect is observed even with the chloride, whereas with the silver halides only the iodide has a homopolar structure. If the difference between the polarisation of the two ions is less marked the sodium chloride structure results, while if both the polarisation and the ionic sizes are very nearly the same a structure of the cæsium chloride type is formed.

AX_2 Compounds. If we consider in a similar way compounds of the type AX_2[1] we find that three different structures are particularly common, viz. :—

(1) The fluorite structure.
(2) The rutile structure.
(3) Structures with layer lattices.

[1] Throughout this book we shall use the letters A, B, etc., to denote cations or atoms of an electropositive nature, and the letters X, Y, Z to denote anions or atoms of an electronegative nature.

In cases in which the anion X is not very readily polarised the ratio of the radii of the ions R_A/R_X is found to be the decisive factor in governing the structure adopted by the compound. If this ratio exceeds about 0·67 the fluorite structure obtains; if it lies between about 0·67 and about 0·43 the structure is of the rutile type, while if it is less than 0·43 the lattice may be either a layer lattice, a molecular lattice, or one of the several silica lattices. If the ion X is easily polarised, or possesses a dipole moment, layer lattices may be formed even when the ratio of the radii exceeds 0·43, as in the cases of $Ca(OH)_2$ and $Cd(OH)_2$. The rule is equally applicable when we are dealing with complex ions, so that we find, for example, that while $NiCl_2$ has a layer lattice $Ni(NH_3)_6Cl_2$ crystallises with the fluorite structure on account of the influence of the larger cation. Similarly, although no simple iodide has the fluorite structure, this structure is observed in the complex iodide $Ni(NH_3)_6I_2$.

ABX_3 Compounds. Compounds of the perovskite type, ABX_3, afford another example of the application of these principles. Such of these compounds as are cubic have a structure in which the unit cell has an A atom at each corner and a B atom at its centre, while its faces are centred by X atoms. It is clear that in such a structure the A—X distance must be $\sqrt{2}$ times as large as the B—X distance, so that if we are to regard all the atoms as spheres in contact their radii must be connected by the relation

$$R_A + R_X = \sqrt{2}\,(R_B + R_X),$$

and this relation will continue to be approximately obeyed even in ABX_3 compounds which are not cubic, so long as the departure from cubic symmetry is small. The measurements show, however, that even in the perovskite structures which are truly cubic the relation is not exactly obeyed, so that these structures cannot be considered as a packing of incompressible, rigid spheres in contact. If instead of the equation as written above, we write

$$R_A + R_X = t\,.\,\sqrt{2}\,(R_B + R_X),$$

where t may be termed a 'factor of tolerance,' we find that the perovskite structure only obtains when t lies within the limits 0·8 to 1·0. For the cubic structures it has a mean value 0·91. If the value of t is less than 0·8 a corundum type of structure is formed, while if it exceeds 1·0 the structure is similar to that of

calcite, or, for very large values of t, to that of aragonite.[1] This criterion for the occurrence of the perovskite structure reveals that a great number of chemically very different compounds, such as KIO_3, $CaTiO_3$, $LaAlO_3$, etc., are isomorphous.

Mixed Crystals. Naturally the conception of ionic sizes and deformabilities is of great significance in the formation of mixed crystals, but here it is not only the ratio of the sizes but also their absolute magnitudes which are important, and we may say that mixed crystals are formed so long as the radii of the components replacing each other differ by less than about 15 per cent. of the radius of the smallest. The internal constitution of the different ions seems to be of less importance, for we find that many compounds of Mg^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} form mixed crystals, while the same is frequently true of members of a principal and sub-group of the periodic table, as, for example, in the case of CaF_2 and CdF_2.

Antisomorphism. There are many lattices which, while geometrically of the fluorite type, differ from this lattice in that the positions of anion and cation are reversed. ThO_2 and Li_2O afford an instance of this phenomenon, which Goldschmidt has termed 'antisomorphism.' The same name may be extended to cover cases in which the lattices are of a non-ionic type if the metallic constituent of one lattice occupies the position of the non-metallic constituent of the other. In this way AgI and NH_4F are antisomorphous, the former having a lattice of the iso-wurtzite type, the latter of the anti-wurtzite type. Similarly we can imagine antilayer-lattices in which it is the cations, instead of the anions, that are the readily polarisable constituents of the structure, and that form the outer sheets of the three-layer units of which such lattices are composed. We should expect, however, that these lattices would be very rare, except perhaps when the cation possesses a strong dipole moment, since the polarising power of anions is usually very small.

Polymeric Isomorphism. A further type of isomorphism which we must also mention is that in which the correspondence between the compounds considered is revealed in a comparison not between the unit cells of the structures but between equivalent groups of several unit cells. The isomorphism of rutile TiO_2 with $FeNb_2O_6$ and $FeTa_2O_6$ is of this type, to which Goldschmidt has given the name 'polymeric isomorphism.' In such cases it is usually found that only orientated overgrowths and not mixed

[1] Zachariasen, *Skr. Norske VidenskAkad.*, Oslo, I. Mat.-Naturv. Kl. Nr. 4, 152 (1928).

crystals are formed. A type of isomorphism which does give rise to mixed crystals, however, even though the formulæ of the isomorphous compounds are not analogous, is that which is observed in the case of CaF_2 and YF_3. Here the yttrium fluoride may be regarded as having a fluorite structure into which an extra fluorine atom has been introduced at the centre and at the middle of the sides of the unit cell without any sensible disturbance of the lattice.[1] The correspondence between Ca^{2+} and Y^{3+} is an example of Goldschmidt's ' diagonal rule ' according to which a metal in a principal group of the periodic table is closely related to that element which immediately follows its next higher homologue.[2] The pairs of ions Sc^{3+}—Zr^{4+}, and Ti^{4+}—Nb^{5+} afford further examples.

Morphotropy. The whole range of phenomena with which we have dealt in this chapter concerning the changes in structure type which take place as one atom or radical is substituted for another in a chemical compound of a given type may be conveniently termed morphotropy. As we have seen, for a given structure the possibility of substitution is limited to a certain range of ion sizes and polarisabilities, and if these limits are exceeded a new structure results. In the case of polymorphous compounds we must conclude that the structure is so sensitive to external conditions that a variation in these conditions is sufficient to occasion a change to a structure of another type. Generally it is the influence of temperature on polarisation which is the principal factor in bringing about this change, and if, for example, the replacement of one cation by another of greater polarising power produces a definite morphotropic transition, we may in general expect that at a sufficiently high temperature a polymorphic transition of the first substance will take place since an increase in temperature usually results in an increase in polarising power.

A particularly interesting example of a morphotropic series, in which the transitional members show polymorphism, is afforded by compounds of the type ABO_3, and the structures of both the nitrates of the alkali metals and the carbonates of the alkaline earths are determined by the size of the cations. If the cation is small the structure is of the calcite type, while if it is large the aragonite structure results. Cations of intermediate size give

[1] Goldschmidt, *Geochemische Verteilungsgesetze*, **7**, 89 (1926). PbF_2 and BiF_3 exhibit the same phenomenon, *cf.* Hassel and Nilssen, *Z. anorg. Chem.*, **181**, 172 (1929).

[2] Goldschmidt, *Geochemische Verteilungsgesetze*, **5**, 58 (1925), and **7**, 90 (1926).

rise to polymorphism and both structures occur, as is shown by the examples given in Table V. Considerations of this kind emphasise the very close relationships which exist between isomorphism, morphotropy, and polymorphism.

TABLE V. *Transition from Calcite to Aragonite Structure* [1]

(The numbers in brackets are the Radii of the Cations)

$LiNO_3$ (0·78) $NaNO_3$ (0·98) KNO_3 (1·33)	$MgCO_3$ (0·78) $CaCO_3$ (1·06)	$ScBO_3$ (0·83) $InBO_3$ (0·92)	Calcite structure.
KNO_3	$CaCO_3$ $SrCO_3$ (1·27) $BaCO_3$ (1·43)	$LaBO_3$ (1·22)	Aragonite structure.

[1] Goldschmidt and Hauptmann. *Nachr. Ges. Wiss. Göttingen*, Math - Phys. Kl. (1932).

CHAPTER IV

THE GEOMETRICAL BASIS OF MORPHOTROPY

We have already discussed the significance of the ratio of the ionic radii in determining the structure adopted by a given compound, and we have seen, for example, that in compounds of the type AX_2 the transition from layer lattice to lattice of the rutile type takes place when the ratio $R_A : R_X$ is about 0·43, while the transition to the fluorite lattice follows when the value of this ratio is about 0·67. An attempt to explain these limiting values of the radius ratios has been made by Goldschmidt from the viewpoint originally due to Magnus,[1] in which a crystal is to be regarded as a packing of rigid ions. According to Magnus, in a complex ion consisting of a positive ion surrounded by a number of negative ions, the maximum co-ordination number of the central ion is governed not only by its charge but also by the ratio of the radii of anion and cation. At a definite value of this ratio the negative ions are in contact with the central ion and with each other. If the radius of the negative ions is increased these ions are forced apart and can no longer all be in contact with the central ion. This separation of the positive and negative ions requires the expenditure of work against the Coulomb forces of attraction so that the potential energy of the ion is increased and its stability reduced. In this way we can see that for a given type of co-ordination there is a corresponding radius ratio giving maximum stability. For three ions X grouped round an ion A at the corners of an equilateral triangle the value of the ratio $R_A : R_X$ is $2/\sqrt{3} - 1 = 0{\cdot}155$, while for four ions tetrahedrally disposed round A it is $\sqrt{6}/2 - 1 = 0{\cdot}225$. If the four ions are situated in a plane at the corners of a square the ratio is $\sqrt{2} - 1 = 0{\cdot}414$, and it is clear that the ratio will have the same value for six ions surrounding A at the corners of a regular octahedron. Finally, if the co-ordination is eight-fold, the X ions being at the corners of a cube, we have $R_A : R_X = 0{\cdot}732$.

Naturally it is not to be expected that the critical values of

[1] Magnus, *Z. anorg. Chem.*, **124**, 288 (1922).

the radius ratios deduced in this simple way will be very exact, for we have assumed the ions to be incompressible spheres and no account has been taken of polarisation. Thus in compounds of the type AX we should expect that the transition from the six-fold co-ordinated sodium chloride structure to the eight-fold co-ordinated cæsium chloride structure would take place at the value of this ratio of 0·73, but actually we find that while the ratio exceeds this value for CsCl, CsBr and CsI, it is also greater than 0·73 for the oxides of the alkaline earth metals, the structure of which, however, is of the sodium chloride type. Again, on the simple theory only CsI of the cæsium halides should show a transition to the sodium chloride structure at high temperatures, whereas actually the bromide and chloride also show this transition. LiBr and LiI also present a difficulty in that they have a sodium chloride structure although from the radius ratio we should anticipate four-fold co-ordination. More recent calculations in which the Van der Waal's forces between the ions are taken into account, give a more satisfactory account of the transition from sodium chloride to cæsium chloride lattice.[1]

In the fluorite structure every A ion is surrounded by eight X ions at the corners of a cube, while in the rutile structure the co-ordination number is six, and the X-atoms are at the corners of an almost regular octahedron. On the simple theory we should expect the fluorite structure to appear whenever the radius ratio exceeds 0·73, while the rutile structure should be stable in the range 0·41 to 0·73. As we saw in the last chapter, the observed range of stability for the rutile structure is 0·43 to 0·67.[2] In SiO_2 the ratio is about 0·3, and here the rutile structure never appears, the co-ordination being always four-fold. In the perovskite structures ABX_3 every B atom is surrounded by six X atoms. For stability the ratio $R_B : R_X$ should therefore lie within the range 0·41 to 0·73 : the observed range is 0·39 to 0·70.

[1] Born and Meyer, *Z. Phys.*, **75**, 1 (1932).

[2] More exact calculations give 0·65 for the critical value of the ratio. Pauling, *J. Amer. Chem. Soc.*, **49**, 765 (1927).

CHAPTER V

LATER WORK ON IONIC RADII

Pauling's Radii. The first attempts to derive theoretical values for the radii of ions on the new quantum theory were made by Pauling in 1927.[1] On the Schrödinger theory the hydrogen atom consists of a nucleus surrounded by a spherically symmetrical distribution of negative electricity, the density of which falls off exponentially with distance so that the greater part of the charge lies within 1–2 A.U. of the nucleus. Pauling proposed a similar model for a many-electron atom, in which each electron is considered to have the distribution in space of a hydrogen-like electron under the influence of an effective nuclear charge $(Z—S_S)e$, where Z is the true nuclear charge and S_S represents the screening effect of the inner electrons. By means of this model we may regard an atom or ion as spherically symmetrical, and in general as consisting of a nucleus embedded in a region of electron density representing the K-electrons, around which are other more or less sharply defined shells of greater electron density corresponding to the L, M, . . . electrons. The size of an ion is governed by the distribution of the outermost electrons, and for similar ions with similar electron distributions is inversely proportional to the effective nuclear charge.

Starting with the observed interionic distances in NaF, KCl, RbBr and CsI, Pauling divided these distances between the two ions, in each case of the same type, in the inverse ratio of their effective nuclear charges, and in this way obtained a series of radii for the alkali and halogen ions. For ions having a similar structure but which were not univalent, so-called 'univalent radii' were calculated in exactly the same way. These univalent radii may be regarded as the radii which the ions would have if they were univalent but retained their electron structure, and may be denoted by R_1. The actual radius of an ion of valency z is then given by

$$R_z = R_1 \cdot z^{-\frac{2}{n-1}},$$

[1] Pauling, *J. Amer. Chem. Soc.*, **49**, 765 (1927); *Z. Kristallogr.*, **67**, 377 (1928).

TABLE VI. *Ionic Radii* (*after* Pauling, 1927). (The Univalent Radii are given in brackets.)

0	I	II	III	IV	V	VI	VII
	H^- 2·08 (2·08)						
He (0·93)	Li^+ 0·60 (0·60)	Be^{2+} 0·31 (0·44)	B^{3+} 0·20 (0·35)	C^{4-} 2·60 (4·14)	N^{3-} 1·71 (2·47)	O^{2-} 1·40 (1·76)	F^- 1·36 (1·36)
				C^{4+} 0·15 (0·29)	N^{5+} 0·11 (0·25)	O^{6+} 0·09 (0·22)	F^{7+} 0·07 (0·19)
Ne (1·12)	Na^+ 0·95 (0·95)	Mg^{2+} 0·65 (0·82)	Al^{3+} 0·50 (0·72)	Si^{4-} 2·71 (3·84)	P^{3-} 2·12 (2·79)	S^{2-} 1·84 (2·19)	Cl^- 1·81 (1·81)
				Si^{4+} 0·41 (0·65)	P^{5+} 0·34 (0·59)	S^{6+} 0·29 (0·53)	Cl^{7+} 0·26 (0·49)
Ar (1·54)	K^+ 1·33 (1·33)	Ca^{2+} 0·99 (1·18)	Sc^{3+} 0·81 (1·06)	Ti^{4+} 0·68 (0·96)	V^{5+} 0·59 (0·88)	Cr^{6+} 0·52 (0·81)	Mn^{7+} 0·46 (0·75)
	Cu^+ 0·96 (0·96)	Zn^{2+} 0·74 (0·88)	Ga^{3+} 0·62 (0·81)	Ge^{4-} 2·72 (3·71)	As^{3-} 2·22 (2·85)	Se^{2-} 1·98 (2·32)	Br^- 1·95 (1·95)
				Ge^{4+} 0·53 (0·76)	As^{5+} 0·47 (0·71)	Se^{6+} 0·42 (0·66)	Br^{7+} 0·39 (0·62)
Kr (1·69)	Rb^{2+} 1·48 (1·48)	Sr^{2+} 1·13 (1·32)	Y^{3+} 0·93 (1·20)	Zr^{4+} 0·80 (1·09)	Nb^{5+} 0·70 (1·00)	Mo^{6+} 0·62 (0·93)	
	Ag^+ 1·26 (1·26)	Cd^{2+} 0·97 (1·14)	In^{3+} 0·81 (1·04)	Sn^{4-} 2·94 (3·70)	Sb^{3-} 2·45 (2·95)	Te^{2-} 2·21 (2·50)	I^- 2·16 (2·16)
				Sn^{4+} 0·71 (0·96)	Sb^{5+} 0·62 (0·89)	Te^{6+} 0·56 (0·82)	I^{7+} 0·50 (0·77)
Xe (1·90)	Cs^+ 1·69 (1·69)	Ba^{2+} 1·35 (1·53)					
	Au^+ 1·37 (1·37)	Hg^{2+} 1·10 (1·25)	Tl^{3+} 0·95 (1·15)	Pb^{4+} 0·84 (1·06)	Bi^{5+} 0·74 (0·98)		
	La^{3+} 1·15 (1·39)	Ce^{4+} 1·01 (1·27)					

where n is a numerical factor whose value depends upon the type of ion concerned.[1] Pauling gives the following values for n :—

He-type ion	$n = 5$
Ne-type	$n = 7$
Ar^- and Cu^+-type . . .	$n = 9$
Kr^- and Ag^+-type . . .	$n = 10$
Xe^- and Au^+-type . . .	$n = 12$

The radii deduced by Pauling are given in Table VI., and the 'univalent radii' are added in brackets. A comparison of these results with those of Goldschmidt given in Table IV. (p. 11) and with the radii of the F^- and O^{2-} ions given by Wasastjerna shows satisfactory agreement. The deviation of interionic distances from additivity in the alkali halides is well known, and is particularly marked in the lithium salts. In the case of the chloride, bromide, and iodide the anions are in contact so that the interionic distance is determined only by the anion radius, but in lithium fluoride the radius ratio is so close to the critical value 0·414, for which anions are in contact both with cations and with each other, that the interionic distance is here determined neither by the sum of the radii alone nor by the radius of the anion alone, and, on account of this double repulsion, must be greater than the distance so calculated. In the sodium halides, too, this effect is appreciable, especially with the iodide, where the radius ratio is 0·44. In the alkali halides of the cæsium chloride type agreement is closer, and the observed interionic distances are about 2·5 per cent. greater than the sum of the radii. Compounds of the alkaline earths with elements of the oxygen group also show very good agreement with Pauling's radii, a fact which is particularly satisfactory since these radii were in no way used in deriving the theoretical values. In MgS and MgSe, as we have seen on p. 5, anions are in contact, while in MgO, where the radius ratio is 0·46, we again have a case of double repulsion resulting in an interatomic distance about 0·5 A.U. greater than the sum of the radii. Good agreement between observed and calculated interatomic distances obtains with the halides of the alkaline earths having the fluorite structure, the only exception being $SrCl_2$ where double repulsion leads to an increase in this distance. The general agreement between Pauling's theoretical radii and those experimentally observed extends as far as compounds of tetravalent cations such as ZrO_2 and CeO_2, but in compounds in which large deformations are to be expected the agreement is poor.

[1] For further details the reader is referred to the original papers quoted.

Zachariasen's Univalent Radii. The conception of 'univalent radii' introduced by Pauling is of great convenience in that it enables interatomic distances to be corrected for the effects of Coulomb forces in a very simple way. As we have seen, however, in comparing his results with experiments, Pauling replaced these univalent radii by calculated radii which should be directly comparable with the empirical radii of Goldschmidt. Zachariasen,[1] approaching the problem from a different point of view, has given a series of empirical radii in univalent form which enable interatomic distances under any conditions of valency and co-ordination to be readily deduced.

