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THE FINE STRUCTURE OF MATTER

PART I

X-RAYS AND THE STRUCTURE OF MATTER

A COMPREHENSIVE TREATISE ON ATOMIC AND MOLECULAR STRUCTURE

By C. H. DOUGLAS CLARK

VOLUME I.

THE ELECTRONIC STRUCTURE AND PROPERTIES OF MATTER

An Introductory Study of certain Properties of Matter in the Light of Atomic Numbers.

CONTENTS: Part I.—GENERAL INTRODUCTION. The Classification of the Elements—The Classification of Atomic Electrons—Line Spectra and Multiplicity—The Transitional and Rare Earth Elements—Valency and Chemical Combination. Part II.—PHYSICAL PROPERTIES AND MOLECULAR CONSTITUTION. Melting-Points and Boiling-Points—Atomic and Molecular Volumes—Atomic and Ionic Radii—Electrical Conductivity—Magnetic Susceptibility—Atomic Magnetic Moments—Cohesional and Other Properties.

VOLUME II. (IN THREE PARTS ISSUED SEPARATELY)

THE FINE STRUCTURE OF MATTER

The Bearing of Recent Work on Crystal Structure, Polarization and Line Spectra.

CONTENTS: Part I.—X-RAYS AND THE STRUCTURE OF MATTER. Space Lattices and X-Rays—The Crystal Structure of Elements—The Crystal Structure of Inorganic Compounds of Type AB—The Crystal Structure of Inorganic Compounds of Type AB_2—The Crystal Structure of Compounds of further Inorganic Types—The Crystal Structure of Compounds of Organic Types—The Crystal Structure of Colloids and Amorphous Substances—The Crystal Structure of Alloys, Intermetallic Compounds and Solid Solutions—Crystal Structure and Molecular Constitution. Part II.—MOLECULAR POLARIZATION. Dielectric Constants—The Debye Theory of Polarization—Molecular Refraction—Polar Molecules—Molecular Fields. Part III.—THE QUANTUM THEORY AND LINE SPECTRA. The Quantum Theory—The General Principles of Line Spectra—The Multiple Structure of Lines—Line Spectra and the Periodic System.

VOLUME III. IN PREPARATION

THE INTERPRETATION OF BAND SPECTRA

An Account of Spectroscopic Investigation in the Field of Molecular Structure.

CONTENTS: Part I.—MOLECULAR SPECTRA. Molecular Energy Levels—Pure Rotation and Vibration-Rotation Spectra—Electronic Bands—Dissociation and Predissociation—Mechanism of Chemical Reaction—Homopolar Valency and the Electronic Configuration of Molecules—Experimental Results in the Infra-Red—Experimental Results in the Visible and Ultra-Violet Regions—Isotopes and Nuclear Structure. Part II.—THE RAMAN EFFECT. Scattering Phenomena—Atomic Linkages and Molecular Frequencies. Part III.—INTRODUCTION TO QUANTUM MECHANICS. Quantum Mechanics and Molecular Structure—Matrix and Wave Mechanics—Achievements of Quantum Mechanics—Some Outstanding Problems—The Human Value of the New Physics.

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THE FINE STRUCTURE OF MATTER

The Bearing of Recent Work on Crystal Structure, Polarization and Line Spectra

Being

VOLUME II

of

A COMPREHENSIVE TREATISE OF ATOMIC AND MOLECULAR STRUCTURE

PART I:

X-RAYS AND THE STRUCTURE OF MATTER

BY

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To
MY MOTHER

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GENERAL PREFACE

THE progress of atomic and molecular theory in recent times has proved remarkably rapid and extensive. The subject has advanced along many different lines more or less independently and the research worker in a specialized branch often encounters no little difficulty in keeping in touch with developments not in his immediate sphere of thought. It has become increasingly difficult, though surely not less important, to correlate work carried out in different branches. It is in the hope that these diverse researches may be enabled to be considered more readily in inter-relation with each other and in respect of the effect of each contribution to the whole that the author has essayed the present task. A work which attempts to view the situation along various avenues of approach may perhaps also prove of value in enabling a given fact or principle to be found conveniently in the original literature.

The introduction of electron spin into physical theory by Uhlenbeck and Goudsmit in 1925 has greatly clarified the general theoretical situation, so that the present time seems appropriate for a review of the present summarizing kind. Moreover, it would appear that sufficient time has elapsed since this important contribution was made for its true significance to be appreciated.

The general plan of the work is that of separate volumes bearing individual titles, each volume being as far as possible complete in itself as an expression of some leading thought. The first three volumes at present projected are intended to deal with different aspects of more purely physical questions. Further volumes are in contemplation which shall be descriptive of matters of special chemical importance.

The treatment is non-mathematical, a few mathematical proofs being collected in appendices to certain chapters. The conclusions reached in *The Basis of Modern Atomic Theory*

(Methuen, 1926), designed to give the experimental background of the fundamental principles, are here assumed, thus saving a considerable amount of space. Methods of reasoning from the results obtained, rather than details of experimental procedure and technique, form the main concern of the present work.

References to the original literature necessarily occupy a considerable amount of space. Titles of papers are given in full; it is hoped that this procedure will facilitate ease of reference. Every attempt has been made to ensure that the references shall be not only as complete as possible, but also accurately quoted. To save space, references to summarizing papers are frequently given, so that in these cases many of the papers quoted in them need not be repeated in the lists.

The thanks of the author are warmly accorded to numerous colleagues who have helped him with advice and co-operation. It is with a deep sense of gratitude that he extends his cordial appreciation of this assistance, which has proved of the greatest value. On the other hand, the author accepts sole responsibility for design and execution, individual expression of opinion and any slips or defects overlooked during revision.

Each volume is brought up to date to the time of publication as far as possible. The author would be pleased to be informed of anything of significance which he may have inadvertently overlooked.

If the work is found to encourage in any measure the wider study and investigation of problems arising in a fascinating field of modern thought, or to assist and direct the energies of the army of workers, the author will be amply repaid for time and care entailed in its production.

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April, 1934.

PREFACE TO VOLUME II

MODERN physics has trained her most powerful weapons on the closely guarded strongholds of Nature. This is particularly true in the field of the fine structure of matter, where the scientific combatant, safely entrenched on high ground already won, glimpses with justifiable satisfaction the fertile lowlands where he may hope to reap the fruits of his campaign. Prominent amongst experimental means which have proved themselves especially efficient are the X-ray, the dielectric cell, and the spectroscope. La Mer,* in the introduction to a symposium on molecular constitution held under the auspices of the American Chemical Society in 1929, recognized these three instruments as assuming special significance at that time. Progress in the intervening period has done much to establish their importance. This matter forms the theme of the present volume, the three named experimental methods being treated in Parts I, II and III respectively (issued for convenience in three separate bindings).

Part I is devoted to discussion of crystal and related structures as determined by X-rays. Space is economized by reference to the valuable *Strukturbericht* (1931) prepared by Ewald and Hermann in connection with the *Zeitschrift für Kristallographie*. The second volume of this work, covering the period 1928 to 1932, has appeared this year (1936), and was therefore not available to the author during the preparation of his manuscript. The method of classification of crystal structures suggested in the 1931 volume has been followed as closely as possible, apart from certain amendments, especially in dealing with organic and intermetallic compounds (Tables XXIII, XXIV, XXV and XXVII). Complex inorganic compounds are classified according to number of atoms per molecule for

*V. K. La Mer: *Chemical Reviews*, 1929, *6*, 445–450.

ease in reference. It is hoped that no outstanding results in the period under review have been overlooked. Space is saved in references by not repeating papers cited by Ewald and Hermann : the present lists are intended to be used in conjunction with their work, so that it is hoped that the experimental data on any given substance may be found quickly and conveniently in the original literature. In the final chapter on the relation between crystal structure and chemical constitution, the author gratefully acknowledges the assistance he received from the fruitful discussion held under the auspices of the Faraday Society in 1929.

The Debye theory of polarization, Fajans' theory of deformation and the derivation and meaning of dipole moments form the leading themes of Part II. The more refined measurements of dielectric constants and refractive indices have played an important part. The comprehensive *Table of Dipole Moments* (1934) of Hampson and Marsden published in the *Transactions of the Faraday Society*, has proved itself remarkably useful in again saving reference space and increasing the availability of experimental data. A detailed account of work on the Kerr Effect closes the Part. Polarization phenomena are found to take their place alongside the other main avenues of approach in providing valuable information about the structure and stereochemistry of organic and inorganic compounds.

Discussion of the results of spectroscopy is commenced in Part III, with special reference to newer adaptations of the quantum theory in relation to line spectra. The treatment is continued in Vol. 3 dealing with band spectra, but the part given separately here seems well able to stand alone, as an introduction to the study of spectra. The derivation of the quantum numbers, omitted from Vol. 1 : 5, is given as carefully as possible. In this connection, acknowledgment is due to the monograph and list of references due to Gibbs in his *Line Spectra of the Elements. I. Early observations and Systems of Classification* (1931), published in the *Review of Modern Physics*. The present author is satisfied if he has met with any success in his attempt to impart to those unfamiliar with recent developments the fascination that he feels in that romantic

department of atomic science, the interpretation of spectra and the inward nature of the periodicity of the elements. More purely chemical considerations receive some attention in the closing chapter of the volume. An electronic periodic table has appeared in time to be included in the Appendix to Part III.

Even with the saving of space effected by utilization of the summarizing works mentioned above and of others referred to in the text, it was soon realized that a very large number of references still remained. The question of the amount of space which should be devoted to their accommodation occupied the attention of the author for some time, as a consequence of which it was decided to depart from previous practice to a certain extent, by omitting the titles of papers in those chapters which dealt mainly with experimental data. It was found possible to retain the titles in other cases, where theoretical aspects seemed particularly important (chapters I, XI, XIV, XV, XVI and XVIII). It is hoped that the change of policy necessitated by exigencies of space will not diminish the usefulness of the book.

The preparation of a work of the present kind by one individual must necessarily be spread over a considerable period of time, and it was deemed preferable to bring the whole volume up to a certain date rather than to add to portions (written at later times) work done after the date. The book is designed to cover the period up to that surveyed by *Science Abstracts* (*Physics*) of January, 1935. From this definite date, more recent work may be found in later numbers of the above and other lists of abstracted papers.

References in the text to *The Basis of Modern Atomic Theory*, mentioned in the General Preface, are given as *Basis*, with sectional reference number.

The author desires to acknowledge with thanks the kind permission of the Editors of the *Philosophical Magazine* to reproduce Fig. CXIII, and to the Editor of the *Proceedings of the Leeds Literary and Philosophical Society* in respect of Figs. CVII and CXXII. In all cases, the diagrams have been specially drawn for this work, and the author's thanks are due to Mr. R. G. A. Dimmick, who prepared some of the original

drafts for this purpose. The kind permission of Professor Planck and Messrs. Methuen, Ltd., to reproduce the quotation facing page 1 is gratefully acknowledged. The author's thanks are also accorded to Miss L. Wilson, for assistance in indexing and proof-reading.

C.H.D.C.

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November, 1936.

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LIST OF SYMBOLS

(VOLUMES I, II, III.)

Note.—As far as possible, in specifying quantum numbers, capital letters refer to atoms; small letters to electrons; large Greek letters to molecules; small Greek letters to molecular electrons.

Symbol

A Atomic weight; area; number of molecules in ground state; Mendeljéeff group; amplitude of wave motion; any constant quantity.

B Constant of rotational spectra; limiting area; Mendeljéeff group; magnetic induction; any constant quantity.

C Curie's constant; specific heat, at constant volume C_V, at constant pressure C_P; any constant quantity.

D Density; electric displacement; spectral series; heat of dissociation; constant of rotational spectra; diffusion constant.

E Energy; molecular surface energy; electric field; number of outermost electrons; extension coefficient; electron affinity.

F Force; electric force acting on a molecule; free energy; spectral series; lowering of surface tension; wave-number of molecular spectral term.

G Co-ordination number.

H Magnetic field strength; quantity of heat; Hermitian polynomial.

I Moment of inertia; ionization energy; electric moment of unit volume (polarization); intensity of magnetization; integration constant.

J Inner quantum number; potential energy; ionization potential; interaction integral.

K Rotational quantum number; Kerr constant; symbol for absolute temperature; equilibrium constant; any constant quantity.

L Serial quantum number; heat of solution.

Symbol

M	Magnetic quantum number ; constant of rotational fine structure of electronic bands ; molecular weight.
N	Avogadro number ; frequency of revolution ; periodic group number ; Weiss molecular field constant.
O	Optical representation of energy level.
P	Vapour pressure ; parachor ; pressure of a gas ; molecular polarization ; spectral series.
Q	Heat of vaporization ; work done on an atom to give ions.
R	Gas constant ; Rydberg constant ; gyromagnetic ratio ; electrical resistance ; molecular refraction ; term multiplicity.
S	Spin quantum number ; heat of sublimation ; spectral series ; entropy.
T	Kinetic energy ; absolute temperature.
U	Lattice energy.
V	Electric potential ; energy in volts ; potential difference ; inner potential of metal ; molecular volume ; volume of a gas ; number of valency bonds ; heat of formation of a vapour from gas ions.
V_0	Zero volume.
W^0	Heat of hydration ; work done ; probability of a state ; negative energy of electron orbit.
X	Magnetic susceptibility.
Z	Atomic number.
Z_e	Effective nuclear charge.

---

a	Constant for spectral series ; van der Waals constant ; amplitude of simple harmonic motion ; atomic radius (a_0 or a_H for hydrogen atom) ; any constant quantity.
b	Number of Bohr magnetons ; van der Waals' constant ; amplitude of simple harmonic motion ; any constant quantity.
c	Velocity of light *in vacuo ;* any constant quantity.
d	Molecular diameter ; distance between unlike centres in crystals ; density of liquid or medium ; symbol for electron of a 10-group.
e	Electronic charge ; electric charge ; base of natural logarithms.
f	Fractional number of molecules per c.c. ; electric force ; symbol for electron of a 14-group.
g	Landé's splitting factor ; group velocity of waves.
h	Planck's constant.

Symbol	
i	Symbol for $(-1)^{\frac{1}{2}}$; chemical constant.
j	Inner quantum number (electron).
k	Mechanical equivalent of heat; azimuthal quantum number; Boltzmann constant; any constant quantity.
l	Serial quantum number (electron).
m	Mass of a body; magnetic quantum number; reduced mass of electron and nucleus; attraction exponent; electric moment; molecular magnetic moment resolved along field axis; induced moment of a molecule "current" number of line series; absolute weight of a molecule.
m_e	Electronic mass.
m_l	Orbital magnetic quantum number.
m_s	Spin magnetic quantum number.
n	Principal quantum number; index of refraction; repulsion exponent; number of molecules of gas per gram or per c.c.; number of electrons in an ion.
n_e	Effective quantum number.
n_r	Radial quantum number.
o	Angular velocity of orbital precession.
p	Angular momentum; number of electron pairs; number of atoms in unit group of crystal; Weiss magneton number; probability; symbol for electron of a 6-group.
q	Heat absorbed; space moved through; Dirac number.
r	Internuclear distance; radius; index of refraction; polar co-ordinate.
r_e	Equilibrium distance between nuclei.
s	Spin quantum number of electron; dipole distance of induced electric moment; symbol for electron of a 2-group.
s_n	Spin quantum number of nucleus.
s_p	Shielding constant.
t	Dipole distance of permanent electric moment; time; temperature (°C).
u	Ionic mobility; wave velocity.
v	Valency; number of valency electrons; velocity of particle; vibrational quantum number.
v_n	Homopolar valency.
v_p	Polar valency.
w	Wave-number of spectroscopic line.
x	Number of charges carried by dipole; constant of vibrational bands; any unknown quantity.
y	Constant of vibrational bands.
z	Effective atomic number; number of outer electrons.

Symbol

Λ Absolute value of orbital quantum number of molecule along nuclear line; wave-length of an electron inside a crystal.

Π Specific polarization.

Σ, Π, Δ Spectral series of molecules.

Φ Eigenfunction.

χ Magnetic susceptibility.

Ψ Space-filling constant; eigenfunction.

Ω Real volume of molecules in one gram-molecule of gas; inner quantum number of molecule.

α Polarizability; deformability; degree of ionization; spin eigenfunction.

β In relativity theory, v/c; coefficient of compressibility.

γ Coefficient of expansion.

δ Lattice distance; symbol for molecular electron.

ϵ Dielectric constant; unit quantum; phase constant of wave motion; eccentricity of ellipse.

η Viscosity coefficient.

θ Angle; polar co-ordinate.

κ Specific inductive capacity.

λ Wave-length; absolute value of orbital quantum number of electron in molecule along nuclear line; electrical conductivity.

μ Intrinsic molecular magnetic moment; total molecular electric moment; magnetic permeability; reduced mass of two nuclei; 10^{-4} cm.; quantum defect.

ν Frequency of spectroscopic line.

ρ Radius ratio; r/r_e.

π Ratio of circumference to diameter of circle; molecular electron.

σ Shielding constant (also s_p); magnetic moment per gram-molecule; saturation moment; surface tension; surface charge density; constant in theory of electron scattering; molecular electron.

τ Harmonic component in wave theory.

ω Angular velocity; vibrational frequency.

ω_e Equilibrium vibrational frequency.

LIST OF ABBREVIATIONS USED IN REFERENCES

Notes.—The reference numbers in the text appear raised above the type: thus [25] indicates "reference number 25" in the list at the end of the chapter in question. Cross-references between different volumes take the form: Vol. 3: 37B, which indicates "section 37, sub-section B of Volume 3." In the reference lists, the Journal is first quoted, as in the reference list below, next the year of publication, then the volume and first and last pages. Thus *Z.E.*, 1925, 31, 417–423 means that the paper is in the "*Zeitschrift für Elektrochemie* for 1925, Volume 31, pages 417 to 423." If the journal is such that it is occasionally renumbered from 1 with a new series number, the latter is placed first in small Roman figures: thus (vii.) 8 means "volume 8 of series number 7." If more than one number of a journal bears the same volume number, then a figure in brackets after the volume number shows this: thus 37 (2) means "the second volume in order of appearance bearing the volume number 37."

A.	*British Chemical Abstracts* (A. Pure Chemistry).
A.C.J.	*American Chemical Journal.*
A.C.P.	*Annales de Chimie et de Physique.*
A.E.S.	*Transactions of the American Electrochemical Society.*
A.F.Q.	*Anales de la Sociedad Espanola Fisica y Quimica.*
A.I.M.	*Memorie della Reale Accademia d'Italia.*
A.J.	*Astrophysical Journal.*
A.J.S.	*American Journal of Science.*
A.L.A.	*Atti delle Reale Accademia Nazionale dei Lincei.*
A.P.	*Annalen der Physik* (*Wiedemann's Annalen*, 1877–1899).
A.P.B.	*Bulletin International de l'Academie Polonaise des Sciences et des Lettres.*
A.P.(*F.*)	*Annales de Physique.*
A.P.P.	*Acta Physica Polonica.*
A.R.	*Annual Reports of the Progress of Chemistry.*
A.S.	*Sammlung Chemischer und chemisch-technischer Vorträge* (*Ahrens*).

A.S.B.	*Annales de la Société Scientifique de Bruxelles.*
A.S.I.	*Bulletin of the Academy of Science of the United Provinces of Agra and Oudh. Allahabad.*
A.T.M.	*Archiv für technische Messen.*
A.W.W.B.	See *W.B.*
B.	*Berichte de Deutschen chemischen Gesellschaft.*
B.A.	See *A.S.I.*
B.A.R.	*Report of the British Association.*
B.B.S.	*Bureau of Standards (Washington).*
B.C.S.J.	*Bulletin of the Chemical Society of Japan.*
B.J.R.	*British Journal of Radiology.*
B.N.C.	*Bulletin of the National Research Council.*
B.T.J.	*The Bell System Technical Journal.*
C.	*Transactions of the Royal Society of Canada.*
C.B.	*Bulletin de la Société chimique Belgique.*
C.I.	*Chemistry and Industry.*
C.J.R.	*Canadian Journal of Research.*
C.L.	*Communications from the Physical Laboratory of the University of Leiden.*
C.P.J.	*Journal of Chemical Physics.*
C.R.	*Chemical Reviews.*
C.Z.	*Chemiker Zeitung.*
D.P.	*Die Physik.*
F.	*Transactions of the Faraday Society.*
G.	*Gazzetta chimica italiana.*
H.	*Helvetica Chimica Acta.*
H.P.A.	*Helvetica Physica Acta.*
I.A.P.	*Proceedings of the Indian Academy of Science.*
I.E.C.	*Industrial and Engineering Chemistry* (Analytical Edition since 1929).
I.J.P.	*Indian Journal of Physics.*
J.A.C.S.	*Journal of the American Chemical Society.*
J.C.P.	*Journal de Chimie physique.*
J.C.S.	*Journal of the Chemical Society.*
J.E.	*Jahrbuch der Radioaktivität und Elektronik* (see *P.Z.*)
J.F.I.	*Journal of the Franklin Institute.*
J.J.P.	*Japanese Journal of Physics.*
J.M.	*Journal of the Institute of Metals.*
J.O.S.	*Journal of the Optical Society of America.*

J.P.	*Journal für praktische Chemie.*
J.P.C.	*Journal of Physical Chemistry.*
J.R.	*Le Journal de Physique et le Radium* (*Journal de Physique* prior to 1920).
J.S.C.I.	*Journal of the Society of Chemical Industry.*
J.S.G.T.	*Journal of the Society of Glass Technology.*
J.T.I.	*The Journal of the Textile Institute.*
J.W.	*Journal of the Washington Academy of Sciences.*
K.B.	*Kolloidchemische Beihefte.*
K.C.S.M.	*Memoirs of the College of Science, Kyoto Imperial University.*
K.M.G.S.	*Arkiv för Kemi, Mineralogi och Geologie* (Stockholm).
K.Z.	*Kolloid-Zeitschrift.*
L.	*Liebig's Annalen der Chemie.*
M.	*Monatshefte für Chemie.*
M.M.	*Mineralogical Magazine.*
N.	*Nature.*
N.C.	*Il Nuovo Cimento* (Bologna).
N.G.T.	*Norsk Geologisk Tidschrift.*
N.W.	*Naturwissenschaften.*
O.	*Observatory.*
P.	*Recueil des Travaux chimiques des Pays-Bas et de la Belgique.*
Pa.	*Physica.*
P.A.S.I.	See *I.A.P.*
P.A.T.	*Proceedings of the Imperial Academy* (*Tokyo*).
P.A.W.A.	*Proceedings d. Koninklijke Akademie van Wetenschappen te Amsterdam.*
P.C.P.S.	*Proceedings of the Cambridge Philosophical Society.*
P.C.R.T.	*Scientific Papers of the Institute of Physical and Chemical Research* (*Tokyo*).
Ph.	*Physics.*
P.I.A.	*Proceedings of the Indian Association for the Cultivation of Science.*
P.I.A.T.	*Proceedings of the Imperial Academy* (Tokyo).
P.L.P.S.	*Proceedings of the Leeds Philosophical and Literary Society* (*Scientific section*).
P.M.	*The London, Edinburgh and Dublin Philosophical Magazine.*

P.M.S.J.	*Proceedings of the Physico-Mathematical Society of Japan.*
P.N.A.	*Proceedings of the National Academy of Sciences.*
P.P.S.	*The Proceedings of the Physical Society.*
P.R.	*The Physical Review.*
P.R. (*Supp.*)	*Physical Review Supplement* (becomes *R.M.P.* after Volume I).
P.R.S.	*Proceedings of the Royal Society.*
P.R.S.E.	*Proceedings of the Royal Society of Edinburgh.*
P.T.	*Philosophical Transactions of the Royal Society of London.*
P.Z.	*Physikalische Zeitschrift* (contains *J.E.* since 1924).
P.Z.S.	*Physikalische Zeitschrift der Sowjetunion.*
R.	*Comptes Rendus hebdomadaires des séances de l'académie des sciences.*
Ra.	*Radiology.*
R.M.P.	*Reviews of Modern Physics.*
S.	*Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.*
S.C.	*Science.*
S.E.	*Stahl und Eisen.*
S.F.	*Societas Scientairum Fennicæ, Acta et Commentationes* (Finland).
S.P.	*Science Progress.*
S.R.T.	*Science Reports of the Tokyo Bunriko Daigaku.*
T.	*Scientific and Technology Reports of the Tohoku Imperial University.*
T.H.	*Science Reports of the National Tsing Hua University* (*Series A*).
T.O.C.	*Transactions of the Optical Society.*
U.	*Nova Acta Regiæ Societatis Scientiarum Upsalensis.*
V.	*Verhanalungen der Deutschen Physikalischen Gesellschaft.*
V.K.A.	*Verschlagen d. Koninklijke Akademie van Weten schappen te Amsterdam* (see *P.A.W.A.*).
W.B.	*Sitzungsberichte der Akademie der Wissenschaften in Wien.*
Z.A.	*Zeitschrift für anorganische und allgemeine Chemie.*
Z.A.P.	*Zeitschrift für Astrophysik.*

Z.E.	*Zeitschrift für Elektrochemie.*
Z.G.	*Zeitschrift für Geophysik.*
Z.K.	*Zeitschrift für Kristallographie.*
Z.M.	*Zeitschrift für Metallkunde.*
Z.P.	*Zeitschrift für Physik.*
Z.P.C.	*Zeitschrift für physikalische Chemie.*
Z.T.	*Zeitschrift für technische Physik.*
Z.W.	*Zeitschrift für angewandte Chemie* (*Angewandte Chemie* since 1932).
Z.W.P.	*Zeitschrift für wissenschaftliche Photographie.*

It is well known that no science develops systematically according to a definite preconceived plan, but that its development depends upon practical considerations, and proceeds more or less simultaneously along different lines, corresponding to the many ways of looking at the problems, and to the time and views of the investigator. . . . It frequently happens that theories are found to be interrelated which were started from essentially different view-points; theories, when extended and completed, turn out to be similar and begin to influence one another, appearing helpful or inimical according to circumstances.

Max Planck, in *A Survey of Physics* (Methuen, 1925).

THE FINE STRUCTURE OF MATTER

PART I

X-RAYS AND THE STRUCTURE OF MATTER

CHAPTER I

SPACE-LATTICES AND X-RAYS

1. The Conception of the Space-Lattice

THE macroscopic properties of a crystal indicate some definite arrangement of its structural units. The development of characteristic plane faces and sharp edges, the method of growth, the action of etching agents, the not infrequent presence of regularly arranged inclusions, and the existence of cleavage planes join in proclaiming the presence of inward symmetry. Regularity of arrangement, however, is not a peculiar characteristic of crystals: it seems to be a more or less general property of all matter.

(A) **The Seven Systems of Crystal Architecture.** The early crystallographers Frankenheim and Bravais initiated the theory of the "space-lattice," thereby laying a new foundation in the science.

A space-lattice may be conceived as consisting of a *net of parallel reference planes* in three dimensions (Figure I). The *lattice-points* occur at the intersections of three, and the *axes of reference* at the intersection of two reference planes. The axes of reference lie in three directions in space, the points along any one axis occurring at equal intervals.

Seven systems of crystals have been distinguished, depending

on the way in which the axes of reference are chosen. These range from the Triclinic (lowest possible symmetry) to the Cubic system (highest possible).[1]

The cell shown in dark outline in Figure I is the " unit cell," which by infinite repetition in three dimensions gives the lattice. The axial lengths are a = OX, b = OY, c = OZ, and the angles α = YOZ, β = XOZ, γ = XOY. The unit cell is formed by

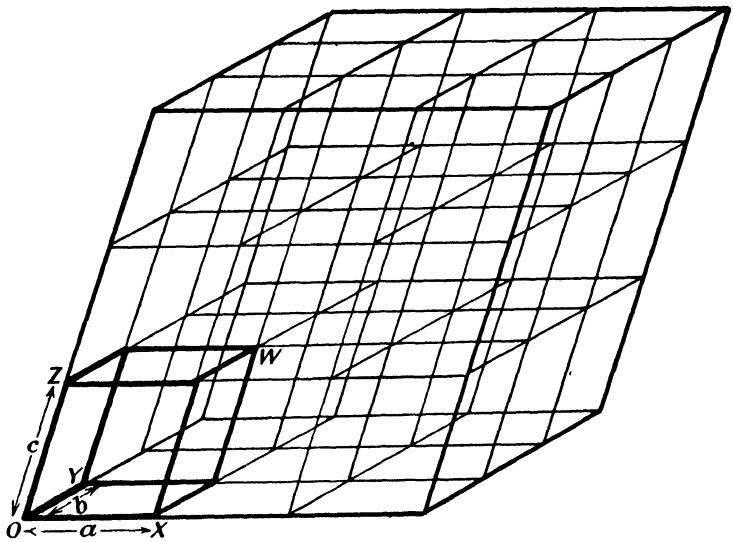

FIGURE I.—A SPACE-LATTICE. The intersections of three lines form the lattice points. The structure may be obtained by repetition of the unit cell OXYZW, the distances a, b and c being known as its primitive translations.

eight points, one at each corner, and contains the equivalent of $8 \times \frac{1}{8} = 1$ point, so that there are as many points as cells.

It is often very convenient to use another type of unit cell, which may have points in positions additional to the eight corners, *e.g.*, centres of faces. Bravais showed that only 14 types of such cells were possible, and that they belonged to the seven crystal systems, as depicted in Figure II. The systems may be defined with reference to the Bravais cells, where the axial lengths and angles are defined in the same way as

for the true unit cells. This is shown in the following scheme :—

Bravais cells	System	Relations between		Specification	
		Axes	Angles	Axes	Angles
I	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	a, b, c	α, β, γ
II, III	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$	a, b, c	β
IV, V, VI, VII	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	a, b, c	.....
VIII	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$; $\gamma = 120°$	a, c	.....
IX	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma$	a	α
X, XI	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	a, c	.....
XII, XIII, XIV	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	a	.....

The Cubic system gives rise to three Bravais cells, viz., cubic (XII), cubic body-centred (XIII) and cubic face-centred (XIV). Figure III shows that the points of the cubic face-centred lattice may be referred to a true unit cell, having one point only at each corner. Similar considerations apply in the other cases.

It may be noted that some authors take the Hexagonal and Rhombohedral systems together as one system (see Appendix to this chapter).

(B) **The Symmetry of Actual Crystals.** The symmetry elements of crystals may refer to planes, axes or points. A *plane of symmetry* is a *reflection* plane, dividing a crystal into halves, such that one half is the mirror image of the other half in the plane. An *axis of symmetry* is a *rotation* axis, such that the crystal may be brought into coincidence with itself by rotation through a specified angle about the axis ; if the smallest angle is 360°, the axis is said to be a one-fold axis, or to possess one-fold or zero symmetry ; if 180°, two-fold ; if 120°, three-fold ; if 90°, four-fold ; if 60°, six-fold. No other cases can arise. A *centre of symmetry* is an *inversion* point, such that a line drawn from any point of the crystal to it and extended an equal distance beyond it encounters a point similar to that at the other end of the line.

Careful examination has shown that whilst a crystal of a given system is always capable of being referred to a lattice having the highest possible symmetry of the system, the crystal as a

whole may have lower symmetry than the highest possible, or " holohedral " symmetry. This is connected with the varying

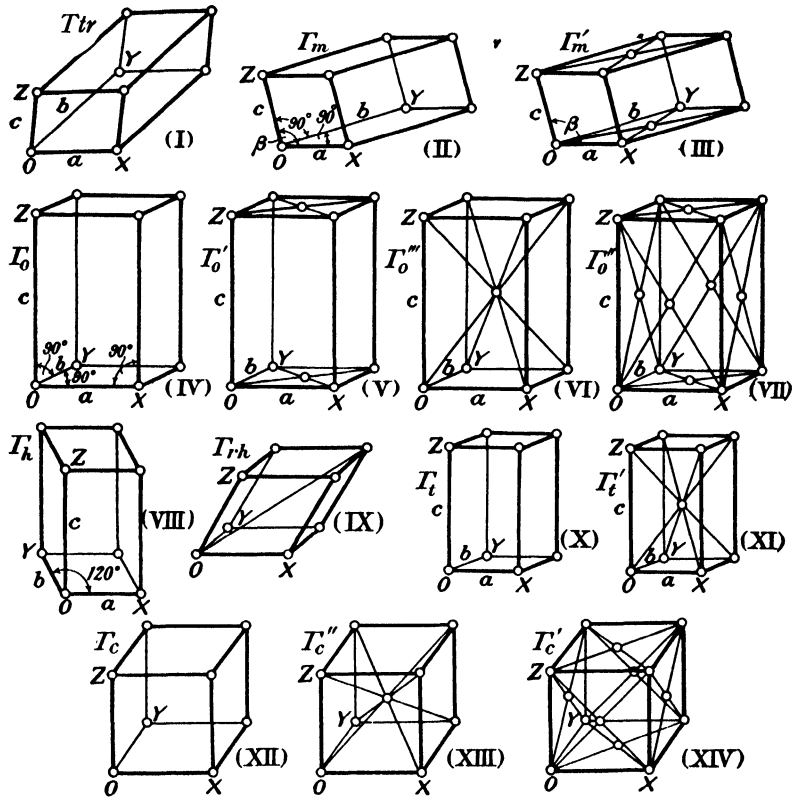

FIGURE II.—BRAVAIS' FOURTEEN TYPES OF UNIT CELLS. The Types are as follows:—(I) Triclinic; (II) Monoclinic; (III) Monoclinic, end face-centred; (IV) Orthorhombic; (V) Orthorhombic, end face-centred; (VI) Orthorhombic, body-centred; (VII) Orthorhombic, face-centred; (VIII) Hexagonal-trigonal; (IX) Rhombohedral (trigonal); (X) Tetragonal; (XI) Tetragonal, body-centred; (XII) Cubic; (XIII) Cubic, body-centred; (XIV) Cubic, face-centred.

The Monoclinic system has 1 2-fold axis (OY); the Orthorhombic, 3 2-fold axes (OX, OY, OZ); the Hexagonal, 1 6-fold axis (OZ); the Rhombohedral, 1 3-fold axis (diagonal from O); the Tetragonal, 1 4-fold axis (OZ); the Cubic, 4 3-fold axes (cube diagonals).

possibilities of the pattern grouped round each lattice point. A description of the " symmetry elements " of a crystal, in terms

of planes, axes and centre of symmetry is termed its " point-group," and crystals within the same system may have different point-groups. It is found that five cases must be distinguished within the Cubic system, leading to 5 Classes. Similarly, in the Triclinic system, there may be a centre of symmetry (Class 2) or no symmetry at all (Class 1). This extension eventually leads to 32 Classes of crystals, discovered by von Lang.

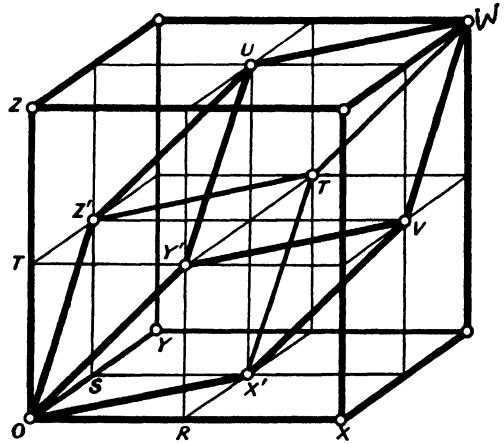

FIGURE III.—FACE-CENTRED CUBIC STRUCTURE. The true unit cell is OX' TZ' UWVY', and is rhombohedral.

(C) **The 230 Space-Groups.** Further consideration of space-lattices, regarded as geometrical systems of points, reveals the existence of a definite set of " space-groups," defining the symmetry elements of such points. The point-groups are derived from the crystal considered as a whole ; the space-groups reveal further detail, and are larger in number than point-groups. New symmetry elements, such as glide-planes (obtained by reflection plus translation parallel to the plane), and screw-axes (by rotation plus translation parallel to the axis) make their appearance. The increased number of cases arises from the fact that a point need not, in a symmetry

TABLE O.—SYSTEMS, CLASSES AND SPACE-GROUPS OF CRYSTALS.

SYSTEMS.	Space Lattices.	CLASSES No.	CLASSES Description	SPACE-GROUPS Nos.	Notation: Schoenflies	Notation: Wyckoff	Notation: Mauguin —I	Totals		
TRICLINIC or ANORTHIC	I	1	Asymmetric	1	C_1^I	1C-1	P1	1		
		2	Central	2	C_1^I or S_2^I	1Ci-1	$P\bar{1}$	1	2	21
MONOCLINIC	II III	3	Planar	3–6	$C_s^{I\text{-}4}$ or $C_{1h}^{I\text{-}4}$	2c-1 to -4	Pm	4		
		4	Digonal polar	7–9	$C_2^{I\text{-}3}$	2C-1 to -3	P2	3		
		5	Digonal equatorial	10–15	$C_{2h}^{I\text{-}6}$	2Ci-1 to -6	P2/m	6	13	15
ORTHORHOMBIC or RHOMBIC	IV V VI VII	7	Di-digonal polar	16–37	$C_{2v}^{I\text{-}22}$	2e-1 to -22	Pmm	22		
		6	Digonal holoaxial	38–46	$D_2^{I\text{-}9}$ or $Q^{I\text{-}9}$ or $V^{I\text{-}9}$	2D-1 to -9	P222	9		
		8	Di-digonal equatorial	47–74	$D_{2h}^{I\text{-}28}$ or $Q_h^{I\text{-}28}$ or $V_h^{I\text{-}28}$	2Di-1 to -28	Pmmm	28	59	74
RHOMBOHEDRAL or TRIGONAL	IX	9	Trigonal polar	143–146	$C_3^{I\text{-}4}$	3C-1 to -4	C3	4		
		12	Di-trigonal polar	149–154	$C_{3v}^{I\text{-}6}$	3e-1 to -6	C3m	6		
		10	Trigonal holoaxial	155–161	$D_3^{I\text{-}7}$	3D-1 to -7	H32	7		
		19	Di-hexagonal alternating	162–167	$D_{3d}^{I\text{-}6}$	3Di-1 to -6	$H\bar{3}m$	6		
		11	Trigonal equatorial	168	C_{3h}^{I}	6c-1	$C\bar{6}$	1		
		13	Di-trigonal equatorial	169–172	$D_{3h}^{I\text{-}4}$	6d-1 to -4	$C\bar{6}m$	4	28	102

	15	Hexagonal alternating	147–148	$C_{3i}^{1\cdot2}$ or $S_6^{1\cdot2}$	3Ci-1 to -2	C_3^-	2		
Hexagonal	14	Hexagonal polar	173–178	$C_6^{1\cdot6}$	6C-1 to -6	C6	6		
	17	Hexagonal equatorial	179–180	$C_{6h}^{1\cdot2}$	6Ci-1 to -2	C6/m	2		
VIII	18	Di-hexagonal polar	181–184	$C_{6v}^{1\cdot4}$	6e-1 to -4	C6mm	4		
	16	Hexagonal holoaxial	185–190	$D_6^{1\cdot6}$	6D-1 to -6	C62	6		
	20	Di-hexagonal equatorial	191–194	$D_{6h}^{1\cdot4}$	6Di-1 to -4	C6/mmm	4	24	126
Tetragonal	22	Tetragonal alternating	75–76	$C^{1\cdot2}{}_4$ or $S_4^{1\cdot2}$	4c-1 to -2	$P\bar{4}$	2		
	26	Di-tetragonal alternating	77–88	$D_{2d}^{1\cdot12}$ or $V_d^{1\cdot12}$	4d-1 to -12	$C\bar{4}2m$	12		
	21	Tetragonal polar	89–94	$C_4^{1\cdot6}$	4C-1 to -6	P4	6		
X	24	Tetragonal equatorial	95–100	$C_{4h}^{1\cdot6}$	4Ci-1 to -6	C4/m	6		
XI	25	Di-tetragonal polar	101–112	$C_{4v}^{1\cdot12}$	4e-1 to -12	P4mm	12		
	23	Tetragonal holoaxial	113–122	$D_4^{1\cdot10}$	4D-1 to -10	P42	10		
	27	Di-tetragonal equatorial	123–142	$D_{4h}^{1\cdot20}$	4Di-1 to -20	P4/mmm	20	68	194
Cubic or Regular	28	Tesseral polar	195–199	$T^{1\cdot5}$	T-1 to -5	P23	5		
	30	Tesseral central	200–206	$T_h^{1\cdot7}$	Ti-1 to -7	Pm3	7		
XII	31	Di-tesseral polar	207–212	$T_d^{1\cdot6}$	Td-1 to -6	$P\bar{4}3m$	6		
XIII	29	Tesseral holoaxial	213–220	$O^{1\cdot8}$	O-1 to -8	P43	8		
XIV	32	Di-tesseral central	221–230	$O_h^{1\cdot10}$	Oi-1 to -10	Pm3m	10	36	230

operation (reflection, rotation, etc.) be brought back to its original position, but may be transferred to a similar position in another cell. The enquiry is purely geometrical, and was made by von Federow and Schoenflies, who described 230 space-groups, as in Table O, where the numbers and names of each of the 32 Classes and the designations of the space-groups for each are shown. In the Schoenflies notation, a capital letter is used, followed by a lower symbol giving the Class, and an upper symbol showing the number of the space-group in the Class; thus C_{2v} refers to Class 7 of the Orthorhombic system, and C_{2v}^{1-22} to 22 space-groups, from C_{2v}^{1} to C_{2v}^{22}. In Wyckoff's system, the first symbol denotes the Class, the second (after a hyphen) the number in the class: thus 2e-1 to 2e-22 denotes the above 22 space-groups of Class 7. The assignment of space-groups to crystals was first made possible by the use of X-rays.[2]

The system of nomenclature has been improved by Hermann and Mauguin,[3] whose symbols make the determination of the space-group in question and its elements of symmetry directly possible, as a chess position may be set up from printed notation. In Mauguin's system, P denotes a simple (or " primitive ") lattice; A, B or C lattices centred on corresponding faces; F, a lattice centred on all faces; I, a body-centred lattice. The numbers following refer, in general, to the principal crystal axis: 1 (one-fold), 2, 3, 4, 6, whilst $\bar{1}$ means a centre of symmetry. Further letters, *m* refer to reflection, and *n*, *a*, *b*, *c* to glide-planes. (For further information, the reader is referred to more specialized works.) Mauguin's notation was adopted by international agreement at a conference held at Zurich in August, 1930. In the present work, however, Schoenflies' space-groups are generally quoted for brevity. Transference to Mauguin's system may be made by reference to the Table at the end of W. L. Bragg's book (see reference list).

It happens that what is a simplification in practice is not so convenient from the point of view of a summarizing Table, since, in Mauguin's system, each space-group has an entirely characteristic symbol of its own. In Table O, therefore, Mauguin's " normalized " symbol for the first space-group only

of each class is recorded. Reference to this Table may be made when one desires to pass from one system of notation to another.

(D) **The Law of Rational Intercepts.** Any three non-parallel planes corresponding to actual crystal faces may be chosen to define the axes by their intersections, but in practice

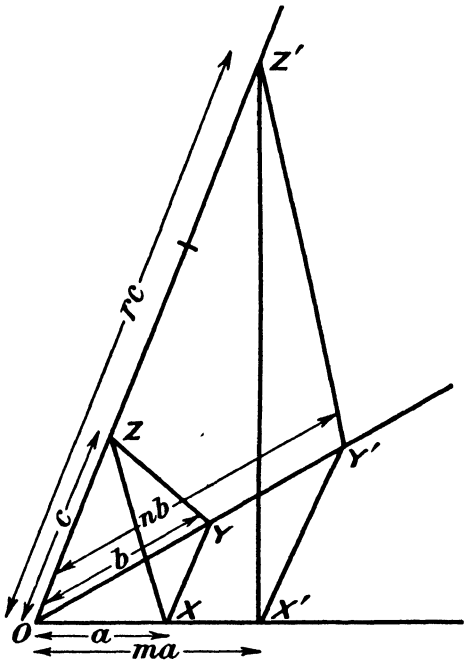

FIGURE IV.—ILLUSTRATION OF THE LAW OF RATIONAL INTERCEPTS.

certain planes present themselves as specially convenient for the purpose. (In the case of a cubic crystal, three faces of the cube are chosen, yielding a set of rectangular axes.) A *reference plane* must next be selected, corresponding to a suitable face which intersects each of the three axes. If XYZ is such a plane (Figure IV), and the intercepts on the axes are a, b, c, then other faces are possible parallel to a plane X'Y'Z', whose intercepts on the axes are ma, nb, rc, where m, n, r, are whole (usually small) numbers (Law of Rational Intercepts).

It has become usual to define a face by its *Miller Indices*, which are chosen so as to be *proportional to the reciprocals* of m, n, r of Figure IV. Thus where $m = 2$, $n = 2$, $r = 3$, the reciprocals are in the ratio $3 : 3 : 2$, and the description of the face X'Y'Z' is (332). The symbol of the reference plane is (111). One zero occurs in the symbol for a face parallel to an axis, and two zeros in that of a face parallel to a plane containing two axes of reference. (The use of reciprocals in this way is found to simplify the mathematical treatment, and leads to the " Law of Rational Indices.")

The eight faces corresponding, for example, to an octahedron or cube, are said to constitute a *form*, denoted by symbols such as {111} and {100}. The respective symbols of the eight faces of an octahedron of form {111} will be denoted by placing negative signs, where necessary, over the digits, corresponding to the sense of measurement along an axis. The octahedral face denoted by (111) is opposite to $(\bar{1}\bar{1}\bar{1})$.

(E) **The Law of Rational Indices.** In a space-lattice, *net-planes* are defined as sets of parallel planes chosen so as to include all the points. Theoretically, it is possible to choose net-planes in an infinite number of ways, and faces of the crystal concerned might be developed parallel to any chosen set. In general practice, however, it is found that only the relatively more thickly-packed, and more widely-spaced, net-planes correspond to actually occurring faces ; though certain exceptions are found, the cause usually being connected with some feature of chemical constitution.

It is not very easy to depict net-planes in three dimensions, but the argument may be readily extended from a figure in two dimensions. Figure V shows a portion of a lattice in one plane. The *unit cell* which gives the figure by repetition is OXWY, the lengths a, b being termed *primitive translations* of the cell. In three dimensions, there will be a third translation c out of the plane of the paper. The line XY corresponds to the *parametral plane* defining the lengths of the axes. The sets of lines marked (11), (21), (31), (41), (51) correspond to net-planes in three dimensions. The numbers chosen in designating rows in Figure V are analogous to the Miller indices for planes. For

example, for lines of the set (21), the intercepts on the axes OX, OY are in the ratio OV : OY $= \frac{1}{2}a : b = a : 2b$; so that the description (21) follows the Miller use of reciprocal ratios.

Where relatively few lattice-points occur on a line, the lines of the set are nearer together than when there are more points per unit distance. Faces corresponding to net-planes suggested by (11) in Figure V are more likely to occur than those

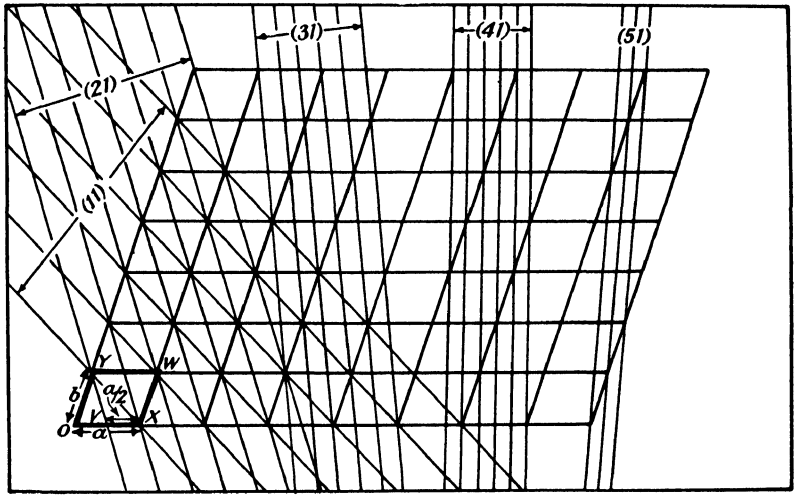

FIGURE V.—LATTICE IN TWO DIMENSIONS, SHOWING DERIVATION OF NET-PLANES.

for (51), for example, the lower indices being favoured in practice. Extending to three dimensions, the planes which contain a relatively large number of lattice-points per unit area are those for which m, n, r are whole, usually small, numbers. The reciprocals giving the Miller indices may therefore generally be expressed in terms of small integers. The Law of Rational Indices follows simply from the Law of Rational Intercepts.

Some historical details concerning the theory of crystals will be found in *Basis:* 17.

2. X-rays and Crystal Structure

The use of X-rays in obtaining diffraction effects with crystals originated with von Laue in 1912, the suggestion being based upon the space-lattice theory, and the probability that X-rays possessed wave-length of the same order of distance as that separating adjacent atoms in a crystal. The experiment of Friedrich and Knipping showed that a crystal at rest did indeed behave as a three-dimensional diffraction grating towards inhomogeneous X-rays passed through it. X-rays here show the quality of wave-structure, with wave-length of the order of an Ångström Unit (1 Å.U. = 10^{-8} cm.).

W. L. Bragg[4] used monochromatic radiation falling at glancing angle on a crystal surface, the angle being varied by rotation of the crystal, and the variation in intensity of the reflected beam with angle being measured by an ionization method. The effect of diffraction of a large number of atoms in a plane is to cause reflection of part of the radiation, the angle of reflection being equal to the angle of incidence; a further part passes on to the next layer of atoms, where part is again transmitted and part reflected. When the angle of incidence is such that the waves from different layers reinforce each other, an intensity maximum is observed for the reflected beam. According to Bragg's Law (see *Basis :* 17, Figure XIII),

$$2d \sin \theta = n\lambda \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where d is the distance between consecutive layers, θ the glancing angle, λ the wave-length of the X-rays, and n is a whole number. By directing the same X-rays upon different faces of an NaCl crystal, the structure was established (this vol.: Figure XIII).

In Laue's method, using heterogeneous radiation, a given net-plane in a crystal selects its own appropriate wave-length, reinforcement being produced in the observed diffraction pattern obtained by developing the emergent radiation on a photographic plate: it has the disadvantage that the spots in the pattern are not all formed by radiation of the same wave-length. In Bragg's development, the use of an ionization

chamber is often laborious: the difficulty may be largely surmounted by the use of an integrating photometer, in which alpha-rays are used to examine the photographic membrane on which reflected X-rays fall.[5]

Another method, developed mainly by Continental workers, known as that of the "rotating crystal," associated with the names of Rinne, Schiebold and Pólányi,[6] uses an homogeneous radiation directed along an axis, at right angles to which the crystal is caused to rotate. The method requires a small crystal, but a definitely developed face for presentation to the X-rays is not necessary. A rotation photograph containing "layer lines," consisting of a number of spots, is obtained on a photographic film bent into a cylinder round the axis of rotation; from this, information is derived respecting the unit cell of the crystal under examination. Linnik[7] has developed an independent rotating crystal method.

Reference must further be made to the "powder" method of Hull[8] and Debye and Scherrer,[9] the method of Davisson and Germer[10] applied to "electron waves," and that suggested by Clark and Duane.[11] A useful account of the methods employed, and the ways in which crystal structures are deduced from the observed intensities, is due to Darrow.[12]

The elucidation of crystal structure has involved a large amount of laborious calculation and a wealth of technical detail and phraseology. The procedure can be supplemented and abbreviated to some extent by the introduction of Fourier series.[13] Bragg[14] has partly avoided the necessity for elaborate calculation by a direct photographic method of superimposing intensities. A photograph is obtained in which blurred spots correspond to the relative positions of atoms in the crystal in question.

Kratky[15] has devised an X-ray apparatus for dealing with crystals of microscopic size, whilst Brill and Pelzer[16] suggest a new method for determining the sizes of particles by the Debye-Scherrer X-ray method. Hägg[17] has suggested the use of long-wave X-rays, such as the K-radiation from calcium, in crystal analysis. Hengstenberg[18] has used X-rays to detect the displacement (polarization) of ions in a KCl crystal in a high

electric field. Coster, Knol and Prins[19] find that not only the amplitude but also the phase of X-rays scattered by atoms is a function of the deflection angle.

Knowing the lattice " parameters " and the density of a substance, it is possible to calculate the number of atoms in the unit cell of its crystal. The calculation is carried out for cubic Na in Vol. I: 18B (end). Conversely, knowing the number of atoms in the unit cell from the determined structure, the density of the substance may be found, affording an often valuable check on the X-ray results.

W. H. Bragg[20] has summarized the development of X-ray analysis of crystal structure following Laue and his successors. The interpretation of X-ray diffraction patterns is possible in an infinite number of arrangements of " electron density." Use is made, in selecting the correct arrangement in a given case, of the centre of symmetry, known unit cell magnitudes and general chemical considerations.

APPENDIX TO CHAPTER I.

HEXAGONAL AND RHOMBOHEDRAL AXES

It is stated in the text that some authors prefer to treat the Hexagonal and Rhombohedral crystal systems as one. The relation between the two unit cells is not very clear from Figure II. However, examination of the rhombohedral unit cell of Figure XXXV (diagram for CALCITE structure) referred to the axes a_R = AD, α = DAF, reveals that the projection of points on a plane passing through A at right angles to the trigonal axis AA is hexagonal in form (see small diagrams at side of Figure XXXV). Hence, the system of points may be referred to a larger hexagonal unit cell having the axes a_H = DF, c_H = AA.

Consideration of the geometry of the figure reveals that transposition between the two sets of axes may be made by means of the following relations :—

(a) *From Rhombohedral to Hexagonal Axes.*

$$\left.\begin{aligned} a_H &= 2a_R \sin\frac{\alpha}{2} = a_R\sqrt{2-2\cos\alpha} \\ c_H &= 3a_R\sqrt{1-\frac{4}{3}\sin^2\frac{\alpha}{2}} = a_R\sqrt{3+6\cos\alpha} \end{aligned}\right\} \quad \ldots\ldots (2)$$

(b) *From Hexagonal to Rhombohedral Axes.*

$$\left.\begin{aligned} a_R &= \tfrac{1}{3}\sqrt{c_H^2 + 3a_H^2} \\ \alpha &= 2\sin^{-1}(a_H/2a_R) \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots (3)$$

The volume of the hexagonal unit cell is

$$V_H = \frac{\sqrt{3}}{2} a_H 2c_H,$$

whence, by equations (2),

$$\begin{aligned} V_H &= 3a_R^3\sqrt{(1-\cos\alpha)^2(1+2\cos\alpha)} \\ &= 3a_R^3\sqrt{1-3\cos^2\alpha+2\cos^3\alpha} \\ &= 3V_R. \end{aligned}$$

Thus the volume of the hexagonal unit cell is three times that of the rhombohedral unit cell (see Neuberger, *Zeit. für Krist.*, 1931, *80*, 112). Hence, if the rhombohedral cell contains n molecules of substance, the hexagonal cell contains $3n$ molecules.

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(*A list of abbreviations used in references will be found on pages* xxxi *et seq.*)

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(*A list of abbreviations used in references will be found on pages* xxxi *et seq.*)

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CHAPTER II

THE CRYSTAL STRUCTURE OF ELEMENTS

3. The Classification of A Types

THE method of classification suggested by Ewald and Hermann[1] is adopted, elements being denoted by A1 to A11 (and further)

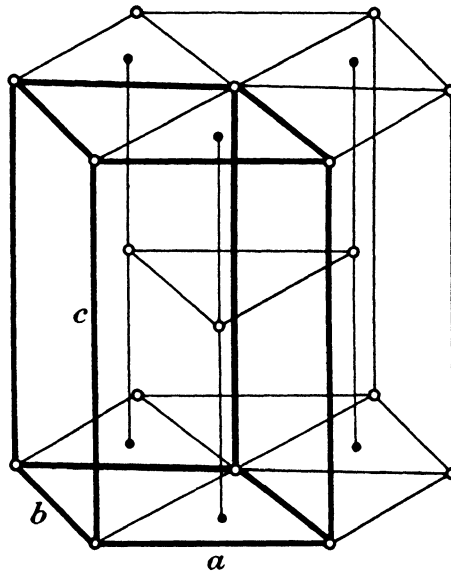

FIGURE VI.—HEXAGONAL CLOSE-PACKING (Magnesium Type). Here $a=b$; angle between a and b is 120°; $c=1{\cdot}63a$.

types. The *Strukturbericht* of these authors contains references to the literature up to 1928. Neuberger[2,47] has provided a useful summary of the lattice constants of elements (1936). The references given are not re-quoted here.

(A) **Cubic and Hexagonal Close-Packing.** "Close-packing" is a characteristic feature of many elementary structures, and is of two types: *cubic* (Figure VIII, Type A1) and *hexagonal* (Figure IX, Type A3). The circles in the Figures denote the centres of spheres in contact, each sphere being placed in a space between three others, so that the four centres form a regular tetrahedron. The centres of spheres lie in horizontal layers, as depicted. In cubic close-packing (Figure VIII), the centres of spheres in layer No. 4 lie vertically over those of layer

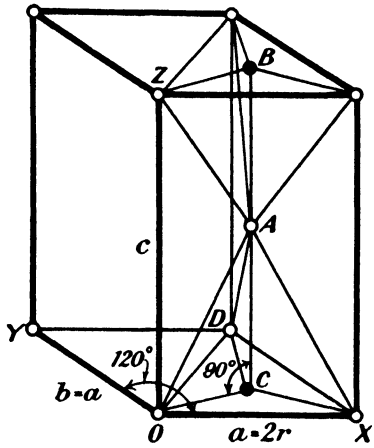

FIGURE VII.—HEXAGONAL CLOSE-PACKING (Unit Cell). The lattice-points (hollow circles) denote centres of spheres of radius r. In the ideal case, $c = 1{\cdot}63a$.

No. 1, layers Nos. 1, 2, 3 forming the structure which by repetition gives the face-centred cubic lattice (see cube drawn within the framework, having corners with double circles). Hexagonal close-packing (Figure IX and Figure XXIII, Vol. 1) has layers Nos. 1 and 2 identical with the corresponding layers in cubic close-packing, but the centres of spheres of layer No. 3 lie vertically above those of layer No. 1, the first two layers by repetition giving the structure. The unit cell is shown in Figures VI, VII, IX. Centres of spheres coincide with centres of the stippled equilateral triangles in Figures VIII and IX. The

nature of the two kinds of packing may be conveniently examined by making models with spheres of equal size, using plasticine to hold the spheres in position.

(B) **Types A1 to A11.** (a) *A1 Type* (Figures II (14), III,

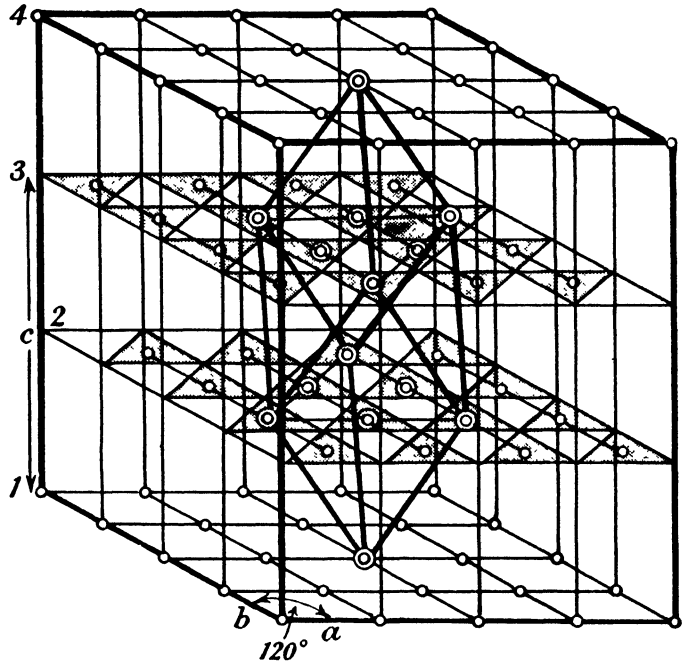

FIGURE VIII.—CUBIC CLOSE-PACKING. This corresponds to the *face-centred cubic lattice*. The unit cell is outlined, and the points in the two middle layers are at the centres of the stippled equilateral triangles. Here $a = b$; $c = 1{\cdot}63a$; $\gamma = 120°$. The points represent centres of spheres in contact. The centres of the fourth layer lie immediately over those of the first layer. The vertical scale is twice the horizontal for convenience in drawing.