He writes for the potential energy of a pair of ions of valency z_1 and z_2 the expression

$$\Phi = -\frac{Az_1 z_2 e^2}{R} + \frac{B}{R^n},$$

where A is the Madelung constant, R is the distance between the ions, and the term B/R^n is that introduced by Born to represent the effect of the repulsive forces between the ions, forces which become appreciable at close approach. The equilibrium value of R will be that for which $\frac{\partial \Phi}{\partial R} = 0$, whence at once

$$R = \sqrt[n-1]{\frac{B}{Az_1 z_2 e^2}} \quad \ldots\ldots\ldots \quad 5{\cdot}1$$

or for univalent ions

$$R = \sqrt[n-1]{\frac{B}{Ae^2}} \quad \ldots\ldots\ldots \quad 5{\cdot}2$$

If now we imagine some compound AX which can exist having the cæsium chloride, sodium chloride, and zincblende structures, we see that in general the A—X distance will be different in each of the lattices since both A and B are functions of the lattice type. Taking the interionic distances in the six-fold co-ordinated sodium chloride lattice as standard we shall be able to write

$$R_{CsCl} = R_{NaCl}\sqrt[n-1]{\frac{A_{NaCl} \cdot B_{CsCl}}{A_{CsCl} \cdot B_{NaCl}}}, \qquad R_{ZnS} = R_{NaCl}\sqrt[n-1]{\frac{A_{NaCl} \cdot B_{ZnS}}{A_{ZnS} \cdot B_{NaCl}}}.$$

The constant A is, of course, known for each of the lattices, but the value of B is less certain. In crystals where no anion-anion contact occurs the overwhelming contribution to the repulsion

[1] Zachariasen, *Z. Kristallogr.*, **80**, 137 (1931).

potential is given by the cation-anion contacts. With a good approximation we may therefore put the coefficient B proportional to the number of these contacts per molecule, *i.e.*, to the co-ordination number. We then have, introducing at the same time the numerical values of A,

$$R_{CsCl} = R_{NaCl}\sqrt[n-1]{\frac{8\,.\,1{\cdot}748}{6\,.\,1{\cdot}762}}, \qquad R_{ZnS} = R_{NaCl}\sqrt[n-1]{\frac{4\,.\,1{\cdot}748}{6\,.\,1{\cdot}640}}.$$

The value of n we have already seen to be a function of the electron configuration of the ion. Using the mean value $n = 9$, we find a 3·3 per cent. contraction in the transition from cæsium chloride to sodium chloride lattice, and a 4·3 per cent. contraction in the transition from sodium chloride to zincblende lattice, both in good agreement with Goldschmidt's empirical values.[1] The contraction in passing from the fluorite to rutile structure is almost exactly the same as that between the cæsium chloride and sodium chloride lattices, while again the contraction between the rutile and quartz lattices is nearly the same as that between the sodium chloride and zincblende lattices. If we define the co-ordination number of a compound as the number of anions round a cation, so that, for example, the co-ordination numbers of the fluorite, rutile, and quartz lattices are 8, 6, and 4 respectively, we can summarise these results by saying that the difference in interionic distance for different co-ordination numbers depends only on the values of the co-ordination numbers and not on the lattice itself. In passing from 8 to 6 co-ordination the contraction is in the ratio $\sqrt[n-1]{1{\cdot}296}$, and from 6 to 4 co-ordination in the ratio $\sqrt[n-1]{1{\cdot}391}$. In both cases these values are averages derived from compounds AX and AX_2. Table VII. below, shows the variation of interionic distance with co-ordination number and n, expressed in terms of the distance unity for co-ordination number 6.

It will be seen from this table that the correction to interionic distances for co-ordination number may be very large, and must always be taken into account to obtain accurate values.

In addition to the correction for co-ordination just discussed, Zachariasen's univalent radii must also be corrected for valency. A comparison of equations (5·1) and (5·2) shows that the distance between two ions of valencies z_1 and z_2 is related to the distance

[1] Goldschmidt, *Geochemische Verteilungsgesetze*, **8**, 69 (1926).

which would separate them if they were univalent by the relation

$$R_{z_1 z_2} = R_{11} \Big/ \sqrt[n-1]{z_1 z_2}$$

As an example of the application of these two corrections we may consider the calculation of the Na—O distance in eight-fold co-ordination. The univalent radii of the Na^+ and O^{2-} ions are 0·98 and 1·76 A.U. respectively. Both ions have the neon electron configuration for which $n = 7$, and Na^+ is univalent while O^{2-} is divalent. The sum of the radii, 2·74 A.U., divided by $\sqrt[6]{2}$ therefore gives the interionic distance which would obtain under six-fold co-ordination, namely 2·44 A.U. The distance in eight co-ordination is obtained by multiplying by the factor 1·044 from Table VII., giving the final result of 2·55 A.U.

TABLE VII. *Interionic Distance as a Function of Co-ordination Number*

n	5	6	7	8	9	10	11	12
C.N. 12	1·160	1·126	1·104	1·088	1·077	1·068	1·061	1·056
C.N. 9	1·087	1 069	1 057	1·048	1 043	1·038	1·034	1·031
C.N. 8	1 067	1 053	1 044	1·038	1 033	1 029	1·026	1 024
C.N. 6	1 00	1 00	1·00	1·00	1·00	1·00	1·00	1·00
C.N. 4	0·920	0 936	0·946	0 954	0·959	0 963	0·967	0·970
C.N. 3	0·862	0 889	0·906	0·919	0·928	0 936	0·942	0 947
C.N. 2	0·793	0·834	0·857	0·877	0·890	0·902	0·911	0 919

Table VIII. contains a number of univalent empirical radii deduced by Zachariasen. These radii were derived in the following way. Reliable observations on interionic distances

TABLE VIII. *Univalent Radii of Ions with Rare Gas Electron Configuration* (*after* Zachariasen)

			H^-	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}		
			1·36	0·68	0·55	0·42	0·38	0·35		
C^{4-}	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}
2·49	2·02	1·76	1·33	0·98	0·89	0·79	0·69	0·66	0 64	0·63
Si^{4-}	P^{3-}	S^{2-}	Cl^-	K^+	Ca^{2+}	Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}
2·97	2·56	2·20	1·81	1·33	1·17	1·03	0·88	0·82	0·70	0·68
	As^{3-}	Se^{2-}	Br^-	Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}	Nb^{5+}	Mo^{6+}	
	2·62	2·29	1·96	1·48	1·34	1·19	1·07	0·98	0·90	
	Sb^{3-}	Te^{2-}	I^-	Cs^+	Ba^{2+}	La^{3+}	Ce^{4+}			
	2·77	2·47	2·19	1·67	1·49	1·30	1·14			
							Th^{4+}			
							1·24			

were selected from existing material, and these distances were corrected for co-ordination and valency in the manner described above. From the corrected interionic distances the individual radii were deduced by taking 1·33 A.U. and 1·81 A.U. as the radii of the K^+ and Cl^- ions respectively. These radii were chosen as the starting point because both Goldschmidt and Pauling are in complete agreement as to these values, and because the same radii are obtained by Landé's method. The general agreement between the values given in Table VIII. and those of Pauling is good for ions of small valency, but for higher valencies differences of the order of 10 per cent. often occur.

In many cases we find in complex structures pairs of anions which may be regarded as simultaneously co-ordinating two different cations, and in these cases, if the valencies or co-ordination numbers of the two cations are different, an ambiguity arises in the calculation of the radius of the anions. If we regard the anions as lying at the corners of polyhedra surrounding the cations, such structures will be characterised by the fact that neighbouring polyhedra have one or more edges in common. In these cases it is found that the lengths of these common edges always have the smallest possible value, being determined by the cation with the largest charge and smallest co-ordination number. Similar considerations lead at once to the calculation of the smallest possible distance between anions for a given co-ordination number. For oxygen Zachariasen finds that the effective radius, for six-fold co-ordination round a univalent cation, lies between 1·53 and 1·62 A.U., the exact value depending on the value of n. This gives for the smallest oxygen-oxygen distance about 3·15 A.U., which is considerably greater than Goldschmidt's value 2·64 A.U. Empirical data is in good agreement with the higher result. With cations of higher charge much smaller distances can, of course, occur, and in rutile we deduce an oxygen-oxygen distance of 2·4 A.U., which is also in good agreement with experiment but cannot be reconciled with Goldschmidt's conception of a constant oxygen radius.

Zachariasen's radii can naturally be used to predict the co-ordination in any structure, for we have already seen the close relationship that exists between co-ordination number and radius ratio. In several cases disagreement with experiment is found, but in general the agreement is good, and such discrepancies as occur are easily explained. Thus, for example, the difference between the calcite structure, where the co-ordination number has the value 6 to be expected from the radii, and the aragonite

structure where it is 9, is explained by the fact that in the latter structure edges are shared between the CaO polyhedra and the

TABLE IX. *Comparison of observed Interatomic Distances with those derived from the Radii of Zachariasen, Goldschmidt, and Pauling*

A—X	Observed Distance.	Compound.	C.N.	Calculated Distance.		
				Zachariasen	Gold-schmidt.	Pauling.
Li—O	2·15	$LiNO_3$	6	2·13	2·10	2·00
Li—F	2·01	LiF	6	2·01	2·11	1·96
Li—S	2·47	Li_2S	4	2·42	2·38	2·31
Li—Cl	2·57	LiCl	6	2·49	2 59	2·41
Li—I	3·03	LiI	6	2·87	2·98	2·76
Be—Te	2·43	BeTe	4	2·40	2·34	2 41
Na—O	2·46	$NaClO_3$	6	2·44	2·30	2·35
Na—O	2·40[1]	Na_2O	4	2·31	2·37	2·42
Na—F	2·31	NaF	6	2·31	2·31	2 31
Na—S	2·82	Na_2S	4	2·75	2 59	2 66
Na—Cl	2·81	NaCl	6	2·79	2 79	2 76
Mg—O	2·10	MgO	6	2·10	2·10	2·05
Mg—F	1·99	MgF_2	6	1·98	2·11	2·01
Mg—S	2·59	MgS	6	2 53	2·52	2·49
Mg—Se	2 73	MgSe	6	2 64	2·69	2·63
Mg—Te	2·76	MgTe	4	2·74	2·78	2·75
Al—N	1·87	AlN	4	1·84		2·09
Al—F	1·79	Topaz	6	1·77	1·90	1·86
Al—P	2·36	AlP	4	2·34		2·50
Al—Sb	2·64	AlSb	4	2·64		2·83
Si—O	1·55—1·65	Silicates	4	1·64	1·63	1·71
K—O	2·95	$KClO_3$, $KBrO_3$	9	2·93	2·78	2·86
K—O	2·82	KH_2PO_4	8	2·90	2 75	2·83
K—F	2·66	KF	6	2·66	2·66	2·69
K—Cl	3·14	KCl	6	3·14	3·14	3·14
K—Br	3·29	KBr	6	3·29	3·29	3·28
Ca—F	2·36	CaF_2	8	2·35	2·48	2·44
Ca—S	2·84	CaS	6	2·83	2·80	2·83
Ca—Te	3·17	CaTe	6	3·14	3·17	3·20
Ti—O	1·96	TiO_2	6	1·96	1·96	2·08
Ti—S	2·42	TiS_2	6	2·38	2·38	2·52
Rb—Cl	3·29	RbCl	6	3·29	3·30	3·29
Rb—I	3·66	RbI	6	3·67	3·69	3·64
Cs—F	3·00	CsF	6	3·00	2·98	3·05
Cs—Br	3·71	CsBr	8	3·72	3 70	3·73
Ba—O	2·77	BaO	6	2·76	2·75	2·75
Ba—F	2·68	BaF_2	8	2·68	2·85	2·80
Ba—Se	3·30	BaSe	6	3·28	3·34	3·33

CO_3 triangle. In such cases where anion-anion distances are shortened by sharing with other co-ordination spheres, greater co-ordination numbers may naturally occur.

[1] Zintl and Baumbach, *Z. anorg. Chem.*, **198**, 88 (1931).

In Table IX. a comparison is given between the observed values of certain interionic distances and those calculated from Zachariasen's, Goldschmidt's, and Pauling's radii. It will be seen that in general Zachariasen's values are in best agreement with experiment. In some cases, as, for example, with MgS and MgSe, the agreement is poor, but this is due to the fact that in these lattices anion-anion contact occurs and no correction for double repulsion was made. On the other hand, in MgTe, where there is no anion-anion contact, the agreement is good. The general applicability of Zachariasen's radii is perhaps best illustrated by comparing the interionic distances between one cation and anions of different valency, as, for example, Li—F and Li—O, Mg—O and Mg—F, etc. These cases show definitely the necessity of using the radii in their univalent form. An interesting observation which arises out of this work is that the ammonium radical may be satisfactorily regarded as an ion with the krypton electron configuration, for which $n = 10$, having a radius of 1·44 A.U.

Attempts to extend Zachariasen's treatment to ions which do not have an inert gas shell have been rewarded with very much less success.

CHAPTER VI

THE CRYSTAL CHEMISTRY OF AX, AX_2 AND A_2X COMPOUNDS

In the previous chapters we have shown that the structure of a crystal is determined primarily by the ratio of the sizes of its constituents and by their polarisation properties. Before passing on to consider the structure of more complex substances we give in the present chapter a brief summary of the crystal chemistry of some very simple compounds.

AX Compounds. If the compound is to be regarded as consisting of rigid ions the co-ordination number is determined by the radius ratio $R_A : R_X$.

If $R_A : R_X$ lies in the range	0·155–0·225	the co-ordination number is	3.
„ „ „	0·225–0·414	„ „ „	4.
„ „ „	0·414–0·732	„ „ „	6.
„ is greater than	0·732	„ „ „	8.

As an example of a structure with three-fold co-ordination we may instance the boron nitride or graphite type. It is not to be expected that the forces in such a structure would be ionic in nature, yet we find that the radii of the ions B^{3+} and N^{3-} give a radius ratio 0·208 appropriate to three-fold co-ordination. If the boron is replaced by the larger aluminium a four-fold co-ordinated structure is to be expected, and in fact AlN has the wurtzite structure. If the still larger scandium is introduced in place of the aluminium the radius ratio is 0·510 and the sodium chloride structure results. An exactly similar change of co-ordination with increasing radius of cation is observed between BeO and MgO, or between ZnO and CdO; in both cases the structure changes from the wurtzite to the sodium chloride type.

The same progressive increase in co-ordination accompanying a change in radius ratio can, of course, be brought about by reducing the size of the anion instead of increasing that of the cation. An example is provided by the compounds of cadmium with Te, Se, S and O. Of these CdTe has a zincblende structure, CdSe and CdS are both dimorphous and crystallise with the

zincblende and wurtzite structures, while in CdO the co-ordination is six-fold, and the structure is of the sodium chloride type. In many cases the transition from one state of co-ordination to another is determined by the influence of polarisation, as in the transition from the structure of CdS to the sodium chloride structure of CaS which takes place in spite of the fact that the radii of the Ca^{2+} and Cd^{2+} ions are very nearly the same.

The alkali halides demonstrate particularly clearly that other factors beside the ratio of the radii of the ions play an important part in determining the structure of a compound. Thus for the cæsium chloride structure it is not sufficient that the radius ratio should lie between 0·73 and 1·37 (= 1/0·73), but, as Goldschmidt has shown,[1] it is also necessary that there should be a close similarity of the two ions A and X in their polarisation properties. In this way we can see how it is that the oxides of the alkaline earth metals, while having a suitable radius ratio, do not have the cæsium chloride structure, since in these compounds the polarisability of the cation in relation to that of the anion is much too small. On the other hand it is equally clear why the cæsium chloride and closely related structures are so common among intermetallic compounds.

We have already discussed the transition of the sodium chloride lattice into the zincblende and wurtzite types due to the influence of an increase in the polarising power of the cation on the anion. If, however, the electropositive constituent A of the lattice is one of the transition elements Cr . . . Cu, Mo . . . Pd, or W . . . Au, increasing polarising power may give rise to a lattice of the nickel arsenide type. The appearance of a lattice of the zincblende or wurtzite types is conditioned by the Grimm-Sommerfeld Rule, which states that in such lattices the constituent A stands in the periodic table as many places in front of the group of tetravalent elements as the constituent B stands after this group. Similarly the appearance of a lattice of the nickel arsenide type is associated with the existence of an incomplete electron shell in the atom A.[2] The transition from sodium chloride to nickel arsenide structure involves no change in co-ordination number, but all crystals with the latter structure are semi-metallic in nature, so that they must contain free or

[1] Goldschmidt, *Geochemische Verteilungsgesetze*, **7**, 74 (1926).

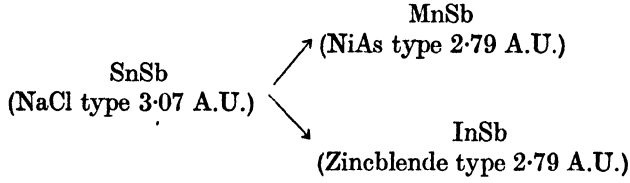
[2] It must be emphasised here that MnS and MnSe form an exception to the Grimm-Sommerfeld Rule in that they have a sodium chloride and not a nickel arsenide structure, while MnS also exhibits a four-co-ordinated structure. For a discussion of the anomalous behaviour of manganese see Horst Schnaase, *Z. phys. Chem.* (B), **20**, 89 (1933).

loosely bound electrons. The morphotropic transition between these structures is shown very clearly in Table X.

TABLE X. *Transition from NaCl to NiAs Lattice*

	Ca.	Mn.	Fe.	Co.	Ni.
Radius of divalent Cation.	1·06	0·91	0·83	0·82	0·78
O	NaCl	NaCl	NaCl	NaCl	NaCl
S	NaCl	NaCl / ZnS	NiAs	NiAs	NiAs
Se	NaCl	NaCl (ZnS ?)	NiAs	NiAs	NiAs
Te	NaCl	NiAs	NiAs	NiAs	NiAs

If we start with a compound of the sodium chloride structure such as SnSb it is possible, according as we replace the tin by a transition element or by a different element of sufficiently strong polarising power, to produce compounds of the nickel arsenide type in the former case, and of the zincblende or wurtzite type in the latter, in both of which, however, the interatomic distances are practically the same. The example depicted graphically below will make the point clear.



In compounds of the type AX it should be possible, as Hund [1] has pointed out, for layer lattices to be formed when the polarising influence of the cation on the anion is very strong, and in confirmation Ernst [2] has reported that in LiOH such a lattice is observed.

AX_2 Compounds. Compounds of the type AX_2 afford a number of excellent examples of the transition from one lattice type to another brought about by changes in the sizes of the constituents

[1] Hund, *Z. Phys.*, **34**, 833 (1925).
[2] Ernst, *Naturwissenschaft*, **20**, 124 (1932); *Z. phys. Chem.* (B), **20**, 65 (1933).

and by changes in the degree of polarisation. On geometrical grounds it is easy to see that in compounds of this type the co-ordination number of one ion must be twice that of the other, so that we have to deal with the following possibilities :—

Co-ordination numbers 4 and 2, as in the different forms of SiO_2 and in the cuprite structure.

Co-ordination numbers 6 and 3, as in the various forms of TiO_2, in the layer lattices of $CdCl_2$ and CdI_2, etc.

Co-ordination numbers 8 and 4, as in the fluorite structure.

We shall consider first the dioxides of a number of tetravalent elements, and give below the radius ratios for certain compounds of this type.

Oxide	. SiO_2	TiO_2	ZrO_2	CeO_2	ThO_2
R_A/R_X	. $<0{\cdot}30$	0·49	0·66	0·78	0·83

In all the known forms of silica the silicon atom is surrounded by four oxygen atoms tetrahedrally disposed, an arrangement in conformity with the radius ratio 0·30 appropriate to four-fold co-ordination. In all the crystalline forms of TiO_2 the co-ordination is six-fold, which is again to be expected from the radius ratio. In the case of ZrO_2 the radius ratio is not far from the transition value 0·73, and the only simple modification has the fluorite structure with a co-ordination of eight. Tetragonal and monoclinic modifications reported appear to resemble a distorted fluorite structure. In CeO_2 and ThO_2 eight-fold co-ordination of the cation is to be expected, and in fact these oxides also have the CaF_2 structure. Germanium in the sub-group of the fourth group of the periodic table forms a dioxide for which the radius ratio is 0·36, and which is dimorphous, having structures of the α-quartz [1] and rutile [2] types. GeO_2 shares with SiO_2 and BeF_2 the property of readily forming glasses.

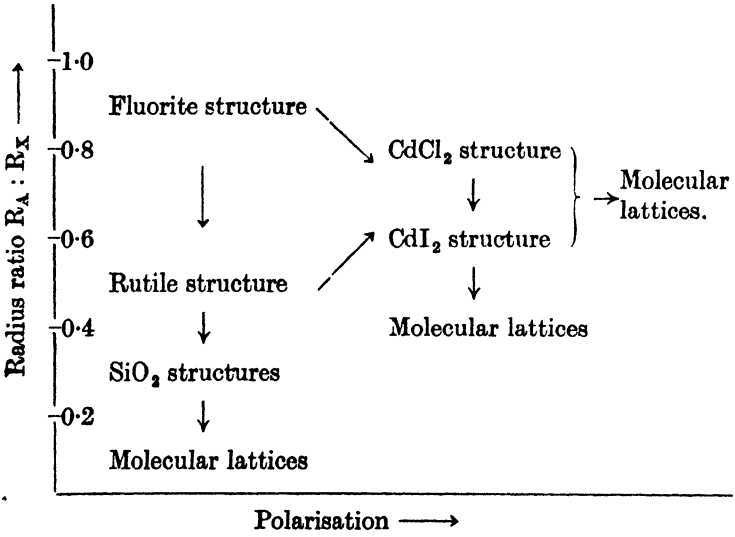
Exactly similar observations could be made concerning the fluorides of divalent metals, and here again the structures observed are in general those to be expected from the radius ratios. BeF_2 is of particular interest in that the radius ratio is so small, less than 0·4, that a four-fold co-ordination of the beryllium is to be expected, and indeed the structure is found to be that of β-cristobalite.[3]

If in the fluorides or oxides we replace the anion by a more

[1] Zachariasen, *Z. Kristallogr.*, **67**, 226 (1928).
[2] Goldschmidt, *Z. phys. Chem.* (B), **17**, 172 (1932).
[3] Brandenberger, *Schweiz. min. petrogr. Mitt.*, **XII**, 243 (1932).

easily polarised ion we can readily produce structures having layer lattices. Thus, for example, the rutile structure of MgF_2 and the fluorite structure of CdF_2 are both converted to a layer lattice of the cadmium chloride type if the fluorine is replaced by chlorine. When the chlorine is replaced by the still more readily polarised iodine, or by a complex ion which possesses a dipole moment, a layer lattice of the cadmium iodide type results. In the same way the rutile lattices of the oxides can be converted into layer lattices, as in the case of the transition from TiO_2 into $TiSe_2$ and $TiTe_2$, which last two compounds both have the cadmium iodide structure. These morphotropic transitions between compounds of the AX_2 type can be conveniently summarised graphically in the form of a diagram as in Table XI., in which the polarisation increases from left to right and the radius ratio from bottom to top.[1]

TABLE XI



Certain other compounds of the general type AX_2 remain to be discussed, and we may consider first those which possess the iron pyrites structure. This structure, in which the two X-atoms form a complex within which the forces are probably homopolar, is very common among sulphides, selenides and tellurides, as well as in the platinum compounds PtP_2, $PtAs_2$, and $PtSb_2$. The criterion for the appearance of this structure seems to be the

[1] Goldschmidt, *Geochemische Verteilungsgesetze*, 8, 101 (1927).

radius of the metallic component in the free state, for it is found that if the radius of the metal is relatively small the pyrites structure obtains, but if the radius in the metallic state exceeds a certain value a layer lattice results. We can imagine that in the latter case electrons are readily given up to the molecule X_2 which is thereby disrupted into two negative ions, but that in the former case this can happen only with great difficulty. This point is clearly illustrated by the examples given in the table below.[1] The radii of the metal atoms there quoted are those which obtain under twelve-fold co-ordination.

TABLE XII

Metal.	Radius				Structure.
Zr	1·60	ZrS_2	$ZrSe_2$		CdI_2 type
Sn	1·58	SnS_2			CdI_2 type
Ti	1·45	TiS_2	$TiSe_2$	$TiTe_2$	CdI_2 type
W	1·41	WS_2	WSe_2	WTe_2	MoS_2 type
Mo	1·40	MoS_2	$MoSe_2$	$MoTe_2$	MoS_2 type
Pt	1·38	PtS_2	$PtSe_2$	$PtTe_2$	CdI_2 type
Pd	1·37			$PdTe_2$	CdI_2 type
Os	1·34	OsS_2	$OsSe_2$	$OsTe_2$	Pyrites type.
Ru	1·32	RuS_2	$RuSe_2$	$RuTe_2$	
Mn	1·30	MnS_2		$MnTe_2$	
Fe	1·27	FeS_2			
Co	1·26	CoS_2	$CoSe_2$		
Ni	1·24	NiS_2	$NiSe_2$		

Layer lattices.

There are many compounds of the type AX_2, particularly among the silicides, which are still more metallic in their properties, and among such silicides a characteristic feature is always the mutual binding between the silicon atoms. Thus in $CaSi_2$ [2] corrugated layers of silicon atoms extend through the whole lattice perpendicular to the trigonal axis, and these layers can be recognised in the lattice of crystallised silicon itself. The lattice of $MoSi_2$ can be regarded as a deformed molybdenum lattice in which two-thirds of the molybdenum atoms are replaced by silicons.[3]

A_2X Compounds. Many X-ray investigations have also been carried out on compounds of the type A_2X, particularly on the

[1] *Cf.* Goldschmidt, *Fortschr. Min.*, **15**, 100 (1931).
[2] Böhm and Hassel, *Z. anorg. Chem.*, **160**, 152 (1927).
[3] Zachariasen, *Z. phys. Chem.*, **128**, 39 (1927).

oxides and sulphides of univalent metals. Since in these cases the radius of the anion is large compared with that of the metal, we shall in general expect structures of low co-ordination, and in fact, many of the structures so far investigated are of the anti-fluorite type. On the other hand Ag_2O and Cu_2O have lattices of the cuprite type with four-fold co-ordination of the oxygen atoms although a higher co-ordination might be expected, that we must conclude that the binding forces in these compounds are different from those which obtain in compounds such as the oxides of the alkali metals having the anti-fluorite structure.

More Complex Compounds. Before closing this account of the crystal chemistry of simple compounds we may mention that many important observations have been made concerning the relations which exist between atom size, polarisation, and crystal structure in more complex compounds, but that so far it has not been possible to formulate any simple rules such as those which we have discussed in this chapter for compounds of the type AX and AX_2. Space does not permit a detailed discussion, but we may here remark that in compounds, the cations in which have relatively high charges, layer lattices and molecular lattices must be increasingly common. Even among compounds of the type AX_3 the number with layer lattices is very large.

CHAPTER VII

PAULING'S PRINCIPLES OF IONIC STRUCTURE

THANKS to the work of many investigators, much of which we have described in earlier chapters, it is now possible to predict with considerable success the co-ordination of any ion in an ionic crystal from a knowledge of the ionic radii and polarisabilities. Only in very simple cases is this knowledge sufficient to give an unambiguous indication of the exact structure. Even in the case of quite complex structures, however, we are often able, by means of the rules which Pauling [1] has formulated, so to reduce the number of possible arrangements that with the help of relatively few and simple X-ray data we can readily arrive at the correct structure. Pauling's rules frequently lead to a close packing of the large ions, a configuration which is in fact often encountered, as in the silicate structures investigated by W. L. Bragg and his school.

As an illustration of the application of Pauling's rules we may consider the various crystalline modifications of TiO_2. In both rutile and anatase the co-ordination number of the titanium atom is six, and the oxygens surround the titaniums, being situated at the corners of an almost regular octahedron. The Ti—O distance is 1·95 A.U., and if the octahedra were quite regular their edges would be 2·75 A.U. long. In fact some of the edges are shorter and others correspondingly longer, and it is found that those edges which are shorter than 2·75 A.U. are common to two TiO_6 octahedra, while those which are longer belong only to one such octahedron. In rutile every octahedron has two such common edges, in anatase four. In determining the structure of brookite, the third form of TiO_2, Pauling and Sturdivant [2] started from the assumption that here, also, the octahedral co-ordination of the titanium atoms occurred, and in this way they were able to reduce the number of possible structures to two. The selection of the correct structure was

[1] Pauling, *J. Amer. Chem. Soc.*, **51**, 1010 (1929).
[2] Pauling and Sturdivant, *Z. Kristallogr.*, **68**, 239 (1928). See also Pauling's work on pseudobrookite, *Z. Kristallogr.*, **73**, 97 (1930).

then readily made by a simple X-ray investigation. The same method was applied to the structure of topaz,[1] and a structure was predicted in which every aluminium was surrounded by four oxygens and two fluorines in the form of a regular octahedron, and every silicon was surrounded by four oxygens, the O—O and the O—F distances being both 2·72 A.U. The structure involves the determination of 15 parameters, and Pauling's predictions were completely confirmed by the investigations of Alston and West.[2]

Pauling's rules are applicable to ionic crystals in which the cations are small and highly charged ($R_A < 0{\cdot}8$ A.U., valency 3 or 4), and the anions have a radius greater than about 1·35 A.U. The polarisability must not be too large.

The First Rule. The first rule states that :—

Every cation is surrounded by a polyhedron of anions, the cation-anion distance being determined by the radius sum and the co-ordination number of the cation by the radius ratio.

It was at the time clearly emphasised by Pauling that in the case of aluminium a radius ratio appropriate to six-fold co-ordination was sometimes accompanied by four-fold co-ordination, a fact which accounts for the replacement of silicon by aluminium in silicates.

The Second Rule : the Electrostatic Valency Principle. The strength of a valency bond between a cation and an anion is defined by Pauling as the number z/n where z is the valency of the cation and n is the number of anions which surround one cation. If y is the valency of the anions, Pauling's second rule states that if we consider one given anion the sum of the strengths of all the valency bonds from the neighbouring cations to this anion is equal to its valency, *i.e.*, $\Sigma\, z/n = y$. Expressed in words :—

The total strength of the valency bonds which reach an anion from all the neighbouring cations is equal to the charge of the anion.

This rule is merely an expression of the fact that negative constituents of a lattice tend to occupy positions of maximum positive potential. In general the rule is not rigidly obeyed, but it is necessarily fulfilled in cases where all the anions are in crystallographically equivalent positions. Large departures from the rule are not to be expected and have never been observed.

The electrostatic valency rule enables us to determine how

[1] Pauling, *Pr. Nat. Acad. Sci. Wash.*, **14**, 603 (1928).

[2] Alston and West, *Proc. Roy. Soc. A*, **121**, 358 (1928); *Z. Kristallogr.*, **69**, 49 (1928).

many anion polyhedra will share a common corner ; it can tell us nothing, however, about the number of corners common to two given polyhedra. This point may be illustrated by considering again the various forms of TiO_2. In rutile, anatase, and brookite the strength of every electrostatic valency bond is $4/6 = 2/3$, since the charge on the cation is four, and every cation is surrounded by six anions. In all these structures three oxygen octahedra meet in a common oxygen atom so that the valency rule is satisfied. The number of edges, however, which a given octahedron shares with other octahedra is in rutile two, in brookite three, and in anatase four. In none of these structures have two oxygen octahedra more than two corners in common.

The Third Rule. A third rule of Pauling may be formulated :—

The existence of edges, and particularly faces, common to two anion polyhedra reduces the stability of a structure. This effect is particularly marked if the cation is highly charged or has a low co-ordination, and, ceteris paribus, *is greater the nearer is the radius ratio of the polyhedron concerned to the lower limit of stability.*

The basis of this rule is the fact that a face common to two anion polyhedra necessitates the close approach of two cations, resulting in a corresponding increase in the potential energy. It is readily deduced that for a tetrahedron of anions the cation-cation distance is reduced in the ratio 1 : 0·58 for the transition from a common corner to a common edge, and in the ratio 1 : 0·33 for the transition from a common corner to a common face. For an octahedron of anions the effects are smaller, viz. 1 : 0·71 and 1 : 0·58 respectively. These calculations do not, of course, take any account of the deformations of the polyhedra which generally take place. In fact these deformations are greater the greater the radius ratio $R_A : R_X$. In this way it is easy to understand why SiO_4 tetrahedra usually share only corners, while TiO_6 octahedra may have common edges, and AlO_6 octahedra common faces. In the modifications of TiO_2 the radius ratio $R_{Ti} : R_o$ is so large that the difference in stability between the different forms is relatively small. The influence of the charge of the cation is reflected by the fact that SiO_4 tetrahedra share only corners with AlO_6 octahedra, but may have an edge in common with MgO_6 octahedra.

The Fourth Rule. Pauling's fourth rule states that :—

In a crystal containing different cations those with high valency and small co-ordination number tend not to share polyhedron elements with each other.

This rule follows directly from the fact that cations with high

electric charge tend to be as far apart as possible, in order to reduce their contribution to the Coulomb energy of the crystal.

The rule requires that in silicates the SiO_4 tetrahedra share no elements with each other if the oxygen : silicon ratio is equal to or greater than four (as in topaz, zircon, olivine, and the orthosilicates in general). If stoichiometrically necessary, corners will be shared between tetrahedra, but not edges or faces. In the various forms of silica all four corners of each tetrahedron are shared with adjoining tetrahedra. In silicates containing the Si_2O_7 group this group is formed by two tetrahedra sharing a corner. The metasilicates with an oxygen : silicon ratio of three should not contain groups of two tetrahedra with a common edge, but rather chains or rings, each tetrahedron sharing two corners.[1] It is of interest to note that the electrostatic valency rule requires that corners shared between two oxygen tetrahedra be not also shared with other polyhedra. In fact this is not always the case, as in diopside, where certain oxygen atoms are bound not only to two silicon atoms but also to two calciums, so that the strength of the valency bonds terminating on these oxygen atoms is $2\frac{1}{2}$ instead of 2.

The Fifth Rule : the Principle of Parsimony. Pauling's fifth rule states that :—

The number of essentially different kinds of constituents in a crystal tends to be small.

According to this rule the electrostatic bindings of all chemically similar anions must be the same whenever possible. Thus in topaz every oxygen atom is bound to two aluminiums and one silicon, and every fluorine atom to two aluminiums. The rule does not, however, require all the atoms of one kind to be crystallographically equivalent, and in topaz the oxygen ions are crystallographically of three kinds. Often the preceding rules do not permit all the atoms of one kind to be alike, as, for example, in the silicates with an oxygen : silicon ratio greater than four. In these cases, however, the number of different kinds of anions will be small. The rule further requires that polyhedra circumscribed about all chemically identical cations should, if possible, be chemically similar, and similar in their immediate environment. For example, each aluminium octahedron in topaz has as corners four oxygen and two fluorine ions, and each shares two edges with other octahedra and four corners with silicon tetrahedra. The titanium octahedron in rutile shares two edges, in brookite three, and in anatase four, but no structure is known in

[1] Machatschki, *Zbl. Min., Geol., Paläont.*, Abt. A and B (1928), 97.

which these different octahedra occur together. The polyhedra which are similar in these respects need not be crystallographically equivalent, for they may differ in their remote environment.

We have already remarked that the existence of edges or faces common to two polyhedra results in the shortening of the corresponding edges, and in the case of simple structures it is possible to calculate from the energy of the lattice the amount of this shortening. In more complex structures the calculation cannot usually be effected, but for oxygen polyhedra around trivalent or tetravalent cations it is found that all shared edges are shortened to about 2·50 A.U. In some structures it is to be anticipated that cation-cation repulsion will operate to displace the cations from the centre of their co-ordinated polyhedra. This action will be large only when the radius ratio approaches the lower limit of stability, so that the size of the polyhedron is partially determined by the characteristic anion-anion repulsive forces.

It has been pointed out by Bragg[1] that the application of Pauling's rules to silicate structures, based on the conception of a packing of Si^{4+} and O^{2-} ions, rests on rather insecure grounds, and that the use of the radius ratio in the case of so small an ion as Al^{3+} to determine the co-ordination number must also be somewhat uncertain. Nevertheless the $Al^{3+} : O^{2-}$ ratio of about 0·4 accounts very satisfactorily for the occurrence of aluminium in four- and six-fold co-ordination. Bragg expresses the view that the electrostatic valency rule constitutes Pauling's most important contribution to the theory of complex ionic lattices. In all cases where the oxygen atoms occupy equivalent positions it is necessarily fulfilled as a consequence of the chemical valencies, but where the oxygen atoms are not crystallographically equivalent its fulfilment is no longer self-evident, and, as we have already mentioned, in many complex structures it is not valid. In all silicates we find, however, that the total strength of the bonds which terminate on an oxygen atom is approximately two, and of those which terminate on a fluorine atom or OH group approximately one. It is easy to see that the energy of a lattice will be a minimum if the valency bonds from each ion are as short as possible, and the electrostatic valency rule is simply an expression of this condition.

[1] W. L. Bragg, *The Structure of Silicates*, 2nd edition (Leipzig, 1932), p. 57 *et seq.* This work differs only in the addition of a few pages from the paper *Z. Kristallogr.*, **74**, 237 (1930).

CHAPTER VIII

THE CRYSTAL CHEMISTRY OF THE SILICATES

THE application of X-ray methods to the study of the silicates has led to advances as notable and important as in any other branch of chemistry, and provides a particularly beautiful illustration of the principles of crystal chemistry laid down by Goldschmidt and Pauling. Fundamental to the understanding of the silicate structures is the four-fold co-ordination of oxygen atoms round silicon. As we have already seen, the nature of the forces within the SiO_4 group may be regarded in more than one way, and we can follow Goldschmidt and consider the group as formed by the packing of rigid ions, or we can take the view that the bindings are essentially homopolar in nature, resembling rather those which occur in organic molecules. On either view the SiO_4 group plays the part of a discrete unit in all silicates. The four-fold co-ordination of silicon follows at once from the radius ratio of about 0·3 for $Si^{4+} : O^{2-}$. The radius ratio for $Al^{3+} : O^{2-}$ is according to Goldschmidt's radii 0·43, and according to Pauling's 0·36. Both of these values are not very far from the critical value for transition from four to six co-ordination, and it is therefore not surprising that aluminium occurs in silicates with both of these co-ordinations. In addition to Si^{4+}, the ions Be^{2+} and Zn^{2+} occur in silicates exclusively in four-fold co-ordination, although from the Goldschmidt radius six-fold co-ordination would be expected for zinc. Sc^{3+} and Ti^{4+} always have a co-ordination number 6, and Zr^{4+} a co-ordination number 8. Other ions occur in general in the silicates with different co-ordination numbers.