VIII). The FACE-CENTRED CUBIC LATTICE (cubic close-packing) has $(6\times\frac{1}{2})+(8\times\frac{1}{8})=4$ atoms in the Bravais cell No. 14 (the six spheres at the centres of faces each contribute half a sphere, and the eight spheres at the corners contribute one-eighth of a sphere to the Bravais cell). The smallest unit cell is rhombohedral (Figure III) and contains 1 atom. Results are

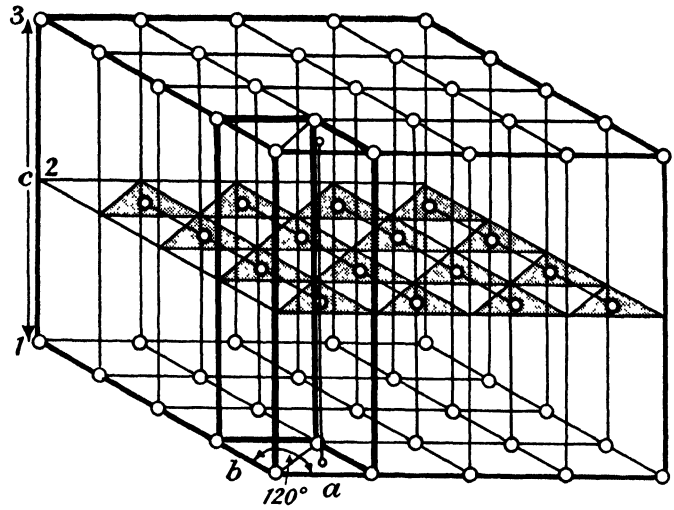

FIGURE IX.—HEXAGONAL CLOSE-PACKING. The points denote centres of spheres in contact, and lie, in the alternate layers, at the centres of the stippled equilateral triangles. The unit cell is outlined; $a = b$; $c = 1{\cdot}63a$; $\gamma = 120°$. The centres of the third layer lie immediately over those of the first layer. The vertical scale is twice the horizontal for convenience in drawing.

in Table I. Where allotropic modifications exist, low temperature forms are denoted by α, higher temperature forms by $\beta, \gamma \ldots\ldots$

TABLE I.—A1 TYPE FACE-CENTRED CUBIC ELEMENTS (Schoenflies Space-Group O_h^5).

Z	Element	a	Z	Element	a	Z	Element	a	Z	Element	a
10	Ne	4·52[2]	28	Ni	3·518[4]	47	Ag	4·077[2,4,9]	79	Au	4·070[2,3]
13	Al	4·041[2,4]	29	Cu	3·608[2,4,6,7]	54	Xe	6·18[10]	81	β-Tl	4·841[2]
18	A	5·42[1,2]	36	Kr	5·59[2], 5·79[8]	57	β-La	5·296[11]	82	Pb	4·940[2]
20	α-Ca	5·56[1,2,5]	38	Sr	6·08[1,2]	58	β-Ce	5 12[1,2]	90	Th	5·074[2]
26	γ-Fe	3·63[1,2]	45	Rh	3·795[2,3,4]	77	Ir	3·831[2,4]			
27	β-Co	3·55[1,2]	46	Pd	3·885[4]	78	Pt	3·916[2]			

Atomic numbers are denoted by Z, and lengths of cube-edges a are in Å.U. (10^{-8} cm.).

Thin layers of Al studied by electron diffraction[41] are reported to have face-centred tetragonal structure, whilst thicker layers have the normal structure. Pt has been examined by the same method,[42,43] certain orientation effects being observed.

(b) *A2 Type* (Figure II (13)). The BODY-CENTRED, or CUBE-CENTRED CUBIC LATTICE has $1 + (8 \times \frac{1}{8}) = 2$ atoms in the Bravais cell No. 13. The true unit cell is monoclinic. Atomic numbers Z and lengths of cube edges a in Å.U. are in Table II.

TABLE II.—A2 TYPE BODY-CENTRED CUBIC ELEMENTS (Schoenflies Space-Group O_h^9).

Z	Element	a	Z	Element	a	Z	Element	a	Z	Element	a
3	Li	3·46[a]	24	β-Cr	2·88[a]	37	Rb	5 62[1,2]	56	Ba	5·02[a]
11	Na	4·24[a]	26	α-Fe	2·8611[2,3]	41	Cb	3·30[a]	73	Ta	3·311[e]
19	K	5·33[a]	26	β-Fe	2·90[1]	42	Mo	3·140[2,4]	74	α-W	3·159[4,12]
23	V	3·01[a]	26	δ-Fe	2·93[1]	55	Cs	6·05[1,2]	92	U(?)[35]	3·43[a]

(c) *A3 Type* (Figures VI, VII, IX). HEXAGONAL CLOSE-PACKING is shown in Figure VI, where three unit cells are shown, a single cell being denoted by thick lines and containing $1 + (8 \times \frac{1}{8}) = 2$ atoms. The ideal ratio between the axes $c/a = 2\sqrt{\frac{2}{3}} = 1{\cdot}63$, since c is given by twice the height of the regular tetrahedron OXAD, where $OA = a$, $OC = a/\sqrt{3}$, so that $c = BC = 2AC = 2\sqrt{\frac{2}{3}}.a$ (Figure VII). If r is the radius of a sphere, $a = 2r$, whence the volume of the cell is $8\sqrt{2}.r^3$, and the volume of two atoms contained in it $2 \times \frac{4}{3}\pi r^3$, so that the "space-filling fraction" is $\pi/(3\sqrt{2}) = 0{\cdot}74$ (see Vol. I: 18B). Results are shown in Table III, whence it is noted that Zn and Cd depart rather widely from the ideal ratio.

(d) *A4 Type* (Figures X, XI). Each atom in the DIAMOND LATTICE is surrounded symmetrically and tetrahedrally by four others, the angle between the "valency" directions being 109° 24′. The structure consists of two interpenetrating face-

TABLE III.—A3 TYPE HEXAGONAL CLOSE-PACKED ELEMENTS
(Schoenflies Space-Group D_{6h}^4).

Z	Element	a	c	a/c	Z	Element	a	c	a/c
1	para-H_2†	3·75	6·12	1·633[12]	44	Ru	2·695	4·27	1·58[8]
4	α-Be°	2·268	3·594	1·585[14]	48	Cd	2·974	5·608	1·885[15]
7	β-N_2‡	4·03	6·57	1·63[21]	57	α-La	3·72	6·06	1·63[2]
12	Mg	3·202	5·196	1·624[2,15]	58	α-Ce	3·65	5·91	1·62[2]
22	Ti	2·95	4·69	1·59[1,2]	59	Pr	3·657	5·85	1·60[17]
24	β-Cr	2·717	4·418	1·626[2]	68	Er	3·74	6·09	1·63[2]
27	α-Co	2·51	4·11	1·63[1,2]	72	Hf	3·20	5·08	1·59[1,2]
28	Ni*	2·474	4·06	1·64[19,20]	75	Re	2·755	4·448	1·615[16]
30	Zn	2·659	4·934	1·856[15,16]	76	Os	2·72	4·31	1·58[8]
40	Zr	3·22	5·12	1·59[1,2]	81	α-Tl	3·450	5·520	1·600[2]

* High temperature β-Be recorded[18]. * Spluttered metal examined by electron diffraction.
† at 14°K. ‡ Stable above 35°K.

centred cubic lattices, and may be obtained by dividing the Bravais face-centred cubic cell into eight smaller cubes, placing an atom at the centre of *each alternate* smaller cube (Figure X). The cell depicted contains $4 + (6 \times \frac{1}{2}) + (8 \times \frac{1}{8}) = 8$ atoms. The distance between adjacent carbon atoms in diamond is $d = 1{\cdot}54$, whence the cube diagonal is $4 \times 1{\cdot}54 = 6{\cdot}16$ and the cube edge $a = 6{\cdot}16/\sqrt{3} = 3{\cdot}56$ Å.U. Figure XI shows a section of the lattice. Data for four cases of the A4 type are in Table IV.

TABLE IV.—A4 TYPE DIAMOND AND DIAMOND-LIKE ELEMENTS
(Schoenflies Space-Group O_h^7).

Z	Element	a	d	Z	Element	a	d
6	C[1,2] (Diamond)	3·560	1·540	32	Ge[2]	5·647	2·444
14	Si[1,2]	5·42	2·346	50	α-Sn[1,2]	6·46	2·80

Robertson and collaborators[22] have found absorption evidence of the existence of two types of diamond, whose X-ray patterns are the same, but whose intensities of reflection are somewhat different.

(e) *A*5 *to A*8, *A*10 *and A*11 *Types.* Results are tabulated on page 27.

It is worthy of notice that the A7 type corresponds to slightly

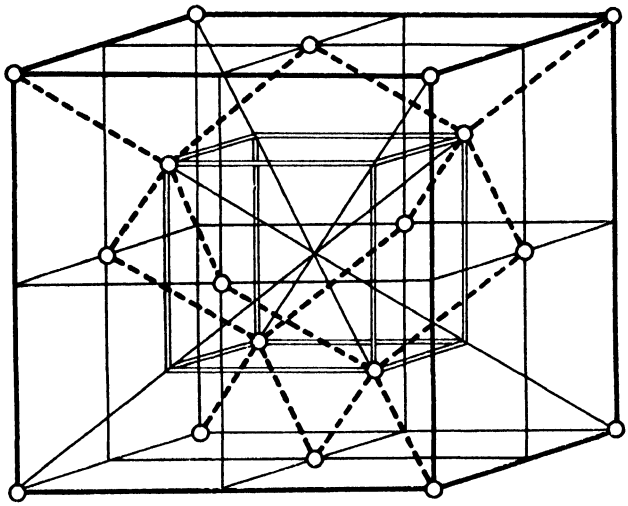

FIGURE X.—THE STRUCTURE OF DIAMOND. The diamond framework may be referred to two interpenetrating cubic face-centred lattices, of which the outer and inner cubes here shown are respectively parts. When the atoms of one lattice differ from those of the other, the zinc blende type of structure is obtained.

distorted simple cubic arrangement, and may also be referred to two interpenetrating face-centred rhombohedral lattices, with 8 atoms in the unit cell, with the following dimensions :— P[2] *a* 5·96, *α* 60° 47′ ; As[2] *a* 5·60, *α* 84° 18′ ; Sb[7] *a* 6·24, *α* 87° 24′ ; Bi[6] *a* 6·58, *α* 87° 34′. Laves[32] has found the orthorhombic space-group V_h^{18} for Ga.

(f) *A*9 *Type* (Figure XII, a and b). GRAPHITE,[2] a modification of carbon, has the hexagonal space-group D_{6h}^4 or C_{6v}^4, with 4 atoms in the unit cell, having the dimensions *a* 2·46, *c* 6·78. Hexagonal rings of carbon atoms lie in parallel planes

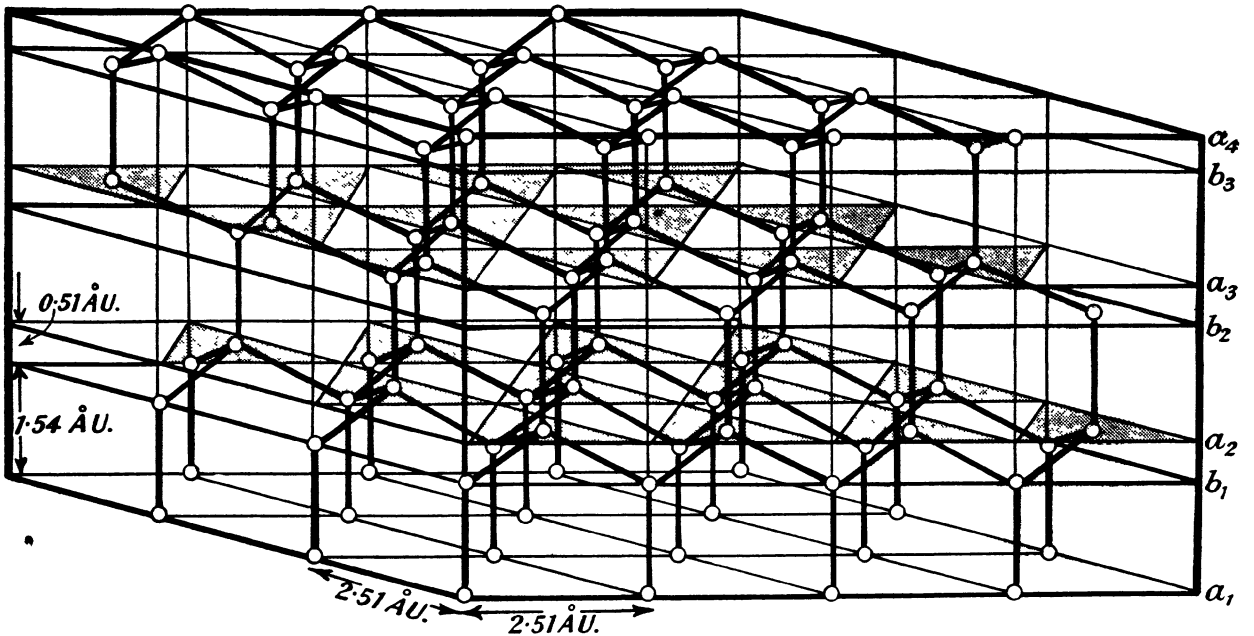

FIGURE XI.—THE DIAMOND FRAMEWORK. The planes contain atoms of carbon arranged at the corners of regular hexagons. Atoms in the planes b_1, a_1; b_2, a_2; b_3, a_3; lie respectively exactly over each other, whilst a_4 is a repetition of a_1. Atoms in the planes a_2, a_3, lie at the centres of the stippled equilateral triangles. The two interpenetrating face-centred cubic lattices are here represented by atoms in a and b planes respectively. The dimensions of the structure are shown, the distance between the centre of one carbon atom to that of a proximate neighbour being 1·54 Å.U. This representation of the structure shows the arrangement in rings of six atoms, as well as the tetrahedral symmetry of the connecting bonds starting from any given atom. The zinc blende structure is easily obtained from this.

TABLE IVa.—CRYSTAL STRUCTURE OF A5 TO A8, A10 AND A11 TYPES.

Type	Z	Element	Cell and Number of Units	Space-Group	a	c	α
A5	50	β-Sn[2,11,22]	Tetragonal Body-Centred (4)	D_{4h}^{19}	5·82	3·16	
A6	25	γ-Mn[1,2,45*]	Tetragonal Face-Centred (4)	D_{4h}^{17}	3·77	3·53	
	49	In[22,24]			4·582	4·936	
A7	15	Black P[2]	Body-Centred (2) Rhombohedral	D_{3d}^{5}	5·14		34° 7′
	33	As[2]			4·15		53° 49′
	51	Sb[2]			4·50		57° 5′
	83	Bi[2,4]			4·75		57° 16′
A8	34	Hex. Se[2]	Hexagonal (3)	D_3^1 or D_3^6	4·34	4 94	
	52	Te[2]			4·50	5·91	
A10	80	Hg[1,2]	Rhombohedral (1)	D_{3d}^{5}	3·00		70° 32′
A11	31	Ga[1,2]	Tetragonal (8) (?) [22]	D_{4h}^{16}	4·51	7·64	

* Above // 1100°C.

(Figure XIIb). Figure XII shows the structure, which is that of a " layer " lattice. The carbon atoms lie in the planes nearer together than in diamond : C–C (graphite) 1·42, (diamond) 1·54. The planes are separated by 3·39, with low cohesion between the planes, giving rise to cleavage and softness.

Whilst Hönig[28] has developed a crystal model of graphite different from that assigned by the use of X-rays, experiments on electron diffraction have confirmed the classical structure.[26,27]

Krishnamurti[29] pointed out that, whilst amorphous carbon has been generally regarded as identical with finely-divided graphite, there are marked differences according to the method of preparation. Mukherjee[30] has found the lattice spacing of amorphous carbon to be different from that of graphite, and assumed that either there was a difference in structure, or that the small graphite crystals were differently spaced. Warren[31] finds carbon black to consist of a heterogeneous mixture of particles, from single layers to several layers in thickness.

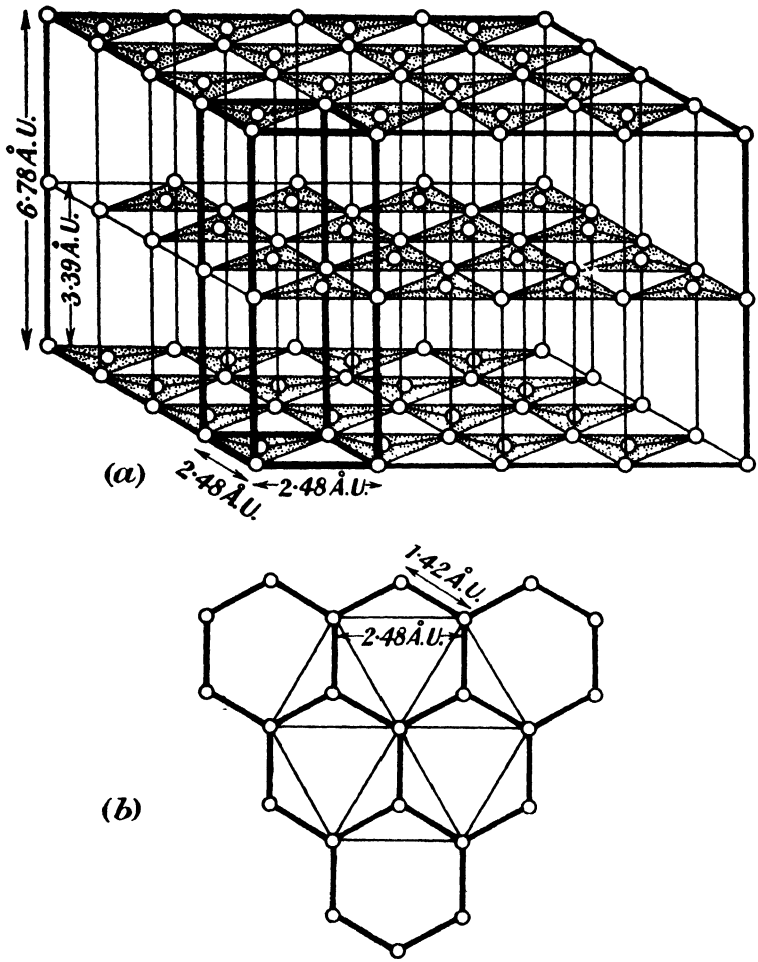

FIGURE XII a AND b.—THE STRUCTURE OF GRAPHITE. The carbon atoms lie on the corners of the hexagonal framework, with additional atoms at the centres of the stippled equilateral triangles. The carbon atoms are in the planes in the form of hexagonal rings. Figure XII b shows a portion of a plane in plan. The unit cell is shown in outline in Figure XII a.

(C) **Unclassified Cases, Ax Type.** Various elements exist in forms included in none of the above A Types, and these are here provisionally classified together as of Ax type. For

example, Mn exists in three forms, of which α—Mn and β—Mn are cubic of low symmetry, the transition temperature being about 750°C. Above 1100°[33] (1191 ?[34]) γ—Mn is the stable form (A6 type). Some of the lattices are molecular in type, the units being groups of atoms, such as N_2, O_2, I_2. S has 128 atoms[2] in the unit cell, arranged in groups of S_4, S_8 and S_{16}. Se_8 is probably the basal unit in red selenium. Ruhemann[21] finds solid oxygen to have two forms, the X-ray lines of which do not agree with the orthorhombic cell assigned by McLennan and Wilhelm.[2] Thirteen cases of Ax type are here shown.

TABLE IVb.—CRYSTAL STRUCTURE OF ELEMENTS OF UNCLASSIFIED Ax TYPES.

Type	Z	Element	Cell and Number of Atoms	Space-Group	a	b	c	β
Ax	7	α-N_2[1,2,21]	Cubic (8)	T^4	5·67			
	8	O_2[1,2]	Orthorhombic, Body-Centred (2) (?)[21]	?	5·50	3·82	3·44	
	15	White P[1,2]	Cubic (16)	?	7·17			
	16	S[2]	Orthorhombic, all Face-Centred (128)	V^{24}_h	10·61	12·87	24·56	
	24	γ-Cr[2]	Cubic, Body-Centred (58)	T^3_d	8·717			
	25	α—Mn[1,2]			8·894			
	25	β-Mn[1,2]	Cubic (20)	O^6 or O^7	6·30			
	31	Ga[22]	Orthorhombic (8)	V^{18}_h ?	4·506	4·506	7·642	
	34	α-Se[27,28]	Monoclinic (32)	C^2_{2h}	8·99	8·97	11·52	91° 34′
	34	β-Se[28]		C^5_{2h}	12·74	8·04	9·25	93° 4′
	53	I_2[1,2]	Orthorhombic (8)	V^8_h	4·795	7·255	9·780	
	74	β-W[2,12]	Cubic (8)	O^3 or O^3_h	5·038			
	92	U[26]	Monoclinic (2)	C^3_{2h}	2·829	4·887	3·308	

(D) **Crystal Structure and the Periodic Classification.** Hume-Rothery[39] has discussed the crystal structure of elements of B sub-groups of the Mendeljéeff classification, and has argued

TABLE V.—THE LATTICE TYPES OF ELEMENTS.

PERIODIC GROUPS.

O	I	II	III	IV	V	VI	VII	VIII		
2He	3Li A2	4Be A3	5B	6C A4, A9	7N Ax, A3	8O Ax	9F			
10Ne A1	11Na A2	12Mg A3	13Al A1	14Si A4	15P A7, Ax	16S Ax	17Cl			
18A A1	19K A2	20Ca A1	21Sc	22Ti A3	23V A2	24Cr A2, A3, Ax	25Mn A6, Ax	26Fe A2, A1	27Co A1, A3	28Ni A1, A3
	29Cu A1	30Zn A3	31Ga Ax, A11 (?)	32Ge A4	33As A7	34Se A8, Ax	35Br			
36Kr A1	37Rb A2	38Sr A1	39Y	40Zr A3	41Cb A2	42Mo A2	43Ma	44Ru A3	45Rh A1	46Pd A1
	47Ag A1	48Cd A3	49In A6	50Sn A4, A5	51Sb A7	52Te A8	53I Ax			
54X A1	55Cs A2	56Ba A2	57La A1, A3	72Hf A3	73Ta A2	74W A2, Ax	75Re A3	76Os A3	77Ir A1	78Pt A1
	79Au A1	80Hg A10	81Tl A1, A3	82Pb A1	83Bi A7	84Po	85	RARE EARTHS		
86Nt	87	88Ra	89Ac	90Th A1	91Pa	92U Ax, A2 (?)		58Ce A1, A3	59Pr A3	68Er A3

that, whilst Zn, Cd, Hg, In, are true metals having distorted ions in their structure, elements in the fifth and sixth B groups are not true metals, and contain covalent and molecular linkages. Bernal[25] thought metallic bonds were present in these cases. Hume-Rothery[40,46] has further given an empirical formula connecting lattice constants of elements with other constants depending on the position of the elements in the Periodic Classification. The crystal types are set out in periodic relation in Table V.

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CHAPTER III

THE CRYSTAL STRUCTURE OF INORGANIC COMPOUNDS OF TYPE AB

4. The Classification of B Types

EWALD and Hermann[1] have classified binary compounds in relation to crystal structure into B1 to B13 (and further) types. A general crystallographic survey of compounds of Type AB is provided by Niggli.[2,3] Further results are given by Goldschmidt.[4] Intermetallic compounds are chiefly considered elsewhere: this vol.: 19, 20. The cases included in the present discussion involve pairs of atoms, of which *at least one* in each instance is chosen from Groups IV, V, VI and VIIB (with boron in Group III) of the Periodic Classification.

(A) **Types B1 to B13.** (a) *B1 Type* (Figure XIII). The SODIUM CHLORIDE or ROCK SALT type contains two symmetrically interpenetrating face-centred cubic lattices of the two kinds of atoms respectively, with four AB groups in the unit cell. The important suggestion that the units are ions instead of atoms was made by Debye and Scherrer[5] for uni-univalent crystals (LiF), and by Gerlach[5] for bi-bivalent crystals (MgO). No other assumption accounts satisfactorily for the alternation of the two kinds of atoms in the structure, and for the absence of any grouping into pairs corresponding to AB molecules. The structure is such that each ion is symmetrically surrounded by six of the opposite kind. It thus becomes impossible to assign a given ion to its oppositely-charged partner, and the molecule is lost in the symmetry of the crystal. The structure of NaCl was one of the earliest determined by X-rays, by the pioneers W. H. and W. L. Bragg.[6]

Estimates of the distances separating the centres of unlike

contiguous atoms in alkali halide crystals were made by Fajans and Grimm in 1920: see Vol. I: Table XXIII. More recent estimates of the lattice distances of these and other cases are in Table VI. The lattice distance corresponds to the length of cube edge in Figure XIII, and is thus double the separation between contiguous unlike atoms. All references are to the *Strukturbericht*[1] unless another reference number is given.

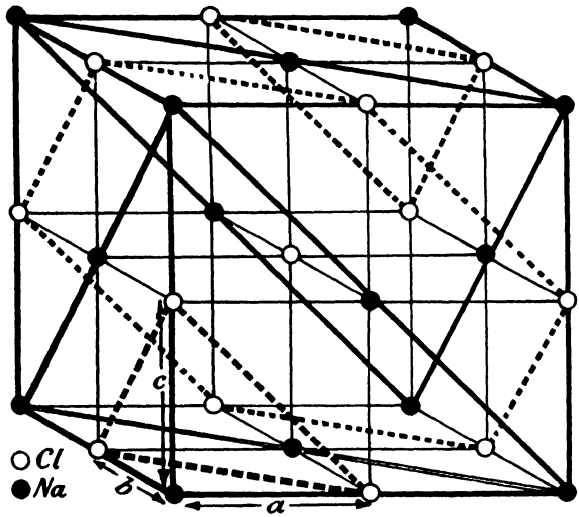

FIGURE XIII.—SODIUM CHLORIDE STRUCTURE. The framework consists of two interpenetrating face-centred cubic lattices of Na^+ and Cl^- ions respectively. The planes outlined by connecting lines contain either Na^+ only, or Cl^- only, alternately, and correspond to the planes of Figure VIII.

An interesting case of mixed crystal formation is described by Goldschmidt (p. 773 of [1]). The mixture which is approximately 8TiN2TiC has sodium chloride B1 structure, with lattice distance 4·24.

(b) *B2 Type* (Figure XIV). The CÆSIUM CHLORIDE Type has a body-centred cubic lattice, the unit at the centre of the cube being different from those at the corners, with 1 AB group in the unit cell. Each ion in the structure is surrounded by eight neighbours of the other kind symmetrically placed in relation

TABLE VI.—LATTICE DISTANCES OF CRYSTALS OF Bi TYPE

(Schoenflies Space-Group O_h^5).

	H	F	Cl	Br	I	SH		O	S	Se	Te
Li	4·08[7]	4·02	5·14	5·49	6·00	—	Mg	4·21	5·19	5·45	—
Na	4·88[7]	4·62	5·63	5·96	6·46	6·05[*8]	Ca	4·80	5·68	5·91	6·35
K	5·70[7]	5·33	6·28	6·59	7·05	6·60[*8]	Sr	5·15	6·01	6·23	6·65
Rb	6·04[7]	5·63	6·54	6·85	7·33	6·93[*8]	Ba	5·53	6·37	6·59	6·99
α-Ag	—	4·92	5·54	5·76	—	—	Pb	—	5·93	6·14	6·44
β-NH_4	—	—	6·53*	6·90*	7·24*	—	Mn	4·44	5·21	5·45	—
Cs	6·38[7]	6·01	—	—	—	—	Sn	—	—	—	6·28

CrN	4·14	CdO	4·69[10]	FeO	4·28	CoO	4·22	NiO	4·17[10,44]	CbN	4·41
SbSn	6·12[9]	ScN	4·44	TiN	4·40	ZrN	4·63	VN	4·28	CbC	4·40
AsSn	5·71[11]	TaC	4·49	TiC	4·31[43]	ZrC	4·76	VC	4·30		

* Higher temperature modifications.

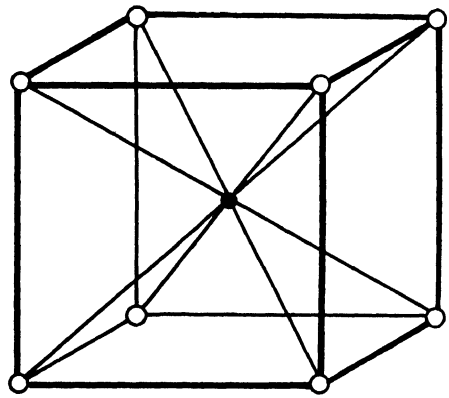

FIGURE XIV.—CAESIUM CHLORIDE STRUCTURE (Body-centred cubic lattice)

to it. Table VII shows examples of the type. Intermetallic compounds of the β-brass type are considered in Section 19B.

TABLE VII.—LATTICE DISTANCES OF CRYSTALS OF B2 TYPE
(Schoenflies Space-Group O_h^1).

The first number in each case gives the distance separating like ions along cube edges = a, and the second that separating the centres of unlike contiguous ions along cube diagonals = $a\sqrt{3}/2$.

	Cl[1]		Br[1]		I[1]		SH[6]		Sb[1]		Bi[1]	
Cs	4·11	3·56	4·29	3·71	4·56	3·95	4·29	3·72				
Tl	3·84	3·33	3·97	3·44	4·20	3·64			3·84	3·33	3 98	3·45
α-NH_4	3·86	3·34	4·05	3·51	4·37	3·78						

The low temperature modifications of NH_4Cl, NH_4Br, NH_4I belong to B2 type, and are isomorphous with CsCl; the high temperature modifications belong to B1 type, and are isomorphous with NaCl. It is in line with earlier adopted convention to denote the low temperature forms by α, though this procedure has not always been followed[12] (see also: Vol. I: 21D).

Bridgman[13] discovered changes of structure in the halides RbCl, RbBr, RbI, which are of Type B1 under ordinary conditions, at high pressures of the order of 5,000 kg./cm.^{2} into other modifications. It would be anticipated that the high-pressure modifications have the CsCl structure B2, but Bridgman doubted whether this was so, since the contractions in volume were found to be much less than those expected from geometrical considerations of the two structures, assuming the "sizes" of the ions to be unaffected by the change. Goldschmidt,[4] however, has observed an increase of 3% in the distance separating nearest centres of anions and cations in changes from NaCl to CsCl structure in the transitions of the ammonium halides with change of temperature. Pauling[14] thus interprets Bridgman's result as indicating the presence of the CsCl type for the rubidium halides under high pressures, the expected contraction in volume accompanying the transition being partly compensated by the increase in distance between unlike ionic centres.

(c) *B3 Type* (Figure XVI). The characteristic structure of the ZINC BLENDE or SPHALERITE modification of zinc sulphide

follows the diamond plan of Figures X and XI. The ions at four corners of the inner cube of Figure X are different from those at the corners and centres of faces of the large cube. There are thus two interpenetrating face-centred cubic lattices, one consisting entirely of ions of one kind, the other of ions of the other kind, arranged so that the corners of cubes of one lattice occupy centres of the small cubes of which eight are shown in Figure X. This has the effect, from the point of view of Figure XI, of forming alternate layers of atoms consisting entirely of one kind or the other. Thus the symmetry requires that the small cube at the centre of Figure X shall be structurally similar to the eight cubes into which the large cube is divided, and identical with four of them but displaced in position (except that the ions are of two kinds, in the case of the zinc blende structure). Substances belonging to this group are shown in Table VIII, where the lengths of cube edges and distances between nearest unlike neighbours are given. There are eight atoms, four of each kind, in the unit cell.

TABLE VIII.—LATTICE DISTANCES OF CRYSTALS OF B_3 TYPE

(Schoenflies Space-Group T_d^2).

The separations of like atoms along cube edges a, and of contiguous unlike atoms along cube diagonals $= \sqrt{3}.a/4$, are given (see Figure X).

CuCl	5·41	2·34		S		Se		Te			P		As		Sb	
CuBr	5·68	2·46	Be	4·86	2·10	5·13	2·18	5·61	2·43	Al	5·45	2·36	5·62	2·43	6·13	2·65
CuI	6·05	2·62	Zn	5·42	2·35	5·66	2·45	6·09	2 64	Ga	5·44	2·36	5·63	2·44	6·12	2·68
β-AgI†	6·47	2·80	Cd	5·82	2·52	6 04	2·62	6·46	2 80	In	—	—	—	—	6·45	2·79
CSi*	4·37	1·89	Hg	5·84	2·53	6·07	2·63	6·44	2·79							

† Stable 145·8 to 500°C. * So-called amorphous modification

The figures in Table VIII are taken from the *Strukturbericht*,[1] except in the case of AgI.[15] Milligan[16] has found the lattice constants of the two forms of CdS to be in agreement with the earlier work of Ulrich and Zachariasen.[1]

(d) *B4 Type* (Figures XV, XVI, XVII). The modification of zinc sulphide, known as WURTZITE, crystallizes in a system consisting of two interpenetrating systems, one of which corresponds approximately to an hexagonal close-packing of zinc atoms and the other to a similar arrangement of sulphur atoms (compare Figure IX). The elementary cell containing 2ZnS

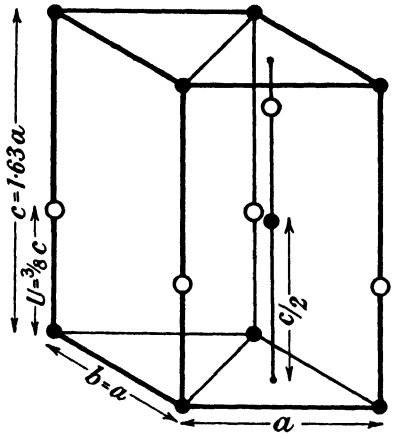

FIGURE XV.—UNIT CELL OF WURTZITE, ZnS.

is shown in Figure XV. For accurate hexagonal close-packing of atoms of one kind only, the axis $c = 1{\cdot}63a$ (see discussion in Chapter II, under A3 type). The " parameter " u, defining

TABLE IX.—LATTICE DISTANCES OF CRYSTALS OF B4 TYPE
(Schoenflies Space-Group C_{6v}^4).

	a	c	c/a		a	c	c/a
ZnS[17]	3·81	6·23	1·64	MgTe[1]	4·52	7·33	1·62
ZnO[18]	3·26	5·24	1·61	CdSe[1]	4·30	7·01	1·63
CdS[16]	4·14	6·72	1·62	AlN[1]	3·11	4·98	1·60
α-AgI[15a]	4·58	7·49	1·64	TaN[1]	3·05	4·94	1·62
BeO[1]	2·69	4·37	1·63	NH_4F[1]	4·39	7·02	1·60
CuH[1]	2·89	4·61	1·60				

* Stable below 145·8°C.

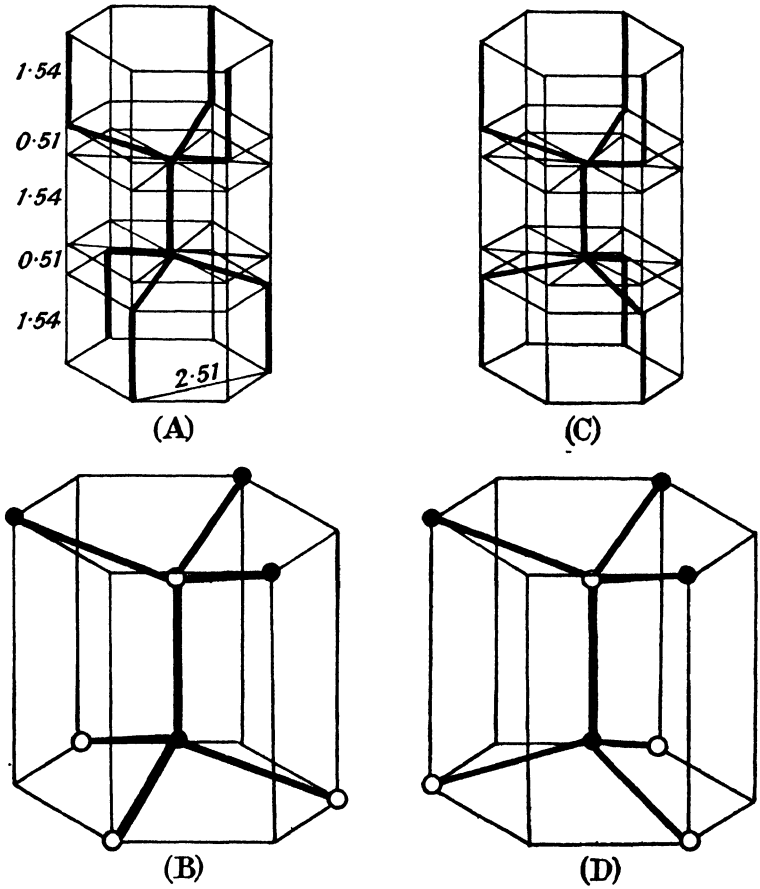

FIGURE XVI.—STRUCTURES OF SPHALERITE (ZINC BLENDE) AND WURTZITE. The two forms of ZnS are here placed side by side for comparison. A and B show sphalerite, C and D zinc blende. B and D are reproductions of the central parts of A and C respectively.

the relative positions of the two sets of atoms, is $\frac{3}{8}$, so that every zinc atom is surrounded tetrahedrally by four sulphur atoms, and *vice versa*. (This condition is also fulfilled for the zinc blende type, though the relative arrangement is different. See Figure XVI.) Repetition of the unit cell gives rise to the structure depicted in Figure XVII. Values of a, c and c/a for substances crystallizing in this way are shown in Table IX.

FIGURE XVII.—STRUCTURE OF WURTZITE, ZnS. The black dots representing centres of zinc atoms in the middle plane lie at the centres of the stippled equilateral triangles. The relation to the diamond structure and the zinc blende structure may be seen by comparison with Figures XI and XVI.

Strock[19] has found β-AgI to contain a cubic body-centred lattice of iodine atoms, with edge length 5·034, the silver ions being arbitrarily distributed in the largest spaces, and behaving as a liquid embedded in the rigid iodine framework.

(e) *B5, B6 and B7 Types.* These three types correspond to different modifications of CARBORUNDUM, CSiIII, CSiII and CSiI respectively.[1] Each has a lattice modelled on a diamond

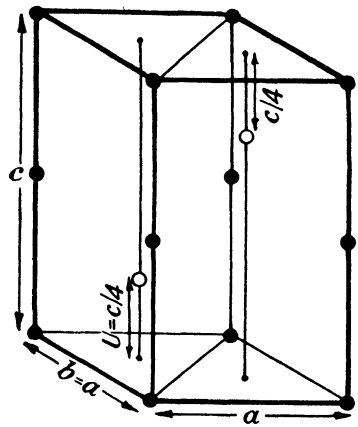

FIGURE XVIII.—UNIT CELL OF NICKEL ARSENIDE, NiAs.

A4 type, but the hexagonal elementary cells have 4, 6, and 15 molecules respectively. The *a* axes are 3·09 in each case, the *c* axes being 10·1, 15·2 and 37·9 respectively, in the ratio 4 : 6 : 15. The Types B3, B4, B5, B6 and B7 have "tetrahedral" lattices. The Schoenflies space-groups are C_{6v}^4 for B5 and B6, and C_{2v}^5 for B7 types.

(f) *B8 Type* (Figures XVIII and XIX). The NICKEL ARSENIDE or NICCOLITE lattice has the unit cell containing two molecules shown in Figure XVIII. The parameter fixing the positions of the atoms within the cell (unlike those at corners and edges) is $u = \frac{1}{4}$. The ideal axial ratio is $2\sqrt{2/3} = 1{\cdot}63$, but there may be wide departure from this, as Table X shows.

(g) *B9 Type.* CINNABAR, HgS[1], may be regarded as possessing a lattice of deformed rock salt type B1. Referred to

hexagonal axes, there are 3HgS in the unit cell, with $a = 4{\cdot}17$, $c = 9{\cdot}50$, $c/a = 2{\cdot}28$.

(h) *B*10 *and B*11 *Types.* These have tetragonal lattices, with 2AB in the unit cell (Space-group D^7_{4h}). B10 type is represented by PHOSPHONIUM IODIDE[1] PH_4I (a 6·34, c 4·62, c/a 0·73), and LITHIUM HYDROXIDE[26] LiOH (a 3·55, c 4·33,

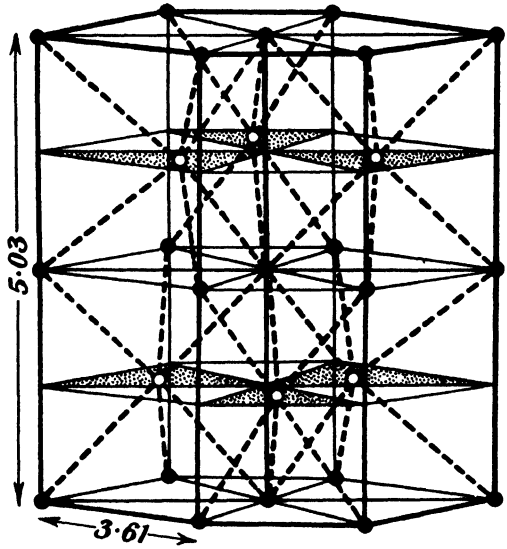

FIGURE XIX.—LATTICE FRAMEWORK OF NICKEL ARSENIDE, NiAs. For convenience of representation, the vertical scale is twice the horizontal (Å.U. units).

c/a 1·22). Ewald and Hermann[1] tentatively classified red PbO (a 3·98, c 5·01, c/a 1·26), SnO (a 3·80, c 4·81, c/a 1·27), and PdO[27] (a 3·03, c 5·31, c/a 1·75) as B10 or B11, which differs from B10 in requiring two parameters, u 0·24 and v 0·74, instead of one to define the positions of the atoms in the unit cells. The positions of the Pb atoms are alike in each (u 0·24). Dickinson and Friauf[1] gave the unit cell of B10, and Levi and Natta[1] of B11, to red PbO. Zachariasen[27] considered PdO to belong to B10 like PbO. Huggins[28] suggested another structure in which each Pd atom was surrounded by four coplanar O's arranged approximately at the corners of a square, somewhat as

TABLE X.—LATTICE DISTANCES OF CRYSTALS OF B8 TYPE (Schoenflies Space-Group D^4_{6h}).
The first figure in each case gives the *a* axis, the second the *c*/*a* ratio. The second figure after a decimal may be uncertain.

	Sn	As	Sb	Bi	S	Se	Te
Ni	4·08 1·27[1]	3·61 1·39[1]	3·91 1·31[1]	4·06 1·32[20]	3·42 1·55[1]	3·66 1·46[1]	3·96 1·35[1]
Co			3·87 1·34[1]		3·37 1·53[1]	3·61 1·46[1]	3·89 1·38[1]
Fe			4·06 1·26[1]		3·43 1·69[1]	3·61 1·63[1]	3·80* 1·49[1]
Cr			4·11 1·33[1]		3·44 1·65[1]	3·59 1·62[1]	3·98 1·56[1]
Mn		3·72* 1·54[1]	4·12 1·40[1]		4·13* 1·39[1]		4·12 1·62[1]
Cu	4·19 1·21[21]						
Au	4·31 1·28[22,46]						
Pt	4·10 1·32[1]		4·13 1·32[23]				
Pd			4·07 1·37[24]				4·13 1·37[25]

* Containing excess of metalloid.

four coplanar S atoms surround each Ni in NiS (B13 type). Bannister and Hey[29] found PtS to have the same structure as that assigned by Huggins to PdO. Red PbO has been confirmed by Darbyshire[30] to be tetragonal, with *a* 3·968, *c* 5·011. Yellow PbO was found by Halla and Pawlek[1] to be orthorhombic. This was confirmed by Darbyshire[30] (see Bx type in Section B below).

(i) *B12 Type* (Figure XX). This is represented by BORON NITRIDE, BN[1], which has a lattice of the graphite type (Figure XII). The unit cell is shown in Figure XX. If the boron

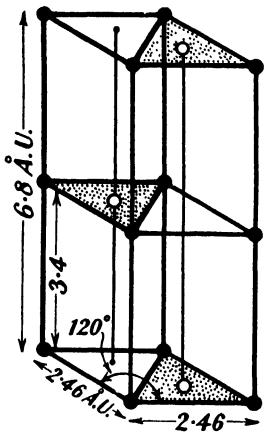

FIGURE XX.—UNIT CELL OF BORON NITRIDE, BN. The empty circles are at the centres of the stippled equilateral triangles.

atoms are supposed to occupy the corners and middle points of the edges of the cell, then the nitrogen atoms are at the centres of the three shaded equilateral triangles, and the cell contains two molecules. The lattice distances are almost the same as for graphite: *a* 2·46, *c* 6·80 (Hassel). Each boron atom is surrounded by three nitrogen atoms symmetrically in a plane, and similarly each nitrogen atom has three boron atoms as immediate neighbours. The space-group is D^4_{6h}.

(j) *B13 Type.* MILLERITE, NiS[1,31], has a rhombohedral unit cell, containing 3NiS, having the dimensions: *a* 5·636, *α* 116° 35′. The probable space-group is C^5_{3v}.

(B) **Unclassified Cases, Bx Type.** Examples are here tabulated :—

TABLE Xa.—CRYSTAL STRUCTURES OF COMPOUNDS AB OF UNCLASSIFIED TYPES Bx.

AB	Cell and Number of Units	Space-Group	a	b	c	α
CO[32]	Cubic (4)	T^4	5·63			
HgO[1]	Orthorhombic (2)		3·30	3·51	5·50	
Yellow PbO[30]	Orthorhombic (4)		5·46	4·72	5·86	
CuS[33]	Hexagonal (6)	D^4_{6h}	3·80		16·43	
GeS[34]	Orthorhombic (4)	V^{16}_h	4·29	10·42	3·64	
PtS[29]	Tetragonal (4)	D^9_{4h}	4·91		6·10	
WC[35]	Hexagonal (1)		2·94		2·86	
FeB[36],[45]	Orthorhombic (4)	V^{16}_h	5·50	4·05	2·95	
FeAs[37]	Orthorhombic (4)		3·37	6·02	5·43	
NaSH[8]	Rhombohedral (1)	D^5_{3d}	3·99			68° 5′
KSH[8]			4·37			68° 51′
RbSH[8]			4·53			69° 20′
NH_4SH[8]	Tetragonal (2)	D_{4h}	6·01		4·01	
$LiClH_3O$[1]	Tetragonal (1)		3 81		3·88	
LiI_3H_3O[1]	Hexagonal (2)		7·45		5·45	
FeSi[38]	Cubic (4)	T^4	4·48			
CrSi[39]			4·62			
MnSi[39]			4·55			
CoSi[39]			4·44			
NiSi[39]			4·44			
Martensite[1] (Fe+ < 6% C)	Tetragonal (L′20 Type)	D^{17}_{4h}	2·84*		2·97	

* 5% C.

Solid α—CO, below 61·5°K, is of the same type as $\alpha - N_2$ (Ax). β—CO[42], above 61·5°K, is like $\beta - N_2$ (A3 type). FeAs and GeS appear to have deformed B8 and B1 lattices respectively.

The diatomic hydrides form an interesting group of compounds. The hydrides from LiH to CsH (B1 type) are polar compounds, and contain the helium-like ion H^-. CuH is probably homopolar, since it has a lattice of diamond-like type (B4), and since its molecular volume is about 5 cubic Å.U.

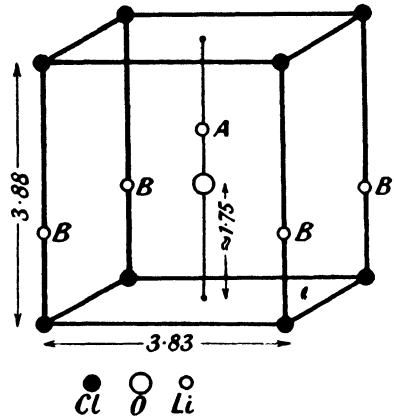

FIGURE XXI.—LATTICE STRUCTURE OF $LiClH_2O$ (Hendricks).

greater than the atomic volume of Cu. Solid HCl, investigated by Simon and Clara v. Simson,[40] is dimorphous, and below 98°K is not cubic; above 98°K, the Cl atoms lie on a cubic A1 lattice, whose edge is 5·54. This high lattice distance, about equal to that of NaCl, suggests a homopolar lattice in which the units are HCl molecules. In such a lattice, the forces between molecules are less than those within molecules, leading to easy separation (low M.P. and B.P.), and high molecular volume and lattice constant (see Vol. 1: 15). Barbara Ruhemann and Simon[41] find HI to have a tetragonal face-centred lattice basis, with c/a 1·08. HBr is possibly orthorhombic face-centred.

$LiClH_2O$, studied by Ott,[1] was found to be cubic, with a 3·83. The difficulty of accommodating three atoms Li, Cl and O in

TABLE XI.—CRYSTAL STRUCTURES OF SOME COMPOUNDS OF TYPE AB.

A \ B	F	Cl	Br	I	H	OH	SH
Li	B1	B1	B1	B1	B1	B10	...
Na	B1	B1	B1	B1	B1	...	Bx, B1
K	B1	B1	B1	B1	B1	...	Bx, B1
Rb	B1	B1	B1	B1	B1	...	Bx, B1
Cs	B1	B2	B2	B2	B1	...	B2
α-NH_4	B4	B2 184·3°	B2 137·8°	B2 -17·6°	...	...	Bx
β-NH_4	...	B1	B1	B1			
α-Ag	B1	B1	B1	B4 145·8°	...	...	...
β-Ag	...	...	...	B3			
Cu	...	B3	B3	B3	B4	...	...
Tl	...	B2	B2	B2	...	...	...
PH_4	...	...	...	B10	...	...	...

A \ B	O	S	Se	Te
Be	B4	B3	B3	B3
Mg	B1	B1	B1	B4
Ca	B1	B1	B1	B1
Sr	B1	B1	B1	B1
Ba	B1	B1	B1	B1
Zn	B4	B4, B3	B3	B3
Cd	B1	B4, B3	B4, B3	B3
Hg	Bx	B3, B9	B3	B3
Cr	...	B8	B8	B8
Mn	B1	B1, (B8)	B1	B8
Fe	B1	B8	B8	(B8)
Co	B1	B8	B8	B8
Ni	B1	B8, B13	B8	B8
Pb	B10 (?) B11 (?) Bx	B1	B1	B1

A \ B	N	P	As	Sb	Bi
Al	B4	B3	B3	B3	...
Ga	...	B3	B3	B3	...
In	...	...	...	B3	...
Sn	...	...	B1	B1	...
Cr	B1	...	...	B8	...
Mn	...	...	(B8)	B8	...
Fe	...	...	Bx	B8	...
Co	...	...	...	B8	...
Ni	...	...	B8	B8	B8
Tl	...	...	...	B2	B2
Pd	...	...	...	B8	...
Pt	...	...	...	B8	...

A \ B	Sc	Ti	V	Cr	Cb	B	Ta	Si	Zr
N	B1	B1	B1	B1	B1	B12	B4	.....	B1
C	...	B1	B1	...	B1	...	B1	B3, B5, B6, B7	B1

the cell was recognized. Hendricks[1] reinvestigated the structure, finding the unit cell tetragonal (Figure XXI). The elongation of the *c* axis leaves room for the small Li^+ ions, in either A or B positions shown.

(C) **Summary of AB Types.** Table XI provides a summary of the leading types discussed in this chapter. Rather striking changes in series are sometimes observed, as at NH_4F, AgI, MgTe and BeO (see this vol. : 25B).

Other Cases (alphabetical order). AlSn B1 ; AuSn B8 ; CO Bx ; CoSi Bx ; CrSi Bx ; CuS Bx ; CuSn B8 ; FeAs Bx ; FeB Bx ; FeSi Bx ; GeS Bx ; $LiClH_2O$ Bx ; $LiI3H_2O$ Bx ; MnSi Bx ; NiSi Bx ; NiSn B8 ; PdO B10 or Bx ; PdTe B8 ; PtS Bx ; PtSn B8 ; SnO B10 (?) ; SnTe B1 ; WC Bx.

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(*A list of abbreviations used in references will be found on pages* xxxi *et seq.*)

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CHAPTER IV

THE CRYSTAL STRUCTURE OF INORGANIC COMPOUNDS OF TYPE AB_2

5. The Classification of C Types

COMPOUNDS of the general type AB_2 are here classified, following Ewald and Hermann,[1] into C1 to C19 (and further) types. Intermetallic compounds are not specially included in this chapter (see this Vol. : 19, 20), though it is clearly impossible to draw a definite line between these and other types of com-

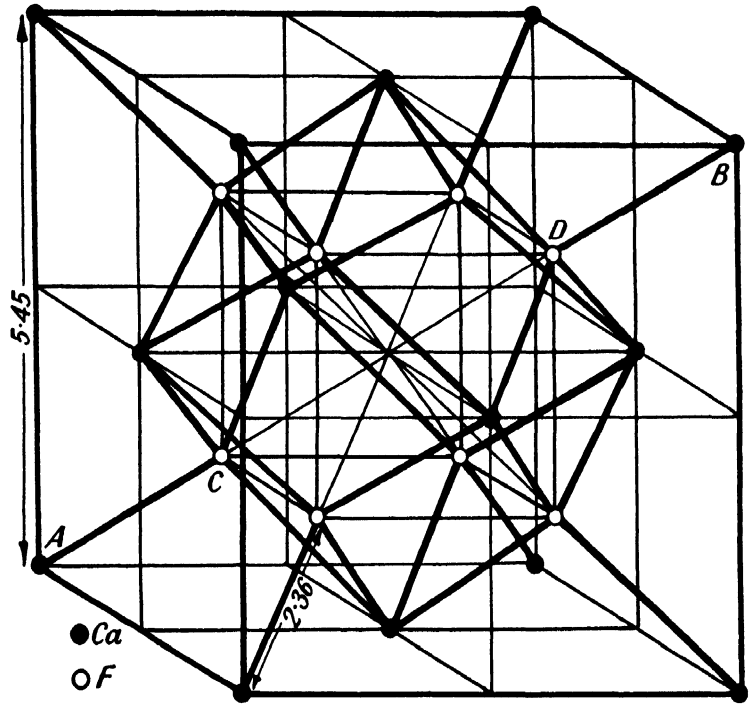

FIGURE XXII.—LATTICE FRAMEWORK OF FLUORSPAR, CaF_2.

pounds. We shall include cases in which either or both A and B are found in Groups IV, V, VI and VIIB (with boron in Group III) of the Periodic Table, in the present section.

Niggli and Brandenberger[2] have treated the stereochemistry of AB_2 types, and derived structures in general agreement with observation.

(A) **Types C1 to C19.** (a) *C1 Type* (Figure XXII). FLUORSPAR, or FLUORITE, CaF_2, is the representative member of C1 type. The unit cell contains four molecules, and consists of a cubic face-centred lattice of Ca^{++} ions, with F^- ions at the centres of the eight small cubes into which the structural unit may be equally divided. Each F^- is surrounded tetrahedrally by $4Ca^{++}$, and each Ca^{++} by $8F^-$. Results are shown in Table XII.

TABLE XII.—LATTICE DISTANCES OF CRYSTALS OF FLUORSPAR TYPE (Schoenflies Space-Group O_h^5).

The numbers given are cube edges (Å.U).

CaF_2	5·45[1]	CeO_2	5·40[1]	OLi_2	4·62[5]	SK_2	7·39[5,6]	$TeNa_2$	7·31[5]
SrF_2	5·78[1]	PrO_2	5·36[1]	ONa_2	5·55[5]	$SeLi_2$	6·01[5,6]	TeK_2	8·15[5]
BaF_2	6·19[1]	ThO_2	5·57[1]	OK_2	6·44[5]	$SeNa_2$	6·81[5]	CBe_2	4·33[7,8]
CdF_2	5·40[1]	UO_2	5·47[1]	SLi_2	5·71[5]	$SeCu_2$	5·75[1]	$SiMg_2$	6·39[1]
β PbF_2*	5·93[1]	SH_2	5·78[3,4]	SNa_2	6 53[5]	SeK_2	7·68[5]	$SnMg_2$	6·78[1]
$SrCl_2$	6·98[1]	SeH_2	6·02[3,4]	SCu_2	5·59[1]	$TeLi_2$	6·50[5,6]	$PbMg_2$	6·75[1]

* Above o 200°C.[9]

(b) *C2 Type* (Figures XXIV and XXV). Lattice C2 is conveniently considered in relation to C1, and developed from it by moving the atoms within the large face-centred cube along diagonals of the smaller cubes of Figure XXII. This gives rise to two cases: (i) where the atoms are moved towards unoccupied cube corners, as with IRON PYRITES, FeS_2; (ii) where the atoms are moved towards occupied corners, as with solid CARBON DIOXIDE, CO_2. If the diagonal AB of Figure

XXII is represented by the top line shown in Figure XXIII, then the other lines represent the corresponding diagonal in Figure XXIV (pyrites type) and XXV (solid CO_2 type) respectively. The parameter u fixes the positions of the atoms along these diagonals. Thus for CaF_2, the cube diagonal is $\sqrt{3} \times 5{\cdot}45 = 9{\cdot}44$ Å.U. The u value 0·25 then fixes the distance between nearest unlike neighbours Ca-F as 0·25 ×

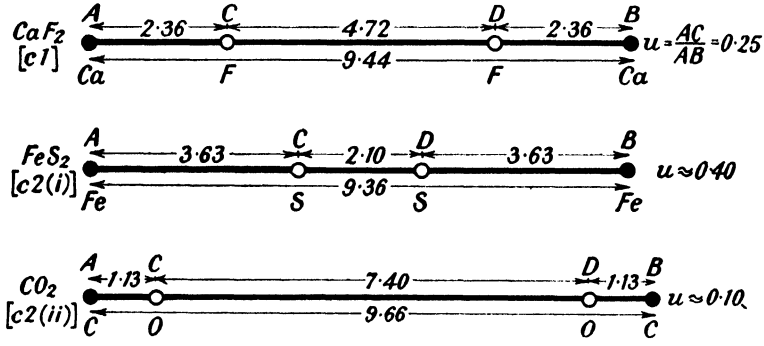

FIGURE XXIII.—DISTANCES ALONG CUBE DIAGONALS OF FLUORSPAR, IRON PYRITES AND SOLID CARBON DIOXIDE. The points A, C, D, B correspond to those having the same lettering in Figures XXII, XXIV and XXV for the three cases respectively.

$9{\cdot}44 = 2{\cdot}36$. For crystals of FeS_2 type, u approximates to 0·4, giving the distance Fe-S along the diagonal of the FeS_2 cube as $9{\cdot}36u = 9{\cdot}36 \times 0{\cdot}388 = 3{\cdot}63$. It follows that the distance between two neighbouring sulphur atoms of a pair is 2·10. Pyrites has relationship with polar NaCl; if the Fe ions of Figure XXIV are replaced by Na^+, and the centres of gravity of each S_2 group by Cl^-, the structure of Figure XIII is obtained. The arrows in Figure XXIV indicate the directions along the cube diagonals shown in which atoms inside the cube must be moved in order to derive the pyrites from the fluorspar structure. The lines are continued dotted outside the cube to indicate the relative positions of adjacent sulphur atoms. Figure XXV shows the structure assigned to solid CO_2 in a similar way. The effect of $u = 0{\cdot}1$ is to bring the two oxygen atoms of the CO_2 molecule close to the carbon atom, so that the

structure is molecular, in agreement with other considerations. The three atoms are collinear.