The application of X-ray methods to the analysis of the more complex silicates is primarily due to W. L. Bragg, and has become possible only by the development of the method of absolute intensity measurements. The conception of a silicate structure as built up to a close approximation of a close-packed arrangement of oxygen atoms has also been of great value, while Machatschki's [1] classification of the silicates has proved very

[1] Machatschki, *Zbl. Min., Geol., Paläont.*, Abt. A (1928), 97.

useful. This classification is based on the nature of the binding between neighbouring SiO_4 tetrahedra in the lattice. The first class of silicates comprises those in which no tetrahedra share an oxygen atom. In these structures the oxygen atoms are linked together by other cations, and they may be regarded as true orthosilicates. The remaining silicates are classified according to the way in which the tetrahedra are linked together. A linkage in which tetrahedra are joined in pairs through a common oxygen atom gives rise to the group Si_2O_7, while the addition of a third tetrahedron produces the group Si_3O_{10}. If every tetrahedron is linked to two neighbours we shall obtain either endless chains or closed ring systems, which will in both cases have the composition SiO_3, while if each tetrahedron shares three corners two dimensional sheets of composition Si_2O_5 will be produced. Finally, if the tetrahedra share all corners, a three-dimensional network results having the composition SiO_2, and such an arrangement is illustrated by the structure of silica itself, and by the felspars. A classification of this kind is, however, attended by certain difficulties. Thus, as we have already seen, aluminium can occur in the silicates in four-fold co-ordination, and sometimes exists actually replacing silicon atoms, and we are therefore compelled to treat four co-ordinated aluminium atoms in the same way as silicon atoms in any scheme of classification. Machatschki himself treats the BeO_4 group in the same way, and is also inclined to believe that B^{3+} can behave similarly. Since, however, Be^{2+} and Zn^{2+} are in many silicates precisely equivalent, we must also regard the ZnO_4 and SiO_4 groups as analogous.[1]

Simple Orthosilicates. As an example of a structure which was among the earliest to be investigated, and which is to be considered as a typical orthosilicate we may instance olivine $(Mg, Fe)_2SiO_4$.[2] The SiO_4 tetrahedra in this structure are linked together through Mg^{2+} (and Fe^{2+}) ions, while these cations are surrounded by an octahedral arrangement of oxygens. Pauling's electrostatic valency rule leads us to expect that every oxygen atom will be bound to three divalent ions, since the strength of the O—Si bond is $4/4 = 1$, and that of one O—Mg

[1] According to Barth and Posnjak, *Z. Kristallogr.*, **81**, 376 (1932), the structure of α-carnegite ($NaAlSiO_4$) may be regarded as derived from that of the high temperature form of cristobalite by replacing half the silicon atoms by aluminium, a sodium atom being introduced with each aluminium in order to satisfy the valency requirements. Na_2CaSiO_4 may be regarded in a similar way. If we accept this view we must clearly consider the CaO_4 and SiO_4 groups as analogous, a conception which appears very remarkable in terms of our earlier knowledge.

[2] Bragg and Brown, *Z. Kristallogr.*, **63**, 538 (1926).

bond only 2/6 = 1/3, leaving a strength of 2/3 still to be satisfied. We therefore conclude that each oxygen is linked to three magnesiums. A somewhat idealised representation of the structure is shown in Fig. 1, which illustrates a projection of the rhombic lattice on the *b*—*c* plane. It is readily seen that the tetrahedra of oxygen atoms occur with their apices pointing alternately up and down, while it is also clear that the magnesium ions are of two kinds in that only one half of them, namely those starred in the figure, lie at symmetry centres. On account of the

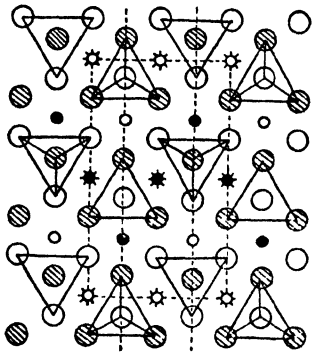


Fig 1.—Idealised Structure of Olivine projected on *b*—*c* plane.

○ = Mg in plane of paper
◉ = O at height $a/4$
● = Mg ,, $a/2$
○ = O ,, $3a/4$.

The atoms starred are at centres of symmetry.

existence of these two kinds of magnesium atoms the structure of monticellite $MgCaSiO_4$ may be regarded as that of olivine in which one half of the magnesium atoms have been replaced by calciums.[1] In both these structures the arrangement of oxygen atoms approximates to that of hexagonal close packing. Closely related to the structure of olivine are the structures of the compounds $Mg(F, OH)_2 . nMgSiO_4$, viz., norbergite $n = 1$, chondrodite $n = 2$, humite $n = 3$, and clinohumite $n = 4$. The first and third are orthorhombic with the space group *Pnma*, the second and fourth monoclinic with the space group $P2_1/c$. In all four structures two dimensions of the unit cell are about 4·7 and 10·2 A.U., while in the orthorhombic silicates the length in the *c* direction, and in the monoclinic silicates the projection of the third dimension in a direction normal to the (001) plane, are a

[1] Brown and West, *Z. Kristallogr.*, **66**, 154 (1927).

multiple of about 1·45 A.U. All the structures approximate to a hexagon close packing of oxygen and fluorine ions, and the distance 4·7 A.U. embraces two layers of such an arrangement of oxygens. Certain regions in the structures are the same as in the olivine lattice, but these regions are separated from each other by layers containing F and OH groups so disposed that no silicon atom is directly bound to either of these radicals. The oxygens which surround the silicon atoms are also each linked to three magnesiums, as are the F and OH groups, and it is in fact possible to construct all these structures by the juxtaposition of units of the composition $Mg(OH)_2$ and Mg_2SiO_4. In this way the structure of still undiscovered members of this series of minerals can be predicted, and in fact the structure of the last known member was predicted by Taylor and West before it was formally analysed.

In all the silicates so far discussed the metal ion has been surrounded by an octahedral arrangement of oxygen ions. In phenacite Be_2SiO_4 [1] and the isomorphous willemite Zn_2SiO_4 this is no longer the case, and the metal as well as the silicate ions are four-fold co-ordinated with regard to oxygen. In such a structure the strength of the valency bond between metal and oxygen is $\frac{2}{4} = \frac{1}{2}$, so that each oxygen linked to a silicon can be simultaneously bound to only two beryllium ions. The relatively complex rhombohedral lattice of these silicates is merely an expression of the fact that the tetrahedra of oxygen atoms round the beryllium and silicon ions are so linked that every oxygen atom is common to three such tetrahedra. If we attempt to pack three regular tetrahedra in such a way that they all have one corner in common we find at once that this corner lies in the middle of an equilateral triangle, the corners of which are at the centres of gravity of the tetrahedra. In phenacite such triangles are defined by a silicon and two beryllium ions, and such an arrangement leads at once to the complete structure. The phenacite structure differs from that of olivine in that it cannot be regarded as a close packing of oxygen atoms.

If we consider the silicates which contain aluminium we must remember that the co-ordination number of this element relative to oxygen may be four or six, and a very instructive example of this fact is provided by the minerals of composition Al_2SiO_5. In cyanite [2] all the aluminium atoms are six-fold co-ordinated,

[1] Bragg, *Proc. Roy. Soc.*, A, **113**, 642 (1927); Bragg and Zachariasen, *Z. Kristallogr.*, **72**, 518 (1930).

[2] St. Náray-Szabó, Taylor and Jackson, *Z. Kristallogr.*, **71**, 117 (1929); *Proc. Roy. Soc.*, A, **119**, 132 (1928); Cardoso, *Ber. Sächs. Ges.*, **80**, 165 (1928).

while in sillimanite [1] some occur in four-fold co-ordination. Andalusite [2] occupies an intermediate position in that here aluminium atoms occur surrounded by both six and five oxygens. All these modifications of Al_2SiO_5, however, have in common the fact that the AlO_6 groups are linked in chains in such a way that each such group has two oxygen atoms in common with each neighbouring group. This arrangement leads to a spacing along the length of the chains of 5·6—5·7 A.U., and according to the particular way in which the chains are linked together we obtain one or other of the three minerals. In the case of cyanite this linkage takes place in such a way as to lead to an almost cubic close-packed arrangement of oxygens. In all these silicates the SiO_4 groups are independent, so that they are to be regarded as orthosilicates.

While we are discussing the silicates of composition Al_2SiO_5 we may mention the very close resemblance between the interference pictures of sillimanite and of mullite of composition $Al_6Si_2O_{13}$. The unit cell which in sillimanite contains 8 Al, 4 Si, and 20 O, in mullite includes 9 Al, 3 Si, and 19½ O. We may regard mullite as derived from sillimanite by the replacement of one silicon atom by aluminium, the substitution of each silicon being accompanied by the removal of half an oxygen to satisfy valency requirements. The true unit cell of mullite is, of course, necessarily larger than that of sillimanite.[3]

As a final example of an orthosilicate we may consider the structure of garnet $Ca_3Al_2Si_3O_{12}$.[4] This mineral, in which the Al may be replaced by Fe^{3+} or Cr^{3+}, and the Ca by Mg^{2+}, Fe^{2+}, or Mn^{2+}, is characterised by a six-fold co-ordination of the trivalent ions, while the calciums are surrounded by eight oxygen ions all at approximately the same distance. This group is really composed of two groups of four equivalent ions, so that in the case of cations other than calcium the co-ordination is only four-fold. The cubic unit cell of garnet contains 96 oxygen atoms, and affords a particularly good example of a co-ordination structure.

Complex Silicate Groups. So far we have considered exclusively structures in which no oxygen atom is bound to more than one silicon atom. We shall now pass on to discuss some structures in which the SiO_4 groups are no longer independent, but

[1] Taylor, *Z. Kristallogr.*, **68**, 503 (1928).
[2] Taylor, *Z. Kristallogr.*, **71**, 205 (1929).
[3] Taylor, *Z. Kristallogr.*, **68**, 503 (1928).
[4] Menzer, *Z. Kristallogr.*, **63**, 157 (1926), and **69**, 300 (1928).

are linked together through a common oxygen atom. If these groups are linked in pairs we obtain a unit of composition Si_2O_7, such as is found in thortveitite $Sc_2Si_2O_7$,[1] while if every SiO_4 group shares two oxygen atoms with neighbouring groups, chains or rings of composition $(SiO_3)_n$ are formed. Considering first the structures which contain such rings of silicon groups we may instance benitoite $BaTiSi_3O_9$,[2] where the rings contain three such groups, and hexagonal beryl $Be_3Al_2Si_6O_{18}$,[3] in which six silicon groups are linked to form a ring of composition Si_6O_{18}. These rings are superimposed in the structure in the direction of the *c* axis in such a way that the lattice contains wide tunnels parallel to this direction passing through the centre of each ring. Neighbouring rings are bound together by Be^{2+} and Al^{3+} ions, while these ions are surrounded by a tetrahedral and octahedral arrangement of oxygen ions respectively.

Chain Structures. A third type of silicate is that in which the silicon groups are linked together to form endless chains. If this linkage takes place in such a way that each group shares two oxygens with neighbouring groups the silicon : oxygen ratio is 1 : 3, and such an arrangement is found in the pyroxene diopside $MgCa(SiO_3)_2$,[4] (Fig. 2a). If we imagine a reflection plane to pass through the outermost oxygen atoms of this chain we obtain the new type of chain illustrated in Fig. 2b, which gives a silicon :

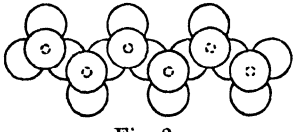


Fig. 2a.

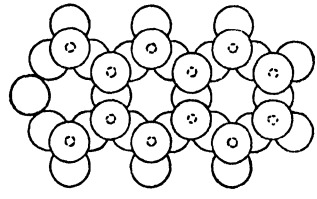


Fig. 2b.

oxygen ratio of 4 : 11. A chain of this type is found in the amphibole tremolite,[5] the general formula of which was previously written $CaMg_3(SiO_3)_4$, but which, in the light of the X-ray investigations, must now be considered to be $(OH)_2Ca_2Mg_5Si_8O_{22}$. In point of fact diopside and tremolite show similarities in their crystallographic properties which may be attributed to the fact

[1] Zachariasen, *Z. Kristallogr.*, 73, 1 (1930).
[2] Zachariasen, *Z. Kristallogr.*, **74**, 139 (1930).
[3] Bragg and West, *Proc. Roy. Soc.*, A, **111**, 69 (1926).
[4] Warren and Bragg, *Z. Kristallogr.*, **69**, 168 (1928).
[5] Warren, *Z. Kristallogr.*, **72**, 493 (1929).

that in both structures the length of the chains is parallel to the *c* axis, and we find that in both minerals the repeat period in this direction is about 5·25 A.U., this distance being four times the radius of an oxygen ion. The same chain-like arrangement of silicon groups is found in the orthorhombic pyroxene enstatite and the orthorhombic amphibole anthophyllite.[1] On account of the very strong forces between the silicon and oxygen atoms such cleavages as take place in these minerals are always parallel to the length of the chains, and the fibrous character of many of the amphiboles is to be attributed to the same cause.[2]

Two-dimensional Networks. If the chains shown in Fig. 2b are symmetrically extended in a direction at right angles to their

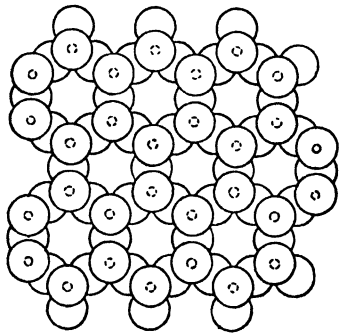


Fig. 3.

length the two-dimensional network illustrated in Fig. 3 is produced. In this arrangement we find not only the repeat period of 5·2 A.U., which occurs in the amphiboles and pyroxenes, but also a period of about 9·1 A.U. in a direction at right angles, and it is this arrangement of silicon tetrahedra which gives to the micas and talc their remarkable properties. The pseudo-hexagonal symmetry, the highly perfect cleavage, which takes place parallel to the nets of silicon atoms, and the silicon : oxygen ratio of 4 : 10 all follow immediately from the structure.[3] The relationships between the different micas and talc is illustrated by writing the formula for muscovite as $(OH)_2KAl_2Si_3AlO_{10}$, a formula which expresses the fact that one quarter of the silicon atoms of the Si_4O_{10} unit have been replaced by aluminiums,

Warren and Modell, *Z. Kristallogr.*, **75**, 1 and 161 (1930).

[2] Warren and Bragg, *Z. Kristallogr.*, **76**, 201 (1930).

[3] Pauling, *Proc. Nat. Acad. Sci., Wash.*, **16**, 123 (1930); Jackson and West, *Z. Kristallogr.*, **76** 211 (1930); **85**, 160 (1933).

while the rest of the aluminiums occur in six-fold co-ordination. If these latter aluminiums are replaced by magnesium we obtain phlogopite mica $(OH)_2KMg_3Si_3AlO_{10}$, while if the remaining aluminiums of phlogopite are replaced by silicons, the potassium atoms being at the same time removed to satisfy the valency requirements, talc $(OH)_2Mg_3Si_4O_{10}$ results. The arrangement of silicon tetrahedra characteristic of the micas is not confined to these structures, and is in fact found in other minerals having pronounced cleavage such as the kaolinites, but it appears always to be associated with the presence of a relatively large number of hydroxyl groups in the structure. The kaolinites show in addition to the mica-like cleavages other cleavages characteristic of the layer lattices of the hydroxides of divalent and trivalent metals.

Three-dimensional Networks. We have already remarked that all the crystalline modifications of silica have structures in which the SiO_4 tetrahedra are linked together to form a three-dimensional network, the linking being such that every oxygen atom is common to two tetrahedra. Such an arrangement, of course, satisfies the electrostatic valency rule. If, however, in

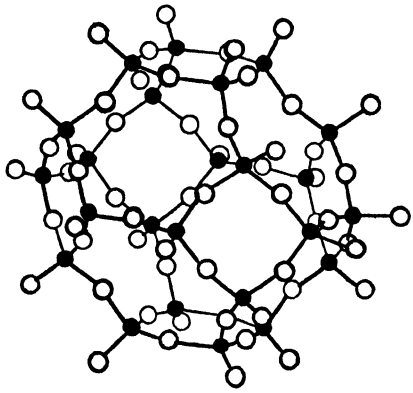


Fig. 4.

such a network some of the silicon atoms are replaced by aluminiums the valency rule can no longer be satisfied unless we simultaneously introduce a cation to balance the excess negative charge, and in this case we obtain a structure of the felspar type. Apart from the felspars, the most important substances whose structures are based on a three-dimensional network of silicon

tetrahedra are the ultramarines and the zeolite analcite. The framework of the ultramarine $Na_6Al_6(SiO_4)_6 \cdot 2\,Na_2SO_4$, is shown in Fig. 4, and has the composition $Al_6Si_6O_{24}^{6-}$ giving the ratio (Al + Si) : O of 1 : 2 required for such a network.[1] The Na^+ and SO_4^{2-} ions are situated in the interstices of the structure. A similar arrangement is found in analcite $NaAlSi_2O_6 \cdot H_2O$, the structure of which contains wide channels that account for the ready dehydration of this mineral and the ease with which the sodium can be replaced by silver and other metals.[2]

Crystal Chemistry of the Silicates. An important principle in the crystal chemistry of the silicates, which follows from the fact that in many of these structures the oxygen atoms form a close-packed arrangement, is that the number of oxygen atoms in the unit cell of a given type of structure is constant. The introduction of further oxygen atoms is manifestly precluded, while the removal of an oxygen atom is likewise impossible as it would lead to the violation of the electrostatic valency principle.

When we pass on to consider the isomorphous replacement of various ions in the silicates, we find that here it is the volume of the ions which is the significant factor, and that the valency is of less importance. As an example we need only instance the replacement of Na + Si by Ca + Al in the felspars. Al^{3+} frequently replaces Si^{4+} in four-fold co-ordination and Mg^{2+} in six-fold co-ordination, and indeed it sometimes happens, as in the amphiboles and pyroxenes, that the aluminium ion occurs in the one structure in both *rôles*. This replacement of silicon by aluminium often leads to an uncertainty in the number of cations in a structure. Thus, for example, the lattice of the ideal tremolite, $(OH)_2Ca_2Mg_5Si_8O_{22}$, contains open spaces which may or may not be occupied by Na^+ or K^+ ions ; the extent to which these spaces are actually filled is determined by the extent to which silicon is replaced by aluminium. Every aluminium thus introduced can be accompanied by a univalent cation without disturbing the valency requirements. Similarly, in mica the number of oxygen atoms in the unit cell is always 48, including 8 as hydroxyls, while the number of cations may be 28 or 32. The importance of the application of principles of this kind to the determination of the true formula of a mineral will be at once apparent, and in fact they have already led to many impor-

[1] Jaeger, *Versl. gewone. Vergad. Akad. Amst.*, 32 (1929); *Trans. Faraday Soc.*, 25, 320 (1929).

[2] Gruner, *Z. Kristallogr.*, 68, 363 (1928); Taylor, *Z. Kristallogr.*, 74, 1 (1930).

tant results, two examples of which, taken from the work of Machatschki, we may mention here.[1]

It was formerly supposed that homilite and gadolinite furnished an example of the isomorphous replacement of calcium by beryllium and boron by yttrium, and the formulæ were written :

Homilite . . .	$FeCa_2B_2Si_2O_{10}$
Gadolinite . .	$FeBe_2Y_2Si_2O_{10}$.

In the light of Goldschmidt's radii, however, it is extremely improbable that the isomorphous replacement of ions of such different sizes would take place (Ca^{2+} 1·06, Y^{3+} 1·06, B^{3+} 0·2, Be^{2+} 0·3 A.U.). On the other hand, the replacement of calcium by yttrium and boron by beryllium is immediately understandable, so that the replacement takes place by ions not of the same valency but of the same size. For comparison with the formula of homilite, that of gadolinite must therefore be written $FeY_2Be_2Si_2O_{10}$.

As a second example we may consider the arsenic mineral berzelite and its relation to the garnets, $Ca_3Al_2Si_3O_{12}$, which have the same structure. If in the garnet structure we replace the three Si^{4+} ions by As^{5+} we obtain an excess of three units of positive charge which must be compensated. This compensation is effected by the replacement of one of the Ca^{2+} ions by Na^+, and of the two Al^{3+} ions by Mn^{2+} or Mg^{2+}. The analogy with garnet is therefore emphasised by writing the formula of berzelite as $Ca_2Na(Mn, Mg)_2As_3O_{12}$.

Crystal Chemistry of the Borates. A series of compounds, the crystal chemistry of which has been very little investigated, but which are nevertheless of particular interest in connection with the chemistry of the silicates, are the salts of boric acid. The radius ratio $B^{3+} : O^{2-}$ is appropriate to three-fold co-ordination of the boron, and in fact Zachariasen[2] has shown that in the mineral hambergite the boron atom lies at the centre of an almost equilateral triangle of oxygen atoms, while a similar arrangement is found in calcium metaborate, CaB_2O_4.[3] These two structures differ, however, in that in hambergite the oxygens surrounding each boron atom are linked to only one such atom, so that independent BO_3 groups are found, whereas in calcium metaborate the triangular groups are so linked that two of the oxygen

[1] Machatschki, *Z. Kristallogr.*, **70**, 211 ; **71**, 45 (1929) ; **72**, 291 ; **73**, 123 (1930).
[2] Zachariasen, *Z. Kristallogr.*, **76**, 289 (1931).
[3] Zachariasen and Ziegler, *Z. Kristallogr.*, **83**, 354 (1932).

atoms of each group are linked also to the boron atom of an adjacent group. In this way endless chains of BO_3 groups are formed, giving a boron-oxygen ratio of 1 : 2.

The Formation of Glasses. Also closely linked with the crystal chemistry of silicon compounds is the question of the structure of glasses. The many similarities, especially in mechanical and elastic properties, between glasses and crystalline substances leads to the conclusion that their structures are closely related to those of the crystals of the corresponding chemical composition, and Randall, Rooksby and Cooper [1] have concluded from X-ray photographs of glasses that these substances have a micro-crystalline structure. Silica glass they find to be composed of crystals of cristobalite of linear dimensions of about 15 A.U. They also conclude that the lattice dimensions in these crystals are about 7 per cent. greater than those observed in ordinary cristobalite crystals, a conclusion which it is very difficult to reconcile with the observed density of the glass.

Arguing from the ease with which silica forms a glass, Goldschmidt has suggested that the ready formation of a glass is associated with the existence of a tetrahedral arrangement of oxygens round the central ion. The fact that BeO, however, in spite of a radius ratio appropriate to four-fold co-ordination, forms no glass indicates that there are other factors of importance, and indeed it is clear that the existence of a stable glass implies that the rate of inversion into the crystalline form is extremely small. This in its turn implies that the difference in the free energy in the glassy and crystalline states must also be small. This last point at once enables us to apply to the problem the principles of crystal chemistry which we have already discussed in earlier chapters. We saw, for example, in the discussion of the various crystalline modifications of SiO_2 and TiO_2 that the energy of an ionic lattice depends primarily on the co-ordination number of the cation and to a lesser extent on the way in which the anion polyhedra are linked together. Space does not permit a complete discussion of this treatment, and here we can only say that by an application of these principles Goldschmidt concludes that for the formation of an oxide glass of composition A_mO_n, the following conditions must be satisfied :—

(1) No oxygen atom is bound to more than two A atoms.
(2) The co-ordination number of A must be small.
(3) The oxygen polyhedra share only corners.

[1] Randall, Rooksby and Cooper, *Z. Kristallogr.*, **75**, 196 (1930).

(4) As a necessary condition for the formation of a three-dimensional structure at least three corners of each oxygen polyhedra must be shared with a neighbouring polyhedron.

It is readily seen that the oxides A_2O and AO cannot satisfy these conditions, but that A_2O_3 and higher oxides can fulfil conditions (1), (3) and (4). For AO_3 and higher oxides the co-ordination number of A must be greater than four, and the fact that no such oxide has yet been found to form a glass suggests that the highest co-ordination permitted by condition (2) is four. In B_2O_3 and P_2O_3 the co-ordination number is three, but in the molecular lattices of As_4O_6 and Sb_4O_6 we can only speak of a three-fold co-ordination to a rough approximation as here the AsO_3 group is not plane. All these four oxides form glasses, and from the above considerations they are the only sesquioxides which are to be expected to form glasses. Among tetravalent ions Si and Ge have a co-ordination number of four relative to oxygen. The higher co-ordination would imply a less-marked tendency to glass formation than in the case of the sesquioxides. The only fluoride which is to be expected to form a glass is BeF_2. The close resemblance of this substance to SiO_2 has already been discussed in Chapter VI., p. 35.

CHAPTER IX

THE STRUCTURE OF RADICALS AND ATOM GROUPS IN CRYSTALS

Zachariasen's Empirical Rules. The numerous X-ray investigations on the structures of inorganic salts have revealed that in many of these substances the acid radical exists as a discrete unit, and for all the common radicals the geometrical disposition of the constituents of this unit has been found. Thus the nitrate and carbonate radicals have a plane structure in which the nitrogen and carbon atoms lie at the centre of an equilateral triangle of oxygens, while the chlorate and bromate ions on the other hand have a pyramidal structure with the radical as a whole still possessing trigonal symmetry, but in which the halogen no longer lies in the plane of the oxygen atoms. An attempt to account for this arrangement of the chlorate ion was made by Zachariasen,[1] who remarked that the three Cl—O bonds were very nearly parallel to the lines drawn from the centre of a regular tetrahedron to three of its corners. The Cl^{5+} ion at the centre of the radical has two electrons in excess of the neon configuration, and he suggested that the electron density of these electrons might be considered as concentrated round the fourth corner of the tetrahedron. In two more recent papers [2] Zachariasen has pursued these ideas further by enquiring whether those radicals in which the central ion has a rare gas electron configuration possess a particularly symmetrical structure, while Hassel [3] has considered the structure of the general radical or molecule of composition AX_m. For the most highly symmetrical structure it is postulated that both the A and X ions must in the radical have a rare gas configuration, so that if the atom X occurs in the tth column of the periodic table, and k is the number of valence electrons in the rare gas which follows X, $m(k-t)$ electrons must be transferred to the X ions in order that they may

[1] Zachariasen, *Ski. Norske VidenskAkad., Oslo*, I. Mat.-Naturv. Kl., No. 4, p. 90 (1928).

[2] Zachariasen, *Phys. Rev.*, **37**, 775 (1931); *J. Amer. Chem. Soc.*, **53**, 2123 (1931).

[3] Hassel, *Tidsskr. Kemi Bergv.*, 1931, 92.

have such a configuration in the radical. If this number is also equal to n, the number of electrons which A must lose in order that it, too, may acquire a rare gas configuration, we may expect the most symmetrical structure of the molecule, and in this case we have $n = m(k—t)$. We define the ' valency electron number ' of the radical as the total number of valency electrons of the ion A and the m ions X, *i.e.*, as the number $n + mt$. If our postulated condition for a structure of highest symmetry is satisfied we see that this number is equal to mk. If the valency electron number exceeds mk the central ion will not be completely deprived of its n electrons and a structure of lower symmetry will result.

When we apply these considerations to the experimental material we find that in many cases there is good agreement with the observations. In the SO_3^{2-} ion, for example, the valency electron number is $8 + 3.6 = 26$, while mk is $3.8 = 24$; we therefore anticipate an unsymmetrical arrangement, and in fact find that the structure of the radical is pyramidal and not plane. For the SO_3 molecule on the other hand, which has two fewer electrons, we should expect a plane structure in the form of an equilateral triangle. Other examples might be given, such as the NO_2^- ion, which experiment [1] shows to be non-linear and for which an unsymmetrical structure is to be anticipated. The trihalides of B and Al on the one hand, and of P, As, and Sb on the other, would furnish a particularly interesting check of the applicability of Zachariasen's rule, but unfortunately the experimental material on the structures of these molecules is very meagre. Measurements of the dipole moments of the molecules in solution, do, however, in fact suggest that while the halides of B and Al have a plane structure, that of the other halides is pyramidal.

The regular tetrahedral structures of the ions PO_4^{3-}, SO_4^{2-}, and ClO_4^-, and of the molecules of the tetrahalides of many tetravalent elements, are further examples of the applicability of Zachariasen's rule, although it must be remarked that it is difficult to regard these halides as composed of ions with the rare gas configuration since the forces are typically homopolar. The difficulty becomes still greater when we consider such molecules as H_2O and NH_3, where the idea of a negative hydrogen ion is clearly absurd. Nevertheless the rule, if formally applied, is of widespread applicability even in such cases, although exceptions are occasionally encountered with compounds containing heavy atoms. Thus the ion ICl_2^- of the rhombohedral

[1] Ziegler, *Phys. Rev.*, **38**, 1040 (1931).

$CsICl_2$ has a linear structure although such a symmetrical arrangement is not to be expected from the rule.

Pauling's Theoretical Treatment. The same problem of the structure of complex molecules and ions has recently been discussed by Pauling[1] in terms of the quantum theory. We cannot here enter into details, for which the reader is referred to the papers quoted, but we may summarise his principal results by saying that he concludes that the *p*-electrons give rise to stronger bonds than the *s*-electrons of the same principal quantum number, and that if an atom takes part in several *p*-electron linkages these links tend to be perpendicular to each other. Thus the oxygen atom has two unpaired electrons, and consequently in the water molecule the two O—H links include an angle of about 90° (but actually somewhat greater owing to the repulsion of the two hydrogen atoms). Similar considerations apply to the nitrogen atom with three unpaired *p*-electrons, so that ammonia has a pyramidal structure. More exact calculations for H_2O and NH_3 show that in both cases the angles between the bonds lie between 90° and 109° 28′; in water the angle is nearer the lower limit, in ammonia nearer the upper. The crystal skutterudite $CoAs_3$ contains As_4^{4-} groups with a square configuration, so that here the bond angles are exactly 90°. The case was also discussed by Pauling in which the number of unpaired electrons available in the atom is smaller than the normal maximum valency. An example is provided by carbon, which in the normal state contains only two unpaired electrons, and the fact that the four bonds are nevertheless completely symmetrical indicates that an alteration in the quantisation of the atom must take place when it enters into combination. The same is true of the nitrogen atom in such radicals as NH_4^+ and $N(CH_3)_4^+$.

The Hydrogen Bond. The structure of the hydroxyl group is of considerable interest, for while in many structures the electrostatic valency rule requires the existence of the —OH group as a discrete unit, there are other structures in which there is considerable evidence for the presence of OHO groups. Thus in many crystals containing H and O, including topaz, $Al_2SiO_4(F, OH)_2$, diaspore, $AlHO_2$, etc., the sum of the strengths of the electrostatic bonds from all cations (except hydrogen) to an anion is either 2 or 1, indicating the presence of O^{2-} and F^- or $(OH)^-$ ions respectively. In some crystals, however, including

[1] Pauling, *J. Amer. Chem. Soc.*, **53**, 1367 (1931); Slater, *Phys. Rev.*, **37**, 481; **38**, 1109 (1931).

KH_2PO_4 [1] the sum of the bond strengths is 2 or $\frac{3}{2}$, the latter value occurring twice for each H. The electrostatic valency rule in this case supports the assumption of $(O^{2-}H^{+}O^{2-})^{3-}$ groups, the hydrogen atom contributing a bond strength of $\frac{1}{2}$ to each of the two oxygen atoms, leaving a strength of $\frac{3}{2}$ still to be satisfied. This so-called hydrogen bond is not, however, confined to the linkage of oxygen atoms, and it is in fact also responsible for the stability of the wurtzite structure of NH_4F, in which each nitrogen is linked to the four fluorine neighbours by such a bond.[2]

The Sulphur Acids. We have already remarked that in the ClO_3^- ion Zachariasen found that the directions of the three Cl—O bonds were very nearly parallel to the lines drawn from the centre of a regular tetrahedron to three of its corners, and the same is true of many other non-planar groups of the type AB_3. One such group is the sulphite ion SO_3^{2-}, and here the arrangement is of particular interest as emphasising the close relation of this ion to the sulphate ion SO_4^{2-} which has a regular tetrahedral structure. Unfortunately no experimental evidence is available for the structure of the thiosulphate ion $S_2O_3^{2-}$, but it seems not improbable that this group is derived from the sulphate ion by the simple replacement of one oxygen atom by sulphur, so that the bonds are still tetrahedrally distributed, although the S—S distance is naturally greater than the S—O distance. The structure of the pyrosulphite ion $S_2O_5^{2-}$ has been determined by Zachariasen[3] by observations on $K_2S_2O_5$, and he has found that this radical may be pictured as derived from the thiosulphate ion by the addition of two oxygen atoms. These oxygens are linked to the second sulphur atom in such a way that the three bonds of this atom are also parallel to the lines from the centre to three corners of a regular tetrahedron. If, finally, we imagine a sixth oxygen atom to be added to this group we obtain a radical S_2O_6 having trigonal symmetry, and the observations on the dithionates of potassium, rubidium[4] and cæsium[5] are in complete agreement with such a structure for the dithionate ion. A second investigation of potassium and rubidium dithionates[6] challenges some of the parameter determina-

[1] West, *Z. Kristallogr.*, **74**, 306 (1930).
[2] Sherman, *Chem. Rev.*, **11**, 93 (1932).
[3] Zachariasen, *Phys. Rev.*, **40**, 113 (1932).
[4] Huggins and Frank, *Amer. Min.*, **16**, 580 (1931).
[5] Hägg, *Z. phys. Chem.* (B), **18**, 327 (1932).
[6] Hägg, *Z. Kristallogr.*, **83**, 265 (1932). See also Helwig, *Z. Kristallogr.*, **83**, 485 (1932).

tions of the earlier measurements but leaves the structure of the acid radical unchanged.

Werner Co-ordination Compounds. Closely associated with the problem of the structure of radicals and atom groups is that of the structure of the Werner co-ordination compounds. The conception of the co-ordination of an atom as the number of its immediate neighbours was first introduced to chemistry by Werner, and it is only relatively recently, with the application of X-ray methods to structure analysis, that this conception has been widely extended to cover structures of a typically ionic kind. As we have seen earlier, the co-ordination number of an ion in ionic structures depends on a number of factors, but is primarily determined by the size and polarisability of itself and its neighbours. In the Werner compounds, however, this is not the case, and here the co-ordination of the central atom is less variable and appears to be determined principally by the influence of the homopolar forces which it exerts on its neighbours.

The complete solution of the structures of certain typical Werner compounds such as $Co(NH_3)_6I_2$ and K_2PtCl_6 has led to a verification of the essential correctness of Werner's ideas, and naturally to an elaboration of them inasmuch as the positions of all the atoms in the structure can now be determined. The X-ray data have also confirmed Werner's views on the structures of those compounds having four-fold co-ordination of the central atom, such as the $PtCl_4^{2-}$ group in K_2PtCl_4, in that in such cases the neighbours of the central atom have a plane distribution.

Extensive researches have also been carried out on the hexammine and hexahydrate compounds of salts of di- and trivalent metals, and this work emphasises the close relationship between these two groups of substances. The compounds are for the most part cubic with structures of the fluorite and closely associated yttrium fluoride types, and in fact it is possible to observe structures of one or other type according as the valency of the complex group is two or three :—

CaF_2 Structure.	YF_3 Structure.
$Co(NH_3)_6I_2$	$Co(NH_3)_6I_3$
$Co(NH_3)_6(ClO_4)_2$	$Co(NH_3)_6(ClO_4)_3$.

The early crystallographic researches on the hexammine salts of trivalent cobalt and chromium, and on those salts in which one or two of the NH_3 groups were replaced by water, showed that the symmetry was entirely unaltered by this substitution,

and the X-ray investigations have confirmed that apart from a trifling change in the lattice dimensions no significant change in the structure takes place. The fact that the X-ray evidence indicates that in such salts as $[Co(NH_3)_5H_2O]SO_4I$ the six molecules bound to the cobalt atom are geometrically and structurally equivalent introduces an obvious difficulty. Hassel [1] has attempted to resolve this contradiction by postulating that the six molecular positions surrounding the cobalt atoms are exactly equivalent and that the water molecule replaces the ammonia in a statistical manner. On this view we can speak of an ' internal mixed crystal ' formation in that, just as in ordinary mixed crystals, equivalent crystallographic positions are occupied by different atoms or atom groups statistically distributed. Similar considerations have been advanced by Pauling [2] in his work on certain fluoroxy salts, such as $(NH_4)_3MoO_3F_3$, in which X-rays reveal the crystallographic equivalence of the oxygen and fluorine atoms. Exactly the same difficulty has arisen in the structures of the spinels AB_2O_4 for which Barth and Posnjak[3] have shown that two structural arrangements exist. In one of these, eight equivalent positions in the unit cell are occupied by the cation A and sixteen other equivalent positions by B. In the other, however, for which we may write the formula $BABO_4$, the sixteen crystallographically identical positions are occupied by equal numbers of the two cations. The former arrangement appears to exist in all the aluminium spinels, while the latter structure has been found for $MgFe_2O_4$, $MgGa_2O_4$, $MgIn_2O_4$, $SnZn_2O_4$, etc. In the case of $MgGa_2O_4$ Barth and Posnjak's result has been confirmed by Machatschki.[4]

The Sizes of Complex Ions. The dimensions of the complex ions of the Werner compounds have been determined principally from a study of the simple halogen salts which have the fluorite or yttrium fluoride structures. In this way, for example, the radii of the $Co(NH_3)_6^{2+}$ and $Ni(NH_3)_6^{2+}$ ions have been found to be 2·60 and 2·58 A.U. respectively,[5] so that here, as in other compounds of Co^{2+} and Ni^{2+}, the nickel salt has the slightly smaller lattice dimensions. The accurate determination of the radii of these complex ions is of great value, for the presence of

[1] Hassel, *Norsk. geol. Tidsskr.*, **10**, 33 and 92 (1928); Hassel and Salvesen, *Z. phys. Chem.*, **128**, 345 (1927).
[2] Pauling, *J. Amer. Chem. Soc.*, **46**, 2738 (1924).
[3] Barth and Posnjak, *J. Wash. Acad. Sci.*, **21**, 255 (1931); *Z. Kristallogr.*, **82**, 325 (1932).
[4] Machatschki, *Z. Kristallogr.*, **82**, 348 (1932).
[5] Bödtker-Naess and Hassel, *Z. anorg. Chem.*, **211**, 21 (1933).

the neutral molecules of H_2O, NH_3, etc., surrounding the central ion robs the cation of the greater part of its polarising influence, and therefore enables measurements to be made of the sizes of readily polarisable anions. In this way, for example, Hassel and Kringstad [1] have found for the radii of the series of ions ClO_4^-, SO_3F^-, and BF_4^- the values 2·36, 2·37, and 2·28 A.U. respectively.