According to Fourier series analysis,[10] the cube edge or lattice constant of iron pyrites is 5·405, and the evidence suggests that the structure is not ionic. Solid CO_2 has been found to have a

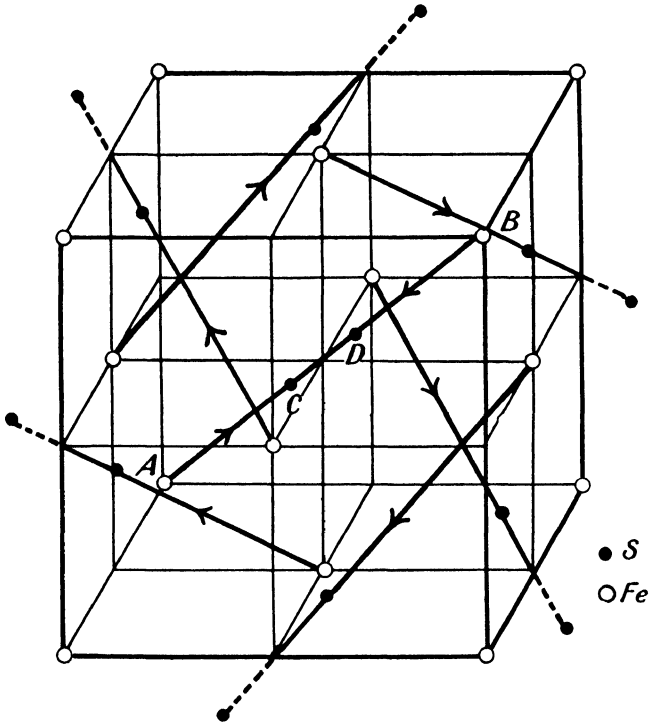

FIGURE XXIV.—LATTICE STRUCTURE OF IRON PYRITES, FeS_2.

lattice constant $a = 5{\cdot}575$ at 83°K,[11] and to vary from 20° to 114°K according to $a = 5{\cdot}540 + 4{\cdot}68.10^{-6}T^2$.

Results are shown in Table XIII. For most of the cases of Type C2 (i) only the distance a is recorded.

(c) *C3 Type* (Figure XXVI). This is the CUPRITE OCu_2 type, and includes OAg_2 and possibly OPb_2. The structure contains two interpenetrating lattices, one body-centred cubic of oxygen atoms, and the other face-centred cubic of metal atoms.[1] Each

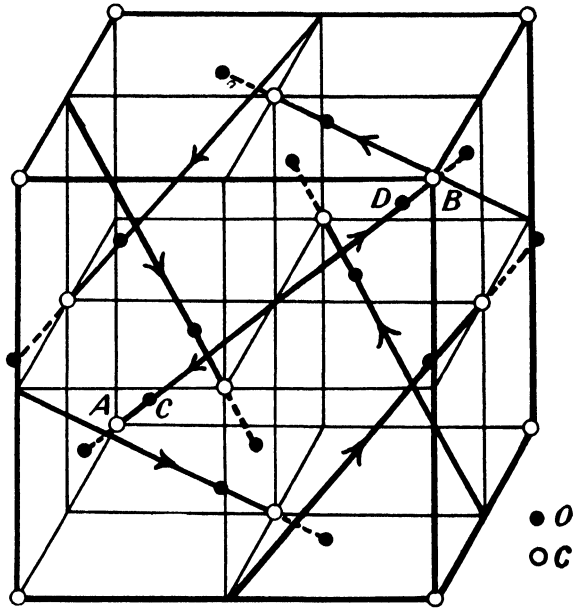

FIGURE XXV.—LATTICE STRUCTURE OF SOLID CARBON DIOXIDE, CO_2.

TABLE XIII.—LATTICE CONSTANTS OF CRYSTALS OF IRON PYRITES TYPE (Schoenflies Space-Group T_h^6).

Type	Substance	a	u	Distance to nearest unlike atom along cube diagonal $a\sqrt{3}.u$	Distance between members of pairs of adjacent atoms B
C2 (ii)	CO_2	5·575[11]	0·12	1·13	2·26
	ON_2	5·72[1]	0·12	1·16	2·32
C2 (i)	FeS_2	5·405[1,10]	0·39	3·63	2·10
	CoS_2	5·64[1]	0·39	3·86	2·05
	NiS_2	5·74[1]	0·39	3·92	2·09

MnS_2	6·08[1]	$NiSe_2$	6·02[1]	$RuTe_2$	6·36[1]	RhS_2	5·57[1]	$OsSe_2$	5·93[1]	$PtAs_2$	5·96[1]
$MnTe_2$	6·94[1]	RuS_2	5·58[1,12]	$PdAs_2$	5·97[1]	$AuSb_2$	6·65[13]	$OsTe_2$	6·37[1]	$PtSb_2$	6·43[1]
$CoSe_2$	5·85[1]	$RuSe_2$	5·92[1]	$PdSb_2$	6·44[1]	OsS_2	5·64[1]	PtP_2	5·68[1]		

oxygen atom lies at the centre of a regular tetrahedron whose corners are occupied by metal atoms. There are four metal

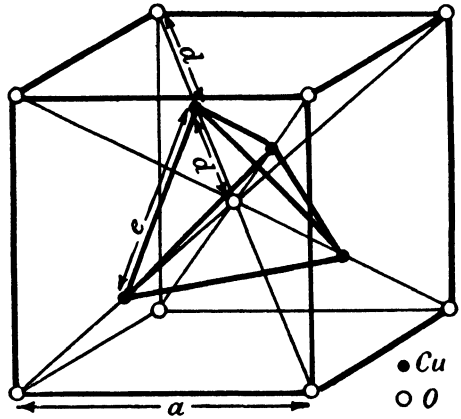

FIGURE XXVI.—LATTICE STRUCTURE OF CUPRONS OXIDE, Cu_2O.

atoms and $1 + (8 \times \frac{1}{8}) = 2$ oxygen atoms in the unit cell, corresponding to $2OMe_2$. If a, d and e are the distances marked,

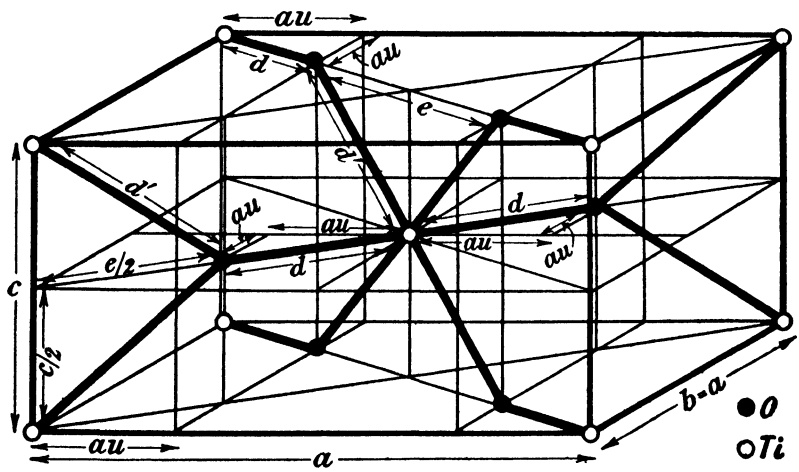

FIGURE XXVII.—CRYSTAL STRUCTURE OF RUTILE, TiO_2.

in Figure XXVI, the approximate values are 4·26, 1·84 and 3·01; 4·74, 2·05 and 3·35 for OCu_2 and OAg_2 respectively,[1]

where $d = \sqrt{3}a/4$, and $e = a/\sqrt{2}$, and correspond to the nearest distances M–O and M–M respectively. A recent measurement yielded 4·252 as the elementary cube edge of OCu_2.[14]

(d) *C4 Type* (Figure XXVII). This is the RUTILE type, corresponding to one modification of TiO_2, and a number of other dioxides, as well as some fluorides of bivalent elements.

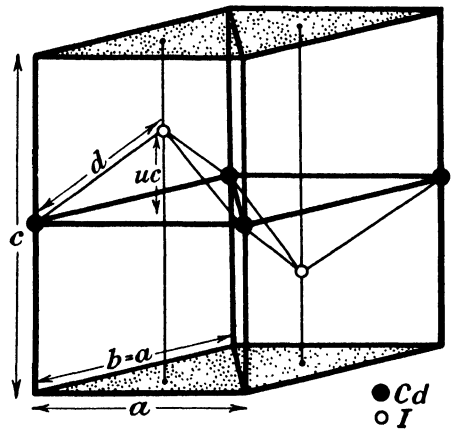

FIGURE XXVIII.—UNIT CELL OF CADMIUM IODIDE, CdI_2. Here $a = 4·24$, $c = 6·84$, $d = 2·99$ Å.U.; $u = 0·25$, $uc = 1·71$ Å.U. The stippled planes denote cleavages.

The unit tetragonal cell shown in Figure XXVII has Ti atoms on a body-centred tetragonal lattice, with oxygen atoms on the diagonals of equidistant planes as shown. A titanium atom is surrounded by 6 oxygen atoms, 4 at distance d', and 2 at distance d; an oxygen atom is surrounded by 3 titanium atoms in one plane, 2 at distance d', and 1 at distance d, given by $au\sqrt{2}$. The distance e may be derived from $a\sqrt{2} - 2d$. The unit cell shown contains $1 + (8 \times \frac{1}{8}) = 2$ atoms of titanium and $2 + (4 \times \frac{1}{2}) = 4$ atoms of oxygen, that is, 2 molecules of TiO_2.

Results are recorded in Table XIV, the numbers being taken directly from the *Strukturbericht*,[1] where references are given to the literature. The value of u remains practically constant.

TABLE XIV.—LATTICE CONSTANTS OF CRYSTALS OF THE RUTILE TYPE (Schoenflies Space-Group D_{4h}^{14})

(The distances given correspond to those marked in Figure XXVII.)

Substance	*a*	*c*	*c*/*a*	*d*	*d'*	*e*	*u*
MgF_2	4·64	3·06	0·66	2·05	1·96	2·47	0·31
ZnF_2	4·72	3·14	0·67	2·10	1·99	2·47	0·32
FeF_2	4·83	3·36	0·70	2·12	2·12	2·60	0·31
CoF_2	4·70	3·19	0·68	2·09	2·01	2·46	0·32
NiF_2	4·71	3·11	0·66	2·06	2·00	2·53	0·31
TiO_2	4·58	2·95	0·64	2·01	1·92	2·46	0·31
SnO_2	4·72	3·17	0·67	2·07	2·03	2·54	0·31

AB_2	*a*	*c*	AB_2	*a*	*c*	AB_2	*a*	*c*
MnF_2	4·87	3·30	TeO_2	4·79	3·77	RuO_2	4·51	3·11
PbO_2	4·96	3·39	MoO_2	4·86	2·79	OsO_2	4·51	3·19
VO_2	4·54	2·88	WO_2	4·86	2·77	IrO_2	4·49	3·14
CbO_2	4·77	2·96	MnO_2	4·40	2·87			

(e) *C*5 *Type*. This is represented by ANATASE, another variety of TiO_2, in which the unit cell is again tetragonal, and contains $4TiO_2$. The Schoenflies space-group is D_{4h}^{19}, and cell dimensions: *a* 3·73, *c* 9·37, *c*/*a* 2·51.[1]

(f) *C*6 *Type* (Figures XXVIII and XXIX). The CADMIUM IODIDE CdI_2 type exemplifies a "layer" lattice. A unit cell, of hexagonal type, is shown in Figure XXVIII, and a portion of the structure in Figure XXIX. The cell contains $4 \times \frac{1}{4} = 1$ atom of cadmium and 2 of iodine, or 1 molecule of CdI_2. Each

cadmium atom has 6 iodine neighbours, arranged at the corners of a deformed octahedron ; each atom of iodine is in contact with three of cadmium, at the corners of an equilateral triangle.

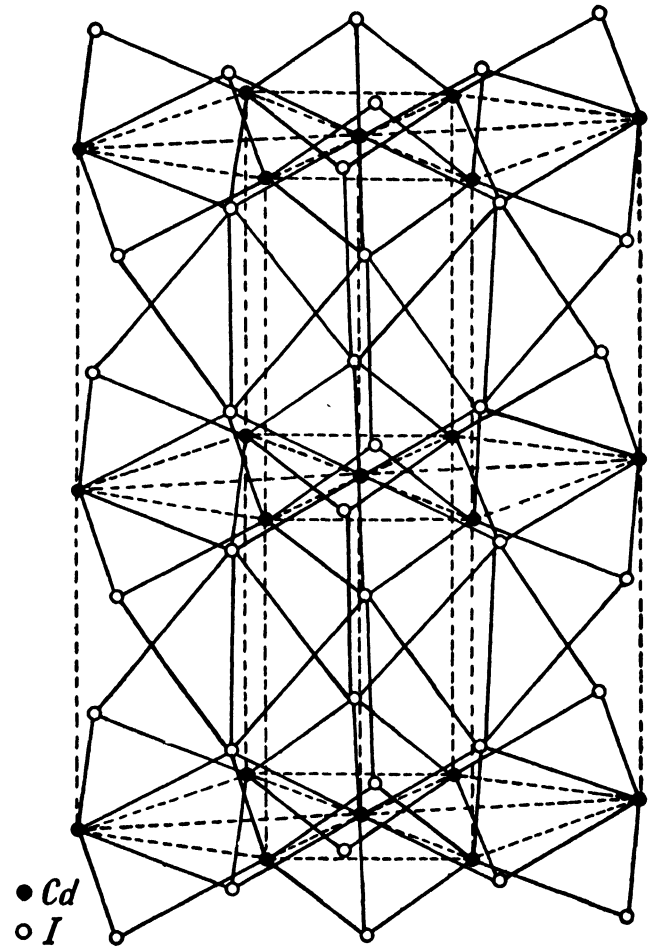

FIGURE XXIX.—LATTICE STRUCTURE OF CADMIUM IODIDE, CdI_2.

The iodine atoms are in hexagonal close-packing (A3 type, Figure IX), or very nearly so, with the smaller cadmium atoms in the interstices of alternate layers. The structure may be

divided into electrically neutral layers by planes parallel to the base of the unit cell placed midway between the parallel sheets of cadmium atoms. The presence of layers of iodine atoms in contact without cementing cadmium atoms is associated with excellent basal cleavage of the crystal. For exact hexagonal close packing of iodine atoms, the c/a ratio should be 1·63 ; the

TABLE XV.—LATTICE CONSTANTS OF CRYSTALS OF THE CADMIUM IODIDE TYPE (Schoenflies Space-Group D_{3d}^3).

AB_2	a	c	c/a	AB_2	a	c	c/a	AB_2	a	c	c/a
FAg_2[21]	2·99	5·71	1·91	$MnBr_2$[15]	3·82	6·19	1·62	ZrS_2[1]	3·68	5·85	1·59
$Mg(OH)_2$[1]	3·11	4·74	1·52	MnI_2[17]	4·16	6·82	1·64	$ZrSe_2$[1]	3·79	6·18	1·63
$MgBr_2$[15]	3·82	6·26	1·64	$Fe(OH)_2$[1]	3·24	4·47	1·38	$Cd(OH)_2$[1]	3·46	4·64	1·34
MgI_2[16]	4·14	6·88	1·66	$FeBr_2$[15]	3·74	6·17	1·65	CdI_2[1]	4·24	6·84	1·61
$Ca(OH)_2$[1]	3·52	4·93	1·40	FeI_2[17]	4·04	6·75	1·67	$PdTe_2$[1]	4·03	5·12	1·27
CaI_2[16]	4·48	6·96	1·55	$Co(OH)_2$[1]	3·19	4·66	1·46	SnS_2[1]	3·64	5·87	1·61
TiS_2[1]	3·40	5·69	1·68	$CoBr_2$[15]	3·69	6·12	1·66	PtS_2[1]	3·54	5·02	1·42
$TiSe_2$[1]	3·53	6·00	1·70	CoI_2[17]	3·96	6·65	1·68	$PtSe_2$[1]	3·72	5·06	1·36
$TiTe_2$[1]	3·77	6·54	1·73	$Ni(OH)_2$[19]	3·11	4·17	1·34	$PtTe_2$[1]	4·01	5·20	1·30
$Mn(OH)_2$[1]	3·34	4·68	1·40	α-$Zn(OH)_2$[18]	3·14	5·12†	1·63†	PbI_2[17]	4·53	6·92	1·53

* u=0·31 or 1·19. † Mean values.

actual ratio is 1·61. Other substances of the type depart more widely from the ideal. The ratio u which fixes the positions of the iodine atoms is 0·25 in the ideal case ; this is pretty well satisfied for CdI_2. The iodine atoms are in contact, but the cadmium atoms are separated and lie in the interstices where three iodine atoms rest on three. An iodine atom in contact with three cadmium atoms forms a tetrahedron of atomic centres whose base is an equilateral triangle and whose height is uc ; thus the edge d (giving the distance between nearest unlike centres) is given by $\sqrt{a^2/3 + u^2c^2}$. This gives $d = 2{\cdot}99$, using the values of the structural dimensions of Table XV, corresponding very closely to the sum of the assigned atomic

radii. The distance between iodine centres, on the other hand, is equal to the a axis = 4·24, which is more than twice the iodine radius, showing that atoms carrying like charges may be more widely spaced than the sum of the assigned radii (Bragg's values: Cd = 1·60, I = 1·40). The lattice parameter u is nearly constant for the C6 type, and equal to about 0·25.

(g) *C7 Type* (Figure LXI). MOLYBDENITE, MoS_2, provides another example of a layer lattice. An hexagonal unit cell is shown in Figure XXX, containing $1 + (8 \times \frac{1}{8}) = 2$ atoms of molybdenum and $2 + (8 \times \frac{1}{4}) = 4$ atoms of sulphur, or 2 molecules of MoS_2. Each atom of molybdenum is surrounded by six equidistant sulphur atoms which lie at the corners of a small triangular prism, whilst each sulphur atom is equidistant from three atoms of molybdenum at the corners of an equilateral triangle. The cleavage planes, as in the case of cadmium iodide, divide the structure into layers, each of which has molybdenum atoms in a layer in the centre with sulphur atom layers on both sides. Hexagonal close-packing of the sulphur atoms requires $c/a = 2 \times 1{\cdot}63 = 3{\cdot}26$, but this is not accurately fulfilled. The parametral ratio u defines the positions of the sulphur atom layers, the first group of four sulphur atoms directly above a group of four molybdenum atoms being separated by a distance uc, where $u = \frac{3}{8}$ in the ideal case. The structure differs from Type C6 in that the sulphur atoms on each side of a plane containing molybdenum atoms are opposite to each other and fit into corresponding gaps between atoms of the other kind, whereas in C6 the metalloid atoms fit into different gaps, as Figure XXIX shows. The height of the tetrahedron formed by a molybdenum atom and three sulphur atoms is $c(\frac{1}{2} - u)$, whence d, the distance separating nearest unlike centres, is $\sqrt{a^2/3 + c^2(\frac{1}{2} - u)^2} = 2{\cdot}35$ for MoS_2, in satisfactory agreement with the sum of the estimated atomic radii. Where four sulphur atoms form a tetrahedron, however, the longer edges f may be calculated as 3·66, whereas the diameter of a sulphur atom is 2·10 (Bragg), again suggesting that like atoms may be more widely spaced than unlike. WS_2 also crystallizes in Type C7 (Schoenflies space-group D_{6h}^4). The values of a, c, c/a; d, e, f; u for the two cases are: MoS_2[1], 3·15,

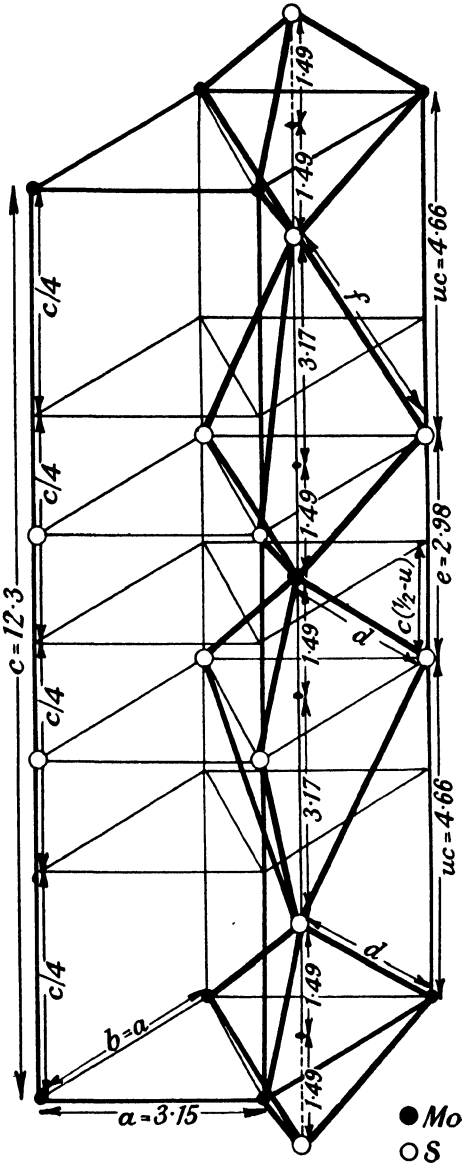

FIGURE XXX.—CRYSTAL STRUCTURE OF MOLYBDENITE, MoS_2.

12·30, 3·90 ; 2·35, 2·98, 3·66 ; 0·379 : WS_2[1], 3·18, 12·5, 3·93 ; 2·48, 3·12, 3·63 ; 0·375, respectively.

(h) *C*8 *Type* (Figure XXXI). The figure denotes the structure of β-QUARTZ, stable above 575°C. The unit cell is hexagonal, and contains $1 + (4 \times \frac{1}{4}) + (2 \times \frac{1}{2}) = 3$ atoms of silicon and 6 atoms of oxygen, corresponding to 3 molecules of SiO_2, as originally calculated by Bragg from the density of quartz. A silicon atom has four oxygen neighbours, and an

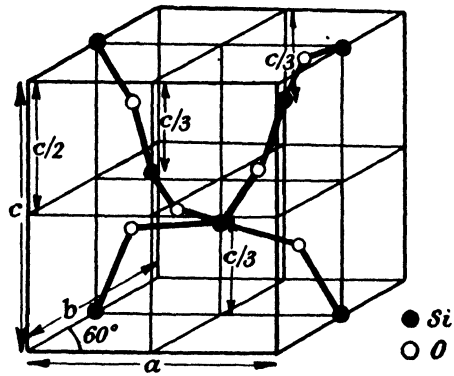

FIGURE XXXI.—UNIT CELL OF β-QUARTZ, SiO_2.

oxygen two silicon atoms. The oxygen atoms do not lie on the lines of centres of neighbouring atoms, but are related tetrahedrally to each atom of silicon. α-quartz has a closely-approximating structure of slightly smaller dimensions, corresponding to its lower molecular volume. It does not appear possible to identify the molecule SiO_2 in the structure. The oxide GeO_2[1] apparently has a similar arrangement, with *a* 4·98, *c* 5·64, *c*/*a* 1·13. The spiral structure of quartz appears related to its peculiar physical properties. The approximate cell dimensions of β-quartz[1] are : *a* 5·01, *c* 5·47, *d* 1·59 (nearest Si-O), *c*/*a* 1·09, *u* 0·50 (space-groups of enantiomorphous forms D_6^5 and D_6^4). For α-quartz,[1] *a* 4·89, *c* 5·38, *c*/*a* 1·10, *u* 0·46 (space-groups D_3^4 and D_3^6).

Very accurate measurements of the lattice constants of α-quartz have been recently made.[20,21] Bradley and Jay[22] find

the dimensions a 4·9029, c 5·3933, $c/a = 1{\cdot}10002 \pm 0{\cdot}00004$, and suggest that this standard be used in accurate lattice measurements.

Meissner[23] examined quartz acoustically and by means of X-rays. Correns and Nagelschmidt[24] find, by X-ray examination, that chalcedony consists of quartz which can be " fibred " in two directions.

(i) *C9 Type.* This is represented by the high temperature form β-CRISTOBALITE, SiO_2, stable above 175°C. (Groth). The structure is not illustrated by a separate figure, but may be readily understood by reference to the diamond structure of Figure X, where each lattice-point must be taken to represent a silicon atom. The oxygen atoms are placed midway on the 16 connecting lines shown. This unit cell is such that each silicon atom is surrounded tetrahedrally by four oxygen atoms, whilst each oxygen has two silicon neighbours (Schoenflies cubic space-group O_h^7). There are $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) + 4 = 8$ atoms of silicon and 16 atoms of oxygen in the unit, corresponding to 8 molecules of SiO_2, though the molecule cannot be identified in the crystal. The edge of the cube is a 7·12, whilst d, the distance of nearest Si-O, given by $\sqrt{3}.a/8$, is 1·54.[1] α-cristobalite is tetragonal, of a different type.

A more recent measurement gives a 7·078.[25] It appears that opals may contain β-cristobalite, or α-cristobalite and quartz.

(j) *C10 Type* (Figure XXXII). The higher temperature form β-TRIDYMITE, another modification of SiO_2, assumes importance in that it corresponds to the structure of ICE, OH_2. C10 type is related to C9 in the same way that B4 (wurtzite) is related to B3 (zinc blende). The unit cell in Figure XXXII, so far as the silicon atoms are concerned, may be obtained from Figure XV by replacing both Zn and S atoms by Si: the oxygen atoms are then placed midway on the lines connecting silicon neighbours. The cell has $(8 \times \frac{1}{8}) + (4 \times \frac{1}{4}) + 2 = 4$ atoms of silicon, and $7 + (4 \times \frac{1}{4}) = 8$ atoms of oxygen, or 4 molecules of SiO_2 (Schoenflies hexagonal space-group D_{6h}^4). Each silicon atom is again surrounded tetrahedrally by four oxygen neighbours, and each oxygen by two atoms of silicon. The lower temperature form, stable below 130°C (Groth),

α-tridymite is orthorhombic. The cell dimensions of β-tridymite[1] are: a 5·03, c 8·22, d (Si-O) 1·54, c/a 1·63. Ice[26] has a similar hexagonal cell, with a 4·535, c 7·41, c/a 1·634, the oxygen atoms being in wurtzite arrangement, with four molecules per unit cell. The positions of the hydrogen atoms on the lines connecting neighbouring pairs of oxygen atoms are uncertain. No change in crystal structure is found from 0° to −183°C. W. H. Barnes considers that the structure is ionic,

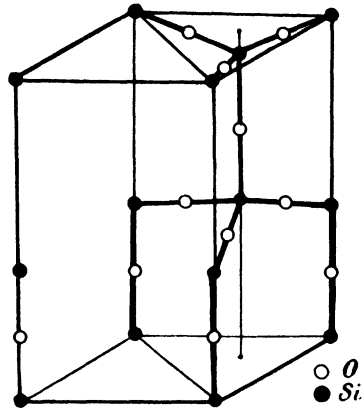

FIGURE XXXII.—UNIT CELL OF β-TRIDYMITE, SiO_2.

and contains H^+ and O^{--}, but certain considerations based on the "Raman effect" tended to favour the existence of molecules of H_2O in ice. The structure is so strongly polar that it resembles an ionic crystal, however, in general properties, and Kinsey and Sponsler[27] suggest that it contains the units H^+ and $H_3O_2^-$ on the basis of Barnes' results.

(k) *C*11 *Type* (Figure XXXIIa). CALCIUM CARBIDE, CaC_2, and MOLYBDENUM SILICIDE, $MoSi_2$, are characteristic of the type. The metal atoms A are on a body-centred tetragonal lattice, with B (carbon or silicon) atoms on the cell edges parallel to the c axis, in positions defined by uc, $c(1-u)$, and on the line through the central atom A parallel to the c axis, in positions defined by $c(\frac{1}{2}-u)$, $c(\frac{1}{2}+u)$. The cell contains $2AB_2$. For CaC_2 type, $u \backsim 0{\cdot}41$, and $c/a \backsim 1{\cdot}63$; for $MoSi_2$

and WSi_2, $u \simeq 0{\cdot}33$ and $c/a \simeq 2{\cdot}45$. The lattice is probably ionic. Results are in Table XVa.

The a values of v. Stackelberg for carbides have been multiplied by $\sqrt{0{\cdot}5} = 0{\cdot}707$, since his figures refer to a face-centred

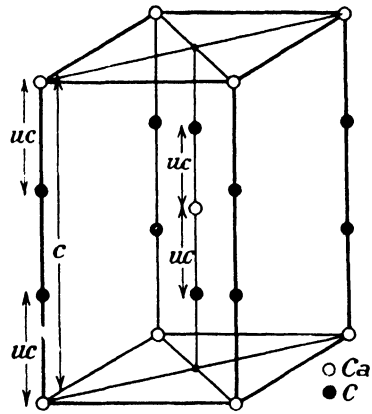

FIGURE XXXIIa.—CRYSTAL STRUCTURE OF CALCIUM CARBIDE, CaC_2.

tetragonal lattice containing $4AB_2$. $SbCu_2$[29] and $AsFe_2$[30] may belong to C11 type, but are here provisionally placed in Cx type (Table XVd, page 67).

TABLE XVa.—LATTICE CONSTANTS OF CRYSTALS OF CALCIUM CARBIDE AND MOLYBDENUM SILICIDE TYPES (Schoenflies Space-Group D_{4h}^{17}(?).

	a	c	c/a		a	c	c/a		a	c	c/a
CaC_2[1]	3·87	6·37	1·65	CeC_2[1]	3·87	6·48	1·67	*ThC_2[8,38,48]	4·14	5·28	1·27
SrC_2[1]	4·11	6·68	1·63	PrC_2[1]	3·85	6·38	1·66	$MoSi_2$[1]	3·20	7·86	2·46
BaC_2[1]	4·40	7·06	1·60	NdC_2[1]	3·82	6·23	1·63				
LaC_2[1]	3·92	6·55	1·67	SmC_2[8,38]	3·75	6·28	1·67	WSi_2[1]	3 21	7·88	2·45

*ThC_2 has probably a different lie of C, groups from CaC_2[26]

(l) *C12 to C18 Types.* Information respecting these cases is in Table XVb, page 66. It may be noted that $MgZn_2$, $MgCu_2$ and

$CuAl_2$ are true intermetallic compounds. They are included here in line with the C type classification.

TABLE XVb.—LATTICE CONSTANTS OF CRYSTALS OF C12 TO C18 TYPES.

Type	AB_2	Cell and No. of Units	Space-Group	a	b	c	α
C12	$CaSi_2$*[81]	Rhombohedral (2)		10·4			21° 30′
C13	Red HgI_2†[1]	Tetragonal (2)	D_{4h}^{15}	4·36		12·36	
C14	$MgZn_2$[1,21]	Hexagonal (4)	D_{6h}^{4}	5·17		8·50	
C15	$MgCu_2$[1]	Cubic‡ (8)	O_h^7	7·03			
	ZrW_2[1,32]			7·61			
C16	$CuAl_2$[1]	Tetragonal (4)	D_{4h}^{18}	6·05		4·88	
C17	BFe_2[1,38,42,54]	Tetragonal (4)	D_{4h}^{18}	5·10		4·24	
C18	FeS_2§[81]	Rhombic (2)	V_h^{12}	5·35	4·40	5·35	
	$FeAs_2$[1]			5·17	4·86	5·80	
	$FeSb_2$[1,30,43]			3·19	5·82	6·52	

* Si atoms not equivalent. † Layer lattice. ‡Compare spinel lattice type H11. §Markasite.

(m) *C19 Type.* CADMIUM CHLORIDE, $CdCl_2$, has a rhombohedral unit cell containing $1CdCl_2$. Cd atoms lie at the eight corners, with Cl atoms on the long diagonal at $\frac{1}{4}$ and $\frac{3}{4}$ positions: thus $u = \frac{1}{4}$, as for CdI_2 (C6 type). The structure comprises a layer lattice like C6 type, but the Cl atoms are in approximate

TABLE XVc.—LATTICE CONSTANTS OF CRYSTALS OF CADMIUM CHLORIDE TYPE (Schoenflies Space-Group D_{3d}^5).

AB	a	α	AB	a	α	AB	a	
$MgCl_2$[1]	6·22	33° 30′	$NiBr_2$*[37]	6·46	16° 40′	$CdCl_2$[1,36]	6·23	36° 2′
$CoCl_2$[1,34]	6·16	33° 26′	NiI_2*[37]	6·92	16° 20′	$CdBr_2$*[35],[18]	7·72	61° 40′†
$NiCl_2$[1]	6·12	33° 30′	$ZnCl_2$[1]	6·32	34° 40′			

* Sublimed specimens. † Referred to unit cell containing $4CdBr_2$.

TABLE XVd.—CRYSTAL STRUCTURE OF COMPOUNDS AB, OF UNCLASSIFIED Cx TYPES.

AB_2	Cell and No. of Units	a	b	c	AB_2	Cell and No. of Units	a	b	c	β
NO_2[41]	Cubic (8)	7·77			SiO_2*[1]	Orthorhombic (64)	9·88	17·1	16·3	
SAg_2[1]	Cubic (2)	4·84			SiO_2†[1]	Cubic (8)	6·94			
NFe_2[1,42]‡	Orthorhombic (4)	2·77	4·82	4·42	TiO_2§[1]	Orthorhombic (8)	9·17	5·44	5·14	
PFe_2[20,43,44]	Hexagonal (3)	5·85		3·45	C-ZrO_2‖[1]	Monoclinic (4)	5·21	5·26	5·32	80° 32′
$AsFe_2$[1,45]¶	Tetragonal (2)	3·63		5·97	B-ZrO_2[1]	Tetragonal	5·07		5·16	
$SbCu_2$[1,25,45]		4·03		6·14	A-ZrO_2[1]	Rhombohedral or pseudo-Hexagonal	3·60		5·88	
$SiCo_2$[46]	Orthorhombic (4)	3·73	4·91	7·10	α-PbF_2[9]	Orthorhombic (4)	3·80	6·41	7·61	
$FeSi_2$[1]	Tetragonal (1) C_{4h}^1	2·69		5·13	$PbCl_2$[49]		4·53	7·61	9·03	
$CrSi_2$[46]	Hexagonal (3)	4·42		6·35	$PbBr_2$[50,51]		4·72	8·02	9·49	
$MnSi_2$[46]	Tetragonal (16)	5·51		17·42	$HgCl_2$[50,51]		4·32	5·96	12·74	
WFe_2[1]	Hexagonal (4)	4·73		7·70	$HgBr_2$[47,49]	Orthorhombic (4)	4·62	6·80	12·45	
α-CW_2[1]	Hexagonal (1)	2·99		4·71	HgI_2[49] (yellow)	(C_{2v}^{12})	4·68	7·32	13·76	
CMo_2[1]		2·99		4·73	$Hg(CN)_2$**[1]	Tetragonal (8)	9·74		8·94	
YC_2[48]	Hexagonal (2)	3·79		6·58	CaC_2[53]	Orthorhombic (2)	6·24	6·43	4·20	
β-$Zn(OH)_2$[52]	Orthorhombic (4)	5·16	8·53	4·92	$Sr(OH)_2.8H_2O$[1]	Tetragonal (1)	6·41		5·81	

(V_h^{16})

* α tridymite. † α-cristobalite ‡NFe_2 given by Hendricks and Kosting[41] as H(2) D_3^1d; 2·70, 4·36. § Brookite. ‖ Stable below 1,000°C.
¶ H.egg[30] gives T (4); 5·13, 5·97 for $AsFe_2$. ** Fm Type.

TABLE XVI.—CRYSTAL STRUCTURE OF COMPOUNDS OF TYPE AB_2.

A / B_2	Mg	Ca	Sr	Ba	Zn	Mn	Cd	Hg	Fe	Co	Ni	Pb
F_2	C_4	C_1	C_1	C_1	C_4	C_4	C_1		C_4	C_4	C_4	C_1
Cl_2	C_{19}	C_x	C_1		C_{19}	C_{19}	C_{19}	C_x	C_{19}	C_{19}	C_{19}	C_x
Br_2	C_6					C_6	C_{19}*	C_x	C_6	C_6	C_{19}*	C_x
I_2	C_6	C_6				C_6	C_6	C_{13} C_x	C_6	C_6	C_{19}	C_6
$(OH)_2$	C_6	C_6			C_6 C_x	C_6	C_6		C_6	C_6	C_6	
C_2		C_{11}	C_{11}	C_{11}								
Si_2		C_{12}				C_x			C_x			

A / B_2	Li	Na	K	Cu	Ag	Pb	O	S	Se	Te
O_2	C_1	C_1	C_1	C_3	C_3	C_4	C_1	C_1	C_1	C_1
S_2	C_1	C_1	C_1	C_1	C_x	C_4	C_4	C_1	C_1	C_1
Se_2	C_1	C_1	C_1	C_1		C_4	C_4	C_1	C_1	
Te_2	C_1	C_1	C_1	C_1		C_1	C_1	C_1		

A / B_2	Ti	Zr	Ce	Pr	Th	Sn	Cr	Mo	W	Mn	Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt
O_2	C_4 C_5C_x	C_x	C_1	C_1	C_1	C_4		C_4	C_4	C_4				C_4		C_4	C_4	C_4	
S_2	C_6	C_6				C_6		C_7	C_7	C_2	C_2 C_{18}	C_2	C_2	C_2	C_2		C_2		C_6
Se_2	C_6	C_6										C_2	C_2	C_2		C_6	C_2		C_6
Te_2	C_6									C_2				C_2		C_6	C_2		C_6
P_2																			C_2
As_2											C_{18}					C_2			C_2
Sb_2											C_{18}					C_2			C_2
C_2			C_{11}	C_{11}	C_{11}		C_x	C_{11}	C_{11}	C_x	C_x								
Si_2																			

A / B_2	U
O_2	C_1
S_2	C_6
Se_2	C_6
Te_2	C_6
P_2	C_2
As_2	C_2
Sb_2	C_2
C_2	
Si_2	

* Layer lattices o $1C_6 + C_{19}$ types combined exist in unsublimed specimens.

cubic close-packing, whilst the I atoms of C6 are in hexagonal packing.

$MnCl_2$[1] and $FeCl_2$[1] are of C19 type, with $\alpha = 35°\ 10'$ and $34°\ 10'$ respectively. $RuCl_2$, $RhCl_2$, $PdCl_2$, $IrCl_2$ and $PtCl_2$ are also of this type.[36] Unsublimed $NiBr_2$[37] and $CdBr_2$[38] belong to a type intermediate between C6 and C19, in which layers of each type are present.

Ferrari and Inganni[40] have found that the binary crystals of C19 type containing $CaCl_2$ as one component do not show complete miscibility, and suggest that the structures may not be rhombohedral. $CaCl_2$[53] is now found to be orthorhombic (see Cx type below).

(B) **Unclassified Cases, Cx Type.** These are tabulated on page 67.

(C) **Summary of AB_2 Types.**

Other Cases (alphabetical order). $AuSb_2$ C2; $AsFe_2$ Cx; BFe_2 C17; CBe_2 C1; CMo_2 Cx; CO_2 C2; CW_2 Cx; $CoAs_2$ Cx; $CuAl_2$ C16; FAg_2 C6; $IrCl_2$ C19; LaC_2 C11; $MgCu_2$ C15; $MgZn_2$ C14; NFe_2 Cx; NO_2 Cx; NdC_2 C11; ON_2 C2; PFe_2 Cx; $PbMg_2$ C1; $PdCl_2$ C19; $PtCl_2$ C19; PtP_2 C2; $RuCl_2$ C19; $RhCl_2$ C19; SH_2 C1; $SbCu_2$ Cx; SeH_2 C1; $SiCo_2$ Cx; $SiMg_2$ C1; SiO_2 C8, C9, C10, Cx; SmC_2 C11; $SnMg_2$ C1; WFe_2 Cx; YC_2 Cx; ZrW_2 C15.

Table XVI contains 129 entries and 151 spaces.

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(*A list of abbreviations used in references will be found on pages* xxxi *et seq.*)

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(*A list of abbreviations used in references will be found on pages* xxxi *et seq.*)

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CHAPTER V

THE CRYSTAL STRUCTURE OF COMPOUNDS OF FURTHER INORGANIC TYPES

THE classification of inorganic compounds of complex types according to crystal structure has been commenced by Ewald and Hermann,[1] who have adopted a system of D, F, G and H types, with added numbering, which is no longer consecutive as in A, B and C types already examined: gaps are left which may become filled as occasion arises. This method does not prove itself very suitable for the present purpose, and a different system is adopted. Classification is here attempted on the basis of *the number of atoms* $X = 3, 4, 5 \ldots$ *present in the molecule*, with cross-reference to Ewald and Hermann's system where possible.

Certain groups containing more than one atom are more conveniently counted as one, with special symbolism (denoted in brackets) as follows: OH (Hy), NH_4 (Am), CN (Cy), SCN (Scy), H_2O (Aq) and NH_3 (Amm), in ammines. For example, Cy may replace a single atom O in compounds of the spinel type, and the method of counting brings similar types, in general, satisfactorily near each other; thus Fe_3O_4 and K_2ZnCy_4 have $X = 7$. The groups within co-ordinated complexes are also always counted as one, independently of whether more than one atom is present within them or not. With this exception, in oxy-groups such as CO_3, NO_3, SO_4. . . . each atom is counted separately: thus $[Co(CO_3)Amm_4]SO_43Aq$ has $X = 1 + 1 + 4 + 5 + 3 = 14$, and AmH_2PO_4 has $X = 1 + 2 + 5 = 8$. Some of the complex silicates, which have no definitely assigned formulæ, are classified separately according to the names of the minerals rather than to the numbers of atoms in the molecule.

Cases where no cell measurements appear to have been made

are generally excluded from the present summary. Intermetallic compounds, including carbides, nitrides. . . . of end-transition elements, are also omitted.

It is evident that only the briefest possible description, except of certain more outstanding types, can be attempted in a very wide field, but it is hoped that the survey provided will enable results to be quickly and conveniently found in the literature. References already given in the *Strukturbericht*[1] are not repeated.

The description of crystal structures is shortened by the introduction of symbols, shown in brackets, to denote the seven systems, as follows: Triclinic (T'), Monoclinic (M), Orthorhombic (O), Hexagonal (H), Rhombohedral (R), Tetragonal (T) and Cubic (C). A number following, within a bracket, denotes the number of molecules in the unit cell, with the Ewald and Hermann symbol, where possible, included in the bracket. The space-group in the Schoenflies system may follow, and then the cell dimensions, distances in Å.U. and angles in degrees and minutes. The dimensions a, b, c and the angles α, β, γ are not usually specified, *the symbols being always given in the order of the Table in Section 1A*; thus $NaNO_3$: R(2-G1)D^6_{3d}; 6·31, 47° 16′ denotes a rhombohedral unit cell containing two molecules, Ewald and Hermann type G1, Schoenflies space-group D^6_{3d}, with $a = 6{\cdot}31$ Å.U., and $\alpha = 47°\ 16'$. Tables of results are arranged in alphabetical order according to chemical symbols.

6. Compounds Containing THREE DIFFERENT ATOMS in the Molecule

CdHyCl[4]: H(2)C^4_{6v}; 3·66, 10·27.	KCN[1]: C(4-F1 ?)T[4]; 6·55.
CoAsS[1]: C(4-F1)T[4]; 5·6.	NiAsS[1]: C(4-F1)T[4]; 5·7.
COS[2]: R(1); 4·08, 98° 58′.	NiSbS[1]: C(4-F1)T[4]; 5·9.
FeAsS[1]: O(8); 6·44, 9·52, 5·63.	PbFCl[3]: T(2)D^7_{4h}; 4·09, 7·21.
FeOCl[5]: O(2)V^3_h; 3·75, 7·95, 3·4.	

FeOCl[5] is of layer lattice type. PbFCl[3] has layers of Pb atoms, with F and Cl atoms alternately between the sheets.

COS[2] was examined at liquid air temperature, and has a different structure from CO_2 (C_{2} type).

7. Compounds Containing FOUR ATOMS in the Molecule

TABLE XVII.—CRYSTAL STRUCTURE OF COMPOUNDS HAVING FOUR ATOMS IN THE MOLECULE.

$AgClO_3$[61]: T(16); 12·17, 6·69.	$KCNO$[1]: T(4-F52)D_{4h}^{18}; 5·67, 6·81
$Ag(Sb,Bi)S_2$[1]: T′(2) 5·67, 5·69, 5 62. 86° 55′, 90° 53′, 93° 18′.	$KCNS$[18,19] O(4)V_h^1; 6·67, 6·65, 7·54.
	KHC_2[1]: T(2); 6·05, 8·42
AlF_3[6]: R(4)D_3^7; 5·03, 58° 31′.	KHF_2[1]: T(4-F52)D_{4h}^{18}; 5·67, 6·81.
$AlHy_3$[7,8] · M(8)C_{2h}^5; 8·624, 5·060, 9·70, 85° 26′.	KN_3[1]: T(4-F52)D_{4h}^{18}; 6·09, 7·06.
$AmClO_2$[61]: T(4)C_{4v}^2; 6 30, 3·73.	LaF_3[13]: H(6)D_6^6; 7·16, 7·33
$AmHF_2$[9,10]: O(4)V_h^7; 8·33, 8·14, 3·68.	MoC_2[20]: O(4)$Q_h^{1,6}$; 3·92, 13 94, 3 66.
AsI_3[11,12]: R(2)C_{3i}^6; 8 25, 51° 20′. H(6); 7·19, 21·39.	$NaBrAq_2$[21] · M(4); 6 59, 10·20, 6·51, 112° 5′.
	$NaHC_2$[1]: T(2); 5·40, 8·17.
BiI_3[11]. H(6); 7·50, 20·68.	$NaHF_2$[1]: R(1-F51)D_{3d}^5; 5·05, 40° 2′.
$CaCN_2$[1]: R(1-F51)D_{3d}^5; 5·11, 43° 50′.	$NaIAq_2$[21] T′(2): 6·85, 5·76, 7·16. 98°, 119°, 68° 30′.
CeF_3[13] · H(6)D_6^6; 7·11, 7·27.	
$CoAs_3$[1]: C(8-D2)T_h^5; 8·18.	NaN_3[1,22]: R(1-F51)D_{3d}^5; 5·48, 38° 43′ · H(3); 3·62, 15·13.
$CrCl_3$[1,14]. R(1); 4·42, 5·75: H(6); 17·3, 6·02.	
CrO_3[15]: O(1)Q_h^{17}; 8·50, 4·73, 5·72.	$NaNCO$[22]: H(3); 3·58, 15·15.
CsI_3[1]: O(4)V_h^{16}; 6·82, 9·95, 11·01.	NdF_3[13]. H(6)D_6^6; 7·02, 7·20.
$CsIBr_2$[1]: O(4)V_h^{16}; 6·57, 9·18, 10·66.	NH_3[1]: C(4-D1)T^4; 5·15.
$CsICl_2$[1]: R(1-F51)D_{3d}^5; 5·05, 40° 2′.	NLi_3[1]: C(4-D1)T^4; 5·50.
$CuFeS_2$[1]: T(1-F61)V_d^3; 3·73, 5·19.	PrF_3[13]: H(6)D_6^6; 7·06, 7·22.
$FeCl_3$[16]: R(2); 6·69, 52° 30′: H(6); 5·92, 17·26.	$PtPdS_2$[23]: T(4)D_{4h}^2; 6·37, 6·58.
	RbN_3[24]: T(1)D_{4h}^1; 4·50, 3·71. (?)[25]
Hg_2Br_2[1]: T(2-D31)D_{4h}^{17}; 4·65, 11·10.	SbI_3[11]: H(6); 7·47, 20·89.
Hg_2Cl_2[1]: T(2-D31)D_{4h}^{17}; 4·45, 10·89.	SmF_3[13]: H(6)D_6^6; 6·98, 7·15.
Hg_2I_2[1]: T(2-D31)D_{4h}^{17}; 4·92, 11·61.	$TlCNS$[19]. O(4)V_h^1; 6·80, 6·78, 7·52.
$KAgCy_2$[17]: H(6)D_{3d}^2 (?); 7·38, 17·55.	Tysonite*[15,26]: H(6)D_{6h}^3; 7·12, 7·28.

* Composition (Ce, La . . .)F_3.

AMMONIA, NH_3[1], in the solid state between $-77°$ and $-160°C$. has the cubic unit cell, containing four molecules, shown in Figure XXXIII, where the positions occupied by nitrogen atoms are indicated. The structure may be developed from Type A1 (face-centred cubic) by moving the atoms along the diagonals of the smaller cubes in the way shown. The edge of the unit cube is 5·15, and the ratio u defining the shift 0·21.

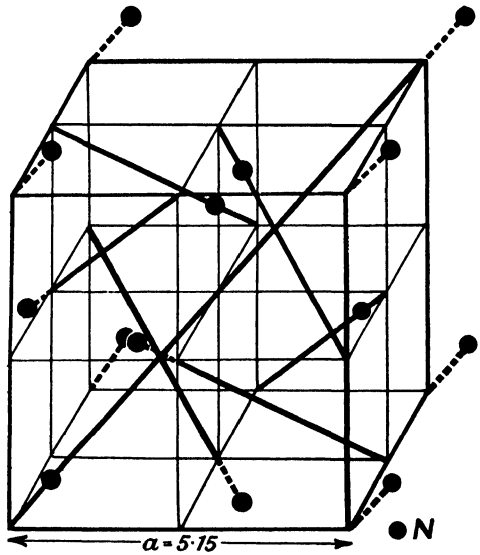

FIGURE XXXIII.—CRYSTAL STRUCTURE OF SOLID AMMONIA, NH_3.

The parameter defining the position of the hydrogen atoms is not determined, but the plane containing three hydrogen atoms does not contain the nitrogen atom, as the existence of dipole moment in NH_3 requires. The axes of the dipoles lie along the diagonals of the smaller cubes. NLi_3 apparently crystallizes in the same way.

$AlHy_3$[8], BiI_3[11], $CrCl_3$[14], $FeCl_3$[16] and MoO_3[20] have layer lattices, $FeCl_3$ being isomorphous with BiI_3. Passing from SbI_3 to AsI_3, the lattices become increasingly molecular. In the series of rare earth fluorides of type MF_3, the cell dimensions diminish with increasing atomic number of M. The name

" braggite " has been suggested for $PtPdS_2$,[23] being the first mineral to be discovered by X-ray methods. Structures of compounds of Type AB_3 have been deduced by Nowacki.[27]

8. Compounds Containing FIVE ATOMS in the Molecule

Figure XXXIV shows the structure of STANNIC IODIDE,

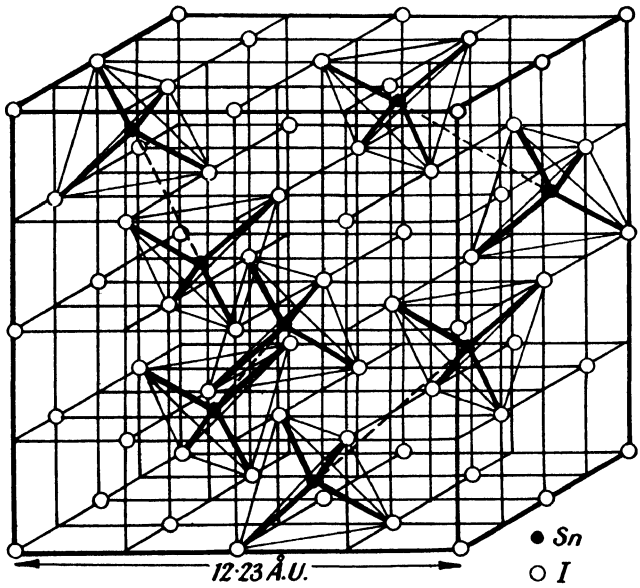

FIGURE XXXIV.—CRYSTAL STRUCTURE OF STANNIC IODIDE, SnI_4.

SnI_4, according to Dickinson. The Sn atoms are arranged in pairs on diagonals of alternate small cubes: each has four iodine atoms symmetrically placed around it, so that they occupy the corners of a regular tetrahedron, forming a " molecular " lattice. There are thus eight atoms of tin in the unit cell, and $(8 \times \frac{1}{8}) + (12 \times \frac{1}{4}) + (30 \times \frac{1}{2}) + (13 \times 1) = 32$ atoms of iodine, corresponding to 8 molecules of SnI_4. The edge of the large cube is 12·23, so that the distance between Sn and a neighbouring I is $\frac{1}{4} \times (\frac{1}{2} \times 12{\cdot}23) \times \sqrt{3} = 2{\cdot}65$, which agrees pretty well with the sum of the assigned " atomic

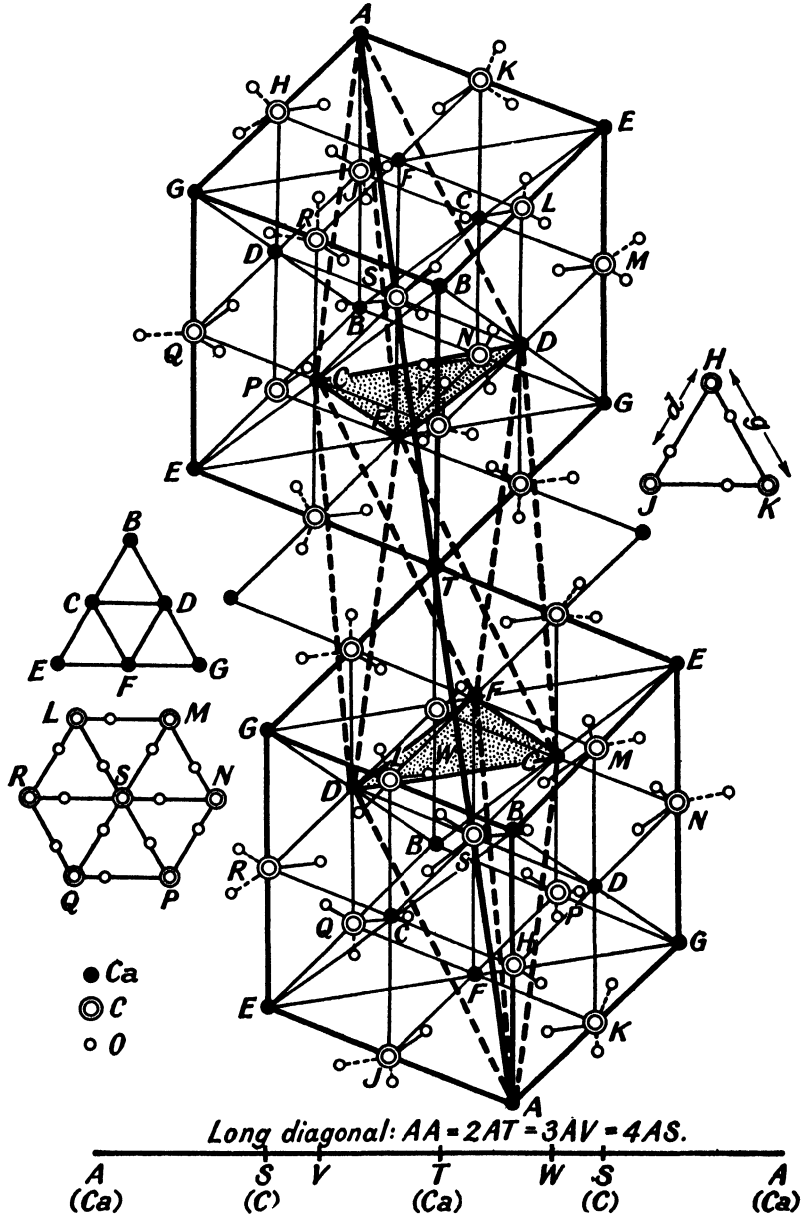

FIGURE XXXV.—CRYSTAL STRUCTURE OF CALCITE, $CaCO_3$. Two cleavage rhombohedra are shown, and the true unit cell is outlined, in barred lines.

radii" (2·80). The distance between an iodine atom and one of a neighbouring molecule is evidently given by $\frac{1}{4} \times 12{\cdot}23 \times \sqrt{2} = 4{\cdot}32$, which is much greater than the assigned diameter of an iodine atom (2·80), but agrees closely with the corresponding distance between iodine centres in CdI_2 (4·24). GeI_4, SiI_4 and TiI_4 crystallize in the same way with slightly smaller structural dimensions.

The structure of CALCITE, $CaCO_3$, is represented in Figure XXXV, in which two "cleavage" rhombohedra limited by the planes AEBG and BGTE are shown. The arrangement is perhaps most easily understood with reference to these rhombohedra, which contain calcium and carbon atoms arranged as in the NaCl type (B1), except that the cubic structure is deformed by compression along a three-fold axis, so that a rhombohedron results having all the edges equal (3·028) and the angle 101° 54′.[46] The oxygen atoms lie on the lines joining adjacent carbon atoms. This rhombohedron contains $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$ atoms of calcium, $(12 \times \frac{1}{4}) + 1 = 4$ atoms of carbon and $(12 \times \frac{1}{2}) + 6 = 12$ atoms of oxygen, or 4 molecules of $CaCO_3$. Planes parallel to BGE and HKJ contain calcium atoms only and carbonate groups only, just as the (111) planes in NaCl contain sodium and chlorine atoms only alternately. Now inspection of Figure XXXV shows that the two rhombohedra are identical as regards calcium and carbon, but differ in respect of the lie of the oxygen atoms. It follows that the true unit cell is not identical with the cleavage rhombohedron. This cell is shown by barred lines, and has its diagonal along those of the two cleavage rhombohedra, and the rhombohedral angle 46° 7′. The cell is observed to contain $1 + (8 \times \frac{1}{8}) = 2$ atoms of calcium, together with 2 of carbon and 6 of oxygen, corresponding to 2 molecules of $CaCO_3$. The long diagonal AA has calcium atoms at A, A and T, the latter being the middle point; the carbon atoms at S, S bisect the lines AT, and the triangles CFD (stippled) have carbon atoms at their corners and intersect AA in points of trisection V, W. Thus AS = 3SV, and the three oxygen atoms of the CO_3 groups lie at the corners of equilateral triangles with carbon atoms at their centres.[48] It is noteworthy that the calcite structure is almost identical with

that of SODIUM NITRATE, $NaNO_3$, where the Na atoms replace Ca, and N replaces C. The cleavage rhombohedron of $NaNO_3$ has the angle 102° 40′, and the unit cell the angle 47° 15′. The lengths of the edges of the unit cells are 6·36 for calcite and 6·31 for $NaNO_3$. The nearest distance C–O in the CO_3 group is 1·24, and that of N–O in the NO_3 group is 1·27. It is somewhat remarkable that the dimensions are so alike, and apparently unaffected by replacing bivalent Ca by univalent Na. It was

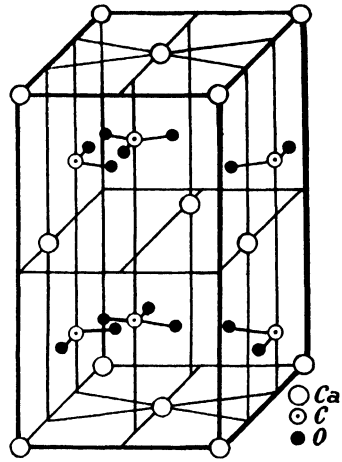

FIGURE XXXVI.—UNIT CELL OF ARAGONITE, $CaCO_3$.

pointed out by Langmuir that the molecules $CaCO_3$ and $NaNO_3$ are " isosteric," and contain 24 outer electrons in each case.

Another form of $CaCO_3$, known as ARAGONITE,[77] is shown in Figure XXXVI, which depicts the rhombic unit cell, containing $(8 \times \frac{1}{8}) + (4 \times \frac{1}{2}) + 1 = 4$ atoms of calcium, $2 + (4 \times \frac{1}{2}) = 4$ atoms of carbon and $10 + (4 \times \frac{1}{2}) = 12$ atoms of oxygen, or 4 molecules of $CaCO_3$. The dimensions of the cell are given by *a* 4·94, *b* 7·94, *c* 5·72, and the distance between nearest neighbours C–O = 1·30. The structure may be regarded as a deformed structure of Type B8 (nickel arsenide, Figure XIX) with Ca replacing As, and CO_3 replacing Ni. The Ca atoms in aragonite are in positions which closely correspond to those in

calcite, but the positions of the carbonate groups are different in the two cases. It has been found that aragonite probably forms the basis of pearl and of nacre (mother-of-pearl). Two other forms of $CaCO_3$ have been described, known as VATERITE A and B respectively. It is suggested that vaterite A has the same structure as calcite, whilst the B form has a different structure (μ-$CaCO_3$). Shôji[184] has discussed the changes of crystal directions for allotropic modifications of $CaCO_3$. The process is described as mainly one of slipping. (Allotropic changes in Fe and ZnS are also discussed. The case of Fe in steel is further considered in Section 20B.)