In the same connection we may mention the fact that the molecular volumes of corresponding salts of $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ are almost identical,[2] while exact X-ray measurements show that the lattice dimensions of the salt with the trivalent cation, having the YF_3 structure, are always slightly smaller than those of the salt of the divalent cation with the CaF_2 structure.

[1] Hassel and Kringstad, *Z. anorg. Chem.*, **209**, 282 (1932).
[2] Biltz and Birk, *Z. anorg. Chem.*, **127**, 34 (1923).

CHAPTER X

THE CRYSTAL CHEMISTRY OF THE METALS

The Structure of the Metals. Any study of the crystal structure and chemistry of the metals must begin with a realisation of the fact that no sharp boundary exists between the metallic and the non-metallic state, and that every possible type of transition is observed between them. Those elements which show particularly pronounced metallic properties all have close-packed structures, but elements of a semi-metallic nature often have structures in which the co-ordination number is less than 12. Just as in the case of ionic lattices, atomic radii in metallic crystals are constant only in lattices of one type, and a comparison of interatomic distances is of little significance unless made between structures of the same co-ordination number. The mean amount by which atomic radii are reduced in passing from close-packed structures to arrangements of lower co-ordination is shown by the following numbers, based on experimental measurements, in which the radii are expressed as fractions of the radius which obtains in twelve-fold co-ordination.

C.N.	Radius.
12	1·00
8	0·97
4	0·88
3	0·81
1	0·72

The Radii of Metal Atoms. Table XIII. contains a list of atomic radii of the metals and certain non-metals for different co-ordinations. The values here given are, of course, not all obtained from observations on the pure elements, but are in many cases derived from measurements on mixed crystals. The use of such measurements is attended by the difficulty that in mixed crystals interatomic distances are in general smaller than the sum of the radii determined by observations on the pure elements. If, however, the two elementary constituents of the mixed crystal are so chosen that their radii do not differ

TABLE XIII. *Atomic Radii* (*after* Goldschmidt)

C.N.	He	Li	Be	B	C	N	O	F				
12		1·57	1·13									
8		1·52	1·10									
4				0·97	0·77	0·71						
3				0·83	0·71	0·62						
1					0·62	0·53	0·41					

C.N.	Ne	Na	Mg	Al	Si	P	S	Cl				
12	1·60	1 92	1·60	1·43								
8		1·86	1·55	1·39								
4					1·17							
1							0·9—1					

C.N.	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
12	1·92	2·36	1·97		1·45	1·36	1·28	1·30	1·27	1·26	1·24
8		2·29	1·91		1·41	1·32	1·24	1·26	1·24	1·22	1·21

C.N.	Cu	Zn	Ga	Ge	As	Se	Br				
12	1·28	1·37		1·39	1·40						
8	1·24	1·34		1·34	1·35						
4				1 22							

C.N.	Kr	Rb	Sr	Y	Zr	Nb	Mo	Ma	Ru	Rh	Pd
12	1·98	2·53	2·16		1·60	1·47	1·40		1·32	1·34	1·37
8		2·46	2·10		1·55	1·43	1·36		1·28	1·30	1·33

C.N.	Ag	Cd	In	Sn	Sb	Te	I				
12	1·44	1·52	1·57	1·58	1·61						
8	1·40	1·47	1·52	1·53	1·56						
4				1·40							

C.N.	X	Cs	Ba	La[1]	Hf	Ta	W	Re	Os	Ir	Pt
12	2·18	2·74	2·25	1·86	1·59	1·46	1·41	1·37	1·34	1·35	1·38
8		2·66	2·18	1·80	1 53	1·42	1·37	1·34	1·30	1·31	1·34

C.N.	Au	Hg	Tl	Pb	Bi	Po	(85)				
12	1·44	1·55	1·71	1·74	1·82						
8	1·40	1·50	1·66	1·69	1·77						

C.N.	Rn	(87)	Ra	Ac	Th	Pa	U				
12					1·80						
8					1·75						

[1] The radii of lanthanum are provisional only. A more recent value is contained in the following list of radii of yttrium and certain rare earth metals in 12-fold co-ordination: Y 1·814, La 1·870, Ce 1·819, Pr 1·824, Nd. 1·819. Quill, *Z. anorg. Chem.*, **208**, 65 and 273 (1932); Rossi, *Rendic, Accad. Naz. Lincei* (6), **15**, 298 (1932); Zintl and Neumayr, *Z. Electrochem.*, **39**, 84 (1933). A collection of lattice constants of the elements is given by Neuburger, *Z. Kristallogr.*, **80**, 103 (1931).

greatly, and they are also chemically similar, this discrepancy is not large. On the other hand the contraction is particularly marked in mixed crystals containing one of the transition

elements. Very occasionally an expansion of the lattice is observed. By using mixed crystals it is frequently possible to determine the atomic radius of an element in a state of co-ordination which for the pure element is not stable. Thus observations on a germanium-copper alloy, which has an hexagonal close-packed structure, have led to a value of the radius of the germanium atom in twelve-fold co-ordination, although no structure with this co-ordination is observed with the pure element.

Numerous attempts have been made to correlate the radius of metallic atoms with the positions of these elements in the periodic table. If we confine our attention to metals which do not belong to the sub-groups we observe in any one series a progressive decrease in the radius with increasing valency, and this decrease in radius is accompanied by an increase in the hardness and an elevation of the melting point, as in the series Na, Mg, Al, Si. The radii of members of the sub-groups, however, increase with increasing valency, as in the series Ag, Cd, In, Sn, Sb, so that for such elements the atomic and ionic radii in a given series change in opposite senses.[1] If, instead of comparing the radii of elements of different valency in a given series, and therefore all with the same principal quantum number, we compare elements of the same valency but with different quantum numbers, as Na, K, Rb, etc., or Zn, Cd, Hg, we find that in both principal and sub-groups the radius increases with increasing quantum number. Naturally, however, in this method of comparison the effect of the lanthanum contraction is very marked, so that Zr and Hf, Nb and Ta, Rh and Ir, and Ag and Au have almost exactly the same radii.

Attempts to express the radii of all metallic atoms by a single formula have been made by Hume-Rothery,[2] who has given the expression

$$R = n\left(\frac{1}{KZ}\right)^{p}$$

for the radius of an atom of atomic number Z and principal quantum number n. K is a constant for any given group of the periodic table, while p is a constant which differs but little from one-third.

[1] See Table IV., p. 11, and Table VI., p. 24, for the ionic radii.
[2] Hume-Rothery, *Phil. Mag.*, **10**, 217 (1930); **11** .649 (1931).

CHAPTER XI

THE CRYSTAL CHEMISTRY OF INTERMETALLIC SYSTEMS

The Chemical Formulæ of Intermetallic Phases. There is no field of inorganic chemistry in which the assignation of stoichiometric formulæ has proved more difficult than in the study of metallic systems. This difficulty arises from the fact that metallic compounds in general possess the capacity of taking up to a greater or less extent an excess of one or other of their components in solid solution. This capacity, however, is limited so that beyond certain bounds the addition of a still further excess of one of the components results in the appearance of a new phase. The range of composition within which a single phase exists we may call the 'region of homogeneity.' This region is in some cases very extensive and embraces a change of composition of several per cent., while in other cases it may be extremely limited. The extent of the region is also a function of the temperature. In a few cases the region of homogeneity is so extremely narrow that even with the application of the modern X-ray methods it has not been possible to establish its existence, although in other cases, where it includes a range of composition of considerably less than 1 per cent., as in $CuAl_2$, Cu_2Mg, etc., its presence has been demonstrated with certainty. If we follow Westgren [1] in believing that all alloys have a definite, although sometimes very narrow, region of homogeneity, we must conclude that a compound of definite proportions in a metallic system can only be regarded as an ideal limiting case. Even in compounds containing non-metallic phases, such as the compounds of the metals with C, N, S, or even O, we find that the composition is somewhat variable, and we are forced to the conclusion that the same limitations apply to the conception of stoichiometric combination in all compounds except those in which the forces are of a pronouncedly polar nature.

The Brasses and Bronzes. When the region of homogeneity is very narrow and does not include any compound of simple

[1] Westgren, *Z. angew. Chem.*, **45**, 33 (1932).

atomic proportions, or when it is so wide that it embraces several possible simple compounds, it is often difficult to find a satisfactory basis for the assignation of a formula: in such cases the evidence from crystal structure is often of great value. As an example we may instance the case of β-brass, the region of homogeneity of which at ordinary temperatures does not include the compound of equal atomic proportions. At higher temperatures, however, the compound of this composition does fall within the homogeneous region, and therefore, although the compound CuZn is not stable at room temperature, we assign this formula to β-brass. The X-ray evidence shows that this phase has a cubic body-centred structure, but on account of the similarity in scattering power of the Cu and Zn atoms it is not possible to distinguish these atoms in the lattice or to assign them to their respective places. It is very probable, however, that the phases AgZn, AuZn and AgMg have the same structure, and here it is easy to discriminate between the two atoms of the structure and to show that the atoms of one kind are situated on a simple cubic lattice while the atoms of the other kind are situated on a second such lattice centring the first. In such cases where structurally equivalent positions in the lattice are occupied by atoms of only one kind the assignation of a formula is greatly simplified. γ-brass provides another example.[1] Here there are 52 atoms in the cubic unit cell divided among four groups of 8, 8, 12 and 24 equivalent positions, and, again by observations on the analogous Ag—Zn and Au—Zn alloys, it is found that the copper atoms occupy one of the eight-fold and the twelve-fold groups, while the zinc atoms occupy the other two groups of positions. The formula of the phase must express this ratio of 20 : 32, and is therefore written Cu_5Zn_8.

Similar considerations apply to γ-aluminium bronze where the unit cell again contains 52 atoms, this time distributed among groups of 4, 4, 4, 4, 6, 6, 12 and 12 equivalent positions.[2] Of these one four-fold and one twelve-fold group are occupied by aluminium atoms and the rest by copper atoms, so that the formula of this bronze is Cu_9Al_4. In many other cases, however, such an ideally regular distribution of the different atoms in the lattice does not occur, and then the assignation of a formula is not so simple. Thus the alloy $Cu_{31}Sn_8$ has 416 atoms in the unit cell although this number is not divisible by 39. In this particular example, however, the formula can be readily deter-

[1] Bradley and Thewlis, *Proc. Roy. Soc.*, **A, 112**, 678 (1926).
[2] Bradley, *Phil. Mag.*, **6**, 878 (1928).

mined by ordinary chemical analysis as the region of homogeneity is very small.

Hume-Rothery's Rule. A general survey of the structures of the alloys compels the conclusion that chemical combination between two metals of different valencies occurs only if the mean number of valency electrons per atom in the compound is considerably removed from a whole number,[1] and Hume-Rothery has formulated the rule that *a given structure type is characterised by a definite electron : atom ratio.* By chemical combination we here imply the existence of a structure significantly different from that of either of the pure components. As an example of this principle we may consider the β-phases CuZn, AgZn, Cu_3Al, Cu_5Sn, etc., in all of which the mean number of electrons per atom is 3/2.[2] The number of valency electrons provided by each atom is just the number of the column in the periodic table in which it stands, except that in the case of the transition elements magnetic measurements show that these metals appear to make no electron contribution. The phases FeAl, NiAl and CoAl therefore all contribute three electrons per molecule, namely those provided by the aluminium atom, so that here also the electron : atom ratio is 3/2. A second series of alloys, which includes the members Ag_3Al, Au_3Al, Cu_5Si, is closely related to the β-brasses, and here too the electron : atom ratio is 3/2.

As an example of a quite different type of structure we may consider the γ-structures already mentioned earlier in this chapter, and enquire whether the average number of electrons per atom is also constant in this series of alloys. Taking the member Cu_5Zn_8 we at once see that here the number of electrons is $5 + 2.8 = 21$, so that the electron : atom ratio is 21 : 13, and the same ratio is found for Ag_5Zn_8 and Au_5Zn_8 and also for the γ-phases Cu_9Al_4 and $Cu_{31}Sn_8$. The γ-phases containing elements of the iron, ruthenium or osmium families combined with zinc or cadmium, such as Fe_5Zn_{21}, or Rh_5Zn_{21}, also have an electron : atom ratio of 21 : 13, but in calculating this ratio we must assume, as before, that the transition element makes no electron contribution.

[1] Dehlinger, *Z. Electrochem.*, **38**, 148 (1932). The work of Zintl, described below, has established that this principle is not without exceptions.

[2] Hume-Rothery, *Jour. Inst. Met., Lond.*, **35**, 313 (1926); *The Metallic State*, Oxford (1931). Recently Laves, *Nachr. Ges. Wiss. Göttingen*, Math.-physik. Kl. III., **27**, 519 (1932), has attempted to explain the dependence of structure type on the number of valency electrons in terms of the relation between this number and the number of atom linkages.

As a final example of the Hume-Rothery rule we may consider the ϵ-phases, which have a hexagonal close-packed lattice in which the atoms are statistically distributed.[1] These structures include the alloys $AgZn_3$, Cu_3Ge, Au_5Al_3, etc., and in all cases the electron : atom ratio is 7 : 4. It seems, however, now to be definitely established that the Hume-Rothery rule is not of universal validity. Thus Zintl and his co-workers [2] have shown that the alloys NaTl, LiZn, LiCd, LiGa, LiIn and NaIn all have the same structure although the number of electrons available is not the same for all these phases. Nor do the alloys LiAg, LiHg, LiTl, MgTl, CaTl and SrTl, which all have the β-brass structure, or the alloys $CaPb_3$, $NaPb_3$, $CePb_3$, $CaTl_3$, $CaSn_3$ and $CeSn_3$, which have a cubic face-centred lattice,[3] satisfy the Hume-Rothery rule.

Interatomic Distances in the Alloys. The researches of Zintl have also provided very valuable information on the interatomic distances in alloys. In the NaTl structure every Na atom is surrounded by four other Na atoms and four Tl atoms, these eight atoms being all at the same distance and situated at the corners of a cube. In such an arrangement the radii of the two atoms must be the same, so that these structures are particularly convenient for atomic radii determinations. The radii found in this way by Zintl for Zn, Cd, Ga, In and Tl are in good agreement with Goldschmidt's values for eight-fold co-ordination, but in the case of the Li and Na atoms Zintl's values are some 15 per cent. smaller. It therefore appears that the radii of the non-noble metals cannot be regarded as constant in the alloys, and it would seem probable that the reduction in the atom size and the failure of the Hume-Rothery rule have a common origin associated with the readiness with which the non-noble constituents of these structures are deprived of their valency electrons.

Compounds of the Metals with Light Non-Metallic Elements

'Interstitial Structures.' Another series of compounds which has been extensively investigated by X-ray methods are those

[1] In some cases, however, an ordered super-lattice is also observed: Bernal, *Nature*, **122**, 54 (1928); Carlsson and Hägg, *Z. Kristallogr.*, **83**, 308 (1932).

[2] Zintl and Dullenkopf, *Z. phys. Chem.*, Abt. B, **16**, 195 (1932); Zintl and Brauer, *ibid.*, Abt. B, **20**, 245 (1933); Zintl and Neumayr, *ibid.*, Abt. B, **20**, 272 (1933).

[3] Zintl and Neumayr, *Z. Electrochem.*, **39**, 86(1933); Zintl and Harder, *Z. phys. Chem.*, Abt. A, **154**, 47 (1931).

of the transition metals with the light elements hydrogen, boron, carbon and nitrogen. Here rules governing the structure types observed have been more difficult to discover, but recently Hägg [1] has succeeded in finding certain regularities among these compounds. When the metal atom is sufficiently large compared with the non-metallic component the lattice is extremely simple in type, but if the radius ratio is less than about 1·7 very complex structures are frequently observed. An explanation of this occurrence is to be found in the fact that in the first case so-called 'interstitial structures' [2] obtain in which the metal atoms are in contact and the non-metallic elements are situated in the interstices between them. In such cases the lattice is usually the same as that of the pure metal and therefore either cubic or hexagonal close packed with a co-ordination number of 12, or body-centred cubic with a co-ordination of 8. Occasionally a simple hexagonal lattice with an axial ratio $c/a = 1$ is observed. The interstitial compounds have in general a wide range of composition within each phase, whereas with the complex structures the range is very narrow.

Of the compounds for which the radius ratio is sufficiently large for the structures to be of the simple interstitial type we may instance the borides of the rare earths and of thorium. The borides of iron and nickel, on the other hand, have a radius ratio less than 1·7 and the structure is more complex, and the same is true of the carbides of the metals Cr, Mn, Fe, Co and Ni. In some cases, as with the borides of Y, Zr, Hf and U, the radius ratio lies so close to the critical value that it is not possible to predict what type of structure will obtain.

Types of Interstitial Structures—The Normal Type. A closer study of the interstitial structures, that is, the relatively simple structures which obtain when $R_M : R_X > 1{\cdot}7$, shows that these structures can be divided into two main types. In the first of these, which we may term the normal type, the non-metallic atoms are individually distributed in the interstices of the lattice, while in the second type, the so-called 'X_2-structures,' the non-metallic atoms are arranged in pairs in these interstices. Considering for the moment only the former of these two types, we find that a characteristic feature of these structures is that the deformation of the metal lattice produced by the introduction

[1] Hägg, *Z. phys. Chem.*, Abt. B, **12**, 33 (1931); **6**, 221 (1929); **7**, 339 (1930); **8**, 455 (1930).

[2] 'Einlagerungsstrukturen': I take the translation from Bragg, "The Crystalline State."

of the non-metallic elements is always very small. Thus, to take an example, the structure of MnN and MoN may be regarded as a face-centred cubic lattice of metal atoms which has become distorted in the direction of one of the tetrad axes, thus in fact producing a face-centred tetragonal lattice. The small extent of the deformation, however, is illustrated by the fact that no case has so far been observed in which the axial ratio of this tetragonal lattice differs from unity by more than about 4 per cent. Similarly those interstitial structures of the normal type which are based on a simple hexagonal arrangement of the metal atoms are usually found to have an axial ratio of about 0·98. In the X_2 type of structures the distortions of the simple lattice are in general considerably larger.

Classification of the Normal Interstitial Structures. On account of the very small scattering power of the light non-metallic elements, the X-ray determination of the exact positions occupied by these atoms in the interstitial compounds is not easy. Certain principles, however, governing the distribution of these atoms have appeared, and it is found that the non-metallic atoms are always in contact with the neighbouring metal atoms, and that they occupy the largest spaces in the structure in which this contact can be achieved. The co-ordination of the non-metal is thus the maximum possible. These principles provide us with the basis of a very convenient classification of the interstitial structures, for we can regard as of one type all those structures which are produced by the occupation of interstices of a given kind in a given type of metal lattice, quite regardless of the number of such interstices which are in actual fact so occupied. On such a classification the type of structure is therefore specified by (1) the nature of the metal lattice and (2) the co-ordination number of the non-metallic atoms.