The NO_2[40] group is apparently not linear, and the ClO_3[49] group is pyramidal in form. A " valency model " is found to represent the structures of oxygenated groups better than a purely ionic structure, on energetic grounds.

Sb_2O_3 (senarmontite) has a diamond-like lattice of Sb_2O_4 molecules. In corundum, α-Al_2O_3, the oxygen atoms are almost in hexagonal close-packing, the Al atoms being in the interstices. Similar structures are assigned to BeO, $MgAl_2O_4$ (spinel), $BeAl_2O_4$ (chrysoberyl), and many silicates.

The D52 type is the rare earth " A " hexagonal type of oxides M_2O_3, whilst the " C " type is represented by the cubic unit cells containing 16 molecules (space-group T_h^7).

The perowskite ($CaTiO_3$) structure is depicted as cubic in Figure LI (KIO_3). It has been observed, however, that in the case of $CsNO_3$[33] the structure is not truly cubic but orthorhombic, and it is suggested that the term " perowskite type " should be discontinued.

Structures of A_2B_3 type have been deduced by Nowacki.[50]

TABLE XVIII.—CRYSTAL STRUCTURE OF COMPOUNDS HAVING FIVE ATOMS IN THE MOLECULE.

$AgBrO_3$[1]: T(8)V_d^{11} ?; 8·59, 8·08. $AgClO_3$[1]: T(8)V_d^{11} ?; 8·48, 7·90. $AgNO_3$[1]: O(8); 6·97, 7·34, 10·14. α-Al_2O_3[1]: R(2-D51)D_{3d}^6; 5·12, 55° 17′. β-Al_2O_3[1,28]: H(12)D_h; 5·56, 22·55. $AmNO_3$[29,30]: (−18 to 32·3°C.) O(2)V_h^{13}; 5·73, 5·43, 4·93: (32·3 to 84·2°) O(4)V_{16}; 7·06, 7·66, 5·80: (84·2 to 125·2°) T(2)C_4^1 ?; 5·75, 5·00: (125·2 to 169·5°) C(1); 4·40. As_2O_3[1]: C(16-D61)O^7; 11·06.

TABLE XVIII—*continued.*

$BaCO_3$[1]: O(4-G2)V_h^{16}; 5·29, 8·88, 6·41. $BaTiO_3$[1]: C(4-G5)O_h^1; 3·97. Be_3N_2[31]: C(16)T_h^7; 8·13. Be_3P_2[31]: C(16)T_h^7; 10·15.

$CaCO_3$ (calcite[1,46,48]): R(2-G1)D_{3d}^6; 6·36, 46° 7′: (aragonite[1]) O(4-G2)V_h^{16}; 4·94, 7·94, 5·72: (vaterite[1]) H(2); 4·11, 8·51. α-Ca_3N_2[31]: C(16)T^5; 11·40. $CaSiO_3$[127]: T′(6); 7·88, 7·27, 7·03, 90°, 95° 16′, 103° 25′. $CaSnO_3$[1]: C(4-G5)O_h^1; 3·92. $CaTiO_3$[1]: C(4-G5)O_h^1; 3·80. $CaZrO_3$[1]: C(4-G5)O_h^1; 3·99. Cd_3As_2[1]: C(2-D61)O_h^4; 6·29. $CdNO_3$[1]: R(2-G1)D_{3d}^6: 6·11, 47° 24′. $CdTiO_3$[158]: R(2-G4)C_{3i}^2; 5·82, 53° 36′. Cd_3P_2[1,31]: C(2-D61)O_h^4; 6·06: C(16)T^7; 12·26. Ce_2O_3[1]: H(1-D52)D_{3d}^3; 3·88, 6·06. Co_2O_3[1]: H(2); 4·64, 5·75. $CoTiO_3$[168]: R(2-G4)C_{3i}^2; 5·49, 54° 42′. Cr_2O_3[1]: R(2-D51)D_{3d}^6; 5·33, 55° 9′. $CsCdCl_3$[1]: C(4-G5)O_h^1; 5·20. $CsHgCl_3$[1]: C(4-G5)O_h^1; 5·44. $CsIO_3$[1]: C(4-G5)O_h^1; 4·66. $CsNO_3$[33]: O(9-G5); 10·74, 7·68.

Ds_2O_3[1]: C(16)T_h^7; 10·63. Er_2O_3[1]: C(16)T^7; 10·54. Eu_2O_3[1]: C(16)T_h^7; 10·84. $FeCO_3$[1]: R(2-G1)D_{3d}^6; 5·82, 47° 45′. $Fe(CO)_4$[32]: M(3)C_{2h}^6; 13·00, 11·41, 11·41, 85° 35′. Fe_2O_3 (haematite[1]): R(2-D51)D_{3d}^6; 5·42, 55° 17′; (γ-Fe_2O_3[34]): C(12); 8·4. $FeMnO_3$[1]: C(16)T_h^7; 9·35. $FeTiO_3$[1,167]: R(2-G4)C_{3i}^2; 5·52, 54° 50′. α-Ga_2O_3[1]: R(2-D51)D_{3d}^6; 5·28, 55° 35′. Gd_2O_3[1]: C(16)T_h^7; 10·79. GeI_4[1]: C(8-D11)T_h^6; 11·89. HIO_3[1]: O(4); 5·53, 5·92, 7·75. Ho_2O_3[1]: C(16)T^7; 10·58. In_2O_3[1]: C(16)T_h^7; 10·12.

$KBrO_3$[1]: R(1)C_{3v}^5; 4·40, 86° 0′. $KCbO_3$[1]: C(4-G5)O^1; 4·01. $KClO_3$[1,35]: M(2)C_{2h}^2; 4·65, 5·59, 7·09. KIO_3[1]. C(4-G5)O_h^1; 4·46. $KMgF_3$[1]: C(4-G5)O_h^1; 4·00. $KNiF_3$[1]: C(4-G5)O_h^1; 4·01. KNO_3[1,36]: O(4-G2)V_h^{16}; 5·43, 9·17, 6·45. $KZnF_3$: C(4-G5)O^1; 4·05.

$LaAl_4$[37]: T(16 ?); 13·2, 10·2 (?). $LaAlO_3$[1]: C(4-G5)O_h^1; 3·78. $LaGaO_3$[1]: C(4-G5)O_h^1; 3·89. La_2O_3[1]: H(1-D52)D_{3d}^3; 3·93, 6·12. $LiCbO_3$: R(2-G4)C_{3i}^2; 5·47, 55° 43′. $LiIAg_3$[121]: H(2); 7·45, 5·45. $LiIO_3$[38]: H(2)D_6^6; 5·47, 5·16. $LiNO_3$[1]: R(2-G1)D_{3d}^6; 5·74, 48° 3′. Lu_2O_3: C(16)T_h^7; 10·37.

Mg_3As_2[1,31,181]: C(2-D61)O_h^4; 6·10: C(16)T_h^7; 12·33. $MgCO_3$[1]: R(2-G1)D_{3d}^6; 5·61, 48° 10′. Mg_3N_2[31,182]: C(16-D61)T_h^7; 9·95: C(12); 9·93. Mg_3P_2[1,31,181]: C(2-D61)O_h^4; 5·92: C(16)$T_h^7O_h^4$; 12·01. $MgTiO_3$[1,168]: R(2-G4)C_{3i}^2; 5·54, 54° 39 $MnCO_3$[1]: R(2-G1)D_{3d}^5; 5·84, 47° 20′. Mn_2O_3[1]: C(16)T_h^7; 9·41. $MnTiO_3$[168]: R(2-G4)C_{3i}^2; 5·62, 54° 16′.

$NaBrO_3$[1]: C(4-G3)T^4; 6·71. $NaCbO_3$[1]: C(4-G5)O^1; 3·89. $NaClO_3$[1,39]: C(4-G3)T^4; 6·57. $NaIO_3$[1]: O(2-G5)V_h^{19}; 5·75, 6·37, 4·05. $NaNO_2$[40]: O(2)C_{2v}^{20}; 3·55, 5·56, 5·37. $NaNO_3$[1,47,49]: R(2-G1)D_{3d}^6; 6·31, 47° 16′. $NiTiO_3$[41,168]: R(2-G4)C_{3i}^2; 5·45, 55° 8′. Nd_2O_3[1]: H(1-D52)D_{3d}^3; 3·84, 6·01. $PbCO_3$[1]: O(4-G2)V_h^{16}; 5·14, 8·45, 6·10. Pr_2O_3[1]: H(1-D52)D_{3d}^3; 3·85, 6·00. (Pten$_2$)Cl_2[97]: T′(1)C_i^1; 8·37, 4·95, 6·86, 100° 46′, 111° 40′, 81° 56′. $RbIO_3$[1]: C(4-G5)O_h; 4·52. $RbNO_3$[31,42].

TABLE XVIII—*continued.*

$R(4)C_{3v}^5$; 7·36, 109° 28′ (?); $H(9)C_{3v}^2$; 10·45, 7·38. Rh_2O_3[1]: $4(2\text{-}D51)D_{3d}^6$; 5·47, 55° 40′.

Sb_2O_3[1]: C(16-D61)O_h^7; 11·14. Sb_2S_3[1,43]: O(4)V_h^{16}; 11·39, 11·48, 3·89. Sc_2O_3[1]: C(16)T_h^7; 9·79. SiI_4[44]: C(8-D11)T_h^6; 11·99. Sm_2O_3[1]: C(16)T_h^7; 10·85. SnI_4[1]: C(8-D11)T_6; 12·23. $SrCO_3$[1]: O(4-G2)V_h^{16}; 5·13, 8·42, 6·10. $SrTiO_3$[1]: C(4-G5)O_h^1; 3·92. $SrZrO_3$[1]: C(4-G5)O_h^1; 4·09.

Tb_2O_3[1]: C(16)T^7; 10·70. $TiBr_4$[45]: C(8-D11)T^6; 11·25. TiI_4[45]: C(8-D11)T_h; 12·00. Ti_2O_3[1]· R(2-D51)D_{3d}^6, 5·42, 56° 32′. Tl_2O_3[1]: C(16)T^7; 10·57. Tm_2O_3[1]· C(16)T_h^7; 10·70. V_2O_3[1]: R(2-D51)D_{3d}^6; 5·43, 53° 53′. $YAlO_3$[1]: C(4-G5)O_h^1; 3·67. Yb_2O_3[1]: C(16)T_h^7; 10·39. Y_2O_3[1]: C(16)T_h^7; 10·60. Zn_3As_2[1,31]. C(2-D61)O_h^1; 5·81: C(16)T_h^7; 11·74. $ZnCO_3$[1]: R(2-G1)D_{3i}^5; 5·62, 48° 20′. Zn_3P_2[1,31]: C(2-D61)O_h^4; 5 68: C(16)T^7; 11·42.

9. Compounds Containing SIX ATOMS in the Molecule

Into this group fall a considerable number of compounds of Type MRO_4, where R in the negative group is surrounded by four atoms of O tetrahedrally. The favoured structures appear to be tetragonal or orthorhombic, with four molecules in the unit cell. $AgMnO_4$ provides an exception, being monoclinic. The β- (high temperature) forms of the perchlorates are cubic.

TABLE XIX.—CRYSTAL STRUCTURE OF COMPOUNDS HAVING SIX ATOMS IN THE MOLECULE.

β-$AgClO_4$[52,53]: $C(4)T^2$; 6·96. $AgIO_4$[54]: T(4-H4)C_{4h}^6; 5·37, 12·01. $AgMnO_4$[55]: M(4)C_{2h}^5; 5·66, 8·27, 7·12, 92° 29′. $AgReO_4$[64,73]: T(4-H4)C_{4h}^6; 5·35, 11·92. α-$AmClO_4$[1,53,55,56]: O(4-H2)V_h^{16}; 9·20, 5·82, 7·45. β-$AmClO_4$[52,53]: $C(4)T_d^2$; 7·65. AmH_2PO_2[57]: O(4)V_h^{21}; 3·98, 7·57, 11·47. $AmOsNO_3$[58]: O(4)V_h^{16}; 5·53, 5·86, 13·54.

$BAsO_4$[59]: $T(2)S_4^2$; 4·46, 6·80. $BaMoO_4$[1]: T(4-H4)C_{4h}^6; 5·56, 12·76: T(1); 3·96, 6·43. $BaSO_4$[1]: O(4-H2)V_h^{16}; 8·85, 5·44, 7·13. $BaWO_4$[1]: T(4-H4)C_{4h}^6; 5·60, 12·69. BPO_4[59]: $T(2)S_4^2$; 4·33, 6·64.

$CaCrO_4$[60]: T(4)D_h^{19}; 7·25, 6·34. $CaMoO_4$[1]: T(4-H4)C_{4h}^6; 5·23, 11·44: T(1); 3·67, 5·69. $CaSO_4$[1]: O(4-H1)V_h^{17}; 6·22, 6·96, 6·97. $CaWO_4$[1]: T(4-H4)C_{4h}^6; 5·23, 11·44. α-$CsClO_4$[1,53,55]: O(4-H2)V_h^{16}; 9·85, 6·03, 7·76. β-$CsClO_4$[52,53]: $C(4)T_d^2$; 7·97. $CsOsNO_3$[61]: O(4)V^2;

TABLE XIX—*continued.*

8·08, 8·35, 7·22. $CsReO_4$[64]: $O(4)V_h^{16}$; 5·73, 5·98, 14·26. Fergusonite (Y(Cb, Ta)O_4): T(8): 7·74; 11·31. Cu_2SnFeS_2[1]: T; 5·58, 5·18.

α-$KClO_4$[1,53,55,56]: $O(4\text{-}H2)V_h^{16}$; 8·83, 5·65, 7·24. β-$KClO_4$[52,53]: $C(4)T_d^2$; 7·49. KIO_4[1]: $T(4\text{-}H4)C_{4h}^6$; 5·75, 12·63. $KMnO_4$[1,55,62]: $O(4\text{-}H2)V_h^{16}$; 9·10, 5·66, 7·40. $KOsNO_3$[63]: $T(4)C_{4h}^6$; 5·65, 13·08. $KReO_4$[64,65]: $T(4\text{-}H4)C_{4h}^6$; 5·62, 12·50. $MgWO_4$[1]: M(2); 4·68, 5·65, 4·92, 89° 35′.

α-$NaClO_4$[53,66]: $O(4)V_h^{17}$; 6·48, 7·06, 7·08. β-$NaClO_4$[52,53]: $C(4)T_d^2$; 7·08 (7·25). $NaHCO_3$[67]: $M(4)C_{2h}^5$; 7·51, 9·70, 3·53, 93° 19′. $NaIO_4$[1]: $T(4\text{-}H4)C_{4h}^6$; 5·32, 11·93. Na_2SO_3[68]: $H(2)C_{3i}^1$; 5·44, 6·13. N_2O_4[69]; $C(12NO_2)$; 7·77; (?)[70] $PbCl_2CuHy_2$[1]: C(32); 15·6. $PbMoO_4$[1]: $T(4\text{-}H4)C_{4h}^6$; 5·41, 12·08: T(1); 3·80, 6·00. $PbSO_4$[1]: $O(4\text{-}H2)V_h^{16}$, 8·45, 5·38, 6·93. $PbWO_4$[1]: $T(4\text{-}H4)C_{4h}^6$; 5·44, 12·01.

α-$RbClO_4$[1,53,55]: $O(4\text{-}H2)V_h^{16}$; 9·28, 5·83, 7·53. β-$RbClO_4$[52,53]: $C(4)T_d^2$; 7·68. $RbOsNO_3$[58]: $O(4)V^4$; 5·57, 5·84, 13·64. $RbReO_4$[64]: $T(4\text{-}H4)C_{4h}^6$; 5·80, 13·17. Sb_2O_4[1]: C(16); 10·22. $SrMoO_4$[1]: T(1); 3·79, 5·97. $SrSO_4$[1]: $O(4\text{-}H2)V_h^{16}$; 8·36, 5·36, 6·84.

α-$TlClO_4$[1,53,55]: $O(4\text{-}H2)V_h^{16}$; 9·41, 5·88, 7·54. β-$TlClO_4$[52,53]: $C(4)T_d^2$; 7·65. $TlOsNO_3$[58]: $O(4)V^4$; 5·42, 5·68, 13·45. $TlReO_4$[64]: $O(4)V_h^{16}$; 5·63, 5·80, 13·33.

$YCbO_4$[1]: T(8); 7·76, 11·32. YPO_4[1]: $T(4\text{-}H3)D_{4h}^4$; 6·88, 6·03. $YTaO_4$[1]: T(8); 7·75, 11·41. YVO_4[72]: $T(4)D_{4h}^{19}$; 7·13, 6·20. Zn_2FeS_3. C; 5·42. $ZnSO_4$[71]: R(4); 8·58, 6·74, 4·76. $ZrSiO_4$[1]: $T(4\text{-}H3)D_{4h}^{19}$; 6·58, 5·93.

10. Compounds Containing SEVEN ATOMS in the Molecule

An important type in this group is the SPINEL type, of general formula $M_2^{III}M^{II}O_4$. The oxygen atoms, in the ideal case, are in cubic close-packing (A1 type), the atoms M^{II}, M^{III} fitting into the spaces between four and six oxygen atoms respectively. The structure as a whole corresponds to a diamond lattice (A4 type) with molecules replacing carbon atoms. MAGNETITE, Fe_3O_4, or $FeFe_2O_4$, belongs to the group. Zinc ferrite is non-magnetic.[101] There appear to be two types of spinel structures, represented by X_2YO_4 and $XYXO_4$.[88]

The normal sulphates of the alkali metals (except Li and Na), Am_2SO_4 and Am_2BeF_4 crystallize in the same way, the anions having tetrahedral structure.[79] β-Li_2SO_4 is apparently of

spinel type,[1] whilst Na_2SO_4 also has high temperature modifications.[103]

The borides MB_6 have CsCl (B2) arrangement of M and B_6, the latter being octahedral.[84,99] The lattice has a network of boron atoms, with metal atoms in interstices. The forces are akin to intermetallic.[102]

TABLE XX.—CRYSTAL STRUCTURE OF COMPOUNDS CONTAINING SEVEN ATOMS IN THE MOLECULE.

The following abbreviations are used in the Table: A for C(8-H11)O_h (spinel type); B for O(4-H12)V_h^{16} (olivine type); D for R(6-H13)C_{3i}^2 (phenacite type).

α-Ag_2HgI_4[74]: T(1)V^1; 6·34, 6·34. β-Ag_2HgI_4[75] (high temperature form): C(1); 6·38. Ag_2MoO_4[1]: A; 9·26. Ag_2SO_4[76]: O(8)V_h^{24}; 5·85, 12·66, 10·25. Ag_3SbS_3[1]: R(2)D_{3d}^6 ?; 7·07, 104° 1′. Al_2BeO_4: B; 4·42, 9·39, 5·47. Al_4C_3[77]: R(1)D_{3d}^5; 8·53, 22° 28′. Al_2CoO_4[1]: A; 8·06. Al_2CuO_4[1]: A; 8·07. Al_2FeO_4[1,78]: A; 8·12. Al_2MgO_4[1,78]: A; 8·09. Al_2MnO_4[1,78]: A; 8·27. AlNaSiO_4[1]· H(8)C_6^6; 10·09, 8·49. Al_2NiO_4: A; 8·05. Al_2ZnO_4[1,78] A, 8·06. Am_2BeF_4[79]: O(4)V_h^{16}; 5·8, 10·2, 7·5. Am_2CrO_4[80]: M(2); 6·10, 6·28, 7·60, 115° 13′. $Am_2CuCl_2Aq_2$[81]: T(2)D_{4h}^1; 7·58, 7·95. Am_2PdCl_4[1]: T(1-H15)D_{4h}^1; 7·21, 4·26. Am_2SO_4[1,82]. O(4)V_h^{16}; 5·96, 10·60, 7·76.

BaB_6[83,84]: C(1); 4·28. BaN_6[24]: M(10); 6·22, 29·29, 7·02. Be_2BO_3Hy[166]: O(8)V_h^{15}; 9·73, 12·18, 4·42. Be_2SiO_4[1,85]: O; 7·68, 108° 1′. CaB_6[83,84,86]· C(1); 4·145 CaB_2O_4[100]: O(4)V_h^{14}; 6·19, 11·60, 4·28. $Ca(ClO_2)_2$[51]: C(2), 5·80. $CaCrO_4Aq$[60]: O(8)V_h^{15}, 7·99, 12·77, 8·11. CeB_6[83,84]: C(1); 4·13 Co_2CuS_4[1]: A; 9·46. Co_3O_4[1]. 8·06. Co_2ZnO_4[1]: A; 8·06. Cr_2CoO_4[1]: A; 8·32 Cr_2FeO_4[1,78] 8·35. Cr_2MgO_4[78]: A; 8·31. Cr_2MnO_4[1,78]· A; 8·46. Cr_2ZnO_4[1,78]: A; 8·31. Cs_2SO_4[1,82]. O(4)V_h^{16}; 6·24, 10·93, 8·23. Cu_3FeS_3[1]. C(8); 10·9. α-Cu_2HgI_4[75]: T(1)V_d^1; 6·04, 6·12. β-Cu_2HgI_4[75] (high temperature form): C(1); 6·10. Cu_3SbS_3[1]: C(8)T_d^3; 10·39. ErB_6[84]. C(1); 4·10.

Fe_2CdO_4[1,87]: A; 8·70. Fe_2CoO_4[1]: A, 8·40. Fe_2CuO_4[1]: A, 8·44. $FeMgFeO_4$[1,78,87,88]: A; 8·36. Fe_2MnO_4[1,78]: A; 8·54. Fe_2NiO_4[1]: A; 8·41. Fe_3O_4[1,78]: A; 8·40. $FeTiFeO_4$[88]: A; 8·50. Fe_2ZnO_4[1,78,87]: A; 8·41. $GaMgGaO_4$[88]: A; 8·26. H_3BO_3[1,89]: T′(4)C_i^1; 7·04, 7·04, 6·56, 92° 30′, 101° 10′, 120°. $InMgInO_4$[88]: A; 8·81.

K_2CdCy_4[1]: A; 12·84. K_2CrO_4[1,90]: O(4)V_h^{16}; 5·92, 10·40, 7·61. $K_2CuCl_2Aq_2$[81]: T(2)D_{4h}^{14}; 7·45, 7·88. K_2HgCy_4[1]: A; 12·76. $K_2OsO_2Cl_2$[91]: T(2)D_{4h}^{17}?; 9·90, 8·75. K_2PdCl_4[1]: T(1-H15)D_{4h}^1; 7·04,

TABLE XX—*continued.*

4·10. K_2PtCl_4[1]: T(1-H15)D^1_{4h}; 6·99, 4·13. K_2SeO_4[1]: O(4)V^{16}_h; 6·0, 10·4, 7·6. K_2SO_4[1,82]: O(4) V^{16}_h; 5·76, 10·05, 7·44. K_2ZnCy_4[1]: A; 12·54.

LaB_6[83,84]: C(1); 4·14. Li_2BeF_4[1]: D; 8·15, 107° 40′. Li_2MoO_4[1]: R(6-H13)C^2_{3i}; 8·77, 108° 10′. Li_2SO_4[92]: M(4)C^5_{2h}; 8·25, 4·95, 8·44, 107° 54′. $LiKSO_4$[1]: H(2-H14)C^6_6; 5·13, 8·60. Li_2WO_4[1]: see Li_2MoO_4. $MgCaSiO_4$[1]: B; 4·82, 11·08, 6·37. Mg_2SiO_4[1]: B; 4·76, 10·21, 5·98. $MgTiMgO_4$[88]: A; 8·41. Mn_3O_4[1]. T(4)D^{19}_4; 5·75, 9·42.

Na_2SiO_4[41]: B; 4·71, 10·11, 5·91. Na_2SO_4[93,95]: O(8)V^{24}_h; 5·83, 12·30, 9·78. NdB_6[84]: C(1); 4·12. Ni_3S_4[1]: A; 9·41 (9·65). $Pb(ClO_2)_2$[51]: T(1); 4·14, 6·25. α-PbN_6[180]: O(12); 6·64, 11·34, 16·25. β-PbN_6[180]: M(8); 5·10, 8·83, 17·60, 90° 49′. P_2O_5[96]: R(12); to H axes, 11·12, 1·12. PrB_6[84]: C(1); 4·12. α-$PtAmm_2Cl_4$[97]: T(2)D^{14}_{4h}; 5·72, 10·37. β $PtAmm_2Cl_4$[97]: O(4); 10·0, 11·2, 6·0. Rb_2SO_4[1,82]: O(4)V^{16}_h; 5·97, 10·44, 7·81. Sb_2O_5[1]: C; 10·22. SrB_6[1,84]: C(1); 4·19. $TeHy_6$[98]: C(4)O^5; 7·83: also second modification: M(4)C^5_{2h}; 5·54, 9·30, 9·74, 104° 30′. ThB_6[84,99]: C(1); 4·32.

Zn_2SiO_4[1,85,94]: D; 8·63, 107° 45′. $ZnSnZnO_4$[41,88]: A; 8·62. Zn_2TiO_4[41]: A; 8·46.

11. Compounds Containing EIGHT ATOMS in the Molecule

The compound Al_2SiO_5 crystallizes in three forms: (1) KYANITE or DISTHENE, (2) ANDALUSITE and (3) SILLIMANITE. The data for the three cases are given in this order in Table XXI.

B_2H_6 (D41 type), DIBORANE,[1] is structurally like ethane, C_2H_6.

X-ray investigations have confirmed that in palladous and platinous tetrammines the four NH_3 groups are in square array.[97,112,113] The configuration is such that the four valencies are not equivalent, but are alike in pairs. The crystal form of $[Co(NO_2)_2(NH_3)_4]I$ has been studied.[114]

CALCIUM DISODIUM ORTHOSILICATE, Na_2CaSiO_4,[1] is an example of a composite lattice of NaCl (B1 type) and CaF_2 (C2 type): the Ca, SiO_4 resembling Na, Cl respectively, and the Na, SiO_4 resembling F, Ca respectively in the two cases.

TABLE XXI.—CRYSTAL STRUCTURE OF COMPOUNDS CONTAINING EIGHT ATOMS IN THE MOLECULE.

Ag_3AsO_4[1]: C(2-H21)T; 6·12. Ag_3PO_4[1]: C(2-H21)T[4]; 5·99. Al_2SiO_5: (1)[1]: T′(4-H51)C_1^1; 7·09, 7·72, 5·56, 90° 5′, 101° 2′, 105° 44′; (2)[1,104]: O(4)V_h^{12}; 7·76, 7·90, 5·56; (3)[1]: O(4)V_h^{16}; 7·25, 7·65, 5·88. AmH_2PO_4[1]: T(4-H22)V_d^{12}; 7·51, 7·52. B_2H_6[1]: H(2-D41); 4·54, 8·69. β-$CaCrO_4Aq_2$[60]: O(8)V_h^{11}; 16·02, 11·39, 5·60. $CaSO_4Aq_2$[1,105]: M(4)C_{3h}^3; 10·47, 15·15, 5·67, 33° 32′; or M(8)C_{3h}^3; 10·47, 15·15, 6·28, 98° 58′. $CuCO_3CuHy_2$[106]: M(4)C_{2h}^5; 9·38, 11·95, 3·18, 91° 3′. CuH_2SiO_4[1]: R(6)C_{3i}^2; 8·8, 111° 42′. Cu_3VS_4[107]: C(1)T_d^1; 5·37. Fe_2TiO_5[1]: O(4)V_h^{12}; 9·78, 9·80, 3·65. KH_2PO_4[1,108]: T(4-H22)V_d^{12}; 7·43, 6·97. Li_2FeO_4[109]: C(1); 4·14. Na $CaSiO_4$[1]: C(4)T^4; 7·50. $Na_2Fe_2O_4$[110]: R($\frac{1}{2}$)D^5; 5·59, 35° 20′. N_4S_4[111]: O(1)V_h^1; 8·87, 8·47, 7·2. Pd[Amm_4Cl_2]Aq[97,113]: T(4)D_{5h}^4; 14·30, 4·27; or T(2): 10·30, 4·34. Pt[Amm_4Cl_2]Aq[97,112]: T(4)D_{4h}^5; 14·76, 4·21.

12. Compounds Containing MORE THAN EIGHT ATOMS in the Molecule

It happens not infrequently that complex structures may be referred to simpler types. Thus K_2PtCl_6[1,118] (H61 type) may be referred to the fluorspar type (C1), Ca atoms being replaced by $PtCl_6$ groups in the form of regular octahedra, and F by K atoms. Similarly, HYDRAZINE HYDROCHLORIDE, $N_2H_6Cl_2$,[1] is structurally related to the iron pyrites type (C2), the N_2H_6 groups and Cl atoms replacing Fe and S atoms respectively.

In general, the crystal structure results have served to confirm and to extend older chemical considerations. In $(MgAq_6)Cl_2$[122] and $(NiAmm_6)Cl_2$[1], the Aq_6 and Amm_6 are arranged at the corners of regular octahedra with the metal atoms at the centre. The structure of CUPRIC SULPHATE PENTAHYDRATE[142] is found to be such that Aq_4 is arranged at the corners of a square round the central Cu atom, the fifth Aq being in contact with two water molecules and two oxygen atoms of the SO_4 group. The general confirmation of Werner's co-ordination theory is noteworthy. The study of a number of groups of the type S_4O_y, notably by Zachariasen,[143] has shown

that in all cases the configurations may be accounted for by single electron pairs joining S and O atoms. In the case of S_2O_8, two tetrahedral SO_4 groups are linked by O atoms. It is suggested that the crystal structure of $B_{10}H_{14}$[163] resembles that of naphthalene. TRICALCIUM ALUMINATE, $Ca_3Al_2O_6$,[140] is built up of CaO and Al_2O_3 groups, and is therefore not correctly described as a true salt.

MERCURIC FULMINATE (formula indeterminate)[180] has O (4); 5·48, 7·71, 10·43.

The structures of complex silicates are generally determined by the O atoms, which control the dimensional relations, whilst metal and Si atoms fit into appropriate interstices between them, and tend to determine the resultant symmetry. BERYL, $Be_3Al_2(SiO_3)_6$,[1] has a local close-packing of O atoms with considerable spaces elsewhere. TOPAZ $(AlF)_2SiO_4$,[1] has apparently an hexagonal close-packing of O^{--} and F^-, which are of about the same size. Similar considerations probably apply to the CHONDRODITE series $Mg_{2x-1}(SiO_4)_xMg(F,OH)_2$,[1] where $x = 1$ (PROLECTITE), 2 (CHONDRODITE), 3 (HUMITE), 4 (CLINOHUMITE). The structure has alternate layers of $Mg(F,Hy)_2$ and complex Mg silicate. In GARNET, $Al_2Ca_3(SiO_4)_3$,[1] (H31 type), each Si is symmetrically surrounded by 4, each Al by 6, and each Ca by 8 O atoms. The O–O distance is approximately constant (2·54 for beryl, 2·52 for tridymite, 2·7 for garnet), whilst Si–O is about 1·62. X-ray investigations indicate that in ZEOLITES the water present does not form an essential part of the lattice.[162] FELSPARS and ZEOLITES[163] have strong frameworks of SiO_4 and AlO_4 groups, forming a three-dimensionally infinite anion. In the isomorphous replacement of felspars, bivalent cations replace univalent cations of about the same size in interstices; the alteration in valency is compensated for by alteration in proportion of Al to Si. The same kind of base exchange may occur in zeolites, but also Ca may be replaced by 2Na. The frameworks are penetrated by channels large enough to permit the movement of cations and Aq molecules without destruction of the lattice. The X-ray examination of SLATE[161] is reported.

Summarizing papers about silicates are due to W. L.

Bragg.[165,169] The structure of complex ionic crystals has also been discussed by Pauling.[170] Four classes of silicates have been described:[165] (1) those containing self-contained groups, as Si_2O_7; (2) those having SiO chains (pyroxenes and amphiboles); (3) those with SiO sheets (micas); (4) those having three-dimensional networks of Si and O (forms of SiO_2). Gossner and co-workers[164] and Schiebold[176] have also contributed largely to the composition and classification of complex silicates. It is found that the SiO_4 group is always tetrahedral.

The composition of ULTRAMARINE[171] has been attacked. It is considered that a certain part of the constituents, easily replaceable by other elements, has no fixed position in the structure. The sulphur present is predominantly "errant," being dispersed throughout the whole crystalline mass, and responsible for the colour of the material.

It is of interest to note that a feeling appears to exist in some quarters that the X-ray results should be received with caution, perhaps even with scepticism. Reviewers of the progress of chemistry have doubted whether conclusions drawn as to chemical structure are always justified.[172] For example, Linnik[173] concluded from the X-ray examination of a thin sheet of heated MICA that heating had caused the cleavage flakes to become separated into such thin layers that the structure no longer behaved as a three-dimensional lattice. Bragg,[174] however, showed that a small rotation of the flakes relative to each other might give rise to the observed effect. Hendricks[183] also opposed Linnik's view. Further, Mauguin[175] pointed out that X-ray rotation photographs of CHLORITE indicated a unit cell three times smaller than the cell of other micas, an unlikely result on general grounds. Similar difficulties arose with BIOTITE. It was supposed that the apparent anomalies could be explained by differing arrangements of cations. Such occurrences will encourage caution in the interpretation of results. On the other hand, the contributions made by the X-ray method to structural inorganic chemistry are far too important to be discredited on account of difficulties of interpretation.

TABLE XXII.—CRYSTAL STRUCTURE OF COMPOUNDS CONTAINING MORE THAN EIGHT ATOMS IN THE MOLECULE.

NINE ATOMS. (Abbreviations: A for $C(4\text{-}G21)T_h$; B for $T(2\text{-}H41)D^1_{4h}$; D for $C(4\text{-}H61)O_h$; E for $M(2)C^3_{2h}$; F for $H(1\text{-}H63)D^1_{3d}$.) $(AlF)_2SiO_4$ topaz[1]: $O(4)V^{16}_h$; 4·64, 8·78, 8·37. $Am_2CuCl_4Aq_2$[1,115]: B; 7·58, 7·96. Am_2PbCl_6[1]: D; 10·14. Am_2PtCl_6[1]: D; 9·84. $Am_2Pt(SCy)_6$[1]: F; 6·77, 10·45. Am_2SiF_6[1]: D; 8·38; second modification[116]: $R(1)D^3_{3d}$; to H axes, 5·76, 4·77. Am_2SnCl_6[1]: D; 10·05. $Ba(NO_3)_2$[1]: A; 8·10. $Ca(NO_3)_2$[1]: A; 7·60. $Cd(ClO_2)_2Aq_2$[51]: M(4); 8·86, 7·12, 9·76, 90° 18′. $(CoAmm_6)Cl_3$[1]: D; 9·87. $(CoAmm_6)I_2$[1]: D; 10·92. $(Co, Cu, Ni)_4S_5$[1]: $C(8\text{-}H11)O^7_h$; 9·43. Cs_2GeF_6[1]: D; 8·99. Cs_2PtCl_6[117]: D; 10·15. $K_2CuCl_4Aq_2$[1]: B; 7·45, 7·88. K_2PtBr_6[118]: D; 10·35. K_2PtCl_6[1,118]: D; 9·73. $K_2Pt(SCy)_6$[1]: F; 6·73, 10·26. K_2SeBr_6[119]: D; 10·36. K_2SnCl_6[1]: D; 9·96. K_2SnHy_6[1]; $R(1\text{-}H62)D^5_{3d}$; 5·67, 70° 1′. $K_2S_2O_5$[120]: $M(2)C^2_{2h}$; 6·95, 6·19, 7·55, 102° 41′. $LiClO_4Aq_3$[121]: $H(2)C^4_{6v}$; 7·71, 5·42. $MgAq_6Br_2$[122]: E; 10·25, 7·40, 6·30, 93° 30′. $MgAq_6Cl_2$[122]: E; 9·90, 7·15, 6·10, 94°. $NaIO_4Aq_3$[1]: $R(1)C^4_3$; 5·58, 65° 1′. $(NiAmm_6)Br_2$[1]: D; 10·48. $(NiAmm_6)Cl_2$[1]: D; 10·09. $(NiAmm_6)I_2$[1]: D; 11·01. $Pb(NO_3)_2$[1]: A; 7·81. $Rb_2CuCl_4Aq_2$[1]: B; 7·81, 8·00. Rb_2PdCl_6[1]: D; 10·02. Rb_2PtCl_6[117]: D; 9·83. $Rb_2Pt(SCy)_6$[1]: F; 6·75, 10·47. $Sr(NO_3)_2$[1]: A; 7·80. $Zn(ClO_2)_2Aq_2$[51]: M(4); 8·67, 6·88, 9·38, 90° 20′.

TEN ATOMS. (Abbreviations: A for $C(4\text{-}H71)$; B for $H(3)D^2_3$; D for $R(2)D^6_{3d}$; E for $M(4)C^6_{2h}$.) $AlAq_6Cl_3$[123]: D; 7·85, 97°. Am_3AlF_6[1]: A; 8·90. $Am_3Co(NO_2)_6$[124]: C(4); 10·81. Am_3FeF_6[1]: A; 9·10. $Am_3MoO_3F_3$[1]; A; 9·10. $BaNiCy_4Aq_4$[125]: M(4); 11·89, 14·08, 6·54, 103° 42′. $BaPtCy_4Aq_4$[125]: M(4). $BeSO_4Aq_4$[1,126]: $T(4)D^{18}_{4h}$; 8·02, 10·75. $CaMg(CO_3)_2$ dolomite[1]: $R(1\text{-}G11)C^2_{3i}$; 6·00, 47° 30′. $CaMg(SiO_3)_2$ diopside[1,127]: E; 9·71, 8·89, 5·24, 74° 10′. $(CoAmm)I_3$[1]; A; 10·88. $(CoAmm_5Aq)I_3$[1]: A; 10·84. $CrAq_6Cl_3$[123]: D; 7·95, 97°. $Cs_2AgAuCl_6$[128]: C(½); 5·33. $Cs_2Au_2Cl_6$[128]: C(½); 5·33. $Cs_3Co(NO_2)_6$[124]: C(4); 11·15. Cs_3FeCy_6[129]: O(2); 11·8, 10·1, 7·0. $Cs_2S_2O_6$[130]: H(2); 6·33, 11·54. Cu_5FeS_4: C(8); 10·9. $K_2BaCo(NO_2)_6$[135]: C(4); 10·45. $K_2BaNi(NO_2)_6$[135]: C(4); 10·67. $K_2CaCo(NO_2)_6$[135]: C(4); 10·17. $K_2CaNi(NO_2)_6$[135]: C(4); 10·29. $K_3Co(NO_2)_6$[124,134,135]: 10·32 (10·44). K_3CrCy_6[129]: O(4); 13·55, 10·60, 8·60. K_3FeCy_6[1,129]: M(4); 13·42, 10·40, 8·38, 90° 6′. K_3IrCy_6[129]: O(4); 13·70, 10·53, 8·34. K_3MnCy_6[129]: O(4); 13·56, 10·60, 8·50. $K_3Ni(NO_2)_6$[135]: C(4); 10·49. $K_2PbCo(NO_2)_6$[134]: C(4); 10·49. $K_2PbCu(NO_2)_6$[134]: C(4); 10·52. $K_2PbNi(NO_2)_6$[134]: C(4); 10·55. $K_2S_2O_6$[131,132,133,136]: B; 9·77, 6·28 (9·82, 6·36). $K_2SrCo(NO_2)_6$[135]:

TABLE XXII—*continued.*

C(4) ; 10·23. $K_2SrNi(NO_2)_6$[135] : C(4) ; 10·49. $LiAl(SiO_3)_2$ spodumene[127] ; E ; 9·50, 8·30, 5·24, 69° 40′. α-Na_3AlF_6[1] : M(2)C^3_{2h} ; 5·39, 5·59, 7·76. $NaSb(AlO_3)_2$[1] : H(2)D^4_{6h} ? ; 5·40, 8·81. $N_2H_6Cl_2$[1] : C(4)T^6_h ; 7·89. $PtAmm_4PtCl_4$ pink salt[137] : O(2) ; 7·9, 8·2, 7·9 ; green salt[137] : T(1)C^1_4 ; 6·29, 6·42. $Rb_3Co(NO_2)_6$[124] : C(4) ; 10·73. $Rb_2S_2O_6$[132] : B ; 10·14, 6·41. $Tl_3Co(NO_2)_6$[124] : C(4) ; 10·72.

ELEVEN ATOMS. $Ag_2Amm_4SO_4$[138] : T(2)V^d_4 ; 8·44, 6·35. $Am_2Cr_2O_7$[139] : M(4)C^6_{2h} ; 7·78, 7·54, 13·27, 93° 42′. Am_3HfF_7[1] : C(4)O^4 ? ; 9·40. Am_3ZrF_7[1] : C(4)O^4 ? ; 9·35. $Ca_3Al_2O_6$[1,140] : C(3); 7·62. $CuSO_4Aq_5$[142]. $Fe_2(CO)_9$[1] : H(2) ; 6·45, 15·8. $K_2Cr_2O_7$[139] : T′(4) ; 7·50, 7·38, 13·40, 82°, 96° 13′, 90° 51′. $KMgCl_3Aq_6$ carnallite[1] : O(12)V^6_h ; 9·53, 16·08, 22·35. $K_2S_3O_6$[141] : O(4)V^{16}_h ; 9·77, 13·63, 5·76. $NaAlSi_2O_6Aq$ analcime[1] : C(16)O^o ; 13·68. Tb_4O_7[1] : C(4) ; 10·56.

TWELVE ATOMS. $AmAl(SO_4)_2$[1] : H(1) ; 4·72, 8·23. $AmFe(SO_4)_2$[1] : H(1) ; 4·83, 8·31. $Am_2S_2O_8$[143] : M(2)C^5_{2h} ; 7·83, 8·04, 6·13, 95° 9′. $Ca_2SiO_4Al_2O_3$ gehlenite[1] : T(4)D^1_{4h} ; 7·80, 5·06. $Cs_2S_2O_8$[143] : M(2)C^5_{2h} ; 8·13, 8·33, 6·46, 95° 19′. $H_4N_4S_4$[144] : O(1)V^1_h ; 12·08, 6·76, 7·86. $KAl(SO_4)_2$[1] : H(1) ; 4·71, 7·96. $KCr(SO_4)_2$[1] : H(1) ; 4·74, 8·03. $K_2S_2O_8$[1] : T′(1) ; 5·11, 6·51, 5·48, 96° 45′, 90° 10′, 95° 15′. $P_3N_3Cl_6$[145] : O(4)V^{16}_h.

THIRTEEN ATOMS. (Abbreviations : A for M(16)C^6_{2h} ; B for O(4)V^4 ; D for C(4-H61).) $Al(PO_3)_3$[1] : C(16)T^6_9 ; 13·63. $(CoAmm_5Aq)SO_4Br$[1] : D ; 10·45. $(CoAmm_5Aq)SO_4I$[1] : D ; 10·62. $(CoAmm_6)SeO_4I$[1] : D ; 10·79. $(CoAmm_6)SO_4Br$[1] : D ; 10·51. $(CoAmm_6)SO_4I$[1] : D ; 10·71. $CoSO_4Aq_7$[1] ; A ; 15·45, 13·08, 20·04, 104° 40′. $FeSO_4Aq_7$[1] : A ; 15·34, 12·98, 20·02, 104° 15′. $MgCrO_4Aq_7$[1] : B ; 11·89, 12·01, 6·89. $MgPtCy_4Aq_7$[1] : T(2)D^{17}_{4h} ? ; 14·6, 3·13. $MgSO_4Aq_7$[1] : B ; 11·89, 12·01, 6·86. $NiSO_4Aq_7$[1] : B ; 11·86, 12·08, 6·81. $Pb_3(PO_4)_2$[1] : H(3) ; 9·66, 7·11. $ZnSO_4Aq_7$[1] : B ; 11·85, 12·09, 6·83.

FOURTEEN ATOMS. $Ba(ClO_4)_2Aq_3$[121] : H(2) ; 7·28, 9·64. $BaTi(SiO_3)_3$ benitoite[1] : R(2)D^2_{3h} ? , to H axes, 6·04, 9·71. $Co_2Amm_4Aq_2Cy_6$[1] : R(1) ; H axes, 10·62, 11·01. $Co_2Amm_5AqCy_6$[1] : R(1) ; H axes, 10·74, 10·85. $CoAmm_5AqFeCy_6$[1] : R(1) ; H axes, 10·74, 10·84. $(CoAmm_4CO_3)SO_4Aq_3$[146] : M(2)C^1_s ? ; 11·80, 10·60, 7·42. $CoAmm_6CrCy_6$[1] : R(1) ; H axes, 11·15, 10·90. $Co_2Amm_6Cy_6$[1] : R(1) ; H axes, 10·89, 10·81. $CoSiF_6Aq_6$[1] : R(1) ; H axes, 9·31, 9·70. $FeSiF_6Aq_6$[1] : R(1) ; H axes, 9·62, 9·68. $K_4FeCy_6Aq_3$[1] : M. $MgSiF_6Aq_6$[1] : R(1) ; H axes, 9·56, 9·89. $MgSnF_6Aq_6$[1] : R(1) ; H axes, 9·77, 10·02. $MgTiF_6Aq_6$[1] : R(1) ; H axes,

TABLE XXII—*continued.*

9·77, 9·88. $MnSiF_6Aq_6$[1]: R(1); H axes, 9·66, 9·75. $NaK_3(SO_4)_2$[1]: H(1)D^3_{3d}; 5·65, 7·3. $NiSiF_6Aq_6$[1]: R(1); H axes, 9·26, 9·51. $NiSnCl_6Aq_6$[147]: R(1); 7·09, 96° 45′. $ZnSiF_6Aq_6$[1]: R(1); H axes, 9·33, 9·64. $ZnSnF_6Aq_6$[1]: R(1); H axes, 9·71, 10·19. $ZnTiF_6Aq_6$[1]: R(1); H axes, 9·55, 9·88. $ZnZrF_6Aq_6$[1]: R(1); H axes, 9·77, 10·11.

FIFTEEN ATOMS. (Abbreviation: A for C(4-H64)T^6.) $(NiAmm_6)(NO_3)_2$[1]: A; 10·96. $(ZnAq_6)(BrO_3)_2$[1]: A; 10·31.

SIXTEEN ATOMS. $Mg_3(SiO_4)_2Mg(F, OH)_2$ chondrodite[1]: M(2); 4·73, 10·27, 7·87, 109° 2′. $(KPbCl_3)_3Aq$[148]: T′(4)C^1_i; 14·35, 9·05, 14·50, 90°, 113°, 90°. $NaCa_2H(SiO_3)_3$ pectolite[127]: T′(2); 7·91, 7·08, 7·05, 90°, 95° 10′, 103°. $P_4N_4Cl_8$[149]: T(2)C^4_{4h}; 10·79, 5·93.

SEVENTEEN ATOMS. $Am_2SO_4(AmNO_3)_2$[1]. O(16); 11·28, 10·18, 38·5. $Ce_2(MoO_4)_3$[1]: T($\frac{1}{2}$); 3·77, 5·89. $La_2(MoO_4)_2$[1]: T($\frac{1}{2}$); 3·78, 5·86. $Mg_2SiO_4(Al_2O_3)_2$ sapphirine[1]: M(8); 9·70, 14·55, 10·05, 105° 29′. $Na_4Ca(SiO_3)_3$[1]: C(2); 7·55. $Nd_2(MoO_4)_3$[1]: T($\frac{1}{2}$); 3·74, 5·79. $Pr_2(MoO_4)_3$[1]. T($\frac{1}{2}$); 3·76, 5·81. Pr_6O_{11}[1]: C(4); 5·53. $Sm_2(MoO_4)_3$[1]: T($\frac{1}{2}$); 3·69, 5·81. $UO_2(NO_3)_2Aq_6$[1]: O(4)V^{17}; 11·42, 13·15, 8·02.

EIGHTEEN ATOMS. $Pb_5(AsO_3)_3Cl$[1]: H(2); 10·2, 6·97.

NINETEEN ATOMS. (Abbreviation. A for M(2)C^{4h}.) $(Al_2SiO_5)_2FeHy_2$ staurolite[1,150]: O(4)V^{17}_h; 7·82, 16·52, 5·63. $Am_2Cd(SO_4)_2Aq_6$[151]: A; 9·35, 12·71, 6·27, 106° 41′. $Am_2Fe(SO_4)_2Aq_6$[151]: A; 9·28, 12·57, 6·22, 106° 50′. $Am_2Mg(SeO_4)_2Aq_6$[151]: A; 9·42, 12·72, 6·30, 106° 27′. $Am_2Mg(SO_4)_2Aq_6$[151]: A; 9·28, 12·57, 6·20, 107° 6′. $Am_2Zn(SO_4)_2Aq_6$[151]: A; 9·21, 12·48, 6·23, 106° 52′. $Bi_4Si_3O_{12}$ eulytine[1,179]: C(4); 10·27. $K_2Mg(SO_4)_2Aq_6$[151]: A; 9·04, 12·24, 6·10, 104° 48′. $Na_2Al_2Si_3O_{10}Aq_2$ natrolite[152]: O(8)C^{19}_{2v}; 18·19, 18·62, 6·58. Sb_6O_{13}[1]: T(16)D^{19}_{4h}. $Tl_2Mg(SO_4)_2Aq_6$[151]: A; 9·22, 12·42, 6·19, 106° 30′.

TWENTY ATOMS. (Abbreviation: A for garnet type C(8-H31)O^{10}_h.) $Al_2Ca_3(SiO_4)_3$ grossularite[1]: A; 11·83. $Al_2CaSi_3O_{11}Aq_3$ scolecite[1]: M. $Al_2Fe_3(SiO_4)_3$ almandine[1]: A; 11·50. $Al_2(Mg, Fe)_3(SiO_4)_3$ pyrope[1]: A; 11·51. $Al_2Mn_3(SiO_4)_3$ spessartite[1]: A; 11·60. $Al_2Na_3(LiF_4)_3$ cryolithionite[1]: A; 12·10. $Cr_2Ca_3(SiO_4)_3$ uwarowite[1]: A; 11·95. $Fe_2Ca_3(SiO_4)_3$ topazolite[1]: A; 12·02.

TWENTY-ONE ATOMS. $Ca(F, Cl)Ca_4(PO_4)_3$ apatite[1]: H(2)C^2_{6h}; 9·41, 6·88. $KH_2Al_3(SiO_4)_3$ muscovite (mica)[1]: M(1)C^6_h; 5·17, 8·94, 10·06, 98° 6′. $Pb_5(PO_4)_3Cl$ mimetite[1]: H(2); 10·0, 7·3. $Pb_5(PO_4)_3Cl$ pyromorphite[1]: H(2; 10·0, 7·4.

TABLE XXII—*continued.*

TWENTY-TWO ATOMS. $(CoAmm_6)(ClO_4)_3$[1] : C(4-H71) ; 11·39.

TWENTY-THREE ATOMS. $Mg_5(SiO_4)_3Mg(F, Hy)_2$ humite[1] : O(4) ; 4·74, 10·23, 20·86.

TWENTY-FOUR ATOMS. (Abbreviation : A for alum type $C(4)T_h^6$.) $AmAl(SO_4)_2Aq_{12}$[1] : A ; 12·14. $AmFe(SO_4)_2Aq_{12}$[1] : A ; 12·17. $B_{10}H_{14}$[153] : $O(2)V_h^{21}$; 14·46, 20·85, 5·69. $CsAl(SO_4)_2Aq_{12}$[1] : A ; 12·31. $KAl(SO_4)_2Aq_{12}$[1] : A ; 12·11. $KCr(SO_4)_2Aq_{12}$[1] : A ; 12·09. $RbAl(SO_4)_2Aq_{12}$[1] : A ; 12·20. $TlAl(SO_4)_2Aq_{12}$[1] : A ; 12·21.

TWENTY-FIVE ATOMS. $Ca_5Al_6O_{14}$[1] . C(3) ; 10·1.

TWENTY-NINE ATOMS. $Be_3Al_2Si_6O_{18}$ beryl[1] : $H(2\text{-}G31)D_{6h}^2$; 9·21, 9·17. $Mg_2Al_4Si_5O_{18}$ cordierite[1] : $O(4)V_h^{17}$; 17·10, 9·78, 9·33.

THIRTY ATOMS. $Mg_7(SiO_4)_4Mg(F, Hy)_2$ clinohumite[1] : M(2) ; 4·73, 10·27, 7·87, 109° 2′.

THIRTY-TWO ATOMS. $Ca_4Al_3NaSi_5O_{19}$ sarcolite[1] . T(6) ; 12·43, 15·6.

FORTY-EIGHT ATOMS. $Mg_6B_{14}O_{26}Cl_2$ boracite[1] . $O(8)C_{2v}^{12}$; 17·0, 17·0, 12·0.

SIXTY-ONE ATOMS. $H_3PW_{12}O_{40}Aq_5$ phosphotungstic acid[154] : $C(2)O_h^4$; 12·14.

EIGHTY-FOUR ATOMS. Type $MPMo_{12}O_{40}Aq_{30}$[155] . M is Gd, Nd or Sa : $C(8)O_h^7$; 23.

EIGHTY-SIX ATOMS. $Be_2SiW_{12}O_{40}Aq_{31}$[155] . $C(8)O_h^7$; 23. $H_3PMo_{12}O_{40}Aq_{30}$ phosphomolybdic acid[155] : $C(8)O_h^7$: 23. Type $M_2SiMo_{12}O_{40}Aq_{31}$[155] : M is Mg or Ni . $C(8)O_h^7$; 23.

MINERALS OF MORE OR LESS ILL-DEFINED COMPOSITION. Actinolite[1] : M. Adularia[1,156] : M. Albite[1,156] : T′. Andesine[156] : T′. Anorthite[1,156] : T′. Apophyllite[1,156] : T. Arfvedsonite[157] : M. Babingtonite[1] : T′. Barkevikite[157] : M. Biotite[1] : M. Boleite[158] : C. Cancrinite[159] : H. Celsian[156] : M. Chabazite[1] : R. Danburite[156] : M. Davynite[159] : H. Enigmatite[157] : T′. Gehlenite[1] : T. Glaucophane[1] : M. Hauyine[1] : C. Helvite[1] : C. Heulandite[1] : M. Hornblende[1] :

TABLE XXII—*continued.*

M. Hyalophane[1,156]: M. Kaolin[1]: M. Karsutite[157]: M. Labradorite[1,156]: T'. Leisite[1]: R. Lepidolite[1]: M. Magnetoplumbite[1]: H. Margarite[1]: M. Melilite[1]: T. Metavoltine[158]: H. Microcline[1,156]: T'. Neptunite[1]: M. Nosean[1]: C. Oligoclase[1,156]: T'. Pennine[1]: M. Phlogopite[1]: M. Prismatine[1]: O. Rhodonite[1]: T'. Ripidolite[1]: M. Sanidine[1,156]: M. Sarcolite[1]: T. Scapolite[1,152]: T. Sodalite[1]: C. Tourmaline[1,160]: R. Ultramarine (Lapis Lazuli)[1]: C. Voltaite[158]: C. Zinnwaldite[1]: M. Zunyite[1]: C.

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CHAPTER VI

THE CRYSTAL STRUCTURE OF COMPOUNDS OF ORGANIC TYPES

THE organic group of crystals is mainly characterized by the presence of molecules as distinct entities. The van der Waals' forces between molecules are weaker than the forces of homopolar union within molecules. The distances separating molecules tend to be greater than those between atoms within them.

The method of classification suggested by Ewald and Hermann[1] has been largely followed. The ten groups follow successive sections or sub-sections of this chapter, except that Group VII (highly-polymerized organic compounds) is left over to Chapter VII, and Group VIII (derivatives of benzene and cyclohexane) has been further subdivided. The following abbreviations are used: Me for CH_3, Et C_2H_5, Pr C_3H_7, Bu C_4H_9, Ay C_5H_{11}, Hx C_6H_{13}, Hp C_7H_{15} and Ph C_6H_5. The further abbreviations and general method suggested in the fifth paragraph of Chapter V (page 72) are continued in Tables XXIV and XXV.

13. Acyclic Compounds

(A) **Inorganic Compounds with Substituted Organic Radicals** (Ewald and Hermann's Group I). Crystals in this group tend to have ionic lattices, and might be classified as inorganic, but for the presence of alkyl or other groups; it contains the alkyl-substituted ammonium halides and oxy-salts, as well as the substituted salts of double ammonium with quadrivalent halides. Symbols for types such as OB4 denote analogy with the inorganic Type B4. Results, roughly in order of increasing molecular complexity, are in Table XXIV, Section A.

(B) **Symmetrical Derivatives of Methane** (Ewald and Hermann's Group II). The structure of solid METHANE CH_4, as determined by McLennan and Plummer[1] and Mooy,[7] is based on a face-centred cubic arrangement of C atoms, the positions of H atoms being indeterminate. CBr_4[1] and CI_4[1] have cubic forms, with a tetrahedral arrangement of halogen atoms ; there are also other modifications known. Experiments on X-ray scattering confirm this molecular form for CCl_4[8] and CBr_4.[9] Guillemin,[10] however, suggested a pyramidal model for CH_4 ; this appears unlikely, however, on general grounds. van Arkel and de Boer[26] showed the tetrahedral forms of CH_4 and CCl_4 to be more stable. Some discussion has taken place as to whether in certain cases, however, a structure having a C atom at an apex, with four atoms or groups in a basal plane, may not be possible. Mark and Noethling[1] established tetrahedral symmetry for $C(CH_3)_4$ and $C(NO_2)_4$, although in the latter case the formula may be $C(O{\cdot}N : O)(N(: O)_2)_3$, with four nitro-groups not chemically equivalent. The case of PENTAERYTHRITOL $C(CH_2OH)_4$ has aroused interest, since Mark and Weissenberg[1] suggested a pyramidal structure, whilst Gerstäcker, Möller and Reis[1] advanced a similar model for the tetracetate $C(CH_2OCOMe)_4$, with the space-group C^3_{4h}. Further examination, notably by Miss Knaggs,[1,11] reasserted the tetrahedral model (space-group C^1_{4h}) for these cases, in conformity with the chemical evidence. The halogen-substituted pentaerythritols are monoclinic,[12] with four C atoms round the central C, the four halogen atoms being in one plane. A similar structure is suggested by electron diffraction.[13] Results are given in Table XXIV, Section B.

(C) **Unsymmetrical Derivatives of Methane without Long-Chain Character** (Ewald and Hermann's Group III). See Table XXIV, Section C.

(D) **Short Chains with Central C-C Symmetry** (Ewald and Hermann's Group IV). The simplest example is solid ETHANE, C_2H_6 (or Me_2), which is of D41 type, and like B_2H_6 Numerous halogen, methyl and hydroxyl substituted derivatives of ethane have been studied by Mrs. Lonsdale (*née* Yardley).[1]

HEXACHLORETHANE, C_2Cl_6, has a plane of symmetry passing through the C atoms and two Cl's, the remaining four Cl's being arranged in pairs at equal distances from the plane. Consideration of the symmetry of this molecule (in particular, the absence of the trigonal axis of symmetry) led Mrs. Lonsdale[25] to the conclusion that the C atom is anisotropic, having 2 " A " valencies, and 2 " B " valencies, perhaps corresponding to linkages involving 2_0 and 2_1 electrons of the C atom. The symmetry results may be explained if the A valencies of one

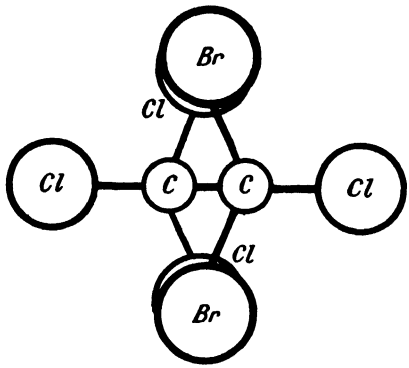

FIGURE XXXVII.—STRUCTURE OF CCl_3CClBr_2.