A justification for this classification is found in the observation that interstitial structures never occur in which more than one type of interstice is occupied by non-metallic atoms, so that such structures never contain more atoms of the non-metal than are required completely to fill all the equivalent positions of one type. When only some of the equivalent positions are occupied we assume that the distribution of non-metallic atoms is the most uniform one possible; if these atoms can form a simple regular lattice such a lattice is formed, otherwise their distribution is statistical. When all the interstices are occupied the distribution is naturally completely ordered.

Following our classification we may regard as the first type

of interstitial structures those in which the metal atoms lie on a face-centred cubic lattice. These structures we may further subdivide according as the co-ordination number of the non-metallic component is 6 or 4. In the former case an NaCl-like arrangement results, and if all the interstices are occupied we obtain a compound of composition MX. If, however, the co-ordination is only four and all the interstices are occupied the structure is of the fluorite type with composition MX_2. The same co-ordination can, however, obtain in a phase of composition MX if only one half of the available interstices are filled, and a zincblende-like structure would in fact be of this kind. The other classes of interstitial structures can be developed in precisely the same way from the hexagonal close-packed, body-centred cubic, and simple hexagonal lattices.

A review of the interstitial structures of what we have called the normal type is given in Table XIV., arranged in conformity with the classification just discussed. Here it will be seen that the structures are divided into four main classes, based on the

TABLE XIV. *Classification of Normal Interstitial Structures*

C.N.	Co-ordinates of Metal Atoms.	C N. of Non-metal Atoms.	Type Symbol and Possible Co-ordinates of Non-metal Atoms.	Condition for Occurrence.
12	12a Face-centred Cubic 0 0 0, 0 ½ ½ ½ 0 ½, ½ ½ 0	6	12a, 6 ½ ½ ½, ½ 0 0 0 ½ 0, 0 0 ½	$R_M : R_X < 2{\cdot}4$
		4	12a, 4 ±¼ ¼ ¼, ±¼ ¾ ¾ ±¾ ¼ ¾, ±¾ ¾ ¼	$R_M : R_X < 4{\cdot}4$
	12b Hexagonal Close Packed 0 0 0, ⅓ ⅔ ½	6	12b, 6 ⅔ ⅓ ¼, ⅔ ⅓ ¾	$R_M : R_X < 2{\cdot}4$
		4	12b, 4 0 0 ⅜, ⅓ ⅔ ⅞ 0 0 ⅝, ⅓ ⅔ ⅛	$R_M : R_X < 4{\cdot}4$
8	8a Body-centred Cubic 0 0 0, ½ ½ ½	4	8a, 4 ±0 ½ ¼, ±½ 0 ¼ ±¼ ¼ 0, ±0 ¼ ¼ ±¼ 0 ¼, ±¼ ¼ 0	$R_M : R_X < 3{\cdot}4$
	8b Hexagonal $c/a = 1$ 0 0 0	6	8b, 6 ±⅓ ⅔ ½	$R_M : R_X < 1{\cdot}9$

type of metal lattice, and that the first two of these are further subdivided according to the co-ordination of the non-metallic element. In the last column of the table is given the radius ratio condition for the occurrence of a structure of a given type. This condition is based on the assumption that the atoms of the non-metallic constituent are always in contact with the neighbouring metal atoms. No structure has yet been found in which this condition is not satisfied. When, however, this condition can be satisfied by the occupation of more than one type of interstice it appears to be always the largest that is filled.

The X_2-structures. The second principal class of interstitial compound, the X_2-structures, as we have already mentioned, are characterised by the fact that here the atoms of the non-metallic component occur grouped in pairs. These structures

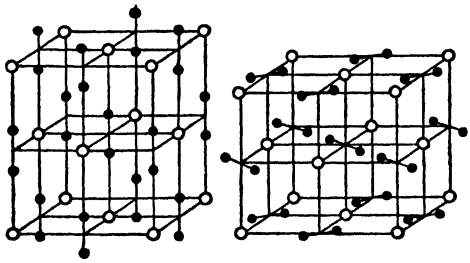


Fig. 5. Fig. 6.

X_2-structures.

are of two kinds, both of which may be most conveniently described in terms of a face-centred cubic lattice, by the distortion of which they are produced. In the first of these, illustrated in Fig. 5, the X_2 groups are all arranged parallel to one edge of the cube, which is thereby extended in this direction ; such a structure is found in LaC_2, CaC_2, PrC_2, NdC_2 and UC_2, in all of which the amount of distortion is measured by an axial ratio of 1·15–1·20. In the second kind of structure, shown in Fig. 6, the X_2 groups lie all parallel to a cube face but with their axes in two mutually perpendicular directions : the distortion thus produced gives rise to a tetragonal lattice with an axial ratio $c : a < 1$. This structure is found in ThC_2 and ZrC_2, in both of which compounds $c : a = 0{\cdot}90$.

Occurrence of Interstitial Structures. A general survey of the interstitial compounds shows that these structures are common among phases of the composition M_4X, M_2X, MX and MX_2, and that of these M_2X and MX occur particularly frequently.

The M_2X phases are characterised by having a very wide region of homogeneity on either side of the composition indicated by the formula, and are usually based on a hexagon close-packed metal lattice. In the MX_2 compounds, on the other hand, the region of homogeneity is generally very narrow, the structures occur only when the radius ratio $R_M : R_X$ is large, and are usually of the X_2 type. The MX_4 phases appear always to have a face-centred cubic lattice of metal atoms, even though this structure is not observed with some of the pure metals concerned. In the MX compounds also, the metal lattice is face-centred cubic, so that here a NaCl-like arrangement is to be expected. In certain cases, however, where the non-metal atom is very small, as, for example, in Ti_2H and Zr_2H, such an arrangement would necessitate a very large radius for the hydrogen atom, and in these cases Hägg has suggested that these atoms occupy the next largest spaces, thus producing an incomplete zincblende-like structure with a reasonable radius of about 0·4 A.U. for the hydrogen atom.

CHAPTER XII

THE CRYSTAL CHEMISTRY OF MOLECULAR COMPOUNDS

THE number of molecular structures which have so far been investigated is very small compared with the number of ionic and atomic structures to which X-ray methods have been applied. Nevertheless it is sufficiently large for many most interesting and important results to have been obtained.

The Structure of Gases at Low Temperatures. The structures of a number of gases at very low temperatures have been determined, among which we may mention particularly the hydrogen compounds of the light elements. In these compounds it would be expected that even at low temperatures the molecule would still possess energy of rotation in the lattice, and in confirmation it is found that lattices based on a close packing of the molecules are here very common. According to Grimm [1] we should find in such cases that the radius of the inert gas atom in its lattice is not very far from that of the corresponding 'pseudo-atom,' and the following comparison of the radius of the argon atom with the molecules of HCl, H_2S, and PH_3 show that this is approximately the case :

A	HCl	H_2S	PH_3
1·92 A.U.	1·92	2·05	2·23

In this connection we may also remark the interesting resemblances between the structures of solid carbon monoxide and solid nitrogen, first pointed out by Vegard.[2] This case is only a special instance of the general resemblance between the structures of an element of atomic number z and the compound AX of elements of atomic numbers $z + n$ and $z - n$, $(n = 1, 2, 3)$. The structures of boron nitride and graphite furnish another example.

Atomic Radii in Molecular Compounds. Just as in other types of lattice, we find that interatomic distances within the molecule in molecular lattices depend on the type of binding forces that

[1] Grimm, *Atombau und Chemie*, in Scheel-Geiger's "Handbuch der Physik," **24**, 466 (Berlin, 1927).

[2] Vegard, *Z. Phys.*, **61**, 185 (1930).

are operative. With forces of a given type, however, the distances to a first approximation may be regarded as constant, so that it is possible to draw up a set of atomic radii by means of which intra-molecular distances in compounds with a given type of binding may be deduced. Table XV contains a few such radii obtained by Pauling[1] from observations on simple co-ordination lattices in which the forces are homopolar, and these radii can therefore be used to calculate interatomic distances in molecules in which such forces occur. The amount of experimental material available for the direct confirmation of Pauling's

TABLE XV. *Radii of Atoms bound by Covalent Forces in Molecules* (*after* Pauling)

Single Bond

H		B	C	N	O	F	Si	P	S
0·29	(0·375 in H_2)	0·89	0·77	0·70	0·66	0·64	1·17	1·10	1·04

Cl	Ge	As	Se	Br	Sn	Sb	Te	I
0·99	1·22	1·21	1·17	1·14	1·40	1·41	1·37	1·33

Double Bond

B	C	N	O	S
0·80	0·69	0·63	0·59	0·94

Triple Bond

C	N	O
0·61	0·55	0 52

radii is very meagre, but a comparison with interatomic distances determined from band spectroscopic data shows in general an agreement to within about 0·02 A.U. These radii are of great value not only in enabling interatomic distances to be deduced, but also conversely in that they permit the type of bonding forces to be determined in molecules in which the interatomic distances have been observed. Thus the interatomic distances in graphite and benzene show that here the carbon-carbon linkage is neither a simple single bond nor a double bond, but a resonance between the two, a fact which found a partial expression in the old Kekulé formula.

A few interatomic distances deduced from Pauling's radii are given in Table XVIa. It must be emphasised, however, that the distances here collected are those between atoms in the same molecule and that they do not necessarily bear any relation to the distance between the molecules themselves, and in fact the absence of any general rules governing the distance between

[1] Pauling, *Proc. Nat. Acad. Sci. Wash.*, **18**, 293 (1932).

atoms in neighbouring molecules constitutes one of the principal difficulties in this branch of crystal chemistry. In certain cases, however, it is possible to give minimum distances between such atoms, and a few distances of closest approach between halogen atoms in neighbouring molecules are given in Table XVIb. In compounds rich in halogens these distances play a particularly important part since here the large halogen atom dominates the structure, so that to a first approximation such compounds, whether they are layer lattices such as CdI_2 or typically molecular

TABLE XVI

(*a*) Intramolecular Atomic Distances.

C—C (aliphatic)	1·5$_4$ A.U.
C—C (aromatic)	1·4$_4$ „
C—N	1 4 „
C—O	1 2 „
C=S	1 6 „
C—Cl	1 8$_2$ „
C—Br	1 9$_6$ „
C—I	2·1$_3$ „

(*b*) Minimum Distance between Atoms of Neighbouring Molecules.

Cl—Cl	3·6 A.U.
Br—Br	3·7 „
I—I	3·9 „

lattices such as SiI_4, $TiBr_4$, TiI_4, etc., may be regarded as having a structure based on a close packing of halogen atoms. In all the particular instances we have quoted the I—I distance is about 4·2–4·4 A.U., and in the lattice of di-iodoacetylene C_2I_2 the distance between the iodines of neighbouring molecules is of the same order. Such a close-packed arrangement of the halogen atoms can, however, be expected only when the distance between the halogen atoms in the molecule is about the same as that between the halogens of neighbouring molecules. In CI_4, for example, we should not expect a close-packed distribution of iodine atoms.

The Structure of AX_4 Compounds. Most of the investigations so far carried out on the tetrahalides of the type AX_4 have revealed a very nearly regular tetrahedral structure for the molecule. In the case of CCl_4 the evidence has come from X-ray and electron diffraction experiments in the gas,[1] while for CBr_4 and CI_4 the direct structure determinations of Mark[2] and of Hassel and Kringstad[3] are available. The same conclusion is reached from the structure determinations on the cubic crystals

[1] Debye, Bewilogua and Erhardt, *Phys. Z.*, **30**, 84 (1929); Debye, *ibid.*, **31**, 142 and 419 (1930); Mark and Wierl, *Naturwissenschaft*, **18**, 205 (1930); Wierl, *Phys. Z.*, **31**, 366 (1930).

[2] Mark, *Ber. dtsch. chem. Ges.*, **57**, 1820 (1924); *Z. angew. Chem.*, **44**, 125 (1931).

[3] Hassel and Kringstad, *Tekn. Ugebl.*, **18**, 230 (1931).

SiI_4, $TiBr_4$, GeI_4 and SnI_4, in all of which structures the iodine atoms appear to lie on a cubic face-centred lattice so that both within the molecule and between neighbouring molecules the iodine-iodine distances are the same.[1]

There are, however, some compounds in which the existence of a tetrahedral arrangement of the atoms or radicals surrounding a carbon atom appears to be more questionable. Thus Mark and Weissenberg[2] found from X-ray investigations that the molecule of pentaerythritol $C(CH_2OH)_4$ possesses a tetrad symmetry axis and must therefore have a plane or pyramidal structure. This result, however, is based on assumptions as to the crystal class, which it is very difficult to substantiate.[3] Experiments on some bodies closely related to pentaerythritol show that these substances have an electric moment in benzene solution which is not to be reconciled with a tetrahedral molecule,[4] although here again the interpretation is ambiguous.[5] No structure appears yet to have been found in which an unsymmetrical distribution of the valencies of a carbon atom has been unequivocably proved, while in the great majority of aliphatic compounds so far investigated the structure is in complete agreement with the classical conception of a tetrahedral distribution of the valencies.

Hexamethylene-tetramine. As an example of the complete structure investigation of an organic substance we may instance the experiments on hexamethylene-tetramine $C_6H_{12}N_4$.[6] This structure is of particular interest since prior to the X-ray investigations the constitution was entirely unknown. The atomic arrangement found is illustrated in Fig. 7, in which the disposition of the carbon and nitrogen atoms is exactly the same as that of the oxygen and arsenic atoms in arsenolite As_4O_6. The position of the hydrogen atoms cannot, of course, be determined by X-rays, and in the figure they are so placed as to satisfy the tetrahedral arrangement of carbon valencies. The complete structure is made up by a repetition of the molecule at the points of a cubic body-centred space lattice.

Long Chain Compounds. X-ray investigations on the long

[1] Hassel and Kringstad, *Z. phys. Chem.*, Abt. B, **13**, 1 (1931); **15**, 274 (1932).
[2] Mark and Weissenberg, *Z. Phys.*, **17**, 301 (1923).
[3] Ebert, *Ber. dtsch. chem. Ges.*, **64**, 114 (1931).
[4] Ebert and Hartel, *Naturwissenschaft*, **15**, 669 (1927); Weissenberg, *ibid.*, **15**, 662 (1927).
[5] Højendahl, "Studies on Dipole Moments," Diss., (Copenhagen, 1928).
[6] Dickinson and Raymond, *J. Amer. Chem. Soc.*, **45**, 22 (1923).

chain aliphatic compounds were carried out as long ago as 1913 by powder photograph methods, and these early experiments revealed in these compounds plane zig-zag chains of carbon atoms with the tetrahedral angle of 109° 28′ between the carbon-carbon bonds. Later work using single crystals of the hydrocarbons and fatty acids has confirmed this structure and shown that in the paraffins these chains are perpendicular to the basal plane of the crystal while in the fatty acids they are inclined to this face. Still more recently the work on the long chain compounds has been further advanced by the investigations of Hendricks[1] on the halogen acid salts of certain primary amines. In the case

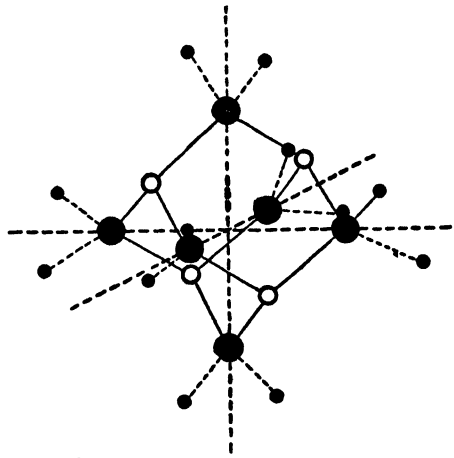


FIG. 7.—Structure of Hexamethylene-tetramine.

● = C. ○ = N. ● = H.

of *n*-amyl-ammonium chloride $NH_2C_5H_{11}.HCl$, to take an example, the structure is tetragonal with two molecules in the cell, and symmetry considerations demand that all the carbon atoms and the nitrogen atom of one molecule shall lie on a line parallel to the *c* axis of the crystal. This arrangement not only necessitates a much smaller C—C distance than that otherwise observed in aliphatic compounds, but also, of course, is not to be reconciled with a tetrahedral distribution of the carbon valencies. The most reasonable explanation of this striking discovery is to be found in the conception of the rotation of atom groups in the crystal, a conception discussed more fully in Chapter XIV below.

The investigations on the alkyl substituted ammonium halides

[1] Hendricks, *Z. Kristallogr.*, **74**, 29 (1930).

have confirmed the picture of a tetrahedrally co-ordinated nitrogen atom in ammonium compounds, and according to the form and size of the cation these structures are found to be closely related to those of either the NaCl or CsCl types.

Aromatic and Cyclic Compounds. Attempts to find the structure of benzene have not yet been successful, but that of the anorthic hexamethyl-benzene has been completely determined by single crystal methods.[1] In this structure the carbon atoms lie in a plane and to a close approximation the molecule as a whole possesses hexagonal symmetry. The distance between the carbon atoms in the ring is very nearly the same as in the graphite structure, namely 1·44 A.U., while the distance between a carbon atom of the ring and that of the associated methyl group is about 1·54 A.U., or close to the characteristic C—C distance found in aliphatic compounds. The plane structure of benzene has been recently completely confirmed by the analysis of anthracene where also the rings are plane.[2]

Another ring compound which is of especial interest is cyclohexane C_6H_{12}, for here the classical conception of a tetrahedrally co-ordinated carbon atom would lead to a highly symmetrical form for the molecule. The experimental demonstration of the existence of such a molecule would establish that this body is to be regarded as essentially aliphatic in nature. Unfortunately, however, the X-ray evidence is not complete, and it can only be said that the experiments so far carried out do not preclude the possibility of the symmetrical structure.[3] The same remarks apply to the investigations on a number of alcohol derivatives of cyclohexane.[4] In the case of 1 : 4-di-iodo-cyclohexane, however, the exact location of the two iodine atoms can be readily established, and here the observed distribution of these atoms leads to two possible values for the distance between the two iodine atoms of the molecular, either of which is consistent with the picture of the highly symmetrical molecule.[5] Experiments on the hexahalide cyclohexanes are in agreement with a molecule containing a puckered cyclohexane ring of tetrahedral carbon atoms.[6]

One further set of experiments on the structures of organic substances which we may mention are the recent investigations

[1] Lonsdale, *Proc. Roy. Soc.*, A, **123**, 494 (1929).
[2] Robertson, *Proc. Roy. Soc.*, A, **140**, 79 (1933).
[3] Hassel and Kringstad, *Tidsskr. Kemi, Bergv.*, No. 7 (1930).
[4] White, *Z. Kristallogr.*, **80**, 5 and 14 (1931).
[5] Halmoy and Hassel, *Z. phys. Chem.*, Abt. B, **16**, 234 (1932).
[6] Dickinson and Bilicke, *J. Amer. Chem. Soc.*, **50**, 764 (1928).

of Hendricks[1] on *p*-dichlorobenzene, *p*-dibromobenzene, and *p*-chlorbromobenzene. In the last of these bodies the chlorine and bromine atoms occupy equivalent positions, thus providing another example of the phenomenon, already discussed in Chapter IX., in which crystallographically identical positions are occupied by chemically different atoms.