C atom lie in the symmetry plane, and the B valencies outside it, the other C atom having B valencies in the plane and A valencies outside it. Similar considerations apply in other cases. Suggested structures for the asymmetrical TETRACHLORDIBROMETHANE, CCl_3CClBr_2, and the symmetrical DIBROMTETRAMETHYLETHANE, CMe_2BrCMe_2Br, are depicted in Figures XXXVII and XXXVIII respectively. Results are in Table XXIV, Section D.

(E) **Short Chains without Central C-C Symmetry** (Ewald and Hermann's Group V). BASIC BERYLLIUM ACETATE, $Be_4O(CO_2Me)_6$ (O41 type), in this group provides an interesting example of a complex molecular lattice which can be referred to a simpler type. The molecule is built up round the unique oxygen atom at its centre, the four Be atoms occupying tetra-

hedral corners regularly around it, and the six acetate groups the six tetrahedral edges. Each molecule is then built into a diamond lattice (A4 type), one molecule replacing one C atom. Results are in Table XXIV, Section E.

(F) **Long Chains** (Ewald and Hermann's Group VI). The earlier work on long-chain aliphatic compounds, summarized in the *Strukturbericht*,[1] showed that each member of an homologous

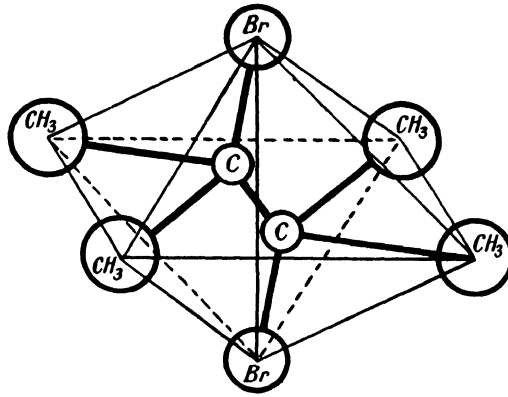

FIGURE XXXVIII.—STRUCTURE OF CMe_2BrCMe_2Br.

series had a " long-spacing " d_1 more or less characteristic of the molecule in question, and " side-spacings " d_2 and d_3 which remained practically constant in a series. The long-spacing tended to increase linearly with the number of C atoms in a chain. A summary is due to Halle.[34]

(a) *Normal Paraffin Hydrocarbons.*[1] The vertical distance between alternate C atoms (2·54) suggests a plane zig-zag arrangement of the hydrocarbon chains. The zig-zag angle may not be the tetrahedral angle (109° 28′) : in the case of $C_{20}H_{60}$, it lies between 76° and 92°. The well-established tendency to alternation in physical properties (melting-points, etc.) amongst the odd and even members of a series was linked by Müller with this peculiarity of arrangement (Figure XXXIX). In the even series, the end layers are identically situated, and the molecules can be brought into coincidence by suitable

parallel shifts: in the odd series, this is true only of pairs of molecules.

Three modifications of paraffin hydrocarbons have been recognized:[33] (i) the normal form, with chains perpendicular to the base of the unit cell, having rectangular cross-section; (ii) type of lower symmetry, without rectangular cross-section, and possible tilting of chains; (iii) rectangular cross-section,

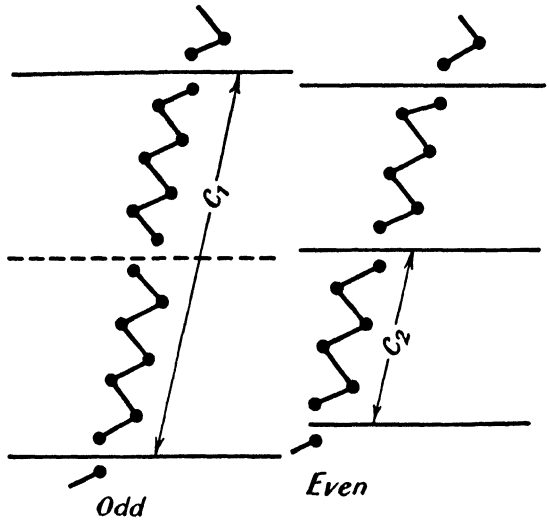

FIGURE XXXIX.—ZIG-ZAG STRUCTURE OF HYDROCARBON CHAINS.

with tilted chains. In the hydrocarbons from C_{21} to C_{29}, there is a change from lower symmetry to hexagonal symmetry near the melting-point: the lower members melt before this symmetry is attained. The effect of increase of temperature from liquid air temperature to the melting-point is to cause expansion in the side-dimensions, without appreciable influence on the long-spacing.[35] The influence of temperature on paraffin wax and vaseline has also been studied by means of X-rays.[36] (See Tables XXIII and XXIV.)

(b) *Normal Alcohols.* The n-alcohols were investigated by Malkin,[37] and, more fully, by Wilson and Ott.[38] In general, two

modifications exist, Type A having molecules perpendicular to the base of the unit cell, and Type B having molecules tilted at an angle of 51° 55′. No measurable change in the long-spacings were found between −50°C. and room temperature. (See Table XXIII.) The unit cells and space-groups of *d*-MANNITOL[39,40] and DULCITOL[39] have been determined. (See Table XXIV.)

(c) *Fatty Acids and their Salts.* (1) *Saturated Monobasic Acids.* De Broglie and Friedel[42] first observed a long-spacing of 43·5 for SODIUM OLEATE. Piper and Grindley[1] found values of 33·5, 38·5 and 43·5 for SODIUM LAURATE, MYRISTATE and PALMITATE respectively, having 12, 14 and 16 C chain atoms respectively, giving a *constant* increase of 5·0 per $2CH_2$ added. Müller and Shearer made experiments on the fatty acids, and found a constant increase of 2·0 per CH_2. Considering the possible arrangement of C atoms in the chains, it was found that even a straight chain of atoms (diameter 1·5, as in this vol.: 3Bd) gave a smaller length of molecule than the long-spacing observed in any given case: it was therefore deduced that pairs of molecules were in contact, joined by their polar carboxyl heads. The increment per CH_2 per molecule was therefore $\frac{1}{2} \times 2{\cdot}0 = 1{\cdot}0$. Assuming spherical carbon atoms, with linkages C–C at the tetrahedral angle, possible structures are as in Figure XL, I and III being plane and II spiral. The arrangement III evidently accorded best with the measurements on the fatty acids. Müller[1] subsequently studied STEARIC, BROMSTEARIC, STEAROLIC and BEHENOLIC ACIDS (monoclinic system), and found chains of C atoms, having their axes approximately parallel, the monoclinic angle being a measure of " tilt " of the chain. It is elsewhere suggested that such tilting of chains may occur, as a result of the work on surface films (see Vol. 1: 33C). The long-spacing may not represent the length of a pair of molecules on this account. The spacing measured by X-rays is the shortest distance between parallel planes in the structure. The " unit cells " are long narrow prisms of height equal to the long-spacing d_1, and of approximately constant side dimensions d_2 and d_3 in the series.

The fatty acids also show polymorphism, which Boer[1] found

to be a temperature effect, with definite transition temperatures between different varieties. A further point of interest is that the K salts of fatty acids appear to have smaller long-spacings than the corresponding Na salts (for results, see Tables XXIII and XXIV). Reference may also be made to the early work of Becker and Jancke[46] on the fatty acids and their Li salts.

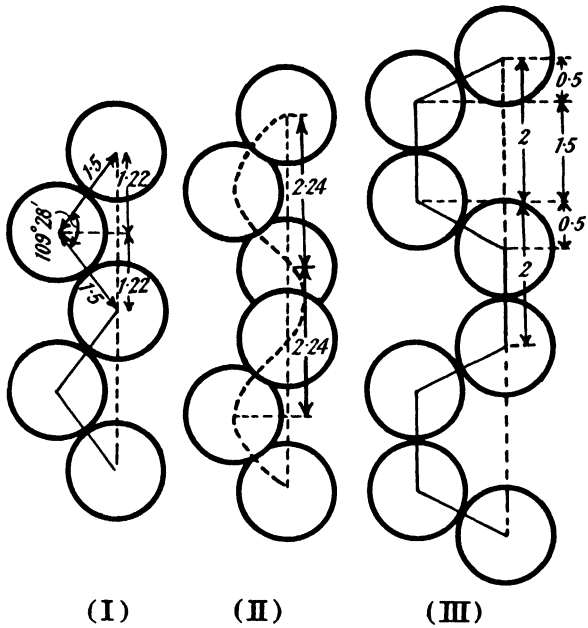

FIGURE XL.—POSSIBLE ARRANGEMENTS OF CARBON ATOMS IN CHAINS.

(2) *Unsaturated Monobasic Acids.* Müller and Shearer[1] investigated the two isomers ERUCIC and BRASSIDIC ACIDS ($C_{21}H_{41}CO_2H$), each containing one double bond, with the possibility of cis-trans isomerism. The results indicated that erucic acid had structure of Type III, and brassidic acid of Type I (Figure XL), which makes the latter the trans-isomer. These two compounds had previously been interchanged. Results are in Tables XXIII and XXIV.

(3) *Dibasic Acids of the Succinic and Alkyl-Malonic Series.*

The long-spacings of dibasic acids of the $(CH_2)_n(CO_2H)_2$ series have been measured by Henderson,[1] Trillat[1] and la Tour and (Miss) Riedberger,[47] the monoclinic cell dimensions being due to Caspari.[1] The acids have a tilted zig-zag structure, as deduced from their cell dimensions, of constant cross-section (mean $ab\sin\beta = 37{\cdot}8$ square Å.U.). The c axes are such that the molecules are in pairs in the odd-numbered series. The values of $c\sin\beta$ agree reasonably well with the long-spacings observed for the even series, but $\frac{1}{2}c\sin\beta$ values are definitely larger than the corresponding spacings in the odd series. Long-spacings in the mono- and di-alkyl malonic acid series are due to Henderson[1] and Coster and van der Ziel.[48] One molecule only is present between successive reflecting planes: after the C_5 member, the lattice spacings alternate. Results are collated in Tables XXIII and XXIV.

(d) *Esters of* (1) *Monobasic*, (2) *Dibasic Acids.*
(e) *Monobasic Acid Amides.*
(f) *Ketones.*
(g) *Dihydrazides.*

} Long-spacings are given in Table XXIII

The esters of monobasic fatty acids studied by Shearer[1] showed an increase of 1·22 per CH_2 added. This is exactly the distance obtained by arranging C atoms in a vertical zig-zag with valency directions from one atom set at the tetrahedral angle (see Figure XL (I)). Malkin[107] has made further measurements, and finds that the esters of palmitic, margaric and stearic acids exist in two forms: A (or α), with vertical zig-zag chains, and B (or β), with tilted chains (smaller long-spacings). The A forms have only one side-spacing, attributed to rotation of the molecule: the B forms have the normal two side-spacings. Similar results have been previously described for the forms of the paraffin and alcohol molecules. In the dihydrazide series, Wolf[49] found the long-spacings to be proportional to numbers of C atoms, the increase per CH_2 being 1·29. For further information, see the *Strukturbericht*[1] and the summarizing paper by Halle.[34]

14. Cyclic Compounds

(A) **Carbocyclic Division.** (a) *Compounds having one Benzene Nucleus* (included in Ewald and Hermann's Group VIII). The crystal structure of BENZENE, C_6H_6,[1,52] was first investigated by Broomé and later by Eastman, by the powder method using X-rays on the solidified substance. Mark applied the rotating-crystal method, and gave provisional measurements of the size of the unit cell. The measurements of Cox yielded the axial lengths, the cell being orthorhombic and containing four molecules. The benzene molecule was shown to possess only a centre of symmetry. The ring is flat, the plane being parallel to the *b*-axis.[53] The structure of HEXAMETHYLBENZENE, $C_6(CH_3)_6$,[1] was determined by Mrs. Lonsdale. The cell is triclinic, pseudo-hexagonal. The results were discussed in relation to the structure of the benzene nucleus.[67] The carbon atoms are arranged, as anticipated, in the form of a closed ring, which is centro-symmetrical. So far as hexamethyl benzene is concerned, the benzene ring is quite flat, and the side-chain carbon atoms are attached radially to their respective nuclear carbon atoms and lie in the plane of the ring. It is natural to draw comparisons here with the graphite structure, where the plane ring arrangement is now generally accepted, the atoms being 1·42 in diameter, as against 1·54 for the atoms in diamond. (See Type A9, and Figure XII.) The structure evidently differs fundamentally from that of diamond, where the rings are " puckered," corresponding to the zig-zag arrangement found for aliphatic chains. The ring of hexamethyl benzene is similar both in structure and in size to the graphite six-membered carbon ring, and the nuclear (aromatic) carbon atoms have three co-planar valencies arranged at 120° to one another as in graphite. Moreover, the assigned diameters of the nuclear and side-chain carbon atoms are about 1·42 and 1·54 respectively. In the case of DURENE, 1.2.4.5 $C_6H_2Me_4$,[62,63] Robertson has found a plane benzene nucleus, with co-planar methyl groups, slightly displaced towards the two unsubstituted positions. On the whole, therefore, whilst the present evidence is in favour of a graphite-like structure of the benzene nucleus, it would appear

unwarranted to assume that this is quite general, until the exact effects of different replacements in the ring are more fully determined.

If a molecule possesses no symmetry, the crystal containing it may have symmetry by association of two or more molecules in the unit cell. Thus the unit cell of BENZOIC ACID, C_6H_5COOH,[1] contains four molecules, A, B, C, D, such that

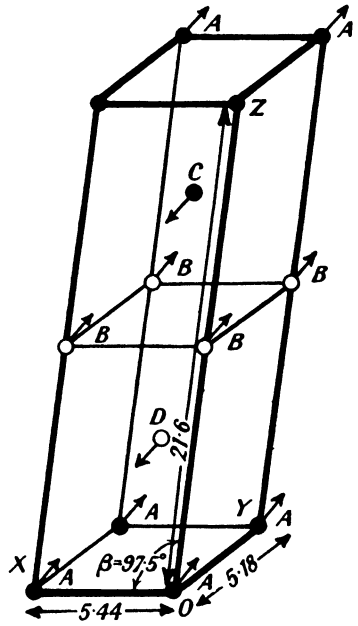

FIGURE XLI.—UNIT CELL OF BENZOIC ACID.

B and D are obtained from A and C by reflection, and C and D from A and B by rotation, providing a centre of symmetry. The unit cell is shown in Figure XLI, and the molecular contribution is evidently $(8 \times \frac{1}{8}) + (4 \times \frac{1}{4}) + 2 = 4$. The structures of the unit cells of α- and β-QUINOL, $C_6H_4(OH)_2$, examined by Caspari,[1] also show growth of symmetry by aggregation of molecules. Here the molecules associate in groups of three, but neither the molecules nor the groups have

symmetry : the groups are associated in larger groups of six for the α- and three for the β-compound, giving 18 and 9 as the total number of molecules in the unit cells, with resulting hexagonal and rhombohedral symmetry respectively. Similarly, the examination of liquid NITROBENZENE[51] and PICRIC ACID[65] has revealed the presence of double molecules, $(PhNO_2)_2$ and $(C_6H_2(NO_2)_3OH)_2$ respectively.

Shearer[1,34] measured the long-spacings of the following three substances of the aromatic class with long aliphatic side-chains : OCTADECYLBENZENE, $C_{18}H_{37}Ph$, $d_1 = 49{\cdot}2$; p-HEXADECYLPHENOL, $C_{16}H_{33}C_6H_4OH$, $d_1, = 46{\cdot}5$; p-OCTADECYLPHENOL, $C_{18}H_{37}C_6H_4OH$, $d_1 = 51{\cdot}3$. The increase for $2CH_2 = 4{\cdot}8$.

X-ray results on benzene and its substituted derivatives are given in Table XXV.

(b) *Compounds having two or more Benzene Nuclei (Uncondensed)* (included in Ewald and Hermann's Group VIII). DIPHENYL, Ph_2, is chemically of considerable interest. Kenner proposed the " butterfly wing " formula, in which the two nuclei are somewhat inclined to each other. The X-ray results apparently confirm this view, for although Dhar[69] found two flat regular hexagons in one plane, Clark and (Miss) Pickett[70,71] reported that the rings, whilst in prolongation rather than doubled over each other, were probably not in the formation of a flat molecule, in agreement with the earlier chemical evidence. Diphenyl has a centre of symmetry. In the case of DIBENZYL $(PhCH_2)_2$, however, the investigations of Dhar[73] and Robertson[72] agree in a non-planar model, the rings being parallel with each other and separated by 0·23. The line connecting the CH_2 groups lies at the tetrahedral angle with the planes of the rings. For results, see Table XXV.

(c) *Compounds having Condensed Nuclei* (Ewald and Hermann's Group IX). NAPHTHALENE, $C_{10}H_8$, and ANTHRACENE, $C_{14}H_{10}$, were amongst the earliest substances investigated by W. H. Bragg[1] using X-rays. The unit cells (Figure XLII) are monoclinic, and contain four molecules. The *c* axes correspond to lengths of single molecules, the increase in length from naphthalene (8·68) to anthracene (11·18) being 2·50, approximately equal to the width of the six-membered C ring of

diamond. It therefore seemed probable that the ring added in passing from naphthalene to anthracene was of the form and size of the diamond six-C ring. Some symmetry is lost between centro-symmetrical benzene derivatives and graphite (hexagonal symmetry), and diamond (cubic symmetry). Further investigation of these substances is due to Robertson[85] and Banerjee.[86] The rings are probably plane in both cases. The two substituted Cl atoms of DICHLORNAPHTHALENE TETRACHLORIDE, $C_{10}H_6Cl_6$, may not lie in the plane of the doubled aromatic ring.[1] NAPHTHALENE TETRACHLORIDE,

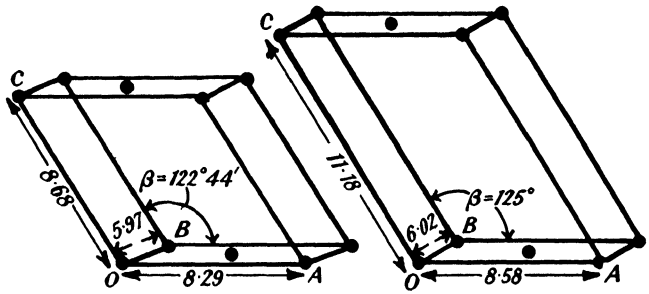

FIGURE XLII.—UNIT CELLS OF NAPHTHALENE AND ANTHRACENE.

$C_{10}H_8Cl_4$, shows elongation of the naphthalene *b* axis, approximately equal to the diameters of two Cl atoms.[1] When the position of a substituent group is moved within a molecule, corresponding changes occur, in general, in axial lengths. When the OH group of NAPHTHOL, $C_{10}H_7OH$, is moved from the α to the β position, the *a* and *b* axes are shortened, and the *c* axis lengthened by an amount, measured along the direction in which the molecule is supposed to lie, which is approximately equal to the diameter of an oxygen atom. Figures XLIII and XLIV show the unit cells of naphthalene tetrachloride and the naphthols respectively. Cell measurements and space-groups are in Table XXV.

(d) *Derivatives of Cyclohexane* (included in Ewald and Hermann's Group VIII). It has been suggested that the cyclohexane ring is of the puckered diamond type.[90,91] This is

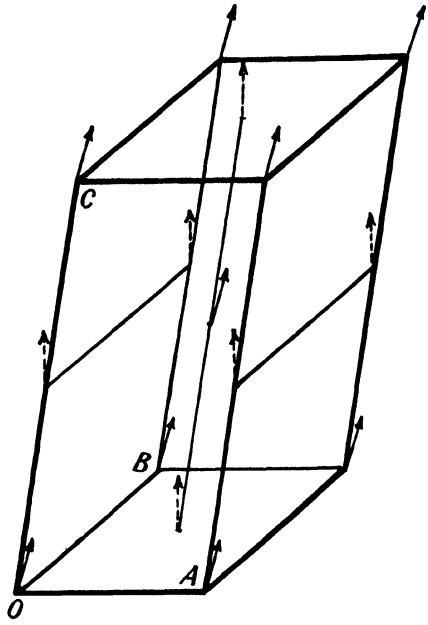

FIGURE XLIII.—UNIT CELL OF NAPHTHALENE TETRACHLORIDE.

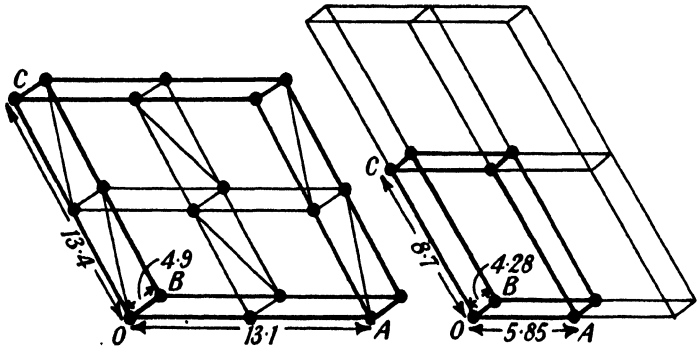

FIGURE XLIV.—UNIT CELLS OF α- AND β-NAPHTHOL.

apparently confirmed by experiments on the diffraction of electrons.[96] Results are in Table XXV.

(B) **Heterocyclic Division** (Ewald and Hermann's Group X). Into this group fall the sugars and their derivatives, which generally possess a pyran (C_5O) or furan (C_4O) ring. It is worthy of notice that the X-ray results led Cox[100] to postulate a ring structure for the pentose β-ARABINOSE, $C_5H_{10}O_5$. Results are given at the end of Table XXV.

The consideration of cellulose, cellobiose and related structures is deferred to the following chapter (Section 17B).

TABLE XXIII.—LONG SPACINGS OF ALIPHATIC CHAIN COMPOUNDS (Å.U.).

SECTION 13Fa.—n-HYDROCARBONS. C_nH_{2n+2}. (Abbreviations: A, B, C for different modifications: p for pressed, and m for melted specimens. The value of n is placed in brackets.) (5) A10·3[1] B7·35[34]. (6) A11·6[1] B8·55[34]. (7) B10·0[34]. (8) A15·0[1] B11·0[34]. (9) B12·8[34]. (10) B13·4[34]. (11) A15·9[34]. (15) A21·0[34]. (16) B20·9[34]. (17) A23·6[34]. (18) A25·3[34] B23·3[34]. (19) A26·2[34]. (20) A27·4[34] B25·4[34]. (21) A28·7[34]. (22) A(30·6)[34]. (23) A31·0[34]. (24) A32·6[34]. (25) A34·3[34]. (26) A35·2[34] C31·1[34]. (27) A37·1[34]. (28) A37·7[34]. (29) A38·8[34]. (30) A40·0[34]. (31) Am41·6[34] Ap43·0[1]. (33) A42·7[34]. (34) A45·3[34] C40·0[34] (35) A47·7[34]. (38) A(50·3)[34] (42) A(55·0)[34]. (60) A78·2[34].

SECTION 13Fb.—n-ALCOHOLS $C_nH_{2n+1}OH$. (Abbreviations: A, B for different modifications; e for crystallized from ether, p for pressed, m for melted, specimens. Values of n in brackets.) (10) Am28·7[38] Bm22·4[38]. (11) Am31·3[38]. (12) Am34·2[38]. (13) Ae36·9[38] Ap36·9[38]. (14) Ae39·7[38] Ap39·4[38]. (15) Ae42·1[38] Ap42·2[38]. (16) Ae44·6[38] Ap44·8[38] Be37·0[38] Bp36·9. (17) Ae47·0[38] Ap47·0[38]. (18) Ae49·6[38] Be41·0[38] Bp41·3[38].

SECTION 13Fc1.—SATURATED FATTY ACIDS AND SALTS. Acids $C_nH_{2n+1}CO_2H$. Salts $C_nH_{2n+1}CO_2M$. Acid Salts $(C_nH_{2n+1}CO_2)_2MH$. (Abbreviations: A, B for different modifications: a for crystallized from acetone, p for pressed, m for melted specimens. Values of n in brackets, followed by H for acid, symbols for M and MH if salt or acid salt respectively.) (oH) formic 5·19[1]. (oK) 6·4[1]. (1H) acetic 6·66[1]. (1Pb) 12·6[1]. (1K) 9·1[1]. (2H) propionic 6·75[1]. (2K) 11·4[1]. (3H) butyric

TABLE XXIII—*continued*

9·65[1]. (3Pb) 14·3[1]. (3KH) 14·9[1]. (4H) valeric 10·1[1]. (4K) 15·6[1]. (4KH) 17·1[1]. (5H) caproic 14·6[1]. (5Pb) 20[1]. (6H) heptylic 16·4[1]. (6Pb) 23·6[1]. (6K) 19·2[1]. (7H) octylic 19·3[1]. (7Pb) 25·4[1]. (7K) 22·3[1]. (8H) nonylic 22·9[1]. (8Pb) 28·2[1]. (9H) capric 23·3[1]. m23·03[41]. (9Pb) 30·6[1]. (10H) undecylic A30·1[1]. B25·8[1]. m25·31[41]. (10K) 27·5[1]. (11H) lauric 27·2[1]. p27·4[1]. p27·29[41]. m27·20[41]. (11Na) 33·5. (11NaH) 35·8[1]. (11Pb) 35·8[1]. (11K) 30·2[1]. (11KH) 35·5[1]. (12H) tridecylic Am34·91[41]. B29·8[1]. (12K) 31·9[1]. (13H) myristic 31·1[1]. 32·2[1]. p36·64[41]. (13Na) 38·5[1]. (13Pb) 41·2[1]. (13K) 34·0[1]. (13KH) 40·5[1]. (14H) pentadecylic A36·1[1]. B34·4[1]. (14K) 35·8[1]. (14KH) 42·9[1]. (15H) palmitic 35·5[1]. 34·7[1]. 35·1[1]. a35·4. m35·7. p41·0. (15Na) 43·5[1]. (15NaH) 46·1[1]. (15Pb) 46·3[1]. (15K) 37·9[1]. (15KH) 45·3[1]. (15Tl) 38·8[1]. (15Fe) 45·9[1]. (15Ni) 46·3[1]. (15Cu) 43·3[1]. (15Zn) 40·1[1]. (15Mo) 44·0[1]. (15Sn) 46·3[1]. (15Sb) 46·1[1]. (15Bi) 47·0[1]. (16H) margaric A41·4[1]. B38·7[1]. Ba39·98[41]. (16Pb) 51·0[1]. (16K) 39·8[1]. (16KH) 48·1[1]. (17H) stearic 39·1[1]. 38·7[1]. m39·9[1]. m39·86[41]. p46·6[1]. a39·62[41]. (17NaH) 50·6[1]. (17Pb) 51·3[1] (17Tl) 42·2[1]. (17K) 42·0[1]. (17KH) 50·5[1]. (18H) nonadecylic a44·07[41]. (18K) 43·8[1]. (18KH) 53·0[1]. (19H) arachidic m44·1[1]. (19K) 46·5[1]. (19KH) 55·7[1]. (20K) heneicosoate 47·9[1]. (20KH) 58·3[1]. (21H) behenic 47·8[1]. m48·6[1]. p48·5[1]. p53·7[1]. (21K) 50·7[1]. (21KH) 60·8[1]. (22H) tricosylic 55·0[1]. p58·5[1]. m52·8[1]. (22Pb) 65·0[1]. (22K) 51·8[1]. (22KH) 54·5[1]. (23H) lignoceric m52·7[1]. p52·9[1]. p58·4[1]. (23K) 63·3[1]. (23KH) 65·9[1]. (24H) 63·0[1]. (24Pb) 71·6[1]. (26H) 65·5[1]. (26Pb) 76·5[1]. (30H) 73·5[1]. (30Pb) 86[1] (31H) 74·0[1]. (31Pb) 92·0[1].

SECTION 13Fc2.—UNSATURATED FATTY ACIDS AND SALTS $C_{17}H_{33}CO_2H$ isoleic. 35·9[1]. oleic· 37·5[1]. 36·2[1]. elaidic: 48·3[1]. $C_{17}H_{33}CO_2Na$ sodium oleate: 43·5[42]. $C_{17}H_{31}CO_2H$ linoleic: 34·4[1] 49·2[1]. $C_{21}H_{41}CO_2H$ erucic· 46·3[1]. brassidic: 59·9[1].

SECTION 13Fc3.—DIBASIC ACIDS OF THE SUCCINIC AND ALKYL-MALONIC SERIES.—Acids $(CH_2)_n(CO_2H)_2$. Monoalkyl Malonic Acids $C_nH_{2n+1}CH(CO_2H)_2$. Dialkyl Malonic Acids $(C_nH_{2n+1})(C_mH_{2m+1})C(CO_2H)_2$. (Values of n, m in brackets, followed by H, MR, MR_2 for the three types respectively.) (1H) malonic 3·77[1]. (2H) succinic 4·5, 4·43[1]. (3H) glutaric 6·40[1]. $\frac{1}{2}c\sin\beta$[44] 6·39. (4H) adipic 6·90, 7·1[1]. $c\sin\beta$[1] 6·82. (5H) pimelic 7·65[1] $\frac{1}{2}c\sin\beta$[1] 8·39. (6H) suberic 9·05, 9·3[1]. $c\sin\beta$[1] 8·88. (7H) azelaic 9·56[1] $c\sin\beta$[1] 10·47. (8H) sebacic 11·2, 11·4[1]. 11·02[47]. $c\sin\beta$[1] 10·95. (10H) 13·04[47]. 13·25[1]. (11H) 13·3[1]. $c\sin\beta$[1] 14·89. (12H) 15·44[47]. 15·4[1]. (14H) 17·41[47]. 17·4[1]. (16H) 19·45[47]. 19·6[1].

TABLE XXIII—*continued.*

(18H) 21·70[47]. (20H) 23·6[1]. (24H) 27·8[1]. (32H) 35·9. (1MR) 5·07[48]. (2MR) 7·36[1]. 7·25[48]. (3MR) 8·70[1]. 8·50[48]. (4MR) 9·83[1]. 9·71[48]. (5MR) 10·82[48]. (6MR) 12·09[48]. (7MR) 12·78[1]. 12·44[48]. (8MR) 14·38[48]. (9MR) 14·61[48]. (10MR) 16·64[48]. (11MR) 16·82[48]. (12MR) 18·90[48]. (13MR) 19·09[48]. (14MR) 21·15[48]. (18MR) 25·59[1]. (2, $2MR_2$) 6·02[1]. (2, $3MR_2$) 6·40[1]. (2, $4MR_2$) 6·94[1]. (3, $3MR_2$) 7·90[1]. (4, $4MR_2$) 9·20[1]. (18, $18MR_2$) 25·59.

SECTION 13Fd1.—ESTERS OF MONOBASIC ACIDS. $C_nH_{2n+1}CO_2C_mH_{2m+1}$ or $C_{n+m+1}H_{2n+2m+2}O_2$. (Values of n,m and n+m+1 in brackets. A and B for different modifications.) (15.1.17) B21·6[107,1]. (15.2.18) B23·0[107,1]. (15.3.19) A27·6[107]. B23·8[107]. (15.4.20) A28·8[107]. (15.8 24) 30·4[1]. (15.16.32) 40·4[1]. (16.1.18) B23·3[107]. (16.2.19) A27·1[107]. B24·6[107]. (16.3.20) A28·6[107]. B25·5[107]. (16.4.21) A30·1[107]. (16.5.22) A31·5[107]. (17.1.19) B23·9[107,1]. (17.2.20) A28·6[107]. B25·5[107,1]. (17.3 21) A30·1[107]. B26·2[107]. (17.4.22) A31·4[107]. B27·7[107]. (17.5.23) B28·8[107].

SECTION 13Fd2.—ESTERS OF DIBASIC ACIDS. $C_nH_{2n+1}CO_2(CH_2)_xCO_2C_mH_{2m+1}$ or $C_{n+m+x+2}H_{2n+2m+2x+2}O_4$. (Values of n,m,x, and n + m + x + 2 in brackets.). (2,0,12,16) 42·1[1]. (2,2,11,17) 22·7[1]. (2,2,12,18) 23·7[1]. (2,0,16,20) 50·5[1]. (2,2,16,22) 28·5[1]. (2,2,20,26) 33·6[1]. (2,2,28,34) 43·7[1]. (2,2,32,38) 49·0[1].

SECTION Fe.—MONOBASIC ACID AMIDES. $C_nH_{2n+1}CONH_2$. (Values of n in brackets) (6) 14·76[1]. (8) 19·56[1]. (13) 29·56[1]. (15) 33·40[1].

SECTION 13 Ff.—KETONES. $C_nH_{2n+1}COC_mH_{2m+1}$ or $C_{n+m+1}H_{2n+2m+2}$. Values of n, m and n+m+1 in brackets.) (6,6,13) 18·7[1]. (1,13,15) 42·4[1]. (1,15,17) 47·6[1]. (1,16,18) 50·0[1]. (2,15,18) 25·2[1]. (6,11,18) 25·2[1]. (1,17,19) 52·9[1]. (3,15,19) 26·3[1]. (2,17,20) 27·3[1]. (3,17,21) 28·9[1]. (6,15,22) 31·1[1]. (11,11,23) 31·6[1]. (6,17,24) 33·6[1], 30·8[1] (dimorphous forms). (13,13,27) 37·0[1]. (15,15,31) 41·1[1]. (17,17,35) 47·2[1].

SECTION 13Fg.—DIHYDRAZIDES. $(CH_2)_n(CONHNH_2)_2$. (Values of n in brackets.) (2) 5·07[49]. 5·84[49]. (3) 8·99[49]. (4) 9·67[49]. (6) 12·24[49]. (7) 13·47[49]. (8) 14·79[49]. (9) 16·05[49]. (10) 17·30[49]. (13) 20·94[49]. (20) 30·25[49]. (24) 35·88[49].

TABLE XXIV.—THE CRYSTAL STRUCTURE OF ACYCLIC ORGANIC COMPOUNDS.

The sectional lettering A to F refers to corresponding sub-sections of Section 13 in the text. Standard abbreviations are on page 72.

SECTION 13A. (The following abbreviations are used: A for $H(2\text{-}OB4)C^4_{6v}$; B for $T(2\text{-}OB10)D^7_{4h}$; D for $T(2\text{-}OB20)C^7_{4h}$; E for $T(1\text{-}OB21)C^1_{4v}$; F for $C(4\text{-}OH61)O^5_h$; G for $M(2)C^2_2$; J for $R(1\text{-}OH62)D^5_{3d}$; K for $C(4\text{-}OH65)T^6_h$.) $TlMe_2Cl$[2]: $T(2)D^{17}_{4h}$; 4·29, 14·01. $TlMe_2Br$[2]: $T(2)D^{17}_{4h}$; 4·47, 13·78. $TlMe_2I$[2]: $T(2)D^{17}_{4h}$; 4·78, 13·43. Me_4SiO_4[3]: $C(4)T^1$; 9·85. NH_3MeCl[1]: E; 4·28, 5·13. NH_3MeBr[1]: D; 5·09, 8·75. NH_3MeI[1]: D; 5·11, 8·95. NH_3EtBr[1]: G; 4·63, 8·32, 6·24, 86° 59′ (γ). NH_3EtI[1]: G; 4·81, 8·68, 6·63, 87° 54′ (γ). NH_3PrCl[1]: E; 4·48, 7·40. NH_3PrBr[1]: E; 4·57, 7·36. NH_3PrI[1]: E; 4·85, 7·33. NH_3BuCl[1]: D; 5·02, 14·85. NH_3BuBr[1]: D; 5·02, 15·23. NH_3BuI[1]: D; 5·18, 15·30. NH_3AyCl[1]: D; 5·01, 16·69. NH_3AyBr[1]: D; 5·00, 16·95. NH_3AyI[1]: D; 5·13, 17·2. NH_3HxCl[1]: D; 4·98, 19·6. NH_3HxBr[1]: D; 4·93, 19·8. NH_3HxI[1]: D; 5·15, 19·5. NH_3HpCl[1]: D; 4·96, 21·1. NH_3HpI[1]: D; 5·17, 21·1. $NHEt_3Cl$[1]: A; 8·38, 7·08. $NHEt_3Br$[1]: A; 8·56, 7·49. $NHEt_3I$[1]: A; 8·78, 7·74. NMe_4Cl[1]: B; 7·78, 5·53. NMe_4Br[1]: B; 7·76, 5·53. NMe_4I[1]: B; 7·94, 5·75. NMe_4ClO_4[4]: $T(2)D^7_{4h}$; 8·29, 6·01. NMe_4MnO_4[4]: $T(2)D^7_{4h}$; 8·44, 6·02. NEt_4I[1]: $T(2)S^2_4$?; 8·87, 6·95. $(NH_3Me)_2SnCl_6$[1]: J; 8·42, 50° 14′. $(NH_3Me)_2PtCl_6$[1]: J; 8·31, 48° 46′. $(NH_3Et)_2SnCl_6$[1]: $H(1\text{-}OH67)D^7_{3d}$; 7·24, 8·41. $(NH_3Et)_2PtCl_6$[1]: $H(1\text{-}OH67)D^3_{3d}$; 7·13, 8·53. $(NHMe_3)_2SnCl_6$[1,5]: K; 12·19. $(NMe_3Et)_2SnCl_6$[1]: K; 13·17. $(NMe_2Et_2)_2SnCl_6$[1]: $T(2\text{-}OH66)C^6_{4v}$; 9·06, 14·12. $(NMeEt_3)_2SnCl_6$[1,5]: K; 13·51. $(NMe_4)_2SiF_6$[6]: $T(2)C^5_{4h}$; 7·88, 11·19. $(NMe_4)_2SnCl_6$[1,5]: F; 12·87. $(NMe_4)_2PtCl_6$[1]: F; 12·65. $BiCl_3SC(NH_2)_2$[1]: R(1)C^4_3; 8·02, 111° 54′. $BiCo(Cy)_6SC(NH_2)_2$: R(1); 9·13, 100° 30′.

SECTION 13B. (Abbreviations: A for $C(1\text{-}O3)T^1_d$; B for $T(2\text{-}O6)V^4_d$; D for $M(1)C^1_{2h}$.) CH_4[1,7]: $C(4\text{-}O1)$; 5·89. CBr_4[1]: A; 5·67. CI_4[1]: A; 5·81. CMe_4[1]: $C(8\text{-}O2)O^7_h$; 11·25. CPh_4[1]: B; 10·86, 7·26. $SiPh_4$[1]: B; 11·32, 7·03. $GePh_4$[1]: B; 11·60, 6·85. $SnPh_4$[1]: B; 11·83, 6·42. $PbPh_4$[1]: B; 12·06, 6·50. $C(NO_2)_4$[1]: C(4); 9·2. $C(CH_2OH)_4$[1]: $T(2\text{-}O4)S^2_4$; 6·01, 8·79. $C(CH_2Cl)_4$[12]: D; 6·91, 6·29, 5·49, 112° 54′. $C(CH_2Br)_4$[12,13]: D; 7·19, 6·33, 5·72, 112° 52′. $C(CH_2I)_4$[12,13]: D; 7·55, 6·43, 6·08. $C(CH_2ONO_2)_4$[1]: B; 9·38, 6·69. $C(CH_2OCOH)_4$[14]: $O(8)V^{15}_h$; 19·80, 9·90, 11·70. $C(CH_2OCOMe)_4$[1,11]: $T(2\text{-}O5)C^4_{4h}$; 11·98, 5·47. $C(COOMe)_4$[24]: $T(2)C^2_{4h}$?; 9·12, 7·02. $C((CH_2O)_2CHPh)_4$[1]: H(3-O7); 6·03, 36·7.

TABLE XXIV—*continued.*

SECTION 13C. (Abbreviation : A for O(4)V^4.) CHI_3[1] : H(2-O11)C_6^5 ; 6·87, 7·61. CHI_3S_8[15] : R(1). $CO(NH_2)_2$[1,16] : T(2-O21) ; 5·70, 4·75. $CS(NH_2)_2$[1,17] : O(4-O22)V_h^{16} ; 5·47, 7·64, 8·54. $CO(NH_2)NHMe$[1,18] : A ; 6·89, 6·96, 8·45. $CO(NHMe)_2$[1] : O(2)V_h^{13} ? ; 4·53, 5·14, 10·92. $CO(NH_2)_2AgNO_3$[19] : M(8)C_{2h}^2 ; 10·23, 16·84, 6·25. $4CO(NH_2)_2CaSO_4$[20] : T′(4) ; 14·74, 14·95, 6·47, 92° 6′, 90° 22′, 86° 50′. $Li(OCOH)Aq$[1] : O(4) ; 6·49, 10·01, 4·85. $Ca(OCOH)_2$[1] : O(8)V_h^{15} ; 10·16, 13·38, 6·28. $Cu(OCOH)_2Aq_2$[21,22] : M(4)C_{2h}^3 ; 8·95, 6·73, 8·24. $Cu(OCOH)_2Aq_4$[22] : M(2)C_{2h}^3. $Sr(OCOH)_2$[1] : A ; 6·86, 8·72, 7·24. $Sr(OCOH)_2Aq_2$[1] : A ; 7·30, 11·99, 7·13. $Ba(OCOH)_2$[1] : A ; 6·78, 8·89, 7·68. $Pb(OCOH)_2$[1] : A ; 6·52, 8·75, 7·41. $CH_2(OCOH)_2$ malonic acid[44] (below 80°C.) . O(16) ; 8·70, 11·53, 17·05. $N(CH_2NO_2)_3$[1] : O(8) ; 11·64, 13·25, 10·80. HN : $C(NH_2)_2HCl$ guanidonium chloride[23] : O(8)V_h^{15} : 7·76, 9·22, 13·06. (HN : $C(NH_2)_2)H_2CO_3$[1] : T(4) ; 6·95, 19·45.

SECTION 13D. (Abbreviation : A for O(4)V_h^{16}.) Me_2[1] : H(2-D41) ; 4·46, 8·19. C_2Cl_6 (below 46°C.)[1] : A ; 11·52, 10·15, 6·39 ; (above 71°C.)[50] : C(2) ; 7·43. $C_2Br_6^6$: A ; 12·07, 10·70, 6·73 C_2Br_5F[1] : A ; 11·84, 10·76, 6·56. C_2Me_6[50] : C(2) ; 7·69. C_2Me_5Hy[1] · O(8)C_{2v}^{21} ? ; 21·35, 10·77, 7·84. $C_2Cl_3Br_3$[1] . A ; 11·77, 10·45, 6·54. $(CCl_2Br)_2$[1] : A ; 11·73, 10·38, 6·51. CCl_3CClBr_2[1] : A ; 11·61, 10·35, 6·51. $(CBr_2Me)_2$[1] : (a) Low temperature form : A ; 11·71, 10·91, 6·56 ; (b) : A ; 11·70, 10·44, 6·57 ; (c) : T(4) ; 8·81, 11·27. $(CBrMe_2)_2$[1] : T(4) ; 10·45, 8·14. $C_2H_4(NH_2)_2H_2SO_4$[1] : T(4)D_4^4 or D_4^8 ; 5·96, 17·99. $(CN_2H_2)_2$[1] : M(4) ; 13·8, 4·4, 6·2, 90°. $H_2C_2O_4$ oxalic acid[1] : O(4) ; 6·46, 7·79, 6·02. $H_2C_2O_4Aq_2$[1] : M(2)C_{2h}^5 ; 6·05, 3·57, 11·9, 106° 12′. $Li_2C_2O_4$[45] : O(4) ; 6·58, 7·74, 6·61. $BeC_2O_4Aq_3$: A ; 6·37, 7·53, 12·45. $K_2Rh(C_2O_4)_3Aq$[1] : H(6)D_3^4 or D_3^6, 11·28, 20·25. $CHBr_2CBr$: $CBrCHBr_2$ hexabromobutylene[27] : M(2)C_{2h}^5 ; 11·55, 6·40, 10·06. cis-$(C_2H_2O_2)_2$ maleic acid : [31,45] M(8)C_{2h}^6 ; 21·5, 6·9, 6·89, 91° 10′. trans-$(C_2H_2O_2)_2$ fumaric acid[1] : M(6)C_{2h}^5 ; 7·60, 15·11, 6·61, 111° 5′. cis-CO_2HCH : $ClCO_2K$[1] : O(8)V_h^{16} ; 7·62, 15·74, 10·95. trans-CO_2AmCH : $ClCO_2Am$[1] : M(2)C_{2h}^2 ; 9·30, 6·70, 6·74, 108° 25′. trans-CO_2AmCH : $CHCO_2H$[1] : T′(4) ; 7·00, 7·44, 6·56, 107° 1′, 117° 58′, 69° 16′. $(CHOHCH_2)_2$ succinic acid : (below 137°C.)[28] : T′(2) ; 5·04, 7·58, 9·75, 67° 23′, 89° 45′, 47° ; (above 137°C.)[1,28,44] : M(2)C_{2h}^2; 5·03, 8·75, 7·48, 133° 37′. $(CH_2CO)_2O$[1] ; O(4) ; 6·93, 11·66, 5·39. $(CH_2CO)_2NH$[1] : O(8)V_h^1 ; 7·50, 9·60, 12·75. $(CH_2CO)_2NI$[1] : T(4) ; 4·45, 15·55. $(CO_2HCHOH)_2$ mesotartaric acid[1] : T′(2) ; 9·24, 6·33, 5·45, 70° 30′, 78°, 79° 30′. *d* and *l* tartaric acids[1,45] : M(2)C_2^2 ; 7·68, 6·03, 6·18, 92° 53′. *d*+*l* racemic acid anhydrous[1] : T′(2) ; 7·18, 9·71, 4·98, 82° 20′, 118°, 72° 58′. *d* + *l* racemic acid Aq[1] :

TABLE XXIV—*continued.*

T′(2) ; 8·09, 10·03, 4·82, 76° 2′, 96° 58′, 120° 8′. meso-$(CHOHCO_2Tl)_2$[1] : T′(4). meso-$(CHOHCO_2K)_2Aq_2$[1] : T′(2). $(CHOHCO_2)_2KH$[29] : O(4) ; 7·61, 10·70, 7·80. $(CHOHCO_2)_2KNa$[1] : O(4) ; 11·91, 14·32, 6·20. $(CHOHCO_2Rb)_2$[1] : H(3)D_3^4 or D_3^6 ; 7·17, 13·19. $(CHOHCO_2)_2NaAm$[1]. $(CHOHCH_2OH)_2$ mesoerythritol[1] : T(8)C_{4h}^6 : 12·76, 6·83. $(CO_2HC\equiv)_2$[45] : acetylene dicarboxylic acid : M(4) ; 7·88, 9·04, 6·62, 111° 6′.

SECTION 13E. (Abbreviations : A for C(8-O41)T_h^4 ; B for M(4)C_{2h}^5 ; D for acetylacetone group CH_2COCH_2COMe.) $(CH_3COH)_4$ metaldehyde[1]. T(8)C_{4v}^9 ? ; 10·34, 4·10. $CH_3CH(OH)NH_2$ acetaldehyde ammonia[1] : R(6)D_{3d}^5 ? ; 8·2, 84° 50′. CH_3CONH_2[1] : R(6)$\dot{C}_{3v}^6$; 8·1, 91° 17′. $CH_2NH_2CO_2H$[32] : M(4)C_{2h}^5 ? ; 5·1, 11·9, 5·43, 111° 38′. $(CH_3CO_2)_2NaH$[1] : C(24)T_h^7 ; 15·98. $Be_4O(OCOMe)_6$[1] : A ; 15·72. $Be_4O(OCOEt)_6$[1]. M(2)C_{2h}^5; 16·00, 9·76, 9·15, 116° 7′. $Be_4O(OCOMe_3)_6$[1] : M(8) ; 19·3, 12·4, 35·4, 91° 21′. $Zn_4O(OCOMe)_6$[1] : A ; 16·4. $(KSO_3CHClCO_2K)_23Aq$[1] : O(4)V_h^{14}. $CO_2HCH_2CO_2H$ malonic acid[1] : T′(2) ; 8·36, 5·33, 5·14, 94° 56′, 103° 56′, 71° 30′. α-AlD_3[1] : B ; 14·1, 7·42, 16·5, 98° 54′. α-CoD_3[1] : B ; 14·2, 7·50, 16·4, 98° 38′. α-CrD_3[1] : B ; 14·2, 7·62, 16·5, 99° 8′. γ-FeD_3[1] : O(16) , 13·68, 15·74, 33·0. α-GaD_3[1] : B , 14·0, 7·63, 16·3, 99° 2′. β-GaD_3[1] : O(4) ; 13·1, 8·20, 16·3. γ-GaD_3[1] : O(16) ; 13·74, 15·71, 32·76. β-InD_3[1] : O(4) ; 13·4, 8·24, 16·5. α-MnD_3[1] : B , 14·1, 7·68, 16·5, 99° 24′. β-ScD_3[1] : O(4) ; 13·52, 8·20, 16·15.

SECTION 13Fa. C_5H_{12}[1] : O(1) ; 3·35, 4·31, 10·3 ; M(1) ; 3·86, 4·61, 10·0, 120°. C_6H_{14}[1] : O(1) ; 3·51, 4·26, 11·6 : M(1) ; 3·87, 4·61, 12·0, 120°. C_8H_{18}[1] : O(1) ; 3·50, 4·36, 15·0 : M(1) ; 3·87, 4·72, 14·4, 120°. $C_{29}H_{60}$[1] : O(4-O32)V_h^{16} ; 7·45, 4·97, 77·2. $C_{35}H_{72}$[1] : O(4) ; 7·43, 4·97, 92·4. $C_{60}H_{122}$[1] : O(4)V_h^{16} ; 7·44, 4·95, 156·4.

SECTION 13Fb. $C_6H_8(OH)_6$ d-mannitol[39,40] : O(4)Q^4 ; 8·66, 16·7, 5·53 ; dulcitol[39] : M(4)C_{2h}^5; 8·61, 11·60, 9·05, 113° 45′.

SECTION 13Fc1. (The following have space-group M(4)C_{2h}^4.) $C_{11}H_{23}CO_2H$ lauric acid[1] : 9·76, 4·98, 36·9, 48° 6′. $C_{15}H_{31}CO_2H$ α-palmitic acid[43,44] : 9·41, 5·09, 45·9, 50° 50′. $C_{17}H_{35}CO_2H$ β-stearic acid[1,43,44] : 5·68, 7·39, 50·7, 63° 38′. $C_{17}H_{34}BrCO_2H$ bromostearic acid[1] : 11·04, 4·90, 52·84, 43° 17′.

SECTION 13Fc2. (Same space-group as Section Fc1.) $C_{17}H_{31}CO_2H$ stearolic acid[1] : 9·55, 4·69, 49·15, 53° 4′. $C_{21}H_{39}CO_2H$ behenolic acid[1] : 9·55, 4·69, 59·10, 53° 30′.

TABLE XXIV—*continued.*

SECTION 13Fc3. (Abbreviation: n value, in brackets, represents symbol $(CH_2)_n(CO_2H)_2$. For (1) malonic acid, see Section C: for (2) succinic acid, see Section D above.) (3) glutaric acid[44]: (below 74°) $M(8)C_{2h}^6$; 10·34, 5·08, 32·9, 129°: (above 74°): $M(4)C_{2h}^6$; 10·06, 4·87, 17·4, 132° 35′. (4) adipic acid[1]: $M(2)C_{2h}^5$; 10·27, 5·16, 10·02, 137° 5′. (5) pimelic acid[1]: $M(4)C_{2h}^5$; 9·93, 4·82, 22·12, 130° 40′. (6) suberic acid[1]: $M(2)C_{2h}^5$; 10·12, 5·06, 12·56, 135°. (7) α-azelaic acid[1]: $M(4)C_{2h}^5$; 9·72, 4·83, 27·14, 129° 30′; β-azelaic acid[34]: $M(4)C_2^2$,; 5·61, 9·58, 27·20, 136° 30′. (8) sebacic acid[1]: $M(2)C_{2h}^5$; 10·05, 4·96, 15·02, 133° 50′. (11) brassylic acid[1]: $M(4)C_{2h}^5$; 9·63, 4·82, 37·95, 128° 20′. (16) hexadecacarboxylic acid[1]: $M(2)C_{2h}^5$; 9·76, 4·92, 25·10, 131° 10′.

TABLE XXV.—THE CRYSTAL STRUCTURE OF CYCLIC COMPOUNDS.

Standard abbreviations are on page 72.

SECTION 14Aa.—ONE RING. C_6H_6 benzene[1,52,53,68]: $O(4)V_h^{15}$; 7·44, 9·65, 6·81.

ONE RING WITH ONE SUBSTITUENT. PhCOOH benzoic acid[1]: $M(4)C_{2h}^5$; 5·44, 5·18, 21·8, 97° 5′. d- and l-$PhNHCH_2COOH$ phenylaminoacetic acid[54]: O(4); 15·2, 5·05, 9·66. PhCH: CHCOOH transcinnamic acid[45]: M(4); 11·65, 14·10, 4·26, 98° 36′. $PhCH_2CH_2COOH$ hydrocinnamic acid[45]: M(4); 12·90, 9·20, 6·98, 103° 36′. Compounds of type PhCH(OH)CHMeNHMeHX[55]: d-pseudoephedrine hydrohalides: X = Cl: $O(4)V^4$; 25·49, 6·48, 6·91; X = Br: $O(4)V^4$; 24·68, 6·93, 6·78; X = I: $O(4)V^4$; 11·39, 6·83, 15·62. l-ephedrine hydrohalides: X = Cl: $M(2)C_2^2$; 12·64, 6·15, 7·34, 102° 6′; X = Br: $M(2)C_2^2$; 12·74, 6·20, 7·62, 100° 48′; X = I: $O(2)V^3$; 25·66, 7·33, 19·14. Type $Ph(CH_2)_nCOOH$[1] (values of n in brackets). (1). $M(4)\ C_{2h}^5$; 14·2, 4·90, 10·10, 101°. (2): $M(8)C_{2h}^5$, 32·2, 9·83, 5·54, 101° 13′. (3): $M(4)C_{2h}^5$; 17·8, 4·90, 10·3, 98° 30′.

ONE RING WITH TWO SUBSTITUENTS. (Details given for di-substituted derivatives of benzene; the substituent groups only given, preceded by o (ortho), m (meta) or p (para) compound.) p-Cl, Cl[56]: $M(2)C_{2h}^5$, 14·53, 4·10, 5·88, 112° 30′. p-Br, Br[56]: $M(2)C_{2h}^5$; 15·46, 4·11, 5·80, 112° 38′. o-I, I[57]: M(4); 8·29, 12·23, 7·91, 93° 8′. m-I, I[57]: O(4); 17·20, 7·08, 6·21. p-I, I[57]: $O(4)V_h^{15}$; 17·00, 7·38, 6·21. o-OH, OH[1]: $M(8)C_{2h}^3$; 17·46, 10·74, 5·48, 94° 15′. m-OH, OH[1]. $O(4)C_{2v}^{10}$; 9·56, 10·25, 5·64. p-OH, OH[1]: (α-modification) $H(18)C_{3i}^1$; 22·06, 5·62: (β) $R(9)C_3^1$; (to H axes) 16·25, 5·53: (γ) $M(4)C_{2h}^5$; 13·24, 5·20, 8·11, 107°. p-O:, O: quinone[45]: M(4); 11·40, 6·43, 6·85, 93° 20′. o-COOH, COOH[45]: M(2);

TABLE XXV—*continued.*

9·33, 7·13, 5·10, 94° 36′. o-NH_2, NH_2[1]: M(4)C_{2h}^4; 7·74, 7·56, 11·76, 121° 10′. m-NH_2, NH_2[1]: O(16)V_h^1 ?; 11·97, 8·14, 23·61. p-NH_2, NH_2[1]: M(8)C_{2h}^2; 8·29, 5·93, 24·92, 112° 58′. o-NO_2, NO_2[1,58]: M(4)C_{2h}^5; 7·95, 13·0, 7·45, 112° 7′. m-NO_2, NO_2[58]: O(4)V_h^{16}; 13·3, 14·1, 3·82. p-NO_2, NO_2[58,59]: M(2)C_{2h}^5; 11·3, 5·51, 5·8, 92° 18′. o-$COCH_2Me$, $COCH_2Me$[1]: T(4); 7·25, 20·47. p-Cl, Br[56]: M(2)C_{2h}^5; 15·15, 4·13, 5·81, 113°. o-I, COOH[60]: M(4)C_{2h}^5; 11·30, 15·17, 4·34, 90° 44′. o-OH, COOH[1]: M(4); 11·56, 11·22, 4·93, 91° 22′. o-OH, NH_2[1]: O(8)V_h^8 ?; 7·26, 7·71, 19·51. m-OH, NH_2[1]· O(4)C_{2v}^4 ?; 6·14, 11·10, 8·38. p-OH, NH_2[1] (1st modification) O(4); 8·25, 5·32, 13·06. (2nd) O(6); 12·07, 11·85, 5·82. o-NO_2, NH_2[1]: O(16); 10·09, 29·44, 8·52. m-NO_2, NH_2[1]: O(4)V_h^{11}; 19·23, 6·48, 5·06. p-Me, NO_2[1]: O(8). o-Me, SO_2NH_2[24]: T(16)C_{4h}^6; 18·8, 9·15. OH, $CH_2CH(NH_2HCl)COOH$ d-tyrosine hydrochloride[24]: M(2)C_2^2 ?; 5·03, 8·97, 22·50, 101° 28′.

ONE RING WITH THREE SUBSTITUENTS. $C_6H_3(NO_2)_3$ 1.3 5 trinitrobenzene[58,61]: O(16)V_h^{11}; 12·8, 27·0, 9·8. $C_6H_3(OH)(NO_2)_2$ 2 6 dinitrophenol[58]: O(8)V_h^{11}; 12·1, 12·7, 9·5.

ONE RING WITH FOUR SUBSTITUENTS. $C_6H_2Me_4$ (1.2.4.5) durene[62,63]: M(2)C_{2h}^5; 11·57, 5·77, 7·03, 113° 18′. $C_6H_2(CN)Br_3$ 2.4.6 tribromobenzonitrile[64]: M(2)C_{2h}^2; 12·50, 10·30, 4·87, 135° 36′. $C_6H_2(NO_2)_2Me_2$ 4.6 dinitro 1.3 xylol[58]. M(2); 11·5, 5·49, 7·2, 98°.

Type $C_6H_2X(NO_2)_3$ *1 X 2.4 6* NO_2. (X only given.) OH picric acid[61,65]: O(8)C_{2v}^5; 9·25, 19·08, 9·68. Cl[61]: M(8)C_{2h}^3; 24·9, 6·8, 11·0, 102° 51′. Br[61]: (1st modification) H(18)$C_6^{2,3}$; 14·90, 25·8, 22·6: (2nd) T′(12); 15·2, 15·4, 15·64, 74°, 98°, 119°. I[61]: T(4)$D_4^{4,8}$; 7·03, 19·80. NH_2[61]: M(4)C_{2h}^5; 15·3, 9·28, 6·01, 99° 12′. NO_2[61]: O(4)V^4; 12·4, 6·15, 13·1. Mc[61]: M(16)C_{2h}^6; 40·5, 6·19, 15·2, 89°. OMe[61]: M(8)C_{2h}^5, 13·7, 9·3, 15·8, 91°. OEt[61]: O(4)C_{2v}^5; 7·34, 23·7, 6·24.

ONE RING WITH FIVE SUBSTITUENTS. $C_6H(NO_2)_3(OH)_2PbO$ lead styphnate[66]: M(4); 10·02, 12·54, 8·00, 92° 51′.

ONE RING WITH SIX SUBSTITUENTS. C_6Cl_6[1,67]: M(2)C_{2h}^5 ?; 8·07, 3·84, 16·61, 116° 52′. C_6Br_6[1]: M(2); 8·50, 4·2, 17·6, 116° 29′. C_6Me_6[1]: T′(1-O52)C_1^1; 9·01, 8·93, 5·34, 44° 27′, 116° 43′, 119° 34′. $C_6(NH_2)_6$[68]: C(16)O_h^3; 15·14.

SECTION 14Ab.—TWO RINGS (UNCONDENSED). Ph_2 diphenyl[1,69,70,71]: M(2)C_{2h}^5; 8·11, 5·67, 9·57, 94° 30′. $C_{12}H_4Cl_6$ hexachlorodiphenyl[1]: O(8)V_h^{16}; 15·80, 8·54, 21·48. $(PhCH_2)_2$ dibenzyl[1,72,73]: M(2)C_{2h}^5; 12·77, 6·12, 7·70, 116°. $(PhCHOH)_2$ isohydrobenzoin[1]: M(2)C_2^2 ?; 12·3, 8·05, 5·8, 92° 53′. $(PhCO)_2$ benzil[1]: R(1)$D_2^{4,6}$; 6·52, 77° 52′. $(C_6H_3Me_2CH_2)_2$ dimesityl[70,71]: M(4)C_{2h}^5; 8·21, 8·58, 22·25, 96° 30′. $(NH_2Me_2C_6H)_2$ 3·3′ diaminodimesityl[71]: M(4)C_{2h}^5; 8·26, 8·58, 22·62, 90°. $(COOHC_6H_4)_2$

TABLE XXV—*continued.*

diphenic acid[71]: O(8)V_h^{13}; 13·80, 11·90, 14·12. (PhCH :)$_2$ stilbene[1,74]: M(4)C_{2h}^5; 12·20, 5·72, 16·00, 113° 48′. $CNC_6H_3(NO_2)CH:CHC_6H_4(OCH_3)$ p-cyano, o-nitro, p′ methoxystilbene[84]: (1st modification): T′(2); 8·50, 7·45, 13·35, 98° 6′, 106° 20′, 75° 40′; (2nd): O(8); 14·2, 27·8, 7·6. (PhC :)$_2$ tolane[74]: M(4)C_{2h}^5; 12·80, 5·68, 15·74, 114° 56′. (PhN :)$_2$ azobenzene[45,75]: M(4)C_{2h}^5; 12·65, 6·06, 15·60, 114° 24′. (PhNH)$_2$ hydrazobenzene[45]: O(4); 11·10, 9·93, 9·33. $NH_2C_6H_4N:NPh$ p-aminoazobenzene[76]: M(4); 13·69, 5·60, 14·18, 81° 49′. (MeC_6H_4N :)$_2$ o-azotoluene[77]: 13·93, 6·60, 14·55, 101° 4′. ($NH_2MeC_6H_3$)$_2$ o-tolidine[70,71]. O(4)V^4; 6·50, 7·48, 23·62. $(C_6H_2(NO_2)_3Cl)(C_6H_2(NO_2)_3Me)$ 2.4.6 trinitrochlorobenzene + 2.4.6 trinitrotoluene[78]: M(16)C_{2h}^6; 40·5, 6·19, 15·2, 89° 29′. (Ph(CH :)$_n$)$_2$ diphenylpolyenes[79] (values of n only in brackets). (2) M(4)C_{2h}^2; 7·71, 11·70, 13·41, 97°. (3): M(2)C_{2h}^5; 6·33, 7·43, 14·43. (4): M(2) ?, 6·25, 7·44, 16·03 (5): O(4)V_h^{15}; 10·25, 7·66, 21·2 (6): O(4) ?, 10·20, 7·60, 23·58. (7) O(4); 10·2, 7·57, 25·95.

THREE RINGS (UNCONDENSED). PhC_6H_4Ph p-diphenylbenzene (triphenyl)[80,81]: M(2)C_{2h}^5; 8·08, 5·60, 13·59, 91° 55′. $CHPh_3$ triphenylmethane[1]: O(8); 15·1, 26·2, 7·66. $COHPh_3$ triphenylcarbinol[1]. R(3) ?, 11·25, 107°. $CBrPh_3$ triphenylbromethane[1]. R(3) ?; 10·8, 81° 30′.

FOUR RINGS (UNCONDENSED). $C_6H_3Ph_3$ 1.3.5 triphenylbenzene[82,83]: O(4)C_{2v}^9; 7·55, 19·76, 11·22. (PhC_6H_4)$_2$ quaterphenyl[83]: M(2)C_{2h}^5; 8·14, 5·64, 18·4, 97°. (PhCH :)$_2$($C_6H_3(NO_2)_3$)$_2$ stilbene + 2 mols. nitrobenzene[84]. T′(2); 12·7, 15·4, 7·7, 102° 16′, 85° 30′, 87° 35′. (For tetraphenyls, see Table XXIV, Section B.)

SECTION 14Ac.—TWO RINGS (CONDENSED). $C_{10}H_8$ naphthalene[1,45,85,86]: M(2-O71)C_{2h}^5; 8·29, 5·97, 8·68, 122° 42′. $C_{10}H_7OH$ α-naphthol[1]: M(4)C_{2h}^4, 13·1, 4·9, 13·4, 117° 10′; β-naphthol[1]: M(4); 11·7, 4·28, 17·4, 119° 48′. $C_{10}H_7NH_2$ α-naphthylamine[1]: O(4)V_h^{20}; 8·62, 14·08, 7·04. $C_{10}H_8Cl_4$ naphthalene tetrachloride[1]: M(4)C_s^4 ?; 7·9, 10·3, 14·2, 112° 40′. $C_{10}H_6Cl_6$ dichlornaphthalene tetrachloride[1]: M(4)C_s^4 ?; 7·8, 12·3, 13·9, 116° 14′.

THREE RINGS (CONDENSED). $C_{14}H_{10}$ anthracene[1,45,85,86]: M(2-O71)C_{2h}^5; 8·58, 6·02, 11·18, 125°. $C_{12}H_{10}$ acenaphthene[1]: O(4)V_h^{20}; 8·32, 14·15, 7·26. $C_{12}H_{10}C_6H(NO_2)_3(OH)_2$ acenaphthene + styphnic acid[87]: M(2); 9·05, 14·8, 6·8, 99°. $C_{12}H_{10}C_6H_2Me_2(NO_2)_2$ acenaphthene + 4, 6 dinitro, 1.3 xylol[88]: M(4)C_{2h}^5; 18·5, 14·2, 7·25, 103°. $C_{13}H_{10}$ fluorene[1]: M(4)C_{2h}^5; 8·48, 5·73, 19·24, 101° 53′. $C_{14}H_{10}$ phenanthrene[1,45]: M(4)C_{2h}^5 ?; 8·60, 6·11, 19·24, 98° 15′. $C_{14}H_8O_2$ anthraquinone[45]: O(2); 12·05, 15·05, 2·69.

FOUR RINGS (CONDENSED). $C_{18}H_{12}$ chrysene[89]: M(4)C_{2h}^6 ?; 8·34, 6·18, 25·0, 115° 48′.

TABLE XXV—*continued.*

SECTION 14Ad.—CYCLOHEXANE DERIVATIVES. $C_6H_6Cl_6$ benzene hexachloride[1,90,91]: C(4-O56)T_h^6; 10·07. $C_6H_6Br_6$[1,90,91]: C(4-O56)T_h^6; 10·42. $C_6H_6(OH)_6$ l-inositol[91]: M(2)C_2^2; 6·17, 9·11, 6·83, 106° 36′; i-inositol[91]: M(8)C_{2h}^5; 6·64, 12·0, 19·7, 105° 48′. $C_6H_6(OH)_6Aq_2$ i-inositol dihydrate[91]: M(4)C_{2h}^5; 8·98, 16·59, 6·19, 109° 48′. $C_6H_7(OH)_5$ quercitol[91]: M(2)C_2^2; 6·83, 8·53, 6·45, 110° 57′. $C_6H_6(OH)_5OMe$ quebrachitol[91,93]: M(2)C_2^2; 6·60, 7·15, 8·65, 90°. $C_6H_{10}Br_2$ 1.4 dibromocyclohexane[92]: M(2)C_{2h}^5; 11·92, 5·56, 6·02, 101° 49′. $C_6H_{10}I_2$ 1.4[92]: M(2)C_{2h}^5; 12·50, 5·72, 6·20, 98°. $C_6H_{10}(OH)_2$ quinitols: α-1.2[94]: O(8)V_h^{15}; 7·62, 8·55, 19·57. γ-1.2[94]: M(8)C_{2h}^6; 19·13, 9·92, 7·23, 103°54′. β-1.4[94,95]: M(6)C_{2h}^5; 6·32, 21·2, 7·27, 96°. $C_6H_{10}(COOMe)_2$ β-1.4 cyclohexane diacetate[94]: M(2)C_{2h}^5; 13·56, 5·83, 6·72, 107° 24′.

SECTION 14B.—HETEROCYCLIC RINGS. (Ring atoms underlined) |–CH(COOH)OCH(COOH)–| maleic acid oxide (cis-ethylene oxide dicarboxylic acid)[1]: M(8)C_{2h}^6; 21·5, 6·9, 6·9, 91° 10′. |–CHCOOCOCH–| maleic anhydride[45]: O(4); 6·58, 11·43, 5·90. |–CH(OH)COOCOCH(OH–| tartaric anhydride[45]: O(2); 6·32, 9·70, 4·83. $C_6H_4(CO_2)_2O$ phthalic anhydride[45]: O(4); 7·74, 13·66, 5·86. |–(CH)$_4$S–| thiophene[97]: T(4); 7·23, 9·54. $(CH_2)_6N_4$ hexamethylene tetramine[1]: C(2-O81)T_d^3; 7·02. $C_3N_3(N_3)_3$ cyanuric triazide[98]: H(2); 5·94, 4·06 |–CEt$_2$(CONH)$_2$CO–| veronal[99]: O(4)V_h^{17}; 7·11, 14·4, 9·7. $C_{16}H_{10}O_2N_2$ indigo[1,45]: M(2)C_{2h}^5 ?; 11·00, 5·8, 10·1, 107° 30′.

Sugars and Derivatives. (Ring atoms underlined.) *Aldo-pentoses:* |–(CHOH)$_4$CH$_2$O–| βl-arabinose[102,103]: O(4)V^4; 6·51, 19·43, 4·85. α- and d-xylose[102,103]: O(4)V^4; 12·64, 9·20, 5·62. *Aldo-hexoses:* |–(CHOH)$_4$CH(CH$_2$OH)O–| d-glucose[101,103]: O(4)V^4; 10·40, 14·89, 4·99. d-mannose[39,40,103]: O(4)V^4; 7·62, 18·18, 5·67. *Keto-hexoses.* |–COH CH$_2$OH)(CHOH)$_3$CH$_2$O–| d-fructose[101,103]: O(4)V^4; 8·06, 10·06, 9·12. sorbose[103]: O(4)V^4; 6·12, 18·24, 6·43. *Methyl aldo-pentose* |–(CHOH)$_4$CHMeO–| Aq d-rhamnose hydrate[102,103]: M(2)C_2^2; 7·96, 7·95, 6·71. *Methyl xylosides.* |–CHOMe(CHOH$_3$CH$_2$O–| α-compound[102]: M(2); 11·28, 6·72, 11·02, 112° 12′. β-compound[105]: M(2)C_2^2; 7·82, 6·89, 7·74, 113° 10′. *Methyl glucoside* |–CHOMe(CHOH)$_3$CH(CH$_2$OH)O–| α-compound[45]: O(4); 10·80, 14·60, 5·61. *Methyl mannosides:* α-compound[104] (formula as α-methyl glucoside): O(4)V^4; 9·38, 9·99, 9·23. β-compound[104]

TABLE XXV—*continued.*

$|\text{-CHOMe(CHOH)}_2\text{CH(CHOHCH}_2\text{OH)O-}|$: O(4)V[4]; 15·87, 11·73, 4·64. *Lactone:* γ-d mannonolactone[106] $|\text{-CO(CHOH)}_2\text{CH(CHOHCH}_2\text{OH)O-}|$: O(4); 14·0, 11·1, 4·73. *Polymethyl d rivatives of lacton.s:* $|\text{-CO(CHOMe)}_2\text{CH(CHOMeCH}_2\text{OMe)O-}|$ 2.3 5.6 tetramethyl γd-mannonolactone[106]: M(2); 9·79, 13·8, 4·50, 93° 18′. $|\text{-CO(CHOMe)}_2\text{CH(CHMeOMe)O-}|$ 2.3 5 trimethyl γl-rhamnolactone[106]: O(4); 12·2,18·3, 4·65. $|\text{-CO(CHOMe)}_3\text{CH}_2\text{O-}|$ 2.3.4 trimethyl δl-arabonolactone[106]: O(4); 10·8, 12·2, 7·30. *Substituted derivatives of hexose-pyranos s* · $|\text{-CHOH(CHOMe)}_3\text{CH}_2\text{O}|$ 2.3 4 trimethyl αd-xylopyranose[106]: M(2); 8·68, 8·31, 6·65, 91°. $|\text{-COH(CH}_2\text{OMe)(CHOMe)}_3\text{CH}_2\text{O-}|$ 1.3.4.5 tetramethyl βd-fructopyranose: O(4); 9·22, 8·97, 14·8. 1.3.4 5 tetracetyl βd-fructopyranose (OMe replaces Me in last formula)[106]. M(2); 10·7, 7·98, 17·0, 144° 30′.

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CHAPTER VII

THE CRYSTAL STRUCTURE OF COLLOIDS AND AMORPHOUS SUBSTANCES

15. Amorphous, Disperse and Mesomorphic Phases

(A) **Amorphous Substances.** The units composing a strictly amorphous body would be quite irregularly distributed, and might be expected to give no indication of structure using the X-ray method. It is actually found, however, that many amorphous substances give evidence of some attempt towards structure in the shape of one or more broad diffuse bands, such as are obtained using pure unstretched rubber. von Weimarn[1a] found that *barium sulphate* particles precipitated from dilute solution were actually crystalline, and gave the diffraction lines of the material in bulk, and thus found support for his view that the truly amorphous state is not existent in nature.

Debye and Scherrer[1b] believed that *amorphous carbon* consisted of minute particles of graphite. Some evidence, however, has been obtained for the view that amorphous carbon is really a third form of the element, giving a single diffuse band[2] (see also this vol. : 3Bf). It was found that by heating at 1,100°C. the graphite lines were gradually developed, indicating a hastening of the change from the amorphous to the crystalline state with rise of temperature. The work seems to suggest a more or less continuous change between the two conditions. X-rays may thus be used to detect the " ageing " of gels as the development of crystalline aggregates proceeds. *Soot* has been found by Ponte[26] and Trendelenberg[27] to consist of small graphite crystals.

In accordance with the view that amorphous substances may be generally regarded as built up of crystallites, it is found

using X-rays that *vitreous silica* consists of small crystals of cristobalite.[3] The same is also true of *silica gel.*[4] According to Zachariasen,[5] *glass* contains small three-dimensional networks, arranged without periodicity or symmetry. Warren[6] finds broad X-ray diffraction rings for *vitreous silica* and *pyrex glass*, leading to spacings of 4·32 and 4·26 Å.U. respectively. The results are attributed to scattering from a non-crystalline random network.

The examination of " *explosive* " *antimony* by X-rays reveals an amorphous structure.[7] On the other hand, " *plastic* " *sulphur* is not amorphous :[8] it has an identity period of 9·35, which corresponds to none of the cell dimensions of rhombic sulphur (see this vol. : 3C), and therefore the unit appears to have an individual structure, which passes into that of rhombic sulphur in a few days. Freshly precipitated hydrous *titanium dioxide* gives no indication of hydroxide formation :[9] the X-ray lines are essentially those of anatase together with absorbed water.

The X-ray work has led to the recognition of a group of substances built up of crystallites arranged according to a definite plan, such that some chief crystallographic direction corresponds to an important direction in the structure. Such substances may be generally included under the title of " fibre-structures." *Cellulose* is an outstanding example, where the crystallites are orientated so that one of the edges of the unit cell lies parallel to the axis of the fibre, which is also the direction of most rapid growth. Other examples are provided by *silk*, *chitin*, *muscle* and *hair*, as well as *pearl* and certain *electrolytic precipitates*. The X-ray method provides a means of distinguishing between natural and artificial pearls,[10] since natural pearls give photographs corresponding to the ordinary powder diagram, whilst artificial Japanese pearls, grown on a nucleus of mother-of-pearl (nacre), give also the diffuse spots caused by this nuclear material. The effect in case of substances precipitated in electrolysis is greatly influenced by the conditions of experiment, but it has been found that in certain circumstances *copper crystals* may be deposited from acid copper sulphate solution in such a way that their (011) axes

stand perpendicular to the plane of the cathode.[11] Similar results have been observed in connection with the deposition of *silver*. Fibre-structures are described in Section 17.

(B) **Colloidal Solutions.** Scherrer, by an X-ray examination of *colloidal gold*, found that the particles were composed of minute crystals, having the same face-centred structure as ordinary gold. As particles become smaller in diameter than 10^{-6} cm., the X-ray diffraction rings become more diffuse and resemble those obtained with amorphous substances. Debye and Scherrer deduced a relationship between size of particle and width of diffraction band, from which the conclusion was drawn that some particles in a purple solution of colloidal gold had a diameter of 18·6 Å.U., that is, about 4·5 times the assigned edge of the lattice unit (4·07). Particles of *colloidal silver* also give evidence of crystalline structure. The coagulation of colloidal gold has been studied by Scherrer and Staub using X-rays.[12]

It has been found that X-rays may exert direct influences upon colloidal solutions. Galecki[13] observed that *gold sols* irradiated with X-rays became partly coagulated, with a corresponding slight colour change. A similar result was obtained by Fernau[14] with *sols of cerium hydroxide* and *albumen*. Further investigation by Crowther and Fairbrother[15] revealed a difference in behaviour between "*positive*" *sols of iron* and *copper* on the one hand, and "*negative*" *sols of silver* and *gold* on the other, the former giving coagulation and the latter stabilization (further dispersion) under irradiation. The effect was attributed to ionization in the double layer surrounding a colloidal particle. Bhatnagar and co-workers[16] investigated the movement of particles in an electric field, and found that, except in the case of partly-dialyzed *sols of iron* and *copper hydroxides*, there was no marked change in the velocity of cataphoresis before and after exposure to X-rays. It was therefore supposed that X-rays act on the sol particles through intermediate action on the electrolytes of the undialyzed sol. X-rays also stimulate nuclei formation of S and P in CS_2.[56]

(C) **Mesomorphic States.** Intermediate between the crystalline and liquid states stands the group of "mesomorphic"

substances, of which Friedel[17] has recognized two classes, the "smectic" and "nematic." The *smectic*, or *soap-like substances*, have units which are ordered in direction, and possess layers with constant separating distance. Such substances are illustrated by the organic chain crystals investigated by Müller and others (see Chapter VI) and by *ethyl p-azoxybenzoate* between 114° and 120°C. In the *nematic*, or *thread-like substances*, the only remaining trace of order is the parallel orientation of the molecules, and to this group belong Lehmann's "liquid crystals," examples of which are provided by *p-azoxyanisole* between 116° and 133°C. and *p-azoxyphenetole* between 135° and 165°C. The transition from crystalline to liquid state through the smectic and nematic mesophases is aided by increase of temperature with definite transition points, and, in solution, by increasing dilution, though both intermediate states may not appear. In McBain's[18,19] study of soaps, the crystalline, smectic and nematic states are represented by his curds, "neat" soaps and "middle" soaps respectively.

In the case of smectic substances, de Broglie and Friedel[17] obtained reflections from planes giving lengths in agreement with molecular lengths deduced from the individual atomic contributions. It thus appeared that the molecules in question were set at right angles to the reflecting planes. Hermann,[28] however, found that the molecules of *thallium oleate* and *stearate* were sloping at 53° and 47° respectively. In these cases, the angle of slope increased from the solid to the smectic phase, in opposition to the usual finding that the molecules tend to become more upright between solid and mesophase. The often curious unspherical forms of droplets of smectic substances observed by Lehmann was studied by Oseen,[30] who found that cylindrical drops with imperfectly plane ends were mathematically possible.

In the true nematic state, there is no sign of parallel plane structure, and the state is described in optical language as "positively uniaxial." The nematic state may, however, merge continuously into another known as "cholesteric," where a twisted structure associated with optical activity and

brilliant coloration appears, the effect being negatively uniaxial, as with *cholesteryl cinnamate* between 156° and 197°C. Thus the aqueous mesophase of *salvarsan* is nematic, but becomes cholesteric on addition of sucrose or dextrose. In the nematic and smectic states, differences of surface tension are found to be responsible for the orientation of the units to the bounding surface.[20] The effect of the surface is demonstrated by showing that *p*-azoxyanisole sets itself perpendicular to a glass surface which has been treated with acid, and parallel to a similar surface treated with alkali. A new type of sol, called " tactosol " by Zocher and Jacobsohn,[21] has been described in which non-spherical particles tend to set themselves spontaneously in parallel order as in a mesophase. Examples are provided by *vanadium pentoxide, ferric oxide, benzopurpurin* and *chrysophenin*. Various effects of applied magnetic and electric fields are described.

It appears that cholesteric substances always contain at least one asymmetric C atom.[29] Oseen[30] has provided mathematical treatment, and finds that the forces acting between molecules are partly magnetic.

The mesomorphic phases represent the primary attempts of a liquid to produce a crystal lattice. Rinne[22] supposes that the swarms of colloidal crystallites attach themselves to a growing nucleus in crystal formation. It may be noted that these phases constitute more or less discontinuous transition stages between crystal and liquid, in contrast to the continuous transition between colloidal or amorphous solids and crystals. The classification of mesomorphic states is summarized by G. and E. Friedel,[23] Ostwald[24] and W. H. Bragg.[25]

(D) **Liquid Crystals.** It may first be noted that for a given substance more than two mesophases may exist. Vorländer[31] and K. Hermann and Krummacher[32] have described cases where as many as four intermediate phases occur, each with its own definite temperature region. According to C. Hermann,[33] who has studied this question from the standpoint of space-groups, as many as 18 intermediate types are possible for mesophases.

Lehmann's liquid crystals were early studied by van der Lingen,[34,35] with a view to deciding between the view of Vorländer, who at first supposed them to have true crystalline structure, and that of Bose, who considered them to consist of " swarms " of similarly orientated molecules. The result was in favour of Bose's theory, no sign of a space lattice being found when the crystals were examined by the Laue method in a strong magnetic field. More recently, Vorländer[36] has expounded the view that the secret of the liquid crystal may lie in a " mixed-dimensional " configuration, and has been at considerable trouble to explain exactly what is intended.[37] In the case of a long molecule, the chief line is one-dimensional; this may be combined with a second dimension, for example, in the width of a benzene ring in p-substituted derivatives.

In electric and magnetic fields, an orienting effect is observed upon the long molecules of a liquid crystal. The nematic phases having similar molecular ends (*e.g.*, p-azoxyanisole) tend to set themselves with their long axes perpendicular to the lines of force in electric fields, whilst molecules with dissimilar ends tend to have their long axes parallel to the lines of force.[38] The effect of a magnetic field was studied by Mauguin[39] by optical methods, and by Kast[40] using X-rays. The orientation of molecules of *p-azoxyanisole* became established. Kast found that the amorphous X-ray ring characteristic of the substance as found by Hückel[42] broke up into two parts in a magnetic field. Further observation[41] has shown that the ring splits into two half-moon " sickles " without change in diameter, which by Bragg's equation corresponds to a dimension measuring the thickness of the molecule. Stewart[43] directed X-rays through the substance at right angles to a magnetic field, and believed he had obtained evidence of " cybotactic " groups similar to, but larger than, those postulated in the case of liquids[43] (see Section 16). It appears difficult, however, to accept the unmodified conclusion that increase in the sizes of groups from liquid to liquid crystal could give rise to discontinuity, as observed, at a fixed transition temperature. Buchwald[44] has examined the parallel arrangement of elongated molecules in liquid crystals and their orientation in magnetic fields mathe-

natically. His results appear to favour the views of Kast (see below) rather than those of Stewart.

The "swarm" theory of liquid crystals has been largely developed by Ornstein,[45,46] Kast,[47,48] and Fréedericksz and Zolina.[49] According to this view, liquid crystals consist of aggregates of sub-microscopic homogeneous ranges or 'swarms," in which the molecules lie parallel. About 10^6 molecules go to form a swarm. The swarms are orientated quite irregularly with their long axes at random. There is a permanent dipole moment in the axis direction; the nematic molecules in a swarm lie so that their anisotropy is magnified. In opposition to Stewart's view of the cybotactic state of a liquid, the molecules are thought to be arranged so that within groups the anisotropy largely cancels, so that a liquid contains isotropic swarms. The effect at surfaces and of electric and magnetic fields is upon the swarms, causing them to align themselves with the field. The theory seems reminiscent of that of the Weiss domains in ferromagnetic materials (see Vol. I: 28); indeed, Foëx[50] has shown certain analogies between nematic and ferromagnetic bodies. The swarm theory, however, is not quite alone in the field: an alternative exists in the 'distortion" theory,[51] according to which the whole substance of a nematic body tends to take up a position such that the axial direction is the same at every point, an applied field disturbing the direction, which changes continuously until an elastic force holds the applied force in equilibrium.

According to the view of Malkin,[52] the molecules in liquid crystals are rotating, as presumed in the case of the A forms of the esters of normal fatty acids (see this vol.: end of Section 13).

The space-groups and cell dimensions of the solid forms of several substances capable of forming liquid crystals have been determined. The results are as follows: (1) $(MeOC_6H_4N:)_2:O$ *p-azoxyanisole* (stable yellow form):[53,54] $M(8)C_{2h}^4$; 16·0, 8·08, 20·5, 104° 30′. (2) $(EtOC_6H_4N:)_2:O$ *p-azoxyphenetole*[53]: $M(4)C_s^4$; 15·4, 5·41, 17·6, 94°. (3) $(MeOC_6H_4CH:N)_2C_{10}H_6$ *anisal* 1·5 *diaminonaphthalene* (stable form)[53]: $M(4)C_{2h}^5$; 21·7, 12·7, 7·7, 119° 30′. (4) $C_{26}H_{43}Cl$ *cholesteryl chloride*[53]: $M(2)C_2^2$; 10·3, 7·0, 21·2, 131°. (5) $C_{26}H_{43}Br$ *cholesteryl bromide*[53]:

(2)C_2^2; 10·7, 7·45, 21·4, 132°. (6) $MeOC_6H_4CNC_6H_4C$: :OOEt *ethyl anisal p-aminocinnamate*[53]: M(4)C_{2h}^5; 6·65, 38, 45·6, 135° 35′.

For further information about liquid crystals, reference may made to the General Discussion inaugurated by the Faraday ›ciety on: "Liquid Crystals and Anisotropic Melts."[55]

16. The Liquid State

(A) **Water and Aqueous Solutions.** Ostwald[57] suggested 1913 that a liquid might have some periodically variable ructure. In 1916, Debye and Scherrer made the first investi- .tion of liquids using X-rays, and discovered the formation of ffraction rings similar to those found for amorphous sub- ances. Interest centres in the intensity-angle curves, the axima of which correspond to the centres of diffraction ınds.

The Debye-Scherrer method was applied to *water* HOH by eyer,[58] who found four maxima, yielding, by Bragg's equation, e following spacings: 3·14, 2·13, 1·35, 0·89. Whilst no ıtirely satisfactory explanation of this result has been found, is possible that the first spacing may be due to diffraction by ıgle molecules, and the second to groups of molecules having mporary existence, for which the name "cybotactic" has ›en coined by Stewart. The investigation of *deuterium oxide*, OD,[59] has yielded similar diffraction maxima with somewhat arper peaks. Good[60] has reviewed the work on water, and ›ncludes that about 15% is in transitory association in the rm of rudimentary ice crystals, which Fowler and Bernal[61] ggest may be quartz-like, ice being like tridymite (C10 type: is vol.: 5Aj). The cybotactic groups may contain perhaps a w hundred molecules.[62] Water containing quartz-like groups found to reproduce the intensity distribution curve most ›arly.[61]

Krishnamurti[63] finds that concentrated *aqueous solutions of nmonium nitrate and acetamide* develop an inner ring, which ›ntracts on dilution, the outer ring expanding and merging ith that of water. Further work on *aqueous solutions of*

starch, tannic acid and *gum arabic*[64] yielded molecular weights of 6,200, 3,134 and 2,810 respectively. Meyer[58] has studied solutions of *lithium and sodium chlorides* and of *sugar* at different temperatures and concentrations. It is found that with increasing temperature and increasing concentration of dissolved substance, the maxima change in position in the same sense.

(B) **Other Inorganic Liquids.** *Liquid sulphur* has been studied from 130° to 260°.[65] The results are interpreted as due to unstable associations of S atoms, the groupings being less pronounced as the temperature rises. There is an abrupt change in the X-ray pattern at 220°, corresponding to the transition from $S\lambda$ to $S\mu$. *Mercury* has been investigated by Debye and Menke,[66,67] who found it to be quasi-crystalline. Kratky[68] examined the results, and found that an hexagonal close-packing of Hg atoms appeared to fit them best. Similar results have been obtained using *liquid gallium* (M.P. 30·1°C.).[67]

(C) **Organic Liquids.** Hewlett[69] in 1922 obtained three maxima in the diffraction-angle curves of *benzene, mesitylene* and *octane*, suggesting the existence of structure in these liquids. Later, Katz and Selman[70] examined numerous liquids, and calculated the distance between neighbouring diffracting centres from the X-ray ring dimensions, using a formula due to Ehrenfest, applicable to scattering by gaseous diatomic molecules. Keesom used the relation : $d' = d/0{\cdot}814$, where d is given by $\lambda = 2d\sin\theta$, the angle of scattering being 2θ. Katz found d' nearly constant (about 5·5) for a number of liquids, and suggested that parallel layers of molecules were present in small groups. The Ehrenfest relation, however, is not strictly applicable to liquids.[65]

Stewart and collaborators[71] have made extensive investigations of organic liquids, in support of the cybotactic theory of the liquid state. *Normal liquid paraffins* (C_5H_{12} to $C_{15}H_{32}$) gave a single maximum on the intensity-angle curve, corresponding to the same Bragg spacing 4·63, which was interpreted as the separation of the molecules (in parallel " square " arrangement within cybotactic groups) in the direction normal to their

lengths. If the volume of one molecule is $(4{\cdot}63)^2$ times the chain length (obtainable from Müller and Saville's results on the solid hydrocarbons), the density is deduced by dividing the molecular weight (multiplied by the mass of an atom of hydrogen) by this volume. Agreement was found to within 2% with experiment. *Normal monobasic fatty acids*, $C_nH_{2n+1}COOH$ (n = 0 to 10) and *normal alcohols*, $C_nH_{2n+1}OH$ (n = 1 to 11), gave two maxima. In the alcohol series, one maximum was fixed (methyl and ethyl alcohols excepted), and corresponded to a Bragg distance of 4·58, attributed to the lateral separation of the molecules in cybotactic groups lying in parallel collinear chains. The other maximum varied from member to member in the series, and corresponded to the chain length, which increased by 1·54 per CH_2 group, in agreement with the results of Müller and Saville (see this vol.: 13F) on solid long-chain hydrocarbons. Density computations led to the conclusion that the OH groups of two molecules are in contact. The cross-sectional area $(4{\cdot}58)^2$ agreed satisfactorily with Adam's measurements (Vol. 1: 33Cc). The fatty acids gave similar results, the lateral spacing when more than five C atoms are present being 4·55, and the longitudinal spacing giving an increase of 1·00 per CH_2 added. Judged by density considerations, the chains are not normal to the basal planes, and the molecules associate in pairs with COOH groups in contact. The *isomers of primary normal alcohols* were examined and found to lead to characteristic X-ray spacings. Attachment of CH_2 to the side of a chain increased the diameter by 0·6, and of OH by 0·4, whilst attachment of both CH_2 and OH gave an increase of 0·65, so that the effect was not additive.

Summaries of Stewart's work and theory, [72,73,74] have appeared. The molecular semi-orderly state called "cybotaxis" is held to correspond to myriads of small groups, a liquid behaving as if composed of tiny imperfect crystals of the substance, although the groups are not permanent.

X-ray diffraction studies on liquids in the neighbourhood of the critical point, in the cases of *ethyl ether*[75] and *isopentane*,[76] reveal the disappearance of cybotactic groups at specific volumes greater than the critical specific volume. Further

work on the effect of temperature on the X-ray diffraction by liquids has shown shifting of maxima in the curves, indicating that in some cases rearrangement may occur within the groups with changes of temperature.[77]

In the Indian school, Banerjee[78] has followed up earlier work by Raman and Ramanathan,[81] and has found that some of the diffraction lines of a solid substance may be preserved in the liquid, whilst others are quenched. A liquid is therefore regarded as the result of degeneration of the crystal lattice set up by thermal agitation.

Trillat[79] has largely confirmed the results of Katz and Stewart, and has also studied the orientation of molecules of liquid at various interfaces. The orientation decreases with distance from the surface.[80]

According to the theory developed by Raman and Ramanathan,[81] a mixture of liquids should give the superimposed X-ray diffraction spectra of the components, whilst Stewart's theory requires a single peak for mixtures, changing in position with proportions of the components. The experimental evidence obtained by Meyer[82] and Parthasarathy[83] is in favour of the view of Stewart. On the other hand, Stewart's theory has been criticized by Müller,[84] who regards the case for it as " not proven."

A number of investigators have turned their attention to the X-ray diffraction of cyclic liquids. Stewart[85] finds that *benzene* and *cyclohexane* rings are flat, of thicknesses 4·70 and 5·10 respectively. The general shape of the ring is unaltered by substitution, but its thickness depends on the positions of substituents, and is apparently least for para-derivatives. Tanaka and Tsuji[86] find that benzene gives two maxima, corresponding to the diameter 4·76 and thickness 3·12, whilst cyclohexane gives one maximum, and is concluded to be " spherical." Ward[87] has reported spacings of 4·68 and 5·09 for benzene and cyclohexane respectively, in agreement with the work of Stewart. Mixtures of the two liquids give two independent peaks, indicating emulsion-type solutions. Krishnamurti[88] has investigated a number of aromatic hydrocarbons using X-rays, and has found that, in general, ortho- and

meta-substituted benzene rings give two interference rings, whilst the para-compounds give only one broad ring. Comparison of the diffraction pattern of *hexamethylbenzene*[89] in the powdered state, as studied by Mrs. Lonsdale, with that in the liquid state indicates an increase in spacings from 3·7 to 4·2, and from 7·7 to 8·2. According to Ishino, Tanaka and Tsuji,[90] who have examined various cyclic and acyclic compounds, cylindrical or disc-shaped molecules give two X-ray maxima, whilst open chain compounds give a single sharp maximum, whose size is practically independent of the number of carbon atoms in the chain.

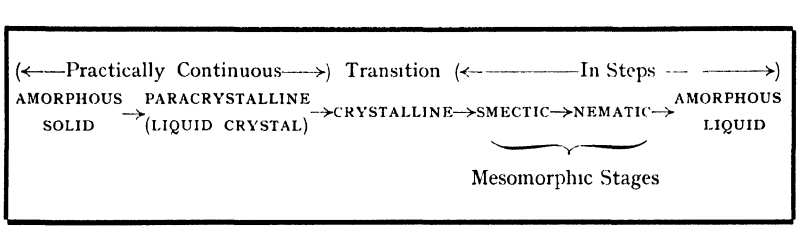
It appears that the X-ray diffraction patterns of *alcohols absorbed on charcoal* do not agree with the superposition of rings due to the pure components.[91] *Carbon bisulphide on charcoal*, however, gives the result expected from superposition.

Dilute non-aqueous solutions are found to give a single ring.[92] A study of concentrated solutions of *lithium chloride* in *ethyl, propyl and butyl alcohols* suggests that lithium and chlorine ions join with solvent molecules in forming the cybotactic unitary structure of the solutions.[93]

Zernicke and Prins[94] have expressed the X-ray scattering by a liquid as a function of angle and the space distribution of molecules, and have endeavoured to ascertain the distribution from the intensity measurements. Warren[95] has applied the method to long-chain liquids.

Further information is given in a summary by Drucker.[96] The X-ray scattering by gases is treated elsewhere (Vol. 3 : 37C).

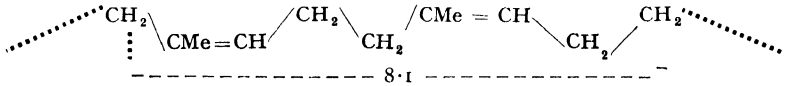
The various types of substances here discussed may be related as in the following scheme :—



17. Fibre Structures

(A) **Rubber and Related Substances.** When X-rays are diffracted by a mosaic of crystals in a random distribution, a complete diffuse ring may be obtained ; when crystal planes are present, spots appear on the circumference of the ring. The method of analysis applicable in such cases has been discussed by Schmid.[97]

Rubber, $(C_5H_8)_n$, provides an example of a substance giving both the above kinds of patterns. Katz[98] found that whilst ordinary rubber gives an amorphous ring, diffraction spots appear on stretching, the spots becoming more distinct as the tension is increased, by a reversible change. It appears that in ordinary rubber the extended isoprene chains are arranged at random, whilst stretching pulls them out into parallel fibres, for which Katz found a periodic spacing of 9·0, and Mark and co-workers[99] of 8·1. The chain structure may be—

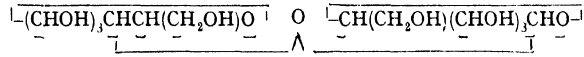


Mark and Susich[99] found an orthorhombic unit cell containing eight molecules, perhaps of space-group V^4, of dimensions 12·3, 8·3, 8·1. Pummerer and Koch[100] isolated crystals from rubber, which Gross found to be monoclinic, with one molecule per unit cell. Other workers have failed to obtain crystals by the method described. Ott[101] found crepe rubber practically completely crystallized, the unit being $(C_5H_8)_6$. Stretched and unstretched rubber have been examined by electron diffraction.[102] *Balata* and *gutta-percha*[103] give diagrams like those of rubber. Meyer and Mark[104] have suggested that the vulcanization of rubber is connected with the formation of sulphur bridge-chains between the isoprene chains.

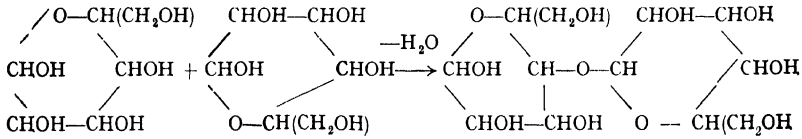
The transitory state of stretched rubber and gutta-percha has been termed " paracrystalline." For intermediate extensions, it is believed that clusters are formed, which may contain 2,000 molecules. Even in the unstretched state, ill-defined crystals may be present : it is noteworthy that if the amplitude of

vibration of crystal units is sufficiently large, X-ray interferences are not obtained. Thus, *benzophenone* gives no interferences at about 3° below its melting-point, although the solid maintains its defined crystal faces.

(B) **Cellulose and Related Cases.** As a result of investigations carried out by Haworth and others, it is found that residues of glucose rings are present in *cellulose*. The glucose molecule has a pyranose ring, and may be represented by —(CHOH)$_4$CH(CH$_2$OH)O—, where the underlined atoms are in the six-membered ring. From this, *cellobiose* may be derived by removal of a molecule of water from two molecules of glucose :—



or $C_6H_{11}O_5$—O—$C_6H_{11}O_5$. The relation between glucose and cellobiose may be depicted as follows :—

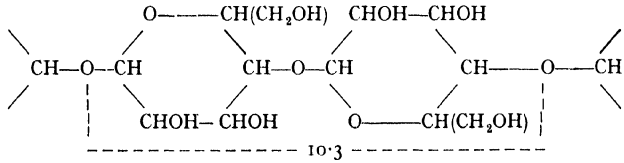


$$2C_6H_{12}O_6 \quad - H_2O \longrightarrow \quad C_{12}H_{22}O_{11}$$

The structure of cellulose is then

. . .—O—$C_6H_{10}O_4$—O—$C_6H_{10}O_4$—O—$C_6H_{10}O_4$— . . .

in an extended chain, and may be obtained by repetition of $(C_6H_{10}O_5)_2$, as follows :—



from which the relation to cellobiose is easily seen.

The cell dimensions of cellobiose using X-rays were determined by Hengstenberg and Mark,[105] (in the notation already specified), as follows: M(2)C_2^2; 5·00, 13·2, 11·1. The early X-ray investigations on cellulose have been conveniently sum-

marized,[1] so that only the more salient results will be noted here. Meyer and Mark[106] found the unit cell to be approximately orthorhombic, its dimensions, containing four molecules, being 8·7, 10·30, 7·85. The *b* axis of length 10·3 shows the periodicity of the fibre chain. More recent results concerning this unit cell, summarized by W. H. Bragg,[107] show it as slightly monoclinic, with the dimensions: 8·35, 10·3, 7·9, 84°. It may be noted that Hess and Trogus[108] have adduced arguments against the cellobiose structure of cellulose, on the ground that its derivatives sometimes give periodic repetition units which are *odd* multiples of $\frac{1}{2} \times 10{\cdot}3$. Yoshida and Matsumoto[112] found a tetragonal cell: T(4); 7·79, 10·26.

The fibre structure of cellulose resembles that of the inorganic silicate *asbestos*, a variety of which, *anthophyllite*, has been found to have a period of 5·27. Cellulose is pictured as containing micelles, which may consist of bundles of parallel chains of variable sizes and lengths. There is therefore little justification for assigning the molecular formula $C_{24}H_{40}O_{20}$, on the ground that the unit cell contains $4C_6H_{10}O_5$. The substance forms a "one-dimensional" lattice, and the cellulose "molecule" consists of a long chain of glucose residues which passes continuously through a series of unit cells. In *ramie* fibre, the chains are arranged parallel to the fibre axis; in *cotton*, there appears to be a screw-like structure of the chains. The micelles may be partly tangled with each other at the bounding surfaces.[130]

The "mercerization" of cotton and cloth, carried out by treatment with concentrated sodium hydroxide solutions, produces a characteristic translucence and dimensional change of the fibres. The change is partly one of hydration, the mercerized product being sometimes called "hydrocellulose." Mark has recently adduced evidence that the water present is chemically combined. Andress[110] found that the characteristic fibre period of 10·3 was present in mercerized cellulose, and concluded that the process altered the relative disposition of the units in the cellulose chain without affecting their absolute dimensions. *He assigned the unit cell: $M(4)C_2^2$; 8·14, 10·30,

*After the sodium hydroxide is washed out, a denser material than before is formed: probably a twisting of the fibres enables closer packing to take place.

9·14, 62°. Burgeni and Kratky[111] reported similar results a little later. Another form, B-cellulose, in the swollen state has an amorphous structure: when dried, it showed the X-ray diagram of ordinary cellulose.[113] Schramek[114] has investigated the possibilities of determining the proportions of native and mercerized cellulose in fibres by means of X-rays.

Cellulose differs from rubber and resembles silk in that its fibres are already fully extended; hence the substance is only slightly extensible, by adjacent fibres slipping over one another in an irreversible change. The " artificial silk " prepared from cellulose hence resembles natural silk. The mechanical strength of hemp and ramie fibres is superior to that of many metallic wires.[116]

It often happens that chemical reagents tend to attack the sides of the cellulose chains, without affecting the characteristic period, as in mercerization. Compounds of cellulose with amines also show a characteristic period which is always about 10·3.[115]

A number of researches have been devoted to *the nitrocelluloses*, which have considerable industrial and theoretical importance. Miles and Craik[117] divided them into three classes, according to the nitrogen content, an increase of which is associated with increased swelling capacity and solubility in acetone. Mathieu[118] took X-ray photographs of films obtained by evaporation of acetone solutions, and found that the solvent acts first as a swelling, then as a dispersing agent: the degree of dispersion increased with the solubility of the nitrated cotton. Trillat[119] also worked on dried and partially dried films, and found evidence of an addition compound with the solvent, formed reversibly and disappearing on complete drying. The formation of compounds of " dissociable hydrate " type was suggested earlier by Trogus, Hess and Katz.[120] Nitrated cotton containing 12·95% N corresponds very approximately to *trinitrocellulose*, in which the hydroxyl groups of the glucose residues have been completely replaced by nitrate groups; specimens containing lower proportions of nitrogen are only partially nitrated. Trillat[121] concludes that in the latter cases some chains of a micelle are completely nitrated, and others are

unaffected, whilst Mathieu[118] advocates a random distribution of nitrate groups down the sides of the glucose chain residues. The latter view is perhaps more probable, since it offers certain analogies with the action of steam on the proteins of wool and hair.

Trogus and Hess[122] found the fibre periodicity of trinitrocellulose to be $25{\cdot}48 \pm 0{\cdot}14$.

Colloidal gels of *nitrocellulose* and *acetylcellulose* are found to behave somewhat as rubber on stretching, but the changes are irreversible. The final state is pseudo-crystalline.[123] Two forms of acetylcellulose have been described, derived respectively from cellulose and hydrocellulose.[124] There is a reversible change between them. The stretching of films of these two substances is accompanied by loss of rotation possibilities of the crystallites.[166]

The gradual addition of camphor to cellulose, forming celluloid, is reported to destroy the orientation of micelles, setting up an isotropic arrangement.[125] The internal X-ray halo of nitrocellulose disappears when 15% of camphor is added. Further work has been carried out by Katz and collaborators[126] and by Jones.[127]

Trimethylcellulose[128] and *higher triacid fatty esters*[129] have been examined by X-rays. Trimethylcellulose gives the characteristic spacing of 10·3, whilst in all cases the aliphatic ester chains lie parallel with each other and perpendicular to the plane of the glucose residue rings.

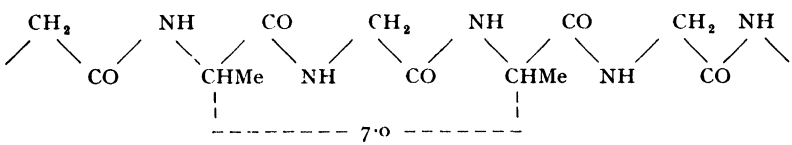
Chitin,[131] which occurs in the external skeletons of insects, has a cellulose structure, with one OH — in each ring replaced by CH_3CONH-. The fibre period is 10·4. Herzog and Gonell[132] have examined *egg-shell*, the *spines of the star-fish and sea urchin*, and other biological structures. Ott[133] has investigated *lichenin*, *starch*, *inulin*, and the *amyloses*. Stillwell[134] has made an X-ray study of the structure of *wood fibre* walls. *Sisal fibres*[135] give the cellulose X-ray pattern; the stretched fibres behave like stretched cotton. The cellulose crystals appear to be more perfectly arranged in more compact woods, as in *oak*.[135] *Coir*[135] gives two cellulose patterns at right angles, suggesting a "natural fabric" structure. Somewhat similar results have

been obtained with the wall of the green alga *valonia ventricosa*,[136] where two patterns crossed at an angle rather less than 90° are observed.

The earlier work on X-rays and fibrous substances was summarized by Polanyi.[137] Adam[138] has described the work done on surface films of cellulose derivatives, whilst Hess[139] has provided a comprehensive review of the X-ray analysis of cellulose structures up to 1930. Further information is given in the Faraday Society General Discussion on the Colloid Aspects of Textile Materials (*Transactions*, 1933).

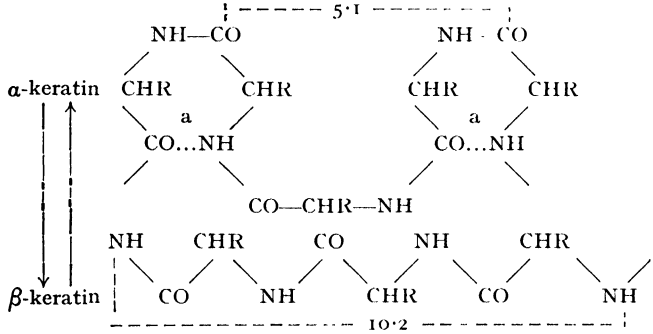
(C) **Proteins.** The early work of Emil Fischer showed that proteins were derived from amino-acids, long chains containing the peptide group —CONH— being formed by numerous condensations (with elimination of water) between the carboxyl group of one amino-acid and the amino group of another. The simplest amino-acid is *glycine*, $CH_2(NH_2)COOH$; more complex cases are derived by introducing various groups R into glycine, with the general formula $RCH(NH_2)COOH$, or RA, where A denotes the amino-acid residue $—CH(NH_2)COOH$. Other amino-acids are : *alanine*, MeA ; *leucine*, $MeCHMeCH_2A$; *arginine*, $NH : C(NH_2)NHCH_2CH_2CH_2A$; *aspartic acid*, $COOHCH_2A$; *glutamic acid*, $COOHCH_2CH_2A$; and *cystine*, ACH_2SSCH_2A.

Natural silk is formed from the protein *fibroin*, which is built up from the two simplest amino-acids glycine and alanine. The first successful interpretation of the X-ray data on silk was made by Meyer and Mark,[140] who suggested that fibroin consisted of crystallites containing bundles of long molecular chains, somewhat analogous to those found in cellulose, built largely of alternating glycine and alanine residues :—



Wool and *hair*, which contain *keratin*, are of peculiar interest. The X-ray photographs could not be accounted for on the

theory which had proved satisfactory for silk until the outstanding discovery was made by Astbury and collaborators[141,142,143] of the characteristics of stretched and unstretched hair keratin, the stretched fibre being found to be analogous to silk. Unstretched hair (α-keratin) has a rectangular unit cell of dimensions 27, 10·3, 9·8; on 30% extension (β-keratin), the dimensions become 9·3, 6·64, 9·8. Keratin is complex, and derived from various amino-acids, of which the chief are leucine, arginine, glutamic acid and cystine, whose unit cell may be described by: H(3); 9·40, 9·42. Deductions based on the known sizes of the atoms concerned and the observed periodicities led to the conclusion that α-keratin had a ring structure, which was capable of rupture and extension into a polypeptide chain, giving β-keratin, as follows:—



The diketopiperazine rings break at the points marked "a," giving a structure whose periodicity is twice as great.[144]

If we divide 10·2 by 3, we obtain the length of an amino-acid residue in the extended chain: this gives 3·4 (more accurately, 3·38). The side dimensions (calculated from the unit cell) are 4·65 and 9·8; taking the density as 1·30 and the average molecular weight of amino-acid residues as 115, the number of molecules in the unit is $(3{\cdot}38 \times 4{\cdot}65 \times 9{\cdot}8 \times 1{\cdot}30)/(115 \times 1{\cdot}65) = 1{\cdot}06$, which nearly equals 1.[145] Hence the cell dimensions appear to be reliable.

Bridge linkages between the R side-chains may occur between members of different chains of hair keratin. Between neigh-

bouring chains, we may have the cystine bridge $\overset{|}{C}H–CH_2–S–S–CH_2–\overset{|}{C}H$, or the internal anhydride bridge (here between glutamic and aspartic acids) $\overset{|}{C}H–CH_2–CH_2–CO–O–CO–CH_2–\overset{|}{C}H$.[144] Speakman and Miss Hirst[146] adduced chemical evidence for the presence of internal salt linkages (here between glutamic acid and arginine) of the type $\overset{|}{C}H–CH_2–CH_2–CO–O^-–NH_3^+–C(:NH)–CH_2–CH_2–CH_2–\overset{|}{C}H$, whilst internal peptide linkages between side-chains of one and the same main chain are also not impossible.[141] These may perhaps introduce contractions and distortions of main chains.

Feather keratin gives rise to a type of X-ray fibre diagram different from that of hair keratin.[147] The fibre periodicity is much longer, equal to at least 24·8, and perhaps as great as 309 (100 amino-acid residues). This gives the amino-acid unit a length of 3·1, as against 3·5 in silk fibroin and 3·4 in β-keratin. Stretched feather keratin gives the unit length 3·3. The 3·1 of unstretched feather keratin is therefore attributed to a slight folding of the protein chain, analogous to that discovered in α-keratin. It is also suggested that the growth of feathers may arise in the formation of extended lateral peptide linkages.

Gelatin and *collagen*[145,148,149] give a fibre period of 8·4, which appears to correspond to three amino-acid residues of length 2·84. The result is attributed to a polypeptide chain twisted about its main axis so that the side-chain pattern is made to occur in sets of three rather than sets of two.[141] If the average molecular weight of the amino-acid residues is 96, the density 1·346, the number of molecules is $(2·84 \times 4·56 \times 10·0 \times 1·346)/(96 \times 1·65) = 1·1$.

Pepsin,[150] after much difficulty, has been made to give an X-ray diagram corresponding to an hexagonal cell of dimensions *a* 67, *c* 154, to within 5%. Using the density 1·32, the cell molecular weight was found to be 478,000. It is inferred from intensity observations that the protein molecules are relatively dense and globular in form. In a later communication,[151] the cell is given as rhombohedral, with dimensions 162, 23° 50′, and an investigation on *insulin* is reported, giving the unit cell: R(1); 44·3, 115°. It is found that the X-ray photographs of *muscle*[152] and α-keratin are closely alike, and that, in fact,

muscle shows phenomena on stretching analogous to the α- and β-keratin change.[153] The muscle protein is *myosin*. Rinne[154] has treated muscles and nerves as of paracrystalline (liquid crystal) type.

The swelling of fibre micelles has been studied by Speakman,[146] and interpreted largely on the basis of the internal salt bridge linkages between protein chains, mentioned above. When a wool fibre is immersed in water, some water enters the micelles, and (by virtue of its high dielectric constant) reduces the attractive force between $-NH_3^+$ and $-COO^-$, so that extension of the fibre is facilitated. Acid or alkaline solutions facilitate extension also by repressing internal ionization. The micelles themselves, however, appear to be relatively impervious to water : the principal swelling must therefore be due to intermicellar action. A micelle thickness of order of 200, with length perhaps ten times as much fs postulated. " Micelle size " has little meaning, however, since it depends on the swelling agent and previous swelling history. Miss Lloyd and Phillips[155] have made a careful study of the hydration of proteins, and have explained the process as one of co-ordination of water molecules with O, N and H atoms of groups in protein chains. A summary on swelling is due to Katz,[156] who states that the intermicellar is the chief kind of swelling in wool, whilst intramicellar and " permutoid " swelling also occur to some extent.

The action of steam on wool is upon the side-chains ; a reaction occurs which destroys the capacity for spontaneous contraction, perhaps by throwing across new " rungs " or bridge chains. This offers a scientific interpretation of the " permanent wave."[144] The " set " of stretched wool fibre may be destroyed by aqueous solutions of sodium sulphide and hydroxide.[157] The subsequent contraction occurs to a length which is actually shorter than the original unstretched length, which suggests a further folding in α-keratin.

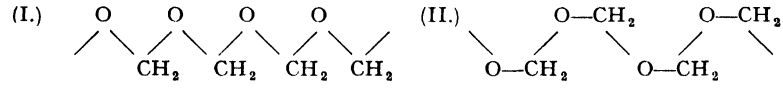
The great strength of natural fibres, previously alluded to, must be attributed mainly to the side cohesion of the chains, and, in particular, to bridge formation between them. The bridges between two chains may be regarded as parallel to each

other, hence the structure is " ladder- " or " grid-like." The grid-like sheets are preserved in stretched and unstretched hair.

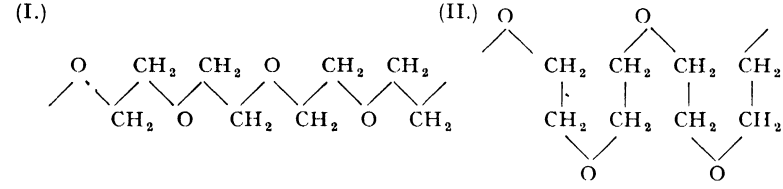
It will be realized that the researches briefly outlined in the present sub-section are of outstanding importance and interest in physical and bio-chemistry. The work of Astbury, Speakman, Bernal and others is beginning to throw light upon complex biological materials, especially in relation to the hitherto almost baffling problem of the fine structure and inward organization of proteins, which play such an essential part in the metabolism of the living organism. Further information will be found in the literature cited.

(D) **Other Complex Types.** Hengstenberg[1] and Staudinger[1] carried out pioneer investigations by the X-ray method on the *polyoxymethylenes* of type $R(OCH_2)_nOR$, where R is H for α-polyoxymethylenes, HSO_3 for β-, Me for γ-, and CH_3CO in diacetates. The highly-polymerized molecules may have n of the order 1,000 to 2,000, so that the nature of the end-groups R may play an unimportant part. Some of the lower diacetates ($n < 20$), however, are soluble, and can be separated by fractional crystallization. When the substances are pressed on celluloid sheets, and subjected to X-ray analysis, long-spacings d were observed in practically linear relation with n: — ($n = 8$) $d = 23{\cdot}7$; (9) 25·2 ; (10) 27·2 ; (12) 32·1 ; (14) 34·6 ; (15) 36·8 ; (16) 38·5 ; (17) 40·4 ; (18) 43·7. For the γ—compounds (dimethyl ethers) were obtained : (10) 24·6 ; (12) 28·6. The mean increase per CH_2O was about 1·9. The unit cell was first found to be hexagonal, and the dimensions, containing $9CH_2O$, were 4·46, 17·35. Taking the latter as the long dimension of the chain, the increase per CH_2O was $17{\cdot}35/9 = 1{\cdot}93$, in good agreement with the value deduced from the increase in long-spacing with increasing n. The side-spacing 7·74 (additional to 4·46) was afterwards added, the space-group type being probably C_2^2 or C_2^3. Further work was done by Ott,[158] who concluded that it was possible to determine the degree of polymerization of β-polyoxymethylenes by the X-ray method, a conclusion which was considered to be erroneous by

Sauter.[159] The hexagonal cell originally suggested was confirmed, with space-group C_3^2 or C_3^3.[160] There were two possibilities of chain arrangement for polyoxymethylenes, as follows :—



Sauter[161] has also studied polyethylene oxides containing $(CH_2CH_2O)_n$ of high molecular weight, and has suggested the presence of macro-thread molecules whose unit cell is probably : $M(36)C_{2h}^4$; 9·5, 19·5, 12·0, 101°. There are again two possibilities of arrangement :—



Methylbixin[162] $COOH(CH:CH.CMe:CH)_2CH:CH(CH:CMe.CH:CH)_2COOMe$ has been found to have monoclinic crystals of the following probable unit cell : $M(4)C_{2h}^5$; 10·56, 13·40, 20·62, 120° 54′. Bixin is the yellow pigment obtained from seeds of *annatto* (*bixa orellana*), and is related to some extent in chain formation with rubber and vitamin A.

Two other X-ray researches may be mentioned here : the work of Mahadevan[163] on the *vitrains* occurring in *coal*, and that of Krishnamurti[164] on the temperature change from amorphous solid to liquid of *shellac* and *rosin*.

The methods used in deducing the structure of organic molecules from X-ray data have been recently discussed by Mark,[165] who points out that the results, whilst very probable, are not necessarily always correct. It would appear that, whilst care is necessary in interpreting the diagrams, account being taken of general chemical and physical properties, the measure of success already attained offers much encouragement and hope for the future in the further investigation of complex organic structures.

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(A list of abbreviations used in references will be found on pages xxxi *et seq.)*

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CHAPTER VIII

THE CRYSTAL STRUCTURE OF ALLOYS, INTERMETALLIC COMPOUNDS AND SOLID SOLUTIONS

18. Solid Solutions of Metals

THE X-ray results on alloy systems and solid solutions are full of complex detail. The difficulty of reporting upon them is fortunately reduced by the earlier preparation of summaries, by Ewald and Hermann,[1] Neuberger,[2,3] and Bernal.[4] The present review purposes to extend the ground covered by these treatises to some extent by reference to recent work. It is hoped that by this means the more detailed results obtained on different systems may become conveniently available in summarizing treatises and in the original literature as required.