The Structure of Natural Fibres

A very important field to which X-ray methods have been recently applied with conspicuous success embraces many complex, naturally occurring organic substances such as cellulose, rubber, silk, etc., and these substances all reveal by the way in which they diffract X-rays an ordered arrangement akin to that in a crystal. It has long been supposed that such substances contain molecules of great size, and it was to the size of the molecule that their characteristic physical properties were attributed. The X-ray experiments, however, have shown, even when the structure cannot be completely determined, that the dimensions of the unit cell are not sufficient to accommodate molecules of any great size. The solution of this difficulty is found in the fact that in such substances the unit cell contains a fraction only of a molecule, and in fact the molecule itself may extend indefinitely through the crystal. The observed spacings are then characteristic repeat distances within the molecule.

Polyoxymethylenes. Among the compounds of this type which we may consider rather more fully are the polyoxymethylenes, the polymerisation products of formaldehyde. These structures have been investigated by Staudinger and his co-workers,[2] who have shown that they have as their foundation a chain of alternate oxygen atoms and methylene groups :

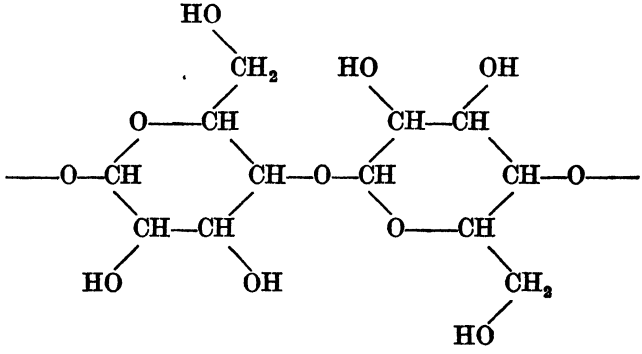
$$—CH_2—O—CH_2—O—CH_2—$$

These chains extend through the crystal parallel to the principal axis, giving rise to a repeat distance in this direction of 17·3 = 3 × 5·77 A.U., a distance which embraces nine —O—CH_2— units. The distance between neighbouring carbon atoms in the direction of the length of the chain is 1·92 A.U., which is very close to the value to be expected assuming that the valencies of the oxygen atom are inclined at 110° and that those of the carbon atom are tetrahedrally disposed.[3] The chain possesses the

[1] Hendricks, *Z. Kristallogr.*, **84**, 85 (1932).
[2] Staudinger, Johner, Signer, Mie and Hengstenberg, *Z. phys. Chem.*, **126**, 425 (1927).
[3] Sauter, *Z. phys. Chem.*, Abt. B, **18**, 417 (1932).

symmetry of a three-fold screw axis. The atoms within the chain are bound together by valency forces while adjacent chains are linked by very much weaker forces of the Van der Waal type.

Cellulose. The structure of cellulose has also been investigated by X-ray methods, and Staudinger predicted that here too chain-like molecules indefinitely extended would be found to form the basis of the structure, and that in fact the fibrous nature of the substance was due to this arrangement. The nature of the molecule composing this chain was suggested by chemical considerations. On partial hydrolysis cellulose is converted into cellobiose $C_{12}H_{22}O_{11}$, the molecule of which is composed of two glucose residues linked by an etheric oxygen atom. Starting from this fact Meyer and Mark [1] postulated that the cellulose chain is composed of a series of cellobiose residues similarly linked together, so that in fact the whole chain may be regarded as a number of glucose residues joined by oxygen atoms. In this way they calculated for the repeat period in the direction of the chain a distance of 10·3 A.U. in close agreement with the experimentally observed spacing. Adjacent glucose residues are not, however, similarly orientated, for the distance 10·3 A.U. embraces two such residues, which must therefore be inclined to one another. Meyer and Mark assume that they are rotated through 180° relative to each other, so that the chain has the symmetry of a screw diad axis. The composition of the chain is represented by the formula



while Fig. 8 illustrates the atomic arrangement of one unit of the chain similarly orientated. Only the carbon and oxygen atoms are here represented.

[1] Meyer and Mark, *Ber. dtsch. chem. Ges.*, **61**, 593 (1928); Sponsler and Dore, *Colloid Symposium Monogr.*, **4**, 174 (1926).

Space does not permit us to give an account of the numerous investigations which have been carried out on other complex organic substances, many of them, such as rubber, silk and wool,

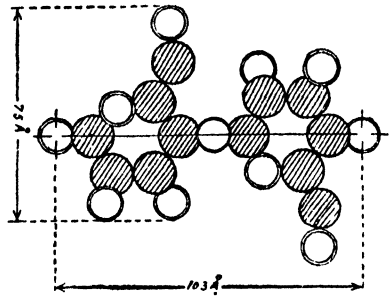


FIG. 8.

of the greatest technical importance, and here we can only remark that the discovery that so many of these compounds have as their basis an indefinitely extended chain-like molecule must be regarded as one of the most important in crystal chemistry.

CHAPTER XIII

A GEOMETRICAL THEORY OF POLYMERISATION IN THE SOLID STATE

THE possibility of deriving significant conclusions concerning the relationships between atoms and atom groups in a crystal from purely geometrical considerations, independently of a complete structure analysis, has led to valuable results in the hands of Reis [1] and of Weissenberg.[2] Of importance to the understanding of their work is the conception of an ' island ' (*Insel* [3]) in a crystal structure, by which term we mean a group of atoms in the lattice which is such that it shares no atom with any other structurally equivalent atom group. In this sense the CO_3 groups in the calcite lattice are to be considered as islands although the $CaCO_3$ groups cannot be so regarded since there is always a second such group having an atom in common with any given group. An island has its own set of symmetry elements and these may include glide planes and screw axes. If there are neither glide planes nor screw axes Weissenberg speaks of an ' islet ' (*Mikroinsel*), while if these symmetry elements are present they may give rise to an island-chain, -net, or -lattice. An island-lattice embraces the whole crystal.

If we now imagine the atoms of a lattice to be displaced in such a way that, while the symmetry of the lattice is preserved, as many atoms as possible are brought into coincidence, the atoms comprising an islet will reduce to a point. Such a point is termed a ' main islet ' (*Mikrohauptinsel*), and to the lattice built up of these points Weissenberg gives the name ' primary point lattice ' (*Leitpunktgitter*). The number of points of this lattice in the unit cell of the structure is the ' primary number ' (*Leitzähligkeit*), and this number is a quantity characteristic only of the space group :

[1] Reis, *Z. Phys.*, **1**, 204 (1920).

[2] Weissenberg, *Z. Kristallogr.*, **62**, 13, 52 and 612 (1925); **63**, 221 (1926); *Z. Phys.*, **34**, 406, 420 and 433 (1925); *Z. phys. Chem.*, Abt. A, **139**, 529 (1928).

[3] A satisfactory rendering of many of the definitions of this theory is very difficult, and it is a not uncommon practice among English writers to employ the German words untranslated. For this reason the original terms are given in parentheses.

TABLE XVII. *Association in Molecular Lattices*

	Contents of Unit Cell.	Space Group.	Primary Number.	Composition of Molecule
		1. *Hydrocarbons*		
Hexamethylbenzene	1 $C_6(CH_3)_6$	P1	1	1 $C_6(CH_3)_6$
Diphenyl	2 $C_{12}H_{10}$	$P2_1/c$	2	1 $C_{12}H_{10}$
Dibenzyl	2 $C_{14}H_{14}$			1 $C_{14}H_{14}$
Phenanthrene	4 $C_{14}H_{10}$			2 $C_{14}H_{10}$
Anthracene	2 $C_{14}H_{10}$			1 $C_{14}H_{10}$
Fluorene	4 $C_{13}H_{10}$			2 $C_{13}H_{10}$
Stilbene	4 $C_{14}H_{12}$			2 $C_{14}H_{12}$
		2. *Halogen Compounds*		
AX_4 (SnI_4, GeI_4, TiI_4, $TiBr_4$, SiI_4)	8 AX_4	Pa3	4	2 AX_4
CHI_3	2 CHI_3	$C6_3$	2	1 CHI_3
Sym. hexachlorcyclohexane	4 $C_6H_6Cl_6$	Pa3	4	1 $C_6H_6Cl_6$
Sym. 1 : 4-di-iodocyclohexane	2 $C_6H_{10}I_2$	$P2_1/c$	2	1 $C_6H_{10}I_2$
		3. *Amines and Amides*		
Urea	2 CON_2H_4	$P\bar{4}2_1m$	2	1 CON_2H_4
p-phenylenediamine $C_6H_4(NH_2)_2$	8 $C_6H_8N_2$	$P2_1/m$	2	4 $C_6H_8N_2$
o-phenylenediamine	4 $C_6H_8N_2$	P2/c	2	2 $C_6H_8N_2$
Acetamide	6 C_2H_5ON	R3c	2	3 C_2H_5ON
		4. *Polyhydric Alcohols*		
d-glucose	4 $C_6H_{12}O_6$	$P2_12_12_1$	4	1 $C_6H_{12}O_6$
d-fructose	4 $C_6H_{12}O_6$			1 $C_6H_{12}O_6$
d-cellobiose	2 $C_{12}H_{22}O_{11}$	$P2_1$	2	1 $C_{12}H_{22}O_{11}$
1 : 4-cyclohexanediol	6 $C_6H_{10}(OH)_2$	$P2_1/c$	2	3 $C_6H_{12}O_2$
1 : 2-cyclohexanediol	8 $C_6H_{10}(OH)_2$	Pbca	4	2 $C_6H_{12}O_2$
1 : 4-cyclohexanediol acetate	2 $C_{10}H_{16}O_4$	$P2_1/c$	2	1 $C_{10}H_{16}O_4$
		5. *Acids*		
Benzoic	4 C_6H_5COOH	$P2_1/c$	2	2 $C_7H_6O_2$
Phenylacetic	4 $C_6H_5CH_2COOH$	$P2_1/c$	2	2 $C_8H_8O_2$
Malonic	2 $C_3H_4O_4$	$P\bar{1}$	1	2 $C_3H_4O_4$
Maleic	4 $C_4H_4O_4$	$P2_1/c$	2	2 $C_4H_4O_4$

its value for each of the 230 space groups is tabulated by Weissenberg.[1]

The significance of these considerations arises from the fact that, according to Weissenberg, the contents of the main islets comprise the units (*Mikrobaustein*) of which the structure is built,

[1] Weissenberg, *Z. phys. Chem.*, Abt. A, **139**, 529 (1928).

and in fact are to be identified with the molecules as they exist in the solid state. Space does not permit us to enter further into a discussion of the physical significance of these ideas, but it is clear that on the chemical side they will be closely concerned with the question of association in molecular structures, and here we shall confine ourselves to this aspect of the problem.

Association in the Solid State. Let us suppose that the volume of the unit cell of a certain substance is V, its density is s, and that the primary number appropriate to its space group is l. If we then denote by M the molecular weight of the (possibly associated) molecule, we shall have, since there are l such molecules in the unit cell:

$$M = V \,.\, s \,.\, N/l,$$

where N is Avogadro's number. All the quantities on the right-hand side of this equation can be readily determined, so that the size of the molecule is geometrically prescribed in terms of the dimensions of the unit cell, the density, and the primary number appropriate to the space group. A comparison of M with the molecular weight given by the empirical formula reveals whether or not association takes place. In Table XVII a number of organic compounds are reviewed in the light of these ideas. In the last column is given the composition of the molecule in the solid, obtained by dividing the contents of the unit cell by the primary number, and it will be seen that in the amines, amides, and organic acids association is common, while the polyhydric alcohols are often unassociated.

The evidence for association given by Weissenberg's theory frequently finds satisfactory confirmation from physical and chemical observations on the solution or vapour, and this is true, for example, of many of the organic acids which in solution are known to show a pronounced tendency to associate. There are, however, naturally many cases in which association may well occur in the solid state although there is no evidence for it in solution or vapour. Among the elements polyatomic molecules appear to be very common, and in the cases of As, Sb and Bi there is evidence for association in the vapour just above the boiling point. In Bi, however, it must be remarked that the two atoms which in Weissenberg's sense constitute the diatomic molecule are separated by a distance greater than that between either of them and its six immediate neighbours. From a physical standpoint the association of these particular atoms appears very surprising.

CHAPTER XIV

THE ROTATION OF MOLECULES IN CRYSTALS

Pauling's Work. We have already mentioned briefly in an earlier chapter the experiments of Hendricks on the structure of *n*-amyl-ammonium chloride which indicate the possibility of a rotation of the carbon chains in the lattice of this body. Before passing on to discuss this case in detail or to give an account of other structures in which a rotation of the molecule appears to take place, we may consider some researches of Pauling who made the first attempt to apply the quantum theory to the problem of the rotation of molecules in a crystal lattice.[1] The work was primarily an attempt to explain the anomalously high entropy of solid hydrogen in terms of the rotation of the molecule. It is to be expected on purely classical grounds that in a molecular lattice in which the forces within the molecules are very much stronger than those between them, the molecule as a whole will possess not only energy of vibration about its mean position but also energy of rotation about the position of equilibrium. The extent to which this rotation takes place will depend on the way in which the potential energy of the molecule varies with its orientation. If the potential energy in the equilibrium position is less than that in other possible positions by an amount appreciably greater than kT per molecule the rotation will be confined to small oscillations about the equilibrium position. If, on the other hand, this difference is never as large as kT the kinetic energy of the molecule will be sufficient to bring about complete rotation.

On the quantum theory this simple picture remains essentially unchanged. In extreme cases when the difference between the maximum and minimum potential energy of the molecule is very large or very small agreement between the two theories is close, and only when this difference in energy assumes intermediate values do significant differences between the classical and quantum treatments arise. In the very simple case of a diatomic

[1] Pauling, *Phys. Rev.*, **36**, 430 (1930). See also Stern, *Proc. Roy. Soc.*, A, **130**, 551 (1931).

arrangement exact calculations show that the H_2 molecule in its lowest quantum state will possess practically free rotation, while molecules with a large moment of inertia, such as I_2, even at relatively high temperatures will execute only small oscillations about their mean position. In many cases it is to be expected that at low temperatures the rotation will be almost completely arrested, although near the melting point practically free rotation takes place. The transition from the state of orientated molecules to that of free rotation, however, naturally does not occur suddenly at a definite temperature, but rather takes place gradually over a small temperature range, since initially only a few of the molecules abandon their orientated positions. The transition is in general accompanied by an increase in the lattice dimensions and a corresponding reduction in the intermolecular forces, and it is therefore to be expected that in the neighbourhood of the transition temperature a volume change will take place while the molecular heat will pass through a maximum. Such a transition appears in fact to occur in methane between 18° K. and 22·8° K., and at the latter temperature the molecular heat shows a pronounced maximum. Between 20° K. and 90·6° K., the melting point, the rotating molecules form a cubic close-packed structure.

Structures containing Rotating Groups. Several other cases have been observed in which thermal properties show similar transitions, while with solid HCl, HBr and HI more than one such transition has been found, each of which may perhaps be due to the inception of rotation about some new axis. In general it is to be expected that molecules and complex ions of reasonably small moment of inertia will possess free rotation below the melting point. A common type of such radical with a small moment of inertia is that in which a large central ion is linked only to hydrogen atoms as in the NH_4 group in ammonium salts. Here the forces between the neighbouring tetrahedral groups are much stronger than in methane and at 20° K. no free rotation takes place. Even here, however, it is to be expected that free rotation will set in below the melting point, and in fact a transition region extending over about 10° has been observed at about 240° K.[1] The effect of the anion on the transition temperature appears to be very small, for in passing from NH_4I to NH_4Cl it rises by only 12° corresponding to an increase in the interionic forces with decreasing radius of anion. The structure

[1] Simon, *Ann. Physik*, **68**, 241 (1932); Simon, Simson and Ruhemann, *Z. phys. Chem.*, **129**, 339 (1930).

remains unaltered at the transition and the volume change is small.

The conception of a rotation of the NH_4^+ ion and H_2O and NH_3 molecules in a crystal lattice can frequently be invoked to account for apparent contradictions between the symmetry of these groups and that demanded by their position in the structure, while the possibility of rotation throws new light on Hendrick's observations on the type of carbon chain in the aliphatic primary amines. In the halides of these bases the cation appears to lie along a tetrad axis, a result which is to be reconciled neither with the classical picture of the carbon atom nor with the X-ray evidence from other long chain carbon compounds. It is easy to see, however, that the moment of inertia about its length of a carbon chain with the classical zig-zag structure will be very small so that rotation about this direction, resulting in an effective higher symmetry, is to be expected at ordinary temperatures. The observations of Hendricks on the same amine salts at liquid air temperatures are in qualitative agreement with this explanation.

Further evidence for the rotation of the carbon chain has been found by Müller,[1] who attributed to this phenomenon the transition which is observed a few degrees below the melting point in the paraffins $C_{24}H_{50}$ to $C_{44}H_{90}$, while Bernal[2] has observed a hexagonal rotating form of the alcohol $C_{12}H_{25}OH$ stable between 16° C. and 24° C. The distance between the carbon chains is 4·76 A.U., which may be compared with the distance of 4·85 A.U. found by Müller in the paraffins.

Among inorganic ionic structures several nitrates, in addition to the ammonium salts already discussed, display characteristic transition phenomena which reveal the possibility of a rotation of the anion in the lattice. Sodium nitrate has been investigated in some detail,[3] and shows a transition between 150° C. and 275° C. resembling that observed in the ammonium halides, in that the greater part of the transition takes place near the upper limit of this temperature interval. The salt crystallises in the rhombohedral system and the crystal class remains unaltered at the transition but the characteristic rhombohedral angle suffers a change of nearly 2°. The X-ray evidence is in agreement with this conclusion, for above a temperature of about 215° C. it is no

[1] Müller, *Nature*, **129**, 436 (1932).

[2] Bernal, *Nature*, **129**, 870 (1932); *Z. Kristallogr.*, **83**, 153 (1932).

[3] Kracek and Posnjak, *J. Amer. Chem. Soc.*, **53**, 1183 (1931); Kracek, *ibid.*, **53**, 2609 (1931); Kracek, Posnjak, and Hendricks, *ibid.*, **53**, 3339 (1931).

longer possible to ascribe any fixed positions to the oxygen atoms in the structure, and the nitrate group as a whole is to be regarded as rotating about the trigonal axis. Powder photographs at high temperatures show good agreement with the pattern to be expected on the assumption that the scattering material of the oxygen atoms is distributed round a ring normal to the trigonal axis and having a radius of $1{\cdot}15 \pm 0{\cdot}005$ A.U.[1] This is somewhat smaller than the N—O distance of 1·24 A.U. found in the low temperature form of the salt. Ammonium nitrate has also been studied,[2] and here it appears that in the cubic modification stable above 125° C. all the rotational degrees of freedom of both the ammonium and nitrate ions are fully excited. The result of this work on the nitrates indicates that rotation of the NO_3 ion is often to be found in these salts, and throws considerable doubt on the accuracy of many of the published structures.

[1] Bijvoet and Ketelaar, *J. Amer. Chem. Soc.*, **54**, 625 (1932).
[2] Kracek, Hendricks and Posnjak, *Nature*, **128**, 410 (1931).

APPENDIX

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'Das Ultrarote Spektrum,' Schaefer and Matossi: Springer, Berlin, 1930.

'Infra-red Analysis of Molecular Structure,' Rawlins and Taylor, Cambridge University Press, 1929.

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