The classification of binary alloys here adopted is based upon division of the metals and metalloids into three classes, six groups A to F being obtained by combining individual members of these classes in pairs, as follows :—

Class I	Class II	Class III
Cu, Ag, Au (Cr), Mo, W Mn Fe, Co, Ni Ru, Rh, Pd Os, Ir, Pt	Li, Na, K, Rb, Cs Be, Mg, Ca, Sr, Ba Zn, Cd, Hg Sc, Y, La Al, Ga, In, Tl Ti, Zr, Hf, Th (Ge), (Sn), (Pb) V, Cb, Ta (Cr) The Rare Earths	H B C, Si, (Ge), (Sn), (Pb) N, P, As, Sb, Bi

Groups	A	Metal of Class I			with	Metal of Class I				*e.g.*,	Au-Cu
	B	,,	,,	,, I	,,	,,	,,	,,	II	,,	Cu-Zn
	C	,,	,,	,, II	,,	,,	,,	,,	II	,,	Mg-Zn
	D	,,	,,	,, I	,,	,,	,,	,,	III	,,	Fe-Si
	E	,,	,,	,, II	,,	,,	,,	,,	III	,,	Mg-Si
	F	,,	,,	,, III	,,	,,	,,	,,	III	,,	Bi-Sb

Metals placed in brackets in the above scheme occur in two different classes, and the structural relations of alloys containing them will decide in which they shall be considered to be placed. Only combinations of the above metals are considered: thus Se and Te are omitted. Alloys are as far as possible written with the more metallic atom placed first: thus Class I is considered from the present point of view as more metallic than Class II, and Class II than Class III, which contains the metalloids. Further, since elements tend to become more metallic with increasing atomic weight, when two elements of the same class are considered, the element coming lower in the list is placed first. Thus, for example, the intermetallic compound containing one atom Ca and three atoms Pb is listed in Table XXVII as Pb_3Ca and not $CaPb_3$, and similarly in like cases.

In a general way, alloys have been classified in three groups: (a) *Solid solutions*, having random replacement; (b) *Intermetallic compounds*, where the atoms of different kinds are more or less symmetrically arranged; (c) Solid solutions having *interstitial additions*, with atoms of one kind occupying spaces in the lattice of atoms of another kind. Westgren and Phragmén[5] pointed out that the distinction between solid solutions and intermetallic compounds is not generally sharply defined. The authors define "ideal" solid solutions as such that all atoms in the lattice are structurally equivalent, and "ideal" compounds as such that structurally equivalent atoms are chemically identical, these ideal types being of rather exceptional occurrence in actual practice. These views were later modified to some extent,[6] the cause of simple stoichiometric proportions found in intermetallic compounds being connected with the relation between the number of valency electrons and the number of atoms present rather than with the structural equivalence of chemically identical atoms. W. L. Bragg and Williams[7] have suggested the introduction of terms "phase-structure" and "atomic distribution" in place of "solid solution" and "intermetallic compound." An alloy is a system in dynamic equilibrium; temperature rise tends to promote disorder, whilst the more ordered systems have lower

potential energy. Two factors must be distinguished in discussing alloys : (1) the arrangement of the atoms irrespective of their nature ; (2) the nature of the atoms occupying the lattice-points (" sites "). The latter may be influenced by heat treatment, as by annealing. With these considerations in mind, we may proceed to discuss cases of " solid solution."

Continuous series of solid solutions through all ranges of concentration appear to be formed between each of the following pairs : Cu-Au,[1,8,9] Ag-Au,[1,10,11,12] Cu-Ni,[1,40] Cu-Pd,[1,13] Cu-Pt,[1] Ag-Pd,[1,123] Au-Pd,[1] Fe-Cr,[1,14] Fe-Mn,[1,15] Mo-W[1] and Bi-Sb.[17] All these mixtures belong to Group A, except the last, in Group F. The crystal structures of the two components are the same in each pair, except for Fe-Cr and Fe-Mn (Chapter II).

The law of linear additivity of Vegard[18] may be expressed in the form $d_{AB} = xd_A + (1 - x)d_B$, where d_{AB}, d_A, d_B are the lattice distances of solid solution AB, pure A and pure B respectively, and x, $1 - x$ are the fractional atomic concentrations of A and B. The law seems to be very nearly obeyed in the above cases, with some deviations, notably in Cu-Au and Ag-Au systems. Some results are plotted in Figure XLV. Slow cooling of certain mixtures gives evidence of rearrangements, which may be attributed to compound formation (see below and following section).

The diffusion of metals into each other is of interest in affording evidence of Bragg's theory of temperature dynamic equilibrium of alloys. Jost[9] has studied the diffusion of Cu into Au using X-rays, Cu wires being coated with Au and kept at 500°C. At first, the powder method gives the separate lines of Au and Cu ; as diffusion proceeds, a continuous variation from the lines of pure Au to pure Cu is observed.

According to the substitutional hypothesis of Rosenhain,[19] the solid solution of one metal in another of the same kind of lattice results in a certain amount of structural distortion, which decreases the solubility of the mixture and increases the hardness. It is pointed out that the hard metals Fe, Co, Ni, Mn, Cr, W tend to form long series of solid solutions, whilst the soft metals like Pb and Sn have no such tendency. Höjendahl[20] pointed out that the introduction of a second element must

reduce the free paths of the atoms, with consequent diminution in electrical conductivity. Tammann observed that silver-gold alloys were unattacked by nitric acid until the proportion of silver reached 50%, and deduced that a regular structure must be present. Borelius[21] criticized this view, and preferred to assume a random distribution. The conclusion seems

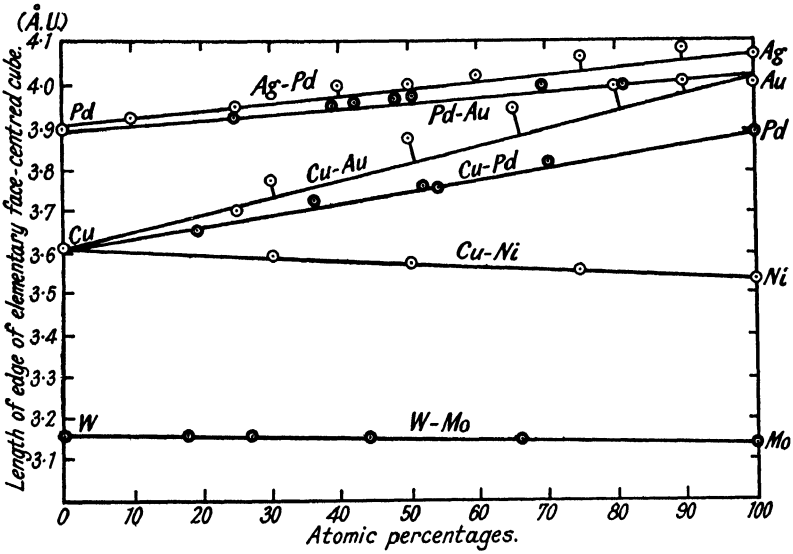

FIGURE XLV.—APPLICABILITY OF VEGARD'S LAW TO SOLID SOLUTIONS OF METALS.

established that where true solid solution is manifest the distribution of atoms between lattice-points is quite irregular, and that this results in increased hardness and decreased conductivity. Tammann[22] has expressed the view that any solid solution may assume a regular structure if suitably annealed, but Johannson and Linde[23] adduce evidence that this will only occur at certain concentrations of the constituents, approximating to the proportions appropriate to the compositions of intermetallic compounds. This change may be regarded as involving an introduction of regularity once more, associated with an *increase* of conductivity. Thus, when the

50% atomic mixture of copper and gold is slowly cooled, a maximum of conductivity is observed corresponding to the *tetragonal* face-centred compound AuCu. Rapid cooling leads to a minimum of conductivity corresponding to this composition, since the effect of adulteration is most strongly noticeable when the atoms are present in equal numbers.

Goldschmidt[24] has used Vegard's law to compute interatomic distances, and thus to obtain estimates of atomic radii, by comparing the lattice distances observed in different cases where no great change in atomic environment occurs. It was observed that the distances between centres were considerably affected by the degree of co-ordination, or number of nearest neighbours of a given atom: hence cases of hexagonal and cubic close-packing were compared, where the " co-ordination number " is 12. Where a pure metal was not found to crystallize in either of these ways, data were obtained from an alloy with another metal, chosen so that both the second metal and alloy possessed the required kind of structure, by the use of Vegard's equation. The values of atomic radii for co-ordination number 12 were thus obtained for different metals, as shown in Table XXVI.

TABLE XXVI.—ATOMIC RADII OF METALS, FOR CO-ORDINATION NUMBER 12 (Goldschmidt).

Metal	r	Metal	r	Metal	r	Metal	r	Metal	r	Metal	r
25 Mn	1·36	29 Cu	1·28	44 Ru	1·32	48 Cd	1·52	76 Os	1·34	80 Hg	1·55
26 Fe	1·27	30 Zn	1·37	45 Rh	1·34	49 In	1·57	77 Ir	1·35	81 Tl	1·71
27 Co	1·26	32 Ge	1·39	46 Pd	1·37	50 Sn	1·58	78 Pt	1·38	82 Pb	1·75
28 Ni	1·24			47 Ag	1·44	51 Sb	1·61	79 Au	1·44	83 Bi	1·82

The rigid applicability of Vegard's law has been discussed by van Arkel and Basart,[25] who prefer a relation of the type $d_{AB}^n = xd_A^n + (1 - x)d_B^n$, where $n = 5$ for the copper-silver system. The question as to how far Goldschmidt was justified in his use of the Vegard equation has been discussed by Westgren and Phragmén,[6] who find on considering alloys of elements

possessing the same kind of crystal structure Cu-Al, Ag-Al, Ni-Al, considerable deviations from Vegard's rule; hence it is concluded that the rule holds only where the components are closely related, as in Mo-W (Figure XLV). The constancy of atomic volume in mixtures must be considered as a first approximation only, the tendency being for departures to occur where the constituents are not closely related in the chemical sense.

In cases of alloys between elements of different crystal types, the tendency is for solid solutions to be formed when only small quantities of one of the constituents is present; the lattice is that of the metal present in larger quantity. Thus small quantities of Zn and Sn make no change in the face-centred Cu and Ag, except to alter the lattice dimensions somewhat, so that a true instance of solid solution is found. With increasing quantities of the second metal, complicated changes occur, usually based upon the formation of compounds, or the formation of what has been described as "solid solutions of compounds in one or other of the pure elements." The investigations have led to the recognition of many different phases, usually distinguished by Greek lettering (see following section). The study of temperature equilibrium diagrams of such systems has provided material for a large number of researches.

Limited solubility ranges of concentration are observed in the following cases:—Group A: Cu-Ag,[1,26,27,32] Cu-Mn,[1,28,29,41] Ag-Pt,[34] Fe-Co,[1] Fe-Ni,[1,16] Fe-Mo,[1] Fe-W,[1] Cr-Co,[1] Cr-Ni[1]; Group B: Mn-Mg,[30] also α-phases of alloys of Cu-Zn type (see following section); Group C: Al-Mg,[32] Zn-Mg[32]; Group D: Fe-C (graphite),[35] Cu-Sb,[36] Ag-Sb[36]; Group E: Sn-As[37]. In Groups D and E, the following have almost complete insolubility: Au-Si,[38] Ag-Si,[38] Pb-Si,[38] Sn-Si,[38] Zn-Si,[38] Cd-Si,[38] Sb-Si,[38] Bi-Si,[38] Pb-Sb.[39] Other cases of limited solubility are discussed in the following section.

It becomes clear that limited solubility ranges tend to occur in cases where the elements have unlike symmetry, although elements of the same type may have limited miscibility (as with Cu-Ag). γ-Mn (stable above 1191°, but obtainable at ordinary

temperatures by quenching) alloyed with Cu[29,41] forms a continuous series of solid solutions over a concentration range approaching 100% Cu, the length of the *a* and *c* axes changing as the concentration of Cu is increased, approaching the value $a = c$ found for pure Cu.

Weist[27] found the solubility of Ag in Cu to be higher for a

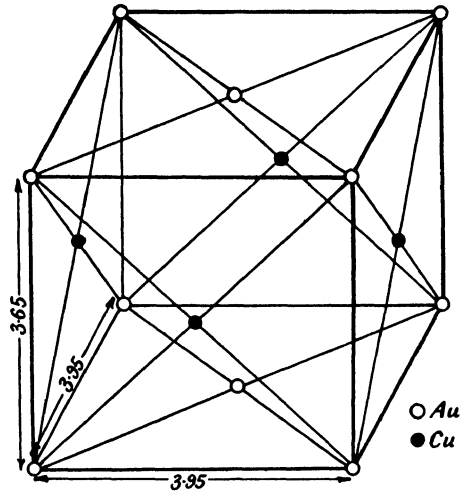

FIGURE XLVI.—STRUCTURE OF THE INTERMETALLIC COMPOUND AuCu.

single crystal than for a crystalline aggregate. Schmid and Siebel[32] report, however, that no difference in lattice parameters occurs in the systems Ag-Cu, Al-Mg and Zn-Mg, whether compounded of single or polycrystalline material.

It is found that the α-phases of Cu-Zn type in Group B sometimes tend not to obey Vegard's law of additivity.[31]

A table of solubilities of metallic pairs is provided by Bernal (p. 372 of [4]).

19. Intermetallic Compounds

(A) **Alloys of Group A.** Two compounds are reported in the system Au-Cu: $AuCu$[1,8] (Figure XLVI), and $AuCu_3$[1,8] (Figure XLVII). The tetragonal face-centred unit cell of

AuCu has $4 \times \frac{1}{2} = 2$ atoms Cu and $(8 \times \frac{1}{8}) + (2 \times \frac{1}{2}) = 2$ atoms Au (2AuCu), and the cubic face-centred unit cell of $AuCu_3$ has $8 \times \frac{1}{8} = 1$ atom Au and $6 \times \frac{1}{2} = 3$ atoms Cu ($1AuCu_3$). Johannson and Linde[1] discovered in 1925 that Cu-Au alloys of $AuCu_3$ composition had Au and Cu atoms distributed at random over the lattice sites : after annealing for

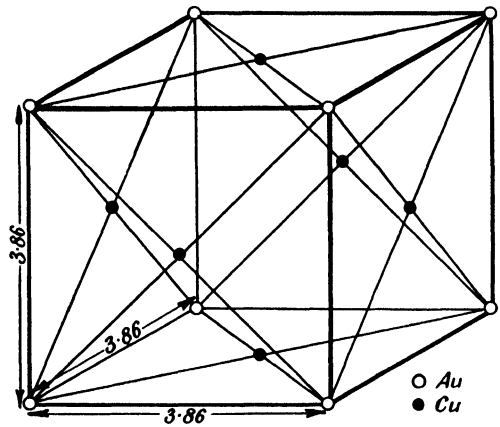

FIGURE XLVII.—STRUCTURE OF THE INTERMETALLIC COMPOUND $AuCu_3$.

several days at 300°, the " superlattice " (Ger. *Überstruktur*) of Figure XLVII appeared, with an increase in electrical conductivity. Similar considerations apply to AuCu, $PdCu$, $PdCu_3$. This has been discussed by Bradley,[29] and by W. L. Bragg and Williams,[7] who suggest that alloys departing from the correct ratio for AuCu and $AuCu_3$ are incorrectly described as solid solutions of Au or Cu in AuCu or $AuCu_3$, since all atoms of each kind play identical parts in dynamic equilibrium. Numerical results are shown for intermetallic compounds of all groups in Table XXVII.

(B) **Alloys of Group B.** (a) *Heusler Alloys.* The structure of the magnetic alloy Cu_3Al[1,3] is depicted in Figure XLVIII. There are present $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$ atoms Al, and $(12 \times \frac{1}{4}) + 9 = 12$ atoms Cu ($4Cu_3Al$). The cell has a cubic face-centred arrangement of Al atoms with a superimposed

body-centred system of Cu atoms. One-third of the Cu atoms may be replaced by Mn giving Cu_2MnAl,[1,3] whilst another substitution gives Cu_2MnSn.[1,3] Persson[48] found that the latter phases were magnetic only if the atomic percentage of Mn exceeded a certain minimum. Heusler[49] discussed the relation between crystal structure and ferromagnetism of these alloys, whilst Bradley and Rodgers[50] attempted to fix the positions of the Mn atoms. It was found that annealing at 500° for several hours gave a non-magnetic alloy of the Cu_9Al_4 type, which

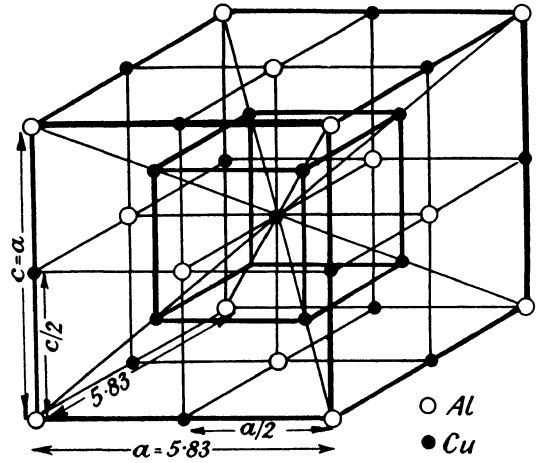

FIGURE XLVIII.—STRUCTURE OF THE INTERMETALLIC COMPOUND Cu_9Al_4

might be written $(Cu, Mn)_9Al_4$, whilst quenching from 800° gave the ferromagnetic arrangement.

(b) *Alloys of the Brass Type.* The following systems give incomplete series of solubility ranges[1]: Ag-Cd, Ag-Sn, Ag-Zn, Ag-Al, Au-Hg, Au-Zn, Cu-Al, Cu-Be, Cu-Mg, Cu-Sn, Cu-Zn, Fe-Zn. In alloys of the brass (Cu-Zn) type,[1] it is found that with increasing Zn content five different phases are shown:— (1) the α-phase (face-centred cubic, or cubic close-packing) containing a solid solution; (2) the β-phase (CuZn, body-centred cubic, Ewald and Hermann's B2 or L20 types); (3) the γ-phase (Cu_5Zn_8, complex cubic, D82 type with 52 atoms in the

unit cell, as in α-Mn); (4) the ε-phase (hexagonal close-packing); (5) the η-phase (hexagonal close-packing, with larger c/a ratio than the ε-phase). In some cases, all of these phases may not appear, whilst in others new phases are shown, distinguished by further Greek lettering, or by accented symbols (β', γ', etc.). Bradley[29] and Ekman[46] have supplied lists showing which phases occur in different cases. Ag-Zn and Ag-Cd are strictly analogous to Cu-Zn. A new δ-phase appears in Cu-Al which has α; $\beta(Cu_3Al)$; $\gamma'(Cu_9Al_4)$; $\delta(CuAl_2)$; ε, whilst Ag-Al has no ε-phase, and the γ-phase is hexagonal. Thus Cu-Zn and Cu-Al are more alike than either of the pairs Cu-Zn, Ag-Al; Cu-Al, Ag-Al.[29] Cu-Cd[62] also shows characteristics where no close analogy with Cu-Zn is found.

The lattice parameters of Cu-Zn alloys over 30% Cu by weight have been measured to within 1 in 4,000.[57] Straumanis and Weerts[63] have followed the transition from the body-centred β-phase to the face-centred α-phase, the change being found to be accompanied by a sequence of slippings.

The Fe-Al system, studied by Bradley and Jay,[58] provides an interesting case. Up to 18 atomic %Al, Al replaces Fe at random. If quenched from above 600°C., the random arrangement persists as far as 25%Al. Between 25 and 26%Al, there is an abrupt change on quenching, the atoms at cube centres are partly Fe and partly Al in varying proportions, the remaining atoms being Fe. Further, carefully annealed specimens of the composition Fe_3Al have the structure of Figure XLVIII, with all the corners, centres of faces and half the cube-centres filled by Fe, and the other half by Al ($4Fe_3Al$). With alloys of the composition 50%Al, all the cube-centres become occupied by Al (CsCl type, B2 and L20). A most interesting diagram accompanies the authors' paper, showing the proportion of atoms of each kind occupying different sites from 0 to 50%Al. Thus, for 40%Al, 80% of the cube-centres are filled by Al, the remaining sites by Fe. The structures are seen to be essentially different from those of the salt type (*e.g.*, NaCl).

(c) *The Hume-Rothery Rule.* An important co-ordinating principle governing the structure of intermetallic compounds was suggested by Hume-Rothery[65,66] in 1926, and extended to

some extent by Westgren and Phragmén[67] a little later, in accordance with which structural similarity is associated with identical " concentration " of valency electrons (ratio of number of valency electrons to number of atoms). Now considering the β-phases of the systems Cu-Zn, Cu-Al, Cu-Sn, which correspond to the molecular compositions CuZn, Cu_3Al, Cu_5Sn respectively, CuZn has the simple body-centred structure (B2), the Heusler alloy Cu_3Al has the structure of Figure XLVIII on a body-centred plan, whilst Cu_5Sn has a body-centred lattice, with the Cu and Sn atoms distributed at random over the lattice-points. It is then noteworthy that the ratio of valency electrons to atoms in each of the three cases is 3 : 2 [CuZn, (1 + 2) : 2 ; Cu_3Al, (3 + 3) : 4 ; Cu_5Sn, (5 + 4) : 6]. Another compound having the same ratio is Ag_3Al, the structure being of a different type, isomorphous with β-Mn, with 5 molecules, *i.e.*, 20 atoms in the unit cell, and $a = 6{\cdot}92$ (*cf.* $a = 6{\cdot}29$ for β-Mn). Now the 20 atoms of Mn in the unit cell of β-Mn, as Preston showed, are divided into two groups of 12 and 8 structurally equivalent atoms. It is therefore clear that all of the 15 atoms of Ag in the unit cell of Ag_3Al cannot be unequivalent to the 5 atoms of Al, if the structures exactly correspond, as the X-ray evidence indicates. It is therefore concluded that the Ag and Al atoms are distributed at random over the two groups of structurally equivalent positions, and atoms which are chemically equivalent are not structurally equivalent. The same argument applies in the cases of Cu_5Si and $CoZn_3$, where the 3 : 2 ratio again occurs, and which has the Mn-β structure. Yet these alloys certainly constitute chemical compounds in the accepted sense of giving constant stoichiometric proportions, so that Westgren and Phragmén are inclined to modify their earlier views as to the difference between an intermetallic compound and a solid solution. The simple and constant proportions may be related to the observation of Hume-Rothery that the stability of a lattice depends on a certain ratio of valency electrons to atoms. It is not yet clear why one or other of these two structures (β-brass and β-Mn) tends to appear whenever this ratio is 3 : 2.

Other illustrations of the Hume-Rothery principle have been

found in the γ- and ϵ-phases, where the ratios are 21 : 13 and 7 : 4 respectively. Compounds of the γ-brass type, Cu_5Zn_8, Ag_5Zn_8, Au_5Zn_8, Ag_5Cd_8, have been shown to resemble α-Mn in structure, and have a unit cell containing 52 atoms (*cf.* α-Mn, 58). The concentration of valency electrons is in every case 21 : 13, which is also true of Cu_9Al_4 and of δ-bronze, $Cu_{31}Sn_8$. In the latter case, however, it has been deduced that there are $52 \times 8 = 416$ atoms in the unit cell, but the structural dimensions are correspondingly doubled ($a = 17{\cdot}91$, as compared with $a = 8{\cdot}86$ for Cu_5Zn_8 and $a = 8{\cdot}89$ for α-Mn). A discrepancy exists here, since 416 is not an exact multiple of $31 + 8 = 39$. Ekman[46] found that alloys of the type M_5Zn_{21}, where M is Fe, Co, Ni, Rh, Pd, Pt, together with Ni_5Cd_{21}, have the γ-brass structure. The ratio of valency electrons to atoms is again 21 : 13, *provided the valency of the transitional element may be taken as zero*, in accordance with an earlier suggestion of Westgren and Phragmén.[67] The ratios 5 : 2 and 6 : 2 give hexagonal structures, *e.g.*, NiAs. Perlitz[69] has extended the work of Hume-Rothery to some extent, by considering the conditions under which structures of different types may be expected. He concludes that β, γ and ϵ structures will not occur in binary alloys if both components have equal numbers of valency electrons. Thus the rule is inapplicable to AgLi,[43] and, more generally, seems to break down whenever Li, Na, Ca, Mg and Sr are present.

Bernal[215] has pointed out that γ-brass and δ-bronze are diamagnetic, whilst the constituent metals are hardly so at all, and has concluded that in these cases homopolar bonds are present. In a cell with a certain number of atoms and a certain number of homopolar bonds, it will be quite indeterminate as to the atoms from which the structure obtains its binding electrons, which may explain the constancy of ratio observed. There appear to be many exceptions to the Hume-Rothery classification, but it seems to be the surest guide so far discovered, and represents the first successful attempt to systematize these groups of intermetallic phases.

Summarizing, the contention that the stability of intermetallic structures is related to the concentration of valency

electrons occurring in them has proved to be largely justified. For a concentration of $\frac{3}{2} = 1{\cdot}50$, two types are possible, the β-brass type (CuZn, Cu_3Al, Cu_5Sn) and the β-Mn type (Ag_3Al, $CoZn_3$, Cu_5Si) ; for $\frac{21}{13} = 1{\cdot}615$, the structure is of α-Mn type (γ-structures) ; for $\frac{7}{4} = 1{\cdot}75$, the structure is that of the ϵ-phases (close-packed hexagonal).

(*d*) *Amalgams. Copper amalgam*[1,3] forms solid solutions when soft, but on setting a change of structure occurs with compound formation. Katoh[52] finds that the solid phase rich in Hg has a γ-structure (Cu_3Hg_4) with 52 atoms in the unit cell, whilst the alloys rich in Cu contain two phases, the Cu lattice and the γ-phase. *Silver*[3,42] yields the γ-phase Ag_3Hg_4, and also at 40%Ag a β-lattice, close-packed hexagonal, with a probable random distribution of Ag and Hg atoms. Gold amalgams[1,3] up to 15%Hg form solid solutions ; the next phase is hexagonally close-packed and corresponds approximately to Au_3Hg. At higher Hg content, two or more phases are present with complex constitution.

Biltz[70] has observed that the heats of formation of intermetallic compounds are greater, the more the atoms uniting are " active " metals : thus the union of Hg + Au provides less heat than Hg + Na.

(e) *Alloy Phases.* Much has been said in preceding paragraphs about alloy phases. It appears worthy of emphasis that although an alloy phase may be described by a formula (*e.g.*, $CuAl_2$) the existence of separate molecules is not implied, somewhat as in the case of the NaCl crystal. There is, however, a distinction : in NaCl, there must be an alternation of Na and Cl, whilst in alloys, especially when quenched from high temperatures, some of the atoms may be in wrong sites. An alloy phase may be defined as a " homogeneous, physically distinct, and mechanically separable portion " of an alloy system.[29]

(C) **Alloys of Group C.** A new type occurs in this group, represented by TlNa,[80] with a cubic unit cell containing 16 atoms. Other members are : InLi,[43] GaLi,[43] CdLi,[43] ZnLi,[43]

and InNa.[73] The Hume-Rothery rule breaks down, for not only is the valency electron to atom ratio different in the series, but also a new type is associated with a 3 : 2 ratio in CdLi and ZnLi. It is noteworthy that in InNa, the radius of the Na atom is 15% smaller than in the pure metal. Other cases include types previously encountered: Pb_8Na_{31}[77] (γ-brass); Pb_3Na,[79] Pb_3Ca,[76] Pb_3Ce,[76] Tl_3Ca,[76] Sn_3Ca[76] ($AuCu_3$ Type L12, as in Figure XLVII); PrMg[78] and NdAl[75] (β-brass). Baroni[71] records CdLi as of β-brass type, whilst Zintl and Brauer[43] find the TlNa type. Pb_8Na_{31} agrees with the Hume-Rothery rule (electron to atom ratio 21 : 13), but there are discrepancies in other cases.

ZnMg,[81] Zn_2Mg (C14 type), and Zn_5Mg[81] form an interesting series, each having 12 atoms in the unit hexagonal cell, so that one cell can be obtained from another by suitable interchanges between Zn and Mg atoms.

The following systems show solid solutions over limited ranges: Zn-Mg,[1] Cd-Mg,[1] Zn-Al,[1,3,82] Hg-Zn,[1,3] Pb-Hg,[1,3] Hg-Sn,[1,3] Pb-Tl[1,3]; whilst Cd-Hg forms a nearly continuous series of solid solutions, with a small gap.

(D) **Alloys of Group D.** This group contains many "interstitial" compounds, treated in Section 20, also members of the B4, B8, Bx, C2, C17, C18 and Cx types of Chapters III and IV. Co_2B and Ni_2B[83] are of Fe_2B C17 type, whilst CoB[83] is like FeB. Cu_5Si[86] is of interest in having the β-Mn structure, with the appropriate electron to atom ratio of 1·5. MoN[95] is like WC, whilst Fe_3Si[58] is like the Heusler alloys (L21 type, Figure XLVIII). The phases of the Cu-Sb[36,99] and Ag-Sb[36,98] alloys have been examined.

(E) **Alloys of Group E.** A number of types encountered in earlier chapters fall into this group. Investigations on the following alloy systems may be noted: Pb-Bi,[103] Sn-Bi[103] and Tl-Sn.[104]

(F) **Alloys of Group F.** The only examples approximating to this type are BN and SiC. Results for all groups are in Table XXVII.

TABLE XXVII.—CRYSTAL STRUCTURE OF INTERMETALLIC COMPOUNDS.

(Intermetallic Compounds are arranged in six groups A to F, in alphabetical order in each group. Where no data are supplied, the reader is referred to an earlier named crystal type: thus, in Group E, AlN $B4$ refers to Ewald and Hermann's $B4$ type (Table IX), and $CoAs_3$: XVII shows that the requisite data are in Table XVII. The other abbreviations follow the method of previous Tables for which see page 72)

GROUP A. $AuCu$[1,8]: T(2-L10)D^1_{4h}; 3·95, 3·68. $AuCu_3$[1,8]: C(1-L12)O^1_h; 3·86. Fe_3Mo_2[1]: H(8); 4·74, 25·63. Fe_2W: Cx. Fe_3W_2[1]: H(8); 4·73, 25·76. $IrOs$[3]: H(1); 2·90, 4·60. Ni_6W[1]: C(A1 type); 3·68. $PdCu$[1]: C(1-L20, B2)O^1_h; 2·99. $PdCu_3$[1,3]: C(1-L12)O^1_h; 3·69. $PtCu$[1,3]: R(1-L11)D^5_{3d}; 3·78, 90° 54′. (2nd modification) C(4-I 13)O^7_h. $PtCu_3$[1,3]: C(1-L12)O^1_h; 3·71.

GROUP B. Ag_3Al[1]: C(5); 6·92. $AgCd$[1]. C(1-L20, B2)O^1_h; 3·33. Ag_5Cd_8[1]: C(4-D82)T^3_d; 9·96. Ag_3Hg_4[42,53]: C(4)O^9_h; 10·09. $AgLi$[43]: C(1-L20, B2); 3·168. $AgMg$[1]: C(1-L20, B2)O^1_h; 3·28. $AgZn$[1,44]: C(1-L20, B2); 3·16. Ag_5Zn_8[1,33,44,51]: C(4-D82)T^3_d; 9·33. $AuSn$[1,45]: H(2-B8)D^4_{6h}; 4·31, 5·51. $AuZn$[1]: C(1-L20, B2)O^1_h; 3·15 $AuZn_3$[3]: C(8); 7·88. Au_5Zn_8[1,3,51]: C(4-D82)T^3_d; 9·27. $CoAl$[46]: C(1-L20, B2)O^1_h; 2·854. $CoZn_3$[46]: C(5); 6·343. Co_5Zn_{21}[46]: C(2); 8·878. $CuAl$[47]: O(16); 4·09, 12·00, 8·64. $CuAl_2$: C16. Cu_3Al[1,3,48,49,50]: C(4-L21)O^5_h; 5·83. Cu_9Al_4[1,3,51,64]: C(4-D83)T^1_d; 8·70. $Cu_{24}Al_{18}$(?)[47]: H(1); 8·08, 1·24. $CuBe$[1]: C(1-L20, B2)O^1_h; 2·69. Cu_5Cd_8[51,62]: C(4-D82)T^3_d. Cu_3Ge[1]: H; 2·63, 4·20. Cu_3Hg_4(?)[52]. C, 9·401 $CuMg_2$[1] O(16); 5·27, 9·05, 18·21. Cu_2Mg: C15. Cu_2MnAl[1,3,48,49,50]. C(4-L21)O_h; 5·95. Cu_2MnSn[1,3,48,49,50]. C(4-L21)O^5_h; 6·17. $CuSn$[54]: H(2-B8)D^4_{6h}; 4·19, 5·09. Cu_3Sn[1,54,55,56,68]. O(16)V^{17}_h, 4·33, 5·55, 38·1. $Cu_{20}Sn_6$[54]: H(1)D^1_{3d}; 7·316, 7·854. $Cu_{31}Sn_8$[1,56]. C(416 atoms -D84); 17·91. $CuZn$[1,57]: C(1-L20, B2)O^1_h; 2·95. Cu_5Zn_8[1,51,57]. C(4-D82)T^3_d; 8·86. $FeAl$[58]: C(1-L20, B2)O^1_h; 2·90. Fe_3Al[7,58]: C(4-L21)O^5_h; 11·56. $FeSn$(?)[59]: H(3); 5·29, 4·40. $FeSn_2$[59]: H(4); 5·317, 9·236. Fe_2Sn[59]: H(2); 5·449, 4·353. $FeZn_7$[60]. H; c/a = 1·6. Fe_3Zn_{10}[1,60]: C(4-D81)O^9_h; 8·93. Fe_5Zn_{21}[46]: C(2); 8·992. $MnZn_3$[61]: H(12). $MnZn_7$[61]: H(2). $NiAl$[1]: C(1-L20, B2)O^1_h; 2·82. Ni_5Cd_{21}[46]: C(2); 9·761. Ni_5Zn_{21}[46]: C(2); 8·904. Pd_5Zn_{21}[46]: C(2); 9·089. Pt_5Zn_{21}[46]: C(2); 18·08. W_2Zr: C15.

GROUP C. Al_3Mg_4[3]: C(1); 4·8. $CdLi$[43,71]: C(8); 6·687: C(1-B2, L20)O^1_h; 3·32. Cd_3Li[71]: C?(8); 8·62. $CeMg_3$[72]: C(4). $GaLi$[43]: C(8); 6·195. $InLi$[43]: C(8); 6·786. $InNa$[73]. C(8); 7·297. $HgCd_3$[4]: T(38); 16·53, 12·69. $LaAl_4$: XVIII. $LaMg_3$[72]: C(4). $NdAl$[75]: C(1-L20, B2)O;

TABLE XXVII—*continued.*

3·73. Pb_3Ca[76]: C(1-L12)O_h^1; 4·891. Pb_3Ce[76]: C(1-L12)O_h^1; 4·864. $PbMg_2$; C1. Pb_3Na[79]: C(1-L12)O_h; 4·873. Pb_8Na_{31}[77]: C(2); 13·27. Pb_3Sr[76]: T(1); 4·955, 5·025. $PrMg$[78]: C(1-B2, L20)O_h^1; 3·88. $PrMg_3$[72]: C(4). Sn_3Ca[76]: C(1-L12)O_h^1; 4·732. $SnMg_2$: C1. Tl_3Ca[76]: C(1-L12)O_h^1; 4·794. $TlNa$[80]: C(8); 7·473. $ZnLi$[43]: C(8); 6·209. $ZnMg$[81]: H(6); 10·66, 17·16. Zn_2Mg: C14. Zn_5Mg[81]: H(2)D_6^5; 9·92, 16·48.

GROUP D. $AuSb_2$: C2. AuSn: B8. $CoAs_3$: XVII. CoB[83]: O(4)V_h^{16}; 3·948, 5·243, 3·037. Co_2B[83]: T(4-C17)D_{4h}^{18}; 5·006, 4·212. CoSb: B8. CoSi: Bx. Co_2Si: Cx. Cr_3C_2[1,3]: O(4); 2·82, 5·52, 11·46. Cr_4C[1,3]: C(24); 10·64. Cr_7C_3[1,3]: H(8), 13·98, 4·52. CrSb: B8. CrSi: Bx. $CrSi_2$: Cx. Cr_3Si[84]: C(2); 4·555. Cu_3As[85]: H(6); 7·118, 7·279. CuH: B4. Cu_2Sb[36]: Cx. Cu_5Si[86]: C; 6·210. $Cu_{15}Si_4$[86,87]: C(4)T_d^6; 9·694. CuSn: B8. FeAs: Bx. $FeAs_2$: C18. Fe_2As: Cx. FeB: Bx. Fe_3B: C17. Fe_3C cementite[2,88,89,90]: O(4)V_h^{16}; 4·52, 5·08, 6·73. Fe_2N: Cx. Fe_3N[91]: H(2)D_6^6; 2·767, 4·417. Fe_4N[1,92,93,116]: C(1-L'10)O_h^1; 3·79. Fe_2P: Cx. Fe_3P[94]: T(8)S_4^2?; 9·09, 4·45. FeSb: B8. $FeSb_2$: C18. FeSi: Bx. $FeSi_2$: Cx. Fe_3Si[58]: C(4-L21)O_h^5. Fe_4W_2C[1]: C(16); 11·04. Martensite: Bx. MoC_3: XVII. Mo_2C: Cx. MoN[95]: H(1); 2·86, 2·80. $MoSi_2$: C11. MnAs: B8. Mn_4N[96]: C(1-L'10)O_h^1; 3·844. MnSb: B8. MnSi: Bx. $MnSi_2$. Cx. Mn_3Si[84]: H(4); 6·898, 4·802. NiAs: B8.' Ni_2B[83]: T(4-C17)D_{4h}^1; 4·980, 4·236. NiBi: B8. Ni_3C[97]: H; 2·646, 4·329. NiSb: B8. NiSi: Bx. NiSn: B8. $PdAs_2$: C2. Pd_2H[119,120]: C; 4·02. PdSb: B8. $PdSb_2$: C2. $PtAs_2$: C2. PtP_2: C2. PtSb: B8. $PtSb_2$: C2. PtSn: B8. WC: Bx. α-W_2C: Cx. WSi_2: C11.

GROUP E. AlAs: B3. Al_4C_3: XX. AlN: B4. AlP: B3. AlSb: B3. BaB_6: XX. BaC_2: C11 BaN_6: XX. Be_2C: C1. Be_3N_2: XVIII. Be_3P_2: XVIII. CaB_6: XX. CaC_2: C11. α-Ca_3N_2: XVIII. $CaSi_2$: C12. CbC. B1. CbN. B1. Cd_3As_2: XVIII. Cd_3P_2: XVIII. CeB_6: XX. CeC_2: C11. CrN: B1. ErB_6: XX. GaAs: B3. GaP: B3. GaSb: B3. InSb: B3. KHC_2: XVII. KN_3: XVII. LaC_2: C11. Li_3N: XVII. Mg_3As_2: XVIII. Mg_3Bi_2[100]: H(1)D_{3d}^3; 4·666, 7·401. Mg_3N_2: XVIII. Mg_3P_2: XVIII. Mg_2Pb: C1. Mg_3Sb_2[100]: H(1)D_{3d}^3; 4·573, 7·229. Mg_2Si: C1. Mg_2Sn: C1. $NaHC_2$: XVII. NaN_3: XVII. NdC_2: C11. PbN_6: XX. PrC_2: C11. RbN_3: XVII. ScN: B1. SmC_2: C11. SnAs: B1. SnSb: B1. SrB_6: XX. SrC_2: C11. TaC: B1. TaN: B4. ThB_6: XX. ThC_2: C11. TiC: B1. TiN: B1. TlBi: B2, L20. TlSb: B2, L20. Tl_7Sb_2[1,3,101]: C(6-L22)Oh; 11·59. VC: B1. VN: B1. YC_2: Cx. Zn_3As_2: XVIII. Zn_3P_2: XVIII. ZrC: B1. ZrH_2[102]: T(2-C11); 4·964, 4·440. ZrN: B1.

GROUP F. BN: B12. SiC: B3, B5, B6, B7.

(G) **General.** The intermetallic compounds may be classified in the following groups[4]:—(1) *Metallic*, as CuAu, CuZn, CuPd, AgCd, $CuAl_2$; (2) *Mixed Metallic and Homopolar*, as $MgZn_2$, $MgCu_2$, Mg_2Cu, Ag_3Al, Ag_3Sb, $FeZn_7$; (3) *Mixed Metallic and Ionic*, as $PbMg_2$, $SnMg_2$, $PdSb_2$, Tl_7Sb_2; (4) *γ-structures*, as Cu_5Zn_8, Ag_5Zn_8, Au_5Zn_8, Ag_5Cd_8, Cu_9Al_4, $Cu_{31}Sn_8$. As intermediate in character between metals and salts, the *adamantine* compounds may be noted. These possess the diamond or some related structure, and include SiC and many compounds of transition elements with the "B" elements of the periodic groups IV, V and VI, notably with S, Se, Te, P, As, Sb.

It is noteworthy that relatively few ternary systems have been examined with X-rays, doubtless mainly on account of experimental difficulties. Even in the binary systems, in spite of a great output of work in recent years, a very large proportion of possible combinations await attention.

The classification of metallic mixtures adopted by Neuberger[2] is in Table XXVIII.

TABLE XXVIII.—CLASSIFICATION OF METALLIC MIXTURES (Neuberger).

Liquid State		Solid State		Examples
Completely Soluble	No Compounds	Completely Soluble		Fe-Mn, Ni-Cu, Au-Cu.
		Partly Soluble		Ag-Cu, Ni-Cr, Zn-Hg.
		Completely Insoluble		Ag-Pb, Pb-Sb.
	One or more Compounds	Compounds and Components	Completely or partly Soluble	Fe-C, Fe-Si, Fe-Ni, Fe-Co, Fe-Cr, Fe-Mo, Mn C, Cu-Al, Cu-Zn, Cu-Sn.
			Completely Insoluble	Pb-Mg
Partly Soluble				Al-Mn.
Completely Insoluble				Fe-Sb, Fe-Pb, Fe-Bi.

20. Interstitial Alloys

(A) **General.** Hägg[105] found that the phases formed between transition elements and B, C and N were more metallic than alloys of these non-metals with non-transitional elements. The effect was attributed to interstitial additions, and was associated with the relatively small atomic dimensions of the non-metals. When the ratio of atomic radius of metal atom to non-metal atom exceeds 1·7, distribution of the added non-metal within spaces occurs. The metal atom structures are usually close-packed or simple hexagonal. If the ratio is less than 1·7, complex structures may arise, as with cementite Fe_3C.[29] This may be contrasted with the observation of v. Stackelberg[106] that the carbides, nitrides, silicides and phosphides of metals may be regarded as ionic lattices, with the anions close-packed, the gaps being filled by a tetrahedral or octahedral arrangement of cations. We are here concerned only with the interstitial addition of relatively small proportions of non-metals to transitional metals, giving non-ionic structures of co-ordination types.

(B) **Steel.** Pure iron has four modifications: α-Fe(A2) $\overset{788°}{\longleftrightarrow}$ β-Fe(A2) $\overset{906°}{\longleftrightarrow}$ γ-Fe(A1) $\overset{1401°}{\longleftrightarrow}$ δ-Fe(A2) (see Chapter II). As varying amounts of C are added to iron up to about 6%, gradual changes occur in lattice dimensions. High temperature steel, or AUSTENITE, is described as an interstitial solid solution of C in γ-Fe. Rapid cooling of austenite gives MARTENSITE, slow cooling CEMENTITE, which is orthorhombic and contains Fe atoms in octahedral formation with C atoms in interstices (Fe_3C).[88,89,90] In the formation of martensite, the body-centred cubic lattice of α-Fe is subject to considerable distortion, so that the unit cell is tetragonal.[107 to 114] It would appear that this distortion is partly responsible for the hardness of martensite. Another factor affecting hardness of steels is grain size, as appears in the X-ray study of Wood,[115] who found that the hardness varied inversely as the surface area of the grains.

(C) **Other Interstitial Alloys.** Hägg[116] investigated the products obtained by passing ammonia over heated iron, and concluded that solid solutions of nitrogen in iron are formed, the nitrogen atoms forcing their way between those of iron, causing a change in the structure with the development of the face-centred cubic lattice, corresponding to γ-Fe. With only 0·2% N, very faint X-ray lines of the face-centred form appear, and at 5·7% N, all lines due to α-Fe have disappeared. The phase of solid solutions of N in γ-Fe has an upper limit corresponding to the composition Fe_4N.[92,93] Between 7·3 and 8·6%N, the lines begin to move inwards, showing an increase in lattice dimensions, with the formation of the ϵ-phase, consisting of a solid solution of N in hexagonal close-packed Fe, the nitrogen atoms being placed at random in the interstices between the iron atoms. The limit of this phase agreed with the composition Fe_3N.[91] Hägg considered that these coincidences in composition with molecular formulæ might be accidental, or they might be related to particular concentrations of the valency electrons. In the Haber synthesis, the iron catalyst is prepared by reduction of the oxide with ammonia, and the suggestion is made that the peculiar activity of the nitrogen in presence of the catalyst may be due to the presence of monatomic nitrogen in the interstices of the iron. Other observers[92,118] confirm the existence of the compound Fe_4N. The regular cubic distribution is shown in Figure XLIX, the unit cell containing $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$ atoms of iron and 1 atom of nitrogen ($1Fe_4N$). The nitrogen atoms enter in the centres of the cubes of close-packed iron, until this composition is reached, with a cell edge 3·79 Å.U. A compound Fe_2N[93] is also described, the iron atoms being in hexagonal close-packing, with N atoms in interstices (Cx type). γ-Fe containing 1·5%N gives a tetragonal phase like martensite.[29,117] The phases in the Mn-N system[96] are similar to those of Fe-N in some ways, and, in particular, in the formation of Mn_4N, structurally analogous to Fe_4N. Blix[94] studied two phases of the Cr-N system, one homogeneous up to 33 atomic %N, containing Cr atoms in hexagonal close-packing, with N atoms distributed at random in interstices, the limit corresponding to about Cr_2N, the other phase being

CrN (B1 type). For further discussion of the binary systems Fe-B, Cr-C, Fe-N, Fe-P, see [1]. Amongst further interstitial compounds may be named: FeB, Fe_2B, Fe_2P, Fe_3P, CoB, Co_2B, Ni_2B, Ni_3C (see Table XXVII, Group D). The Mo-N and W-N systems have also been investigated by Hägg. MoN is structurally like WC.

(D) **Absorption of Hydrogen by Metals.** Hydrogen dissolved in metals gives an interesting case of interstitial solid

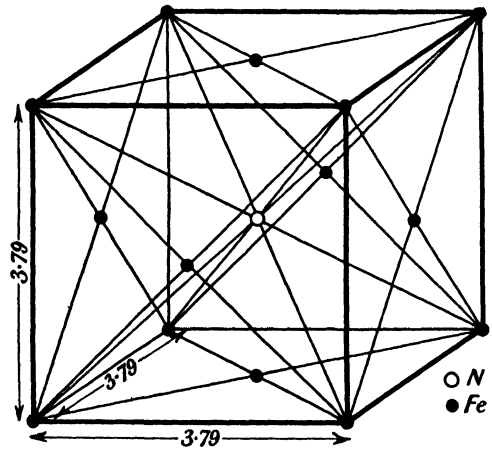

FIGURE XLIX.—STRUCTURE OF THE IRON NITRIDE, Fe_4N.

solution. According to the X-ray investigation of Linde and Borelius,[119] hydrogen is absorbed in palladium in the interstices of the lattice with gradual expansion of the lattice dimensions up to a certain H content. With higher concentrations, a sudden increase appears to occur in the lattice dimensions corresponding to the formation of the compound Pd_2H. Hanawalt[120] has confirmed the existence of this compound, and gives it a face-centred cubic lattice unit with $a = 4{\cdot}02$ (*cf.* Pd, $a = 3{\cdot}87$). Bredig and Allolio[121] find that films of palladium sputtered in hydrogen, prepared in the glow discharge, have the same structure as the pure metal, with continuously increasing lattice dimensions (up to $a = 3{\cdot}98$). Rosenhall[168] confirmed

the results of Linde and Borelius, and found a lattice constant of 4·11 for the hypothetical PdH by extrapolation. Mundt[169] studied the addition of H_2 to Pd-Au alloy, and found two phases, one at low, and the other at high concentrations of H, both being characterized by an increase in lattice dimensions. Hägg[102] reported on the Ti-H, Zr-H, V-H and Ta-H systems, and found in certain cases evidence of compound formation. ZrH_2 is analogous to ThC_2. The systems Pt-H[1] and Ni-H[1] have also been examined : in the latter case, the cubic lattice of Ni expands to an hexagonal formation. Müller and Bradley[1] investigated Wurtz's copper hydride, CuH (B4 type), and found the Cu atoms to be hexagonally close-packed, with $a = 2{\cdot}89$, $c = 4{\cdot}6$, $c/a = 1{\cdot}6$, the space occupied by hydrogen being about the same as in the case of the Pd-H alloys. In these cases therefore it appears that interstitial solid solution of hydrogen is accompanied by the additional effect of increase in lattice dimensions, as distinct from the case of Fe-N, where no increase in size of the unit cell occurs up to about 7%N.

21. The Mechanical Distortion of Crystal Structure

(A) **Cold Working of Metals.** Only a very brief account is attempted, with special reference to the use of X-rays. Considerable progress is due to improved methods of obtaining " single " crystals of metals.[122,123]

The earlier work is summarized by Korber.[124] Baker[125] showed that cylinders of Na and K contracted laterally when stretched giving an elliptical cross-section, with regular surface markings, suggesting the shearing of layers over one another. Andrade[126] obtained similar results with Sn, Pb and solid Hg. Taylor and Elam[127] in 1923 described some remarkable results on the distortion of a single crystal of Al. The work of Weissenberg[128,129] and Polanyi[130,131,132] showed that the stretching of metal wires is accompanied by movements in glide-planes and by rotations, which tend to set up a kind of fibrous structure having parallelism in the direction of extension. Further work[133,134,135] on mechanically treated Al, Ag, Cu, Au and Pt foils confirmed that a preferred orientation of the crystal

aggregates took place. The gliding is accompanied by fine folding in the glide-planes, a result which has been held to account for the increased hardness of cold-worked metals. Star-like figures may appear in the X-ray photographs, an effect known as " asterism."[166]

More recent work may be briefly noted. The effect of torsion on single crystals of Sb,[136] Zn[137] and Al[138] has been studied. Further work on the effect of various stresses on glide-planes,[139] on the fibrous structure of fractured single crystals[140] and the effect of drawing[141] of Al may be noted. The stretching of Cd and Zn crystals[142] and the arrangement of the micro-crystals in a bent tungsten wire[143] have also been examined using X-rays. Burgers[144] found, in drawn tungsten wires, that the lattice distortion is greatest on the surface, although deviations from the average distortion are not large. The X-ray method has been applied to the deformation of single and polycrystals of Cu[145] and of Cu, Al, Ni, Ag, Au and constantan.[146] The cold-working of Cu produces an irregular expansion of the lattice.[147] The rate of production of lattice distortion during cold-rolling has been followed using X-rays.[148]

X-ray studies on the mechanical deformation of alloys of Mg,[149] Cu-Ag[150] and steel[151] are reported. In a study on the X-rays reflected from a bent strip of duralumin,[152] it was found that the transverse contraction of the lattice spacing was proportional to the applied stress until " flow " began.

It is found that the X-ray line breadth is increased, both in cold-working and annealing Fe.[153,154] Broadening also occurs for Cu, Al, Zn, Mg, and electron alloy.[155] Regler[156] considered the two influences to be equivalent.

The mechanical treatment of metals may modify the X-rays reflected by them in widely different ways. Whilst surface treatment, such as grinding, may cause extinctions,[157] deformation in other cases may bring about increased intensities of reflection.[158,159]

(B) **Recrystallization after Distortion.** Wiest[160] has recorded that by deformation of a single crystal of Au-Ag alloy (75 atomic%Au) and recrystallization by heat, diminution

in the lattice constant from 4·0673 for the single crystal to 4·0645 for the polycrystalline material occurs. The recrystallization of Al[161] after deformation is not a random process, but an anisotropic orientation depending on the deformation applied. Crystals of Al[162] and Sn[162,163] may recrystallize and grow at the expense of deformed crystals, but only if not themselves deformed.

(C) **Inorganic Crystals.** Changes occurring in crystals of rock salt[164,165,166] and gypsum[165] on mechanical distortion have been followed using X-rays. The asterisms of deformed NaCl disappear on heating.[166] AgCl and AgBr,[167] when drawn into wires under pressures of 3,500 atmospheres, develop fibrous crystalline structure. The theory of secondary and mosaic structure in crystals arose out of experiments on the breaking stress of rock salt (see appendix to this Chapter).

22. Other Applications of X-rays

(A) **Non-metallic Solid Solutions.** The conditions governing the formation of solid solutions of inorganic salts were discussed by Grimm,[170] who found that, in cases where inert gas-like ions were present, isomorphous mixtures tended to be formed if the structural dimensions of components, as measured by the lattice constant, did not differ very greatly. Substances containing ions of argon and krypton type tended to form solid solutions, but not substances having helium and neon-like, or neon and argon-like ions. Grimm and Wagner[171] found that mixed crystals were formed between $BaSO_4$ and $KMnO_4$ up to 60% $KMnO_4$ molecules at 50°C., but Chlopin and Nitikin[172] regarded these mixtures as a transitional stage between solid solution and layer lattice structure. The conditions under which ionic crystals of AB type may form solid solutions when the ionic charges of like sign of the components are different has been discussed by Stranski.[173]

Mixed crystal formation has been studied between 44 pairs of organic substances containing CH_3, NH_2, OH and other groups.[174] It was found that solid solution did not always occur where it might be expected.

The mixed rhombic crystals of S and Se have been examined.[175]

CuI and AgI[176] were reported to form a continuous series of mixed crystals. This has since been confirmed.[177]

It was argued from the miscibility relations of $CaCl_2$[178] that it would be found not to have C19 type structure. This is now supported by experiment, $CaCl_2$ being found to be orthorhombic (see Cx type).

Vegard[179] first applied X-rays to the problem of the constitution of solid solutions of salts, in order to decide between the view of Retgers, who supposed them to consist of thin superposed laminæ of the components, and that of Tutton[188] and others, who had emphasized the importance of molecular volume in mixture formation, this alternative view being that substitution of atoms occurred in the same lattice with corresponding alteration in dimensions. Vegard proved the latter view to be correct, by showing that superposition of the spectra of the components did not occur unless they were mechanically mixed; when precipitated together, KCl and KBr gave new lines lying between those of the pure components, as shown by comparison of the powder spectrograms of pure KCl, pure KBr and the mixed crystals, proving that the structure of the mixture had dimensions lying between those of the components, substitution in one and the same lattice having produced this result. The additivity law of lattice parameters due to Vegard (this Vol.: 18) holds in the following cases:—CoO-MgO,[179] NiO-MgO,[179] CoO-NiO,[179] BaO-SrO,[180] KCl-KBr,[181] KBr-NH_4Br (up to 40% NH_4Br),[182] AgCl-AgBr,[183] CaF_2-SrF_2,[184] $Ba(NO_3)_2$-$Sr(NO_3)_2$,[185] $Ca(NO_3)_2$-$Sr(NO_3)_2$,[185] $Ba(NO_3)_2$-$Pb(NO_3)_2$[18] and the Ca-Sr-S mixed phosphors.[186] A few results are plotted in Figure L. The additivity law also applies for mixtures of solid CO_2 and N_2O.[187]

The general nature of the substitution process seems to be one of random distribution of substituent atoms and groups. Broomé[189] discussed the system NaCl-AgCl in this connection.

Havighurst, Mack and Blake[190] showed that small amounts of isomorphous impurities in ammonium and alkali metal halides produced negligible effects upon the lattice dimensions.

Photographic emulsions of AgBr containing small quantities of AgI are known to be " faster " than those of pure AgBr. Trivelli[191] advanced the view that this might be connected with the distortion set up by AgI entering the AgBr lattice, associated with strain and stretching of the lattice dimensions. Wilsey[183] found that the fused and cooled AgBr-AgI system contained two phases, one simple cubic with an enlarged lattice

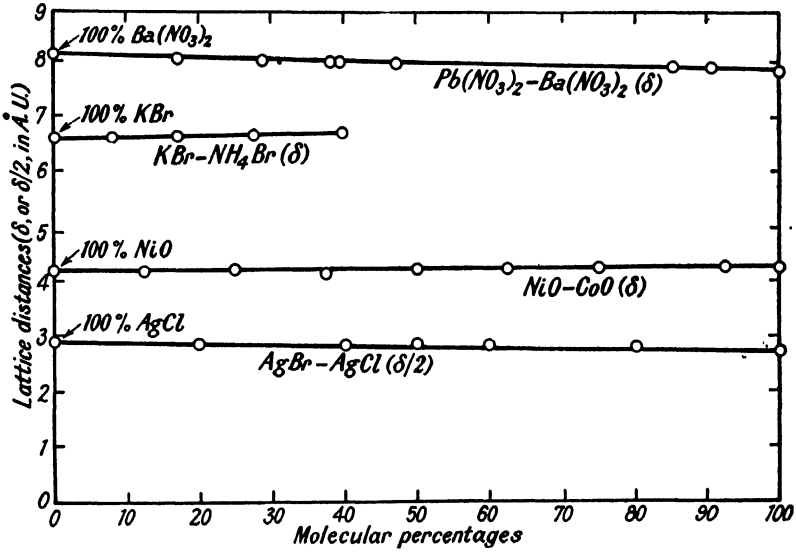

FIGURE L.—APPLICABILITY OF VEGARD'S LAW TO SOLID SOLUTIONS OF SALTS AND THE OXIDE SYSTEM, NiO-CoO.

spacing, and the other diamond cubic (B3 type). Up to 70% AgI, the simple deformed cubic lattice of AgBr (B1 type) predominates. Since the crystal structures of the two forms of AgI (B3 and B4) are different from that of AgBr, the explanation of the increased photographic speed of AgBr containing AgI seems reasonable. No explanation, however, appears to have been given of the way in which the enlargement of the lattice operates to give the observed effect. Where the type of structure is the same, as with AgCl-AgBr, the fused salts on cooling gave a continuous series of solid solutions in one phase (Figure L).

Mixed hydroxides precipitated from solution tend to give solid solutions so long as the cations do not differ too widely in radius[192]; thus $Ni(OH)_2$ gives solid solutions with $Mg(OH)_2$, $Zn(OH)_2$, $Co(OH)_2$, but two-phase mixtures with $Cd(OH)_2$ and $Ca(OH)_2$. It may also be noticed that Vegard found that NaBr would form no mixed crystals with NH_4Br, though KCl-NH_4Cl, KBr-NH_4Br, KI-NH_4I presented continuous isomorphous series.

(B) **Qualitative and Quantitative Chemical Analysis.** (a) *By Characteristic X-rays excited by Cathode Rays.* It is clear from the writings of H. J. G. Moseley that he envisaged the possible application of X-rays to chemical analysis. The first application appears to have been made by Hadding.[193] In 1922, Dauvillier announced the detection of the missing element for which $Z = 72$. Urbain thought it was a rare earth and suggested the name "celtium." Coster and v. Hevesy[194] obtained X-ray lines of the new element, which was shown to be a transition element and a congener of Zr, and suggested the name "hafnium." Other elements which have been discovered in this way are Ma, Re and Il. v. Hevesy and collaborators[195,196] applied the method of line intensity to the quantitative estimation of Hf in Zr and of Ta in Cb, placing the mixtures on the anticathode. The intensity of a line arising from a mixture is proportional to the number of atoms of the constituent element which have been excited. Eddy, Laby and Turner[197] developed the method, and improved its sensitivity. The accuracy was raised to from 0·1 to 1 part of metal per 10^6 parts of alloy; thus, for example, 1 part of Cu in 10^6 parts of Pb was detected.[198,199] The sensitiveness appears to be on the whole rather less for powdered mixtures than for alloys.[200] Fonda and Collins[201,202] used cathode rays passing through a window and falling upon the substance to generate X-rays, and obtained errors within 2% in analyses of Ta and Cb in Mo.

(b) *By Secondary X-Ray Emission.* When the substance forms the anticathode as in the above method, the heat change

may affect the concentration of metals in the surface layers. Coster and Nishina suggested the use of secondary X-rays excited by X-rays from a tube, the substance being placed outside it, in this way avoiding heating effects. Glocker and Schreiber[203,204] and v. Hevesy, Böhm and Faessler[205] used the method. The last-named workers provided tables of comparison elements which may suitably be added as calibrating media for any particular element.

(c) *By X-Ray Absorption Spectra.* Glocker and Frohnmayer[206] applied continuous absorption spectra and measurements on absorption edges to the analysis problem. Caglioti and Agostini[207] used the method to analyse mixtures of Al_2O_3 and NiO containing from 0·2 to 3·98%NiO. Voges[208] has discussed improvements whereby accuracy to within a few tenths of one per cent. may be obtained. Moxnes[209,210] has used X-ray line absorption.

(d) *General.* Nahmias[211] has proposed an analysis method, which he has applied to the estimation of quartz in artificial mixtures and in earths. Terrey and Barrett[212] used a method claimed to overcome difficulties arising in cases where one constituent of a mixture absorbs the radiation the other constituent emits. This work was afterwards critically examined by Eddy and Laby.[213] Calvert [214] applied X-rays to the determination of K in the soil and v. Hevesy and Hobbie[222] to that of minute quantities of Mo and W in igneous rocks. Convenient summaries are due to Laby[215] and v. Hevesy.[216]

The X-ray method has proved its usefulness in the discovery of new elements, and in the rapid detection of minute quantities of impurities in substances which would be difficult to examine chemically. Advantages are: (1) the possibility of working with very small quantities of available material; (2) the fact that the material is unchanged after examination. However, chemical methods have not been ousted by the physical developments, which are not always applicable and involve special technique and often elaborate apparatus.

(C) **Determination of Particle Size and Arrangement.** An excellent summary of the X-ray determination of particle size is due to Mayer.[217] According to Cameron,[218] only the relative values of particle size so far obtained are reliable. Aborn and Davidson[219] have stressed the importance of size distribution, in connection with silica particles. The arrangements of micro-crystals of Cu,[220] Au[220] and Mo[221] deposited in electrolysis have been examined. Fonda[223] has found that the intensity of a diffracted X-ray may be decreased by irregularities on the surface of the target; Wood[232] observed that the intensity from chromium-plated wires varied with the conditions of electro-deposition, hence attention must be paid to the fineness of division of powdered specimens for analysis.

(D) **Further Applications of X-rays.** X-rays may be used in the rapid determination of lead tetraethyl in petrol.[224] Fire-boxes and boilers may be conveniently examined by X-rays: high voltage tubes can be used to detect flaws in thick masses of iron.[225] Genuine and artificial pearls may be distinguished by the powder method: genuine pearls give hexagonal, and artificial pearls fourfold symmetry.[226] In Britain, the chief application of X-rays is in medicine, a review of recent progress in which has been supplied by Anderson.[227]

In the laboratory, X-rays may in certain cases be used in density measurements.[228] X-rays may also promote chemical reactions: for example, the reduction of $K_2Cr_2O_7$ in presence of sulphuric acid. It is found in this case that the action is associated with intermediate formation of H_2O_2.[229] X-ray analysis has also thrown light on the relation between structure and chromoisomerism.[230]

Certain cases where difficulties of interpretation of X-ray results have arisen are noted elsewhere (this Vol.: 12, end).

The article by W. L. Bragg[231] on the architecture of the solid state may be consulted for further information.

APPENDIX TO CHAPTER VIII.

MOSAIC AND SECONDARY STRUCTURE

The mosaic theory of crystal structure is introduced in Vol. I : 21C, where the views of Smekal, Zwicky and Goetz are briefly explained. Smekal's theory [233] was based upon the fact that the breaking stress of rock salt was much less than that calculated : moreover, the crystals showed electrical breakdown for voltages less than theory anticipated. The theory involved the conception of small mosaic blocks of the order of 100 Å.U. width. Smekal rejected the theory that his unit blocks were the same as the " sub-microns " of v. Behren and Traube,[234,235] on account of the larger size of these particles. The submicrons were aggregates left behind after some solution of a crystal had taken place. Asterism, noted in the present chapter, was also regarded as favouring a mosaic theory. Zwicky[236] took up the idea, and formed the conception of surface cracks, which he afterwards extended to the interior of a crystal, giving mosaic structure (M.S.). A secondary structure (S.S.)[237] was also postulated, in which every nth plane of a lattice was peopled by a greater number of atoms than intermediate planes. Zwicky discussed S.S. in relation to electric moments in crystals[238] and the measurement of X-ray wave lengths.[240] Goetz[239,241] adduced evidence of crystalline units in melted bismuth, and found surface markings attributed to mosaic structure on etched single bismuth crystals.[242] With Hergenrother,[243] he studied the influence of magnetic fields on single bismuth crystals, and also found a difference between the thermal expansion of bismuth, as measured by X-rays and optical methods, as further evidence in favour of Zwicky's theory. The observation on thermal expansion is contradicted by Jay.[244] The oldest and best evidence of some sort of M.S., however, comes from the spreading out of reflected X-ray beams from crystals, studied by Darwin.[245] See also [246,247,248] and this Vol. : p. 211. Evjen[248] considered that S.S. might account for the stability of many ionic crystals. On the other hand, Zwicky's theory has been adversely criticized by Orowan,[250] Canfield,[251] Buckley[252] and Buerger,[253] who suggests a " lineage structure " of crystals,[254] according to which minute branched " cracks " spread outwards from the interior of a crystal. The structure is continuously interconnected, but distorted, so that the interlineage boundaries constitute discontinuities. Convenient summaries of M.S. and S.S. structure are provided by Zwicky,[255,256,257] Blank[258] and Goetz.[239]

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(*A list of abbreviations used in references will be found on pages* xxxi *et seq.*)

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CHAPTER IX

CRYSTAL STRUCTURE AND MOLECULAR CONSTITUTION

23. The Classification of Crystals

THERE are two leading ways in which the classification of crystals may be attempted. The first is from the standpoint of the X-ray crystallographer, into space-groups and types of unit cells, as described in foregoing chapters; the second is designed to take account of the general property relations existing between crystals, and forms the main subject of the present chapter. The relation between crystal structure and chemical constitution was discussed under the auspices of the Faraday Society in March, 1929, the opening paper being read by Goldschmidt.[1]

Although a close relation exists between structure and behaviour, it is clear that the two methods of classification may not always lead to the same results. Not only may the purely structural method place together crystals which are chemically unlike (*e.g.*, KBr and TiN, B1 type), but also it may separate substances closely related in properties (*e.g.*, ZnF_2, C4 type, and CdF_2, C1 type). Moreover, K_2PtCl_6 resembles CaF_2 in structure, K replacing F and the complex ion $PtCl_6$ replacing Ca, without any corresponding similarity in properties; the intermetallic compound SbSn has NaCl (B1 type) structure; and similarly in other cases. Further classification is here attempted, based upon physico-chemical behaviour.

von Antropoff,[2] utilizing suggestions made by Grimm, divided crystals into the following four groups: (1) *Metallic*, (2) *Adamantine*, (3) *Ionic*, and (4) *Molecular*. The element C can, in fact, form molecules belonging to each group, as in

Fe_3C; SiC, Na_4C, H_4C respectively. A careful comparison of compounds shows, however, that although certain compounds belong definitely to one or other of these groups, others occupy intermediate positions, and the line of demarcation is not sharply drawn. The forces holding the crystals together in the four types mentioned may be considered to be :—(1) Metallic, between positive metallic ions and electron "gas"; (2) Adamantine, homopolar linkages ("shared" electrons); (3) Ionic, between oppositely charged ions; (4) Molecular, van der Waals' force between molecules (associated with polarization). In connection with case (4), the forces within molecules may be different from the forces between them, and may be homopolar (as in the paraffins) or attraction between ion and permanent dipole (as in the co-ordination compounds); the effective result in either case being the setting up of the "covalent" link found in Type (2). Disregarding this last consideration for the moment, and treating the molecules of Type (4) as units independently of their inner constitution, it is clear that four kinds of linkages between the units in crystals may be recognized as belonging to the four types :—(1) *metallic*; (2) *covalent*; (3) *electrovalent*; (4) *van der Waals*. These linkages may, however, be combined in the same crystal. Thus, in the *layer* lattices, the forces within the layers may be (2), as in graphite, or (3), as in CdI_2; whilst the forces between layers may be grouped under (4). In the *radical-ion* lattices as in $CaCO_3$, and in the *complex-ion* lattices, as in K_4PtCl_6, the forces within the polyatomic groups must be classified under (2), and those between these groups and their oppositely charged partners under (3). The *metalloidal* group (containing FeS_2 and NiAs) may have linkages of Types (1), (2) or (3). Not only may different types of linkage be combined in the same crystal, but also types intermediate between them may occur; thus if the two forms of ZnS are classified as adamantine, it seems reasonable to suppose that the linkages are at any rate partly ionic, and may be described as highly-polarized ionic. The fact that the gradation between the electrovalent and covalent linkage is continuous with intermediate states of "semi-polarity" allows for the existence of such states. In the *silicate* lattices,

as in beryl, whilst electrons of oxygen atoms of SiO_4 groups are shared, the oxygen and silicon atoms appear nevertheless as incompletely ionized, the oxygen atoms having about 9 electrons and the silicons 12, complete ionization requiring 10 each.[33] Taylor[3] has discussed the structure of the SO_4 group, and has shown that whilst chemical evidence suggests that the linkages between S and O are semi-polar, calculations from infra-red spectra have been based upon the assumption of complete ionization, and the mechanical interactions between the atoms can be adequately described by an ionic model. The shared

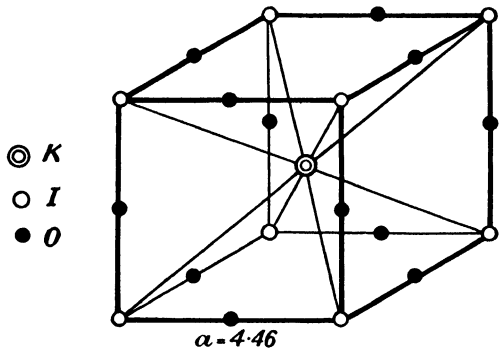


FIGURE LI.—STRUCTURE OF POTASSIUM IODATE (Perowskite $CaTiO_3$ type).

electrons appear to be more effective in screening the oxygen atoms than in screening the central atom of the group, so that, in a mechanical disturbance such as is involved in infra-red vibration frequencies, the binding is " approximately electrostatic." Such considerations illustrate the difficulty which often exists in assigning particular linkages to any one of the four named classes. In the " honeycomb " lattices (Wabengitter), described by Reis,[4] the negative groups are held together by covalent links in a continuous framework throughout the structure, the positive ions fitting into the gaps between, somewhat as in the ideal silicate structures (where no deformation of oxygen close-packing occurs on account of the presence of interstitial positive ions). An example of a honeycomb lattice is provided by KIO_3, of the perowskite type (Table

XVIII and Figure LI). Each iodine atom has 6 oxygens arranged octahedrally about it, and a potassium atom lies in the space between 8 iodate groups, and has 12 oxygen neighbours.

Further suggestions concerning the classification of crystals are made in papers by Reis,[4] Huggins,[5] Ewald,[6] Weissenberg,[7] Goldschmidt,[1,8] Fajans,[9] Grimm,[10] and Steele and Davey.[34]

24. Leading Characteristics of Crystal Types

(A) **Metallic Crystals.** The generally accepted constitution of metals is that of positive ions in an " electron gas," the attraction being responsible for their cohesion. The *melting points* and *boiling points* vary over a wide range, and tend to be widely separated, so that there is a long liquid interval. The crystals are *opaque* to light, and are *good conductors* of heat and electricity and, especially in the case of the alkali metals, show the *photoelectric effect.* Metal alloys are characterized by the property of forming what may be regarded from one point of view as *solid solutions* with the components. When subjected to *stress*, metals yield along their glide-planes. Their *hardness* is attributed to the attraction between positive ions and electron gas. The elements of transition series appear to be harder than the corresponding inert-gas ion formers of the same valency, possibly associated with superimposed magnetic forces. Hardness is often increased by alloying.

The *metalloidal group* of crystals includes compounds of metallic atoms with elements of sulphur and arsenic type. The binding may be homopolar, metallic or ionic. The *opaque* substances of the group tend to resemble metals ; those which are *transparent* to light tend to have high molecular refraction, and are usually *coloured.* Many oxides, sulphides and selenides show *photoelectric conductivity*, and appear thus as related to metals.[11] Other substances showing this amongst the elements are diamond, sulphur, red selenium and iodine. The last-named case is of interest in its relation to metals, in possessing metallic lustre, and, like a metal, having in the liquid state *negative temperature coefficient of electrical conductivity* (see Vol. I : 20C).

An outline of the work of Goetz and others on the possible mosaic structure of a single Bi crystal is in this Vol. : Chapter VIII, Appendix.

(B) **Adamantine Crystals.** The structure of diamond may be represented in two dimensions as in Figure LII. Each carbon atom has four covalent links with surrounding atoms. Similar figures may be drawn for CSi, AlN and ZnS, and provide examples of " atom-lattices," of perfectly continuous structure throughout the framework. The linkages are homopolar, or at

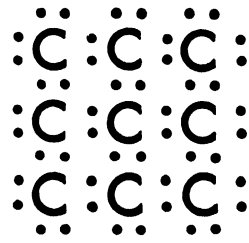


FIGURE LII.—ADAMANTINE DIAMOND LATTICE IN TWO DIMENSIONS.

least highly-polarized ionic, and are formed between elements of the carbon group of the periodic classification, and between an element of a group whose characteristic positive valency is n less than carbon with an element of valency n more than carbon, where $n = 1, 2$ or 3. The molecule is lost in the continuity of the framework.

The diamond-like crystals, if *opaque*, show metalloidal characteristics, and, if *transparent*, have high molecular refraction. The diamond is almost perfectly *non-conducting* to electricity, whilst other members of the group show medium to bad conductivity. The adamantine crystals are *insoluble in water :* if they dissolve in acids, they tend to do so with decomposition. They are very *infusible*, the melting points being high, and are characterized by great *hardness*, especially when composed of fourth group elements only. The metalloidal members are not so hard, where the linkage is in part ionic. The hardness characteristic of diamond and CSi is associated with the stability of the lattice, due to homopolar linkages

symmetrically disposed in space. The arrangement is more open than in close-packed metallic systems, and hence the *specific gravities* of members of the group tend to be lower than for comparable metals.

Graphite provides an example of an adamantine lattice in two dimensions. The forces holding atoms together in the layers are stronger than those between layers, leading to a *plane of cleavage*, and variations of *electrical conductivity* in different directions. Substances which are difficult to volatilize are usually very hard, but graphite in bulk is associated with *softness* and *high melting point*, the former due to the plane of cleavage, and the latter to the strong homopolar forces in the layers. Similar phenomena are observable in *radical-ion lattices*, as in $CaCO_3$. The links binding C to O within the CO_3 group are stronger than those uniting Ca to CO_3, but the strength of an atomic or ionic framework is no greater than that of its weakest link, so the *hardness of calcite* depends upon the weaker ionic linkage, which also gives rise to the *planes of cleavage*. It seems legitimate to consider such cases here, since the linkages within the complex group are at least comparable with those in graphite layers and in diamond. *Honeycomb lattices* of the salts of oxy-acids, silicates, phosphates and arsenates are generally hard. In the *silicate lattices*, the hardness depends on the strength of the Si-O linkage, which is evidently strong, as is shown by the *hardness of quartz*. In these cases of anion-lattices, there are no single anions, just as there are no molecules in the SiC crystals. The anions form a continuous framework with cations interspersed here and there in the interstices. The cations hardly affect the structural dimensions unless they are large, as is the case with Mg^{++} and Fe^{++}. The silicate lattices tend to be *insoluble, hard*, and to have *high melting points*.

(C) **Ionic Crystals.** In ideal ionic crystals, the binding force is electrostatic, and arises from the attraction set up between the oppositely charged ions formed from neutral atoms by the transference of one or more electrons from the metallic to the non-metallic atoms. It is impossible, however,

as previously mentioned, to allocate positively-charged ions to negative partners, the molecule being lost in the symmetry of the crystal. The crystals are *transparent* to light, and, where the ions of low nuclear charge are concerned, are *colourless*. Colour, if present, may be associated with the presence of certain ions, and is often caused by the deforming action of molecules of water of crystallization; thus Cu^{++} is colourless, whilst $Cu(H_2O)_4^{++}$ is blue. Ionic crystals are usually moderately good *insulators* of electricity, and have considerable *hardness*,[12] which increases with decreasing distance between oppositely-charged ions and with increasing ionic charges, which factors are associated with increasing " lattice energy." The *melting points* are high, especially when bivalent ions are present, as in the case of MgO. The *solubilities in water* are greater where univalent ions are concerned than where bivalent ions are present. The general behaviour of ionic crystals conforms with the view that their stability depends on the strength of the electrostatic attractions between oppositely-charged ions, as illustrated by their behaviour towards heat and solvents.

Ionic linkages are also present in other crystals not of purely ionic type. Thus, in *layer lattices* like CdI_2, the linkages in the layers are ionic, and between the layers of the molecular type. In the various cases of *complex-ion* (as with $CaCO_3$) and *radical-ion lattices* (as with K_2PtCl_6) the linkages between the cation and anion are ionic. The linkages within the groups holding them together may be electrovalent or covalent, or may have intermediate character, which may be described as highly-polarized ionic. In the layer lattices also, the linkages in the layers may be covalent, as in the case of graphite.

In the ionic layer lattices, the anion is usually larger than the cation and more polarizable. In *optical properties*, the crystals of this group tend to behave like the adamantine crystals; in *electrical* and *thermal* properties, like the adamantine or molecular crystals. The crystals are characterized by *softness*, *flexibility* and easy *cleavage* between the layers, as already noticed in the case of graphite. The forces in the layers are evidently stronger than those between layers.

The distinction between the electrovalent and covalent types of linkage is only sharp in typical cases. In many cases which are of an intermediate character, it is often difficult to decide to which class they should be assigned, as already noticed in the case of the S-O link in the SO_4 group. Compounds of the type AB may be classified as ionic and homopolar, corresponding to the face- or cube-centred lattices or the diamond or wurtzite lattices respectively.[13] In BeO, transference of electrons from cation to anion seems to occur at least partially, though definite charges cannot be assigned to the individual parts, Ott and others having decided against the presence of Be^{++} and O^{--} ions from measurements of X-ray reflection intensities. The tendency towards ion formation decreases as elements towards the centre of the periodic table are involved; thus SiC is non-polar. The *infra-red characteristic frequencies* can be calculated as vibration frequencies for typically ionic structures like NaCl on the assumption that the building units are ions; but it is noteworthy that the same is true of structures of the ZnS (wurtzite) type, showing clearly that the difference is not absolute, but rather a matter of gradation.[8]

The older conception[14] of inert gas-like ions having cubic shapes is now replaced by the idea of a continuous distribution of electric charge density from the nucleus outwards. The atomic domain is infinite, but the electric density is mainly within a few Å.U. of the nuclear centre. The curves of Havighurst[15] (Figure LIIIa) for Na^+ and Cl^- show humps corresponding to the K, L (and M) rings. Figure LIIIb, due to Brindley,[16] shows the distribution along the line of centres of Na^+ and Cl^- in a rock salt crystal. The construction of these curves, the theory of X-ray scattering and of atomic structure factors is noticed in the Appendix to Part I of this volume.

The presence of *pyro-* and *piezo-electric* phenomena (development of conductivity by heat or pressure respectively) often provides information as to the symmetry properties of charge distribution in crystals, and is generally associated with some lack of symmetrical distribution. Thus the absence of these effects in diamond indicates that complete electron transfer from one atom to another does not occur.

The *molecular refraction* of crystals is treated in Chapter XII. It may be noted here that this increases with their mechanical

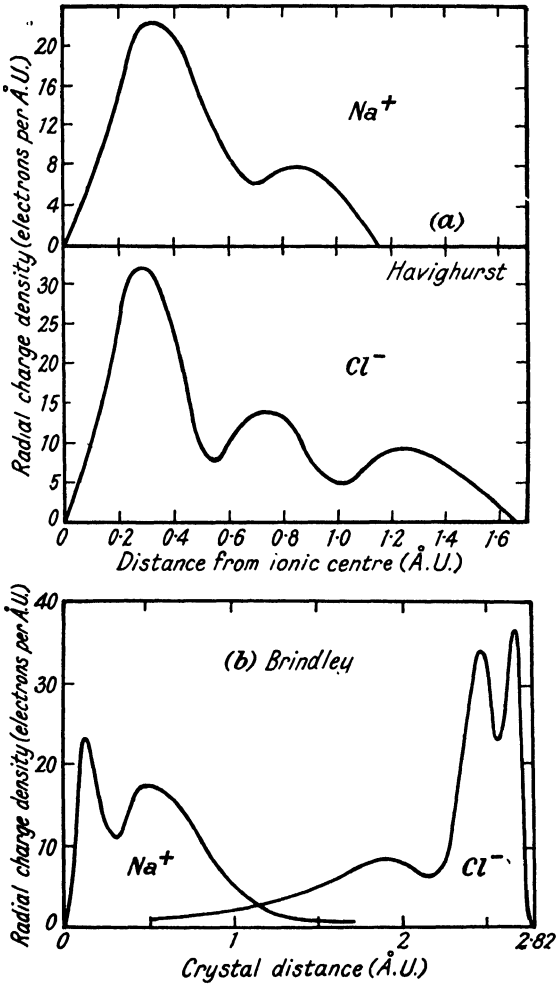


FIGURE LIII, a AND b.—ELECTRON DISTRIBUTION CURVES FOR Na^+ and Cl^-.

and thermal stability, as the lattice energies increase with decreasing distance between ions and increasing charges; thus there is an increase in molecular refraction between LiF and

MgO, BeO and Diamond (CC), CuCl and ZnS, $RbBF_4$ and $BaSO_4$. The *lattice energies* of polar crystals and their *potential constants* are dealt with in Vol. 4 of the present series. The *Raman effect* in the case of crystals is considered in Vol. 3, Chapter XI, dealing with spectroscopic results. The theoretical deduction of the observed parameters of crystals of argon, KCl, CaS, $CaCO_3$ and other carbonates, rutile, potassium chlorostannate and solid CO_2 by Lennard-Jones and Miss Dent[17,18] by means of " intrinsic repulsive forces " may also be noted (see Vol. 1 : 33). Molecular fields are considered in this vol. : Chapter XIV.

(D) **Molecular Crystals.** Examples of this type are provided by the solid inert gases, solid CO_2 and HCl, ice, calomel Hg_2Cl_2, the paraffins and most organic compounds, where the forces between molecules are the van der Waals' fields between permanent or induced dipoles. The forces within the molecules may be described as polar (solid HCl) or homo-polar (solid H_2 or N_2). It is a general feature of molecular crystals that the forces between and within molecules are different in nature, the former being weaker than the latter. Molecular crystals are generally optically *transparent.* The relatively weak forces between molecules lead to lack of resistance to thermal or mechanical treatment, so that the crystals tend to have *low melting points* and to be *soft.*[12] The organic compounds containing the polar groups OH, COOH and CN are generally harder than the corresponding hydrocarbons, on account of the increased forces between molecules due to attractions between the polar radicals. Molecular crystals tend to have *high compressibilities* and *low heats of sublimation.*

In *layer lattices,* the layers may be regarded as vast molecules held together by molecular forces. *Cellulose* provides an example of sets of covalent linkages in one dimension, so that each rod behaves as a single molecule highly polymerized. The forces between the chains are molecular, and weaker than those within them.

Solid HCl evidently differs very greatly from a typical polar salt, the linkages within molecules being only partly ionic, and

between molecules, molecular. The same is probably true of solid CO_2, and possibly also of LiI.[19] In solid argon, the cohesion must be accounted for entirely by molecular forces. The probable origin of the molecular, or van der Waals' force, is discussed in this Vol. : 45.

Goldschmidt[8] has classified the crystal properties determining the kinds of linkages present as follows :—(1) The *geometric arrangements* of the units, leading to the presence or absence of molecules ; (2) The *distances between atom centres ;* (3) The *strengths of linkages* as evidenced by resistance to thermal or mechanical treatment ; (4) The *electrical and optical behaviour* of crystals. Some account has been given in the present section of the way in which these factors appear to operate, leading to the presence of the kinds of linkage described.

25. The Factors affecting Crystal Structure

It has been stated that the classification of crystals according to linkages is often different from that according to the crystal types revealed by X-ray work, the former determining crystal properties. The question of the factors which appear to determine in what way a substance shall crystallize has been considered by Goldschmidt,[8] who gives the following three influence factors, which will be briefly considered here : (A) The *number of atoms in the molecule* ; (B) The *sizes* of the units ; (C) The *polarizabilities* of the units.

(A) **The Number of Atoms in the Molecule.** The influence of this factor is seen by comparison of the crystal types of compounds AB and AB_2, as previously given. The different *Mengenverhältnis* of NaCl, consisting of a mixture of sodium and chlorine ions in equal numbers, as compared with CaF_2, necessitates a different structural arrangement. It is clear, however, that this factor does not alone decide the structure. Compounds of a given molecular type may be further subdivided according to the " co-ordination numbers " (numbers of nearest neighbours) of the units concerned. Table XXIX shows the co-ordination numbers (C.N.) corresponding to

different crystal types for compounds of molecular formulæ AB and AB_2. Thus, the ions of both kinds in rock salt are said to have co-ordination numbers of 6, whilst those in fluorspar have 8 (cations) and 4 (anions).

TABLE XXIX.—CO-ORDINATION NUMBERS OF UNITS IN CRYSTALS OF MOLECULAR TYPES AB AND AB_2.

Compounds AB			Compounds AB_2		
Crystal Type	Type Substance	C.N.	Crystal Type	Type Substance	C.N.
B12	BN	3	C8	SiO_2 (Quartz)	2 and 4
A9	CC (Graphite)	3	C10	SiO_2 (β-Tridymite)	2 and 4
A4	CC (Diamond)	4	C9	SiO_2 (β-Cristobalite)	2 and 4
B4	ZnS (Wurtzite)	4	C3	Cu_2O	2 and 4
B3	ZnS (Zinc Blende)	4	C5	TiO_2 (Anatase)	3 and 6
B1	NaCl	6	C4	TiO_2 (Rutile)	3 and 6
B8	NiAs	6	C6	CdI_2	3 and 6
B2	CsCl	8	C7	MoS_2	3 and 6
			C1	CaF_2	4 and 8

Other factors are evidently concerned in deciding the particular degree of co-ordination of any particular atom or ion belonging to a given molecular type, prominent amongst which is the ratio between the sizes of anion and cation in polar crystals (*Grössenverhältnis*), considered in the following subsection.

(B) **The Sizes of the Crystal Units.** Goldschmidt[1] has collected together information concerning atomic and ionic radii deduced from a study of crystals, together with results obtained theoretically by Pauling, and has also discussed the influence of size upon the way in which a substance crystallizes. It may be noted that the numbers given in Table XXVI are deduced from a study of metals and alloys, and the values

obtained are different from those for corresponding ions in crystalline compounds, and that these numbers, for co-ordination number 12, are reduced if the state of co-ordination is lowered. Thus Ge (C.N. = 12) has $r = 1{\cdot}39$, Ge (C.N. = 8) 1·34, Ge (C.N. = 4) 1·22, whilst the ion Ge^{++++} has $r = 0{\cdot}44$ Å.U. (C.N. = 6). Similarly, Sn has $r = 1{\cdot}58$, 1·53, 1·40 for C.N. = 12, 8, 4 respectively, whilst Sn^{++++} has $r = 0{\cdot}74$ Å.U. for C.N. = 6. The radii of ions of the same atom vary with valency, and contract as the positive valency increases, the nuclear charge becoming more effective as the ratio of its charge to that of the extranuclear electrons increases. In Table XXX, some results are collected together showing the influence on atomic domain of variable valency in ions.

TABLE XXX.—INFLUENCE OF VALENCY ON IONIC RADIUS IN CRYSTALS (Å.U.).

(*Z* gives the nuclear charge of an ion, and *z* the number of extranuclear electrons.)

Ion	*Z*	*z*	*r*	Ion	*Z*	*z*	*r*	Ion	*Z*	*z*	*r*
S^{--}	16	18	1·74	Mn^{++}	25	23	0·91	Te^{--}	52	54	2·11
S^{++++++}	16	10	0·34	Mn^{+++}	25	22	0·70	Te^{++++}	52	48	0·89
Fe^{++}	26	24	0·83	Mn^{++++}	25	21	0·52	Pr^{+++}	59	56	1·16
Fe^{+++}	26	23	0·67	Se^{--}	34	36	1·91	Pr^{++++}	59	55	1·00
V^{+++}	23	20	0·65	Se^{++++++}	34	28	0·35	Tl^{+}	81	80	1·49
V^{++++}	23	19	0·61	Ce^{+++}	58	55	1·18	Tl^{+++}	81	78	1·05
V^{+++++}	23	18	(0·4)	Ce^{++++}	58	54	1·02				

Ionic radius in crystals varies to an approximately constant extent with changes in degree of co-ordination. Goldschmidt's scheme is shown on page 196. It is seen that the variations are small compared with the distances involved, but it is noteworthy that there are regular and appreciable deviations from strict additivity as the co-ordination number changes. If, however, crystals of the same type are compared, the

small departures from additivity may be neglected to a first approximation. Goldschmidt gives a table for ions of inert gas type strictly applicable to C.N. = 6. These numbers are used in the following discussion.

Transition	Change in C.N.	Decrease in Atomic Distance
CsCl type to NaCl type	8 to 6	3 per cent.
NaCl type to ZnS type	6 to 4	5 to 8 per cent.
CaF_2 type to TiO_2 type (rutile)	8, 4 to 6, 3	3 per cent.

It is found that certain remarkable variations in crystal structure in compounds of the same chemical type may be accounted for on the basis of changes in ratio between cationic

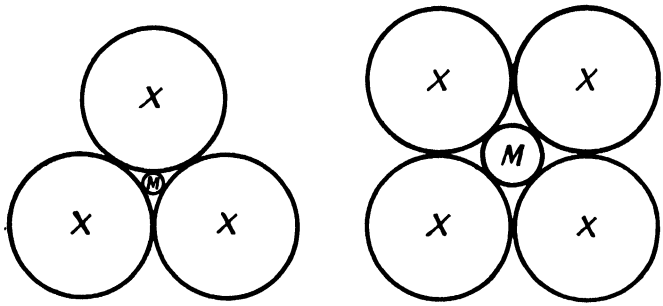


FIGURE LIV.—ARRANGEMENT OF ANIONS X ROUND A METAL ATOM M.

and anionic radius. The hypothesis is made that anions and cations are in mutual contact, and it then becomes a matter of pure geometry to decide the limiting ratios for different degrees of co-ordination. The principle may be understood by reference to Figure LIV, where M represents a cation surrounded by anions X equal in number to the C.N. It is not difficult to prove that an arrangement of three circles X around M is only possible if the radius ratio $r_M : r_X$ exceeds 0·15, and of four circles

if it exceeds the lower limit 0·22. In the case of four anions X, it is clear that if the radius ratio were less than 0·22, the central ion would not touch the outer ions, and hence for contact a lower degree of co-ordination would be necessary. Figure LIV shows the limiting case where the anions are also in contact; this condition is naturally in general not satisfied. Table XXXI gives the limiting ratios for different degrees of co-ordination, space arrangements being assumed, first calculated by Magnus.[20]

TABLE XXXI.—LIMITING RATIOS OF IONIC RADIUS FOR DIFFERING CO-ORDINATION NUMBERS.

Number of Ions X surrounding a central Ion M = Co-ordination Number of M	Arrangement of the X Ions	(Lower) Limiting Ratio $r_M : r_X$
3	Equilateral Triangle	0·15 = $(\frac{2}{\sqrt{3}} - 1)$
4	Regular Tetrahedron	0·22 = $(\sqrt{\frac{8}{3}} - 1)$
6	Regular Octahedron	0·41 = $(\sqrt{2} - 1)$
8	Cube	0·73 = $(\sqrt{3} - 1)$

. Simple proofs of the correctness of the ratios given in Table XXXI are in the Appendix to the present chapter. Table XXXII gives the application to two series of compounds of Type AB and AB_2 respectively.

In the first series shown in Table XXXII, MgO to MgTe, MgTe alone crystallizes like wurtzite, the other members having the NaCl structure, the radius ratio for MgTe being 0·37, less than that required for C.N. = 6 (0·41), but greater than 0·22, the lower limit for C.N. = 4. The noteworthy change in crystal habit in the series is thus accounted for. Similarly, in the second series, MgF_2 to BaF_2, MgF_2 crystallizes like rutile, the other members like fluorspar. The radius ratio for MgF_2 of 0·59 falls below 0·73 required for C.N. = 8 (corresponding to

the co-ordination of anions round cations in fluorspar crystals) but lies above the limit 0·41 for C.N. = 6; hence the rutile arrangement is possible where the cations have this degree of co-ordination. The radii values used are for C.N. = 6, but the variations from additivity are generally small where commensurable crystals are compared: thus the distance between Mg-F is 2·00 in $KMgF_3$ and 1·99 in MgF_2. Moreover,

TABLE XXXII.—CHANGE OF CRYSTAL FORM WITH CHANGING IONIC RADIUS RATIOS.

Compound	Crystal Type	C.N. of M	Lower Limit of r_M r_X for C.N.	r_M (C.N. = 6)	r_X (C.N. = 6)	$r_M : r_X$ found
MgO	NaCl (B_1)	6	0·41	0·78	1·32	0·59
MgS	NaCl (B_1)	6	0·41	0·78	1·74	0·49
MgSe	NaCl (B_1)	6	0·41	0·78	1·91	0·41
MgTe	ZnS (B_4)	4	0·22	0·78	2·11	*0·37*
MgF_2	TiO_2 (C_4)	6	0·41	0·78	1·33	*0·59*
CaF_2	CaF_2 (C_1)	8	0·73	1·06	1·33	0·80
SrF_2	CaF_2 (C_1)	8	0·73	1·27	1·33	0·95
BaF_2	CaF_2 (C_1)	8	0·73	1·43	1·33	1·08

the change in degree of co-ordination from CaF_2 to rutile type only results in a decrease of 3% in interatomic distance, so that the radius ratios are little affected.

Explanations similar to the above have been found in other cases. Of 12 bivalent fluorides, six whose radius ratio is below 0·73 crystallize like rutile (M = Mg, Ni, Co, Fe, Zn, Mn), and six whose ratio lies above this value have the fluorspar structure (M = Cd, Ca, Hg, Sr, Pb, Ba). Of 17 compounds of the type MO_2, 12 having a radius ratio less than about 0·7 crystallize

like rutile, whilst five having a higher series of ratios adopt the fluorspar structure.[1] The influence of ionic size is thus clearly seen, though the fact that the results are only approximately true and not quite general should be noted. Considerations based on limiting radius ratios appear to apply best when ions of the inert gas type are involved, where it seems possible to postulate the presence of charged and incompressible spheres with sufficient approximation to reality.

In the case of structures of the diamond-zinc blende-wurtzite types, the sum of radii seems to be more important than the individual radii or their ratio. Constancy occurs in series, as illustrated by Table XXXIII taken from Goldschmidt's paper.

TABLE XXXIII.—ATOMIC DISTANCES IN DIAMOND-LIKE COMPOUNDS.

Compound	Z_M	Z_X	Distance M–X	Compound	Z_M	Z_X	Distance M–X
SnSn	50	50	2·79	GeGe	32	32	2·43
InSb	49	51	2·79	GaAs	31	33	2·44
CdTe	48	52	2·80	ZnSe	30	34	2·45
AgI	47	53	2·81	CuBr	29	35	2·46

As explained in Vol. I : 19C, Pauling derived a set of ionic radii, based on the conception that calculation of the radii which ions would have if they were univalent might be expected to provide comparable numbers in which the effect of varying valency would be largely eliminated. More recently, this author has shown[21] that the radius ratios obtained from these numbers for a large number of ions lead to the observed co-ordination numbers, using the limiting ratios of Table XXXI.

Goldschmidt[1] has also discussed the transition from ionic to metalloidal crystals of the nickel arsenide type, which are characterized by opacity, electrical conductivity and the property of forming solid solutions with their constituents,

resembling metals in these respects. Thus MnO, MnS and MnSe have NaCl structure, whilst MnTe crystallizes like NiAs. Other examples will be found in Table XI. The nickel arsenide structures occur for transition elements linked with S, Se, Te, As, Sb. The tendency towards formation of this crystal type is linked with (1) increasing radius of the " metalloid " atom, and decreasing electron affinity; (2) decreasing radius and increasing ionization potential of the metallic atom; (3) the presence of an atom having incomplete levels in the " M " shell of electrons.

In ionic crystals, the distances between ions is reduced as their charges increase; thus Na^+F^- has semi-lattice distance 2·31, $Mg^{++}O^{--}$ 2·10; K^+Cl^- 3·14, Ca^{++} S^{--} 2·84 Å.U. This does not occur with change of valency in the case of diamond-like crystals, as Table XXXIII shows, but here purely ionic linkages are not involved.

The existence of a limiting radius ratio in the formation of interstitial compounds is discussed by Hägg (see this vol.: 20A).

Reis and Friederich have investigated *the hardness of crystals*, and some of their results have been noted.[12] The semi-lattice distances *d* of a number of comparable compounds together with numbers representing their hardness are given in Table XXXIV.

In the series MgO-BaO, hardness decreases with increasing distance of separation of the charges, which weakens the electrostatic attractions between oppositely-charged ions. For a similar reason, hardness increases in the series NaF to TiC, the increased charges of the ions being responsible for the increase from NaF to MgO, whilst ScN and TiC are not pure ionic structures; but the fact that hardness increases with increasing valency even in non-ionic structures is shown in the series CuBr to GeGe, where the interatomic distances do not increase. Friederich has given an ingenious explanation of this observation, by showing that although very strong links are present in CuBr, very weak links are also present, and the stability of the structure is naturally determined by its weakest links. Adopting the scheme of representation of Figure LII in the case of

TABLE XXXIV.—SEMI-LATTICE DISTANCES AND HARDNESS OF CRYSTALS.

Compound	MgO	CaO	SrO	BaO	NaF	MgO	ScN	TiC
d	2·10	2·40	2·57	2·77	2·31	2·10	2·23	2·23
Hardness (Ritz)	6·5	4·5	3·5	3·3	3·2	6·5	7–8	8–9

Compound	CuBr	ZnSe	GaAs	GeGe	Metal	Be	Mg	Ca
d	2·46	2·45	2·44	2·43	*d*	2·26	3·20	3·93
Hardness (Ritz)	2·4	3–4	4–5	6	Hardness (Ritz)	5·5	2·8	2·2

CuBr, it is seen that each Cu gives 1, and each Br 7 electrons to the enveloping system. The resulting structure may be represented by

$$\begin{array}{c} \cdot\cdot \quad \cdot\cdot \\ :\,\mathrm{Cu}\,:\,\mathrm{Br}\,: \\ \cdot\cdot \quad \cdot\cdot \\ :\,\mathrm{Br}\,:\,\mathrm{Cu}\,: \\ \cdot\cdot \quad \cdot\cdot \end{array} \qquad \text{or} \qquad \begin{array}{c} \cdot\cdot \quad \cdot\cdot \\ :+1:+7: \\ \cdot\cdot \quad \cdot\cdot \\ :+7:+1: \\ \cdot\cdot \quad \cdot\cdot \end{array}$$

so that the weakest link is between Cu (+1) and the electronic system. In ZnSe, the weakest link is between Zn (+2) and the electronic system, which is stronger than that of Cu (+1). With GaAs, the weakest link is that around Ga (+3), whilst in GeGe all the links are of equal value (+4) which is thus the strongest structure of the series. Returning to Table XXXIV, it is seen that in the series of metals Be, Mg, Ca the hardness decreases with increasing interatomic distance. Thus Li metal is harder than Na, and Na than K. The effect of valency is observed in the cases of Li to Be, Na to Mg and K to Ca, where increasing valency results in increased hardness as in the case of ionic salts. It may also be noted in passing that the elements of the transition series generally seem to be harder and to have

higher melting points than the corresponding inert gas builders of the same valency. It has been suggested that this may be due to magnetic superimposed upon electrostatic forces. The effect on hardness of alloying metals has already been considered.

The property of isomorphism and of solid solution formation is evidently closely linked with the question of ionic size in crystals. Grimm has, however, pointed out that a difference in size may be compensated for by a difference of structure, as may be seen by comparing compounds containing the ion Na^+ with isomorphous compounds containing the ion Ag^+, which is not of inert gas type. Grimm and Wagner[22] have found that $BaSO_4$ and $KMnO_4$ will form mixed crystals (see this vol. : 22A).

In compounds of the Type MBX_3, diminution in the size of M favours the change from aragonite to calcite, and from perowskite to ilmenite types.

Rawlins[23] has noticed that co-ordination number appears to be an important factor in determining the degree of complexity of the infra-red spectra of crystals : thus, in the case of molecular lattices, there is reason to believe that characteristic infra-red vibrations found in the gas phase are conserved with only slight alterations in frequency in the solid crystal.

Niggli[25,26] has discussed compounds of the type ABX_n, developing principles whereby the structures adopted may be predicted. An extension of this work[27,28] involves a general attempt to correlate stereochemistry with atomic valency and co-ordination capacity.

It is noteworthy that in $NaClO_3$ each Na is surrounded by 6, and in $KClO_3$ each K by 9 oxygen atoms.[29]

A notable exception to the Law of Additivity of atomic radii is apparently provided by crystals of the $NaPb_3$ type.[30]

Reinicke[31] has made an extensive study of the tetrahedral symmetry of atoms, in relation to their valencies and the Periodic Law. The paper cited contains full references to earlier work. Attention has also been paid to non-metallic compounds of the type $Mg_3P_2 \longrightarrow Mg_3Bi_2$, with reference to the boundary in the Periodic System where negative ions occur.[40]

Laves[41,42] and Niggli[42] have discussed the relation between co-ordination numbers and the symmetry of space-groups. Onorato[43] finds that the structure of $CaSO_4 2H_2O$ supports the Werner formula in which two water molecules are co-ordinated to Ca. Pauling[44] has enunciated principles which appear to govern the co-ordination of atoms in complex compounds, especially silicates. For further detail respecting these and kindred matters, the reader is referred to the cited literature.

With respect to Goldschmidt's observations on the importance of radius ratio in determining crystal structure, van Arkel[24] has pointed out that crystals within the CsCl limits of radius ratio do not always crystallize in this way. It is here that the third factor mentioned, that of polarizability, enters in, some discussion of which follows.

(C) **The Polarizabilities of the Crystal Units.** The importance of radius ratio becomes less dominating in cases where the ions depart from the theoretical ideal of incompressible and undeformable spheres. The significance of polarization in crystals was emphasized by Hund.[32] Thus it is found that the distance Na-Cl in gaseous NaCl (C.N. = 1) is less than the corresponding distance in the NaCl lattice. The cause of this effect is doubtless to be sought in the symmetrical polarizing influence of neighbouring ions in the crystal, the effect disappearing on volatilization.

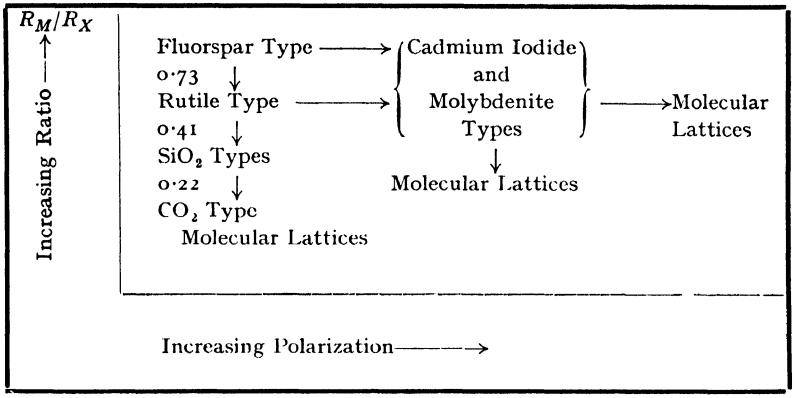
Ionic deformability α is defined by the relation $m = \alpha F$, where m is the electric moment set up by field F, so that α is the moment induced by unit field. The mechanism of the process may be regarded as a displacement of the symmetrical distribution of electronic charges, involving transport of negative charge from the anion towards the cation. Thus the polarization properties of crystals depend on the polarizability of one building unit in the field of another unit. The ion I^- has $\alpha = 6{\cdot}05 \times 10^{-24}$, which is greater than the value for F^-, $\alpha = 0{\cdot}91 \times 10^{-24}$. This difference appears responsible for the different structures of CdF_2 (fluorspar type) and CdI_2 (layer lattice). The increased polarizability of I^- compared with F^-

leads to the formation of electrically neutral layers, in which the weakly polarizable rigid Cd^{++} ions are covered on both sides with layers of strongly polarized I^- ions, the neutral layers corresponding to vast molecules in two dimensions, just as an NaCl crystal forms one giant molecule in three dimensions. The ion I^- is much larger than F^-, and with this is associated its increased polarizability, but that size is not the only determining factor is seen by the consideration that $Cd(OH)_2$ crystallizes like CdI_2, although the OH^- ion has approximately the same size as F^-. Here OH^-, in common with CN^- and the H_2O molecule, has natural dipole moment, associated with an inherent asymmetry of distribution of positive and negative electricity, so that the centres of the opposite kinds of charge do not coincide. The effect of the field of Cd^{++} on OH^- is to orientate the dipoles and to reinforce their moment (see this vol.: Part II). The capacity of negative ions to become polarized is the determining factor in the transition from lattices of the rutile or fluorspar type to lattices of the layer type. $CdCl_2$[35] has a layer lattice structure related to that of CdI_2.

It may be noted here that somewhat different considerations appear to govern transitions between lattices of the pyrite and layer types in the case of certain disulphides, diselenides and ditellurides of the types studied by Thomassen.[36] Here an increase of radius and of valency of the metal ion favours the formation of layer lattices. In pyrite crystals, the S_2 molecule appears in a form which seems analogous to that in S_2 vapour, whilst in the layer lattices, the S_2 is broken up by taking four electrons from the metal, forming two S^{--} ions. Upon the capacity of the metal to cause this fission the appearance of lattices of the layer variety appears to depend. It may be expected that this facility will be greater with metals of larger radii and higher valencies.

The further increase of polarization due to anionic substitution in compounds of the CdI_2 and MoS_2 types leads to the appearance of molecular lattices. The structures of co-ordination, layer and molecular lattices have been represented by Hund as in Figure LV. The effect of radius ratio and of

polarization may be summarized in the following way, due to Goldschmidt :—



Grimm[10] has given examples of polarization influence on the adoption of lattice types. With increasing deforming power of cation (decreasing radius, increasing charge, and transition

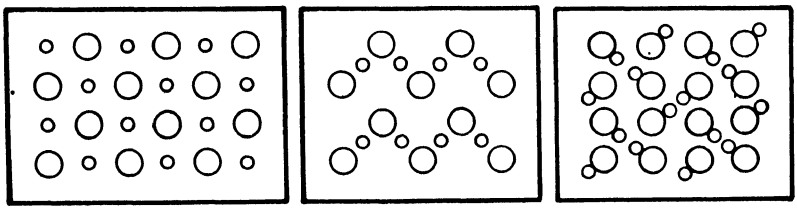
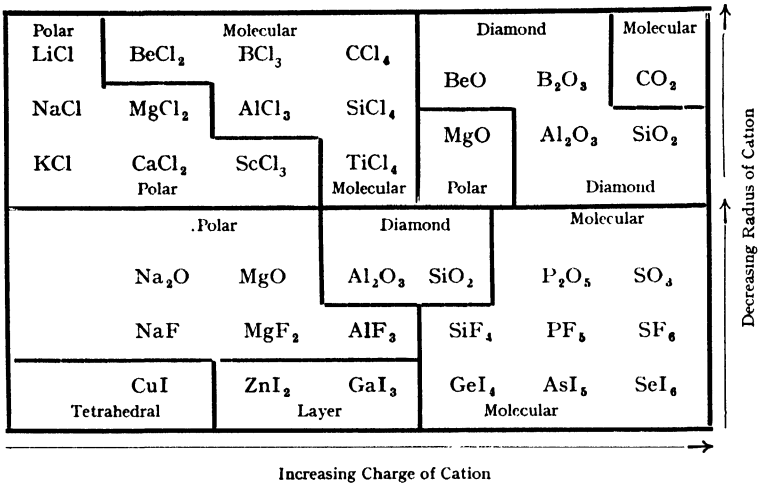


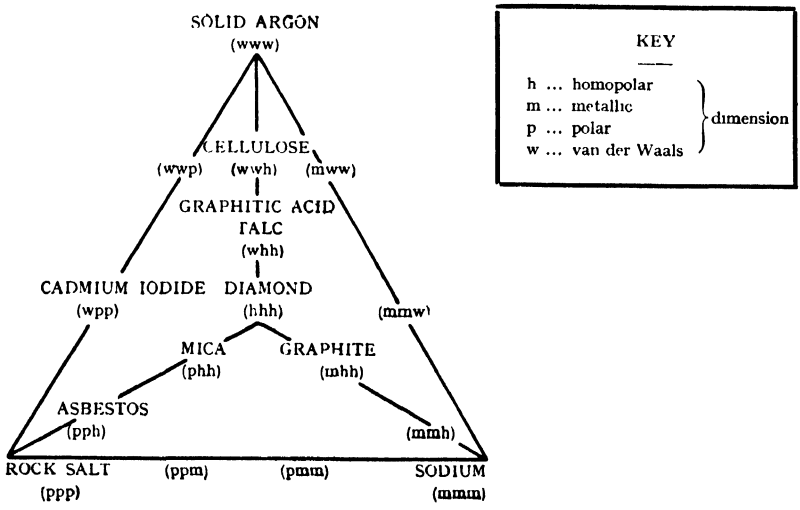
FIGURE LV.—REPRESENTATION OF CO-ORDINATION, LAYER AND MOLECULAR LATTICES RESPECTIVELY (HUND).

from 8 to 18 outermost electrons) and with increasing anionic deformability (increasing size and decreasing charge), the tendency to pass from polar to homopolar crystal types increases. Examples are shown on page 206, the arrows showing direction of increasing polarization.

In the series from CuI to SeI_6, the development of increasing charge of cation leads first to the formation of layer, and then of molecular structures.



The following space-dimensional classification of lattices is due to Grimm :—[37,38]



New developments in the field covered by the present chapter are summarized by Rawlins.[39] It becomes clear that, whilst chemical considerations have played a not unimportant part in the actual determination of structures, they have also, in conjunction with the X-ray results, thrown much new light on the behaviour of matter in the solid state.

APPENDIX TO CHAPTER IX.

LIMITING RADIUS RATIOS FOR DIFFERENT CO-ORDINATION NUMBERS

(1) *Co-ordination Number* 3 (Figure LVI).

Let three spheres of equal radii with centres A, B and C touch an inner sphere with centre D ; and let E be one of the points of

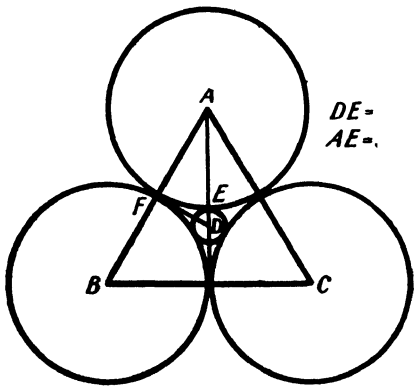


FIGURE LVI.—LIMITING RADIUS RATIO FOR CO-ORDINATION NUMBER 3.

contact. Let the radii DE = r, AE = s ; required the ratio r/s. Here $\sec 30° = AD/AF = (r + s)/s$; whence $r/s = \sec 30° - 1 = (2/\sqrt{3}) - 1 = \mathbf{0{\cdot}15}$.

(2) *Co-ordination Number* 4 (Figure LVII).

Let four outer spheres of radii $s = AF$ touch an inner sphere of radius $r = EF$, and let the tetrahedral edge $AB = a$. Then $EF/AF = r/s = (AE - s)/s = (AE/s) - 1$; whence inserting $s = a/2$, and $AE = \sqrt{3}a/(2\sqrt{2})$, $r/s = (\sqrt{3}/\sqrt{2}) - 1 = \mathbf{0{\cdot}22}$.

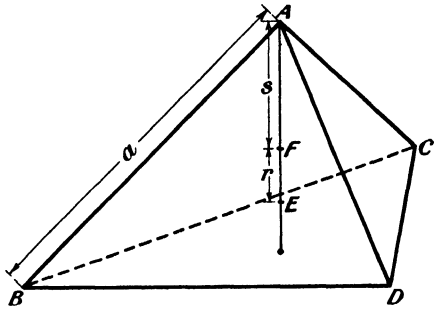


FIGURE LVII.—LIMITING RADIUS RATIO FOR CO-ORDINATION NUMBER 4.

(3) *Co-ordination Number* 6 (Figure LVIII).

Let six spheres of radii s touch an inner sphere of radius r (four spheres only are shown in section in the Figure, those above and

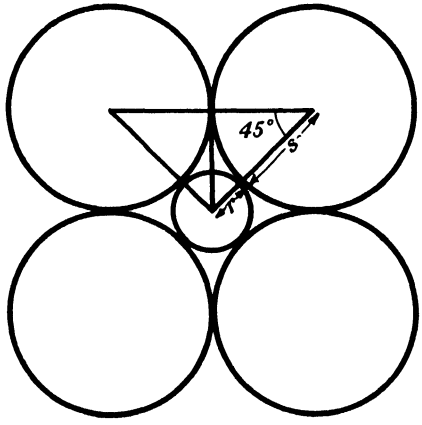


FIGURE LVIII.—LIMITING RADIUS RATIO FOR CO-ORDINATION NUMBER 6.

below the plane of the paper being omitted). Then $\sec 45° = (r + s)/s = 1 + (r/s)$, whence $r/s = \sec 45° - 1 = \sqrt{2} - 1 = \mathbf{0{\cdot}414}$.

(4) *Co-ordination Number* 8 (Figure LIX).

Let eight outer spheres having radii s = AC and centres at the corners of the cube touch an inner sphere of radius r = BC. Then r/s = BC/AC = (AB − AC)/AC = (AB/AC) − 1 = (AB/AE) − 1 = $\sqrt{3} - 1 = \mathbf{0{\cdot}73}$.

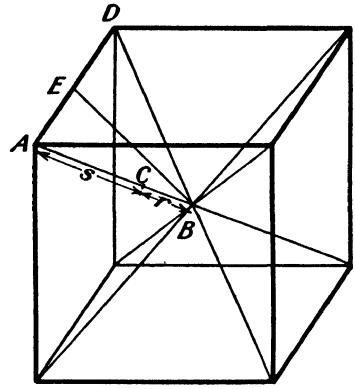


FIGURE LIX.—LIMITING RADIUS RATIO FOR CO-ORDINATION NUMBER 8.

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(*A list of abbreviations used in references will be found on pages* xxxi *et seq.*)

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APPENDIX TO PART I.

ATOMIC STRUCTURE FACTORS

The study of the scattering of X-rays by matter has provided information as to electron distributions within atoms and the imperfection of certain crystals. In 1914, Darwin[1] evaluated expressions for the relation between the amount of radiation reflected by a crystal face and the incident X-ray energy. Use is made of a structure factor F, which measures the scattering power of an atom in relation to that of a single free electron as unit. The formulæ deduced take various forms, and are not reproduced here. It is found that the integrated reflection is proportional to F for perfect, and to F^2 for imperfect (mosaic) crystals. For even orders of reflection from ionic crystals, the structure factors of the ions are added, and for odd orders subtracted. The "atomic F curves" are obtained by plotting F against $\sin\theta/\lambda$, values of θ corresponding to angles of incidence giving maxima of intensity of reflection on different crystal faces: F should therefore be independent, for a given face, of $\sin\theta/\lambda$, that is, of the wave-length of the incident monochromatic radiation. (Actually, small deviations have been found in certain cases: see[2,89].) The measurements of James and Miss Firth[3] on NaCl provide suitable standards which may be used in comparison with other crystals; thus saving labour in calculation. (The value of $F(220)$, or F for second-order reflection on the (110) face for NaCl when $\lambda = 0{\cdot}71$ Å.U. is 15·62.)

Atomic F curves have been calculated theoretically by Hartree[4] by his method of the "self-consistent field." The method applies the classical law of scattering to the Schrödinger wave-mechanical charge distribution in an atom or ion. This has been applied to NaCl.[5] Another method, due to Thomas[6] and Fermi,[7] is based on an approximation applicable to ions of atomic number Z greater than 25. Fourier analysis has also been applied, as in the case of FeS_2[8]. Recent calculations of charge distributions by the Hartree method include Cl^-,[9,10] Cu^+,[10] K^+,[11] Cs^+,[11] F,[12] F^-,[12] and

Ne[12] (see Figure LIII). Wasastjerna[13] has found the electron distributions of atoms and ions of inert gas type calculated from refraction data to be in fairly good agreement with those derived by means of the Hartree self-consistent field. Further applications of quantum mechanics are due to Dirac[14] and Breit.[15] Pauling and Sherman[16] have considered hydrogen-like eigenfunctions, and have obtained scattering factors in agreement with Hartree. Absorption coefficients for X-rays have been calculated from scattering formulæ due to Klein-Nishina, Dirac, Breit and Compton.[17,18]

W. L. Bragg[19] has provided a useful summary of some of the above subjects. Speaking of charge distributions, he says: " Instead of orbits, we get a continuous distribution with spherical symmetry, which may be thought of as density of electron atmosphere or probability of finding an electron in unit volume at different distances from the nucleus."

W. H. Bragg[20] observed the effects of temperature and the phenomenon of " extinction " when the X-rays impinged on a crystal at the reflecting angle. The effect of temperature was worked out by Debye[21,22] and Faxén.[23] If f is the structure factor of an atom at rest, then F at temperature T is found by an exponential relation $F = fe^{-M}$, where M is a function of T. If the atom at the absolute zero possesses " zero-point energy," a small correction in M is required. Waller[24,25] replaced the exponent $-M$ by $-2M$. These formulæ have been found generally satisfactory by many authors. By extinction is meant increased absorption by a crystal in the neighbourhood of the reflecting angle. The reflection cannot be independent of the planes of atoms passed by the emergent X-ray beam from a crystal, for each plane encountered is in the correct position to reflect it: multiple reflections of the reflected beam therefore take place. Primary extinction refers to this effect in perfect crystals, secondary extinction to mosaic crystals, where parallel blocks may reduce the intensity of emitted reflection. The corrections in the scattering formula for primary and secondary extinction were found by Darwin,[1,26] whose results were confirmed by Ewald,[27] for the case of a perfect crystal. Moseley and Darwin,[28] Compton[29] and W. L. Bragg and collaborators[30,31] showed that experiment agreed with Darwin's formula for a mosaic crystal. Ewald[32] found that calcite and diamond behaved more as perfect than as mosaic crystals.

The application of structure factors to the determination of

crystal structure in the case of a crystal having many parameters has been considered by W. L. Bragg and West,[33] and the method applied to topaz[34] and diopside.[35]

The structure factor method has been applied to many salts, and salt-like compounds: NaCl,[36,37,38,39,40,41] KCl,[38,42,43,44,45,46,47,50,51] NaF,[38,48,49,50,51,52,53,54,55,56] LiF,[38] NH_4Cl,[57] CaF_2,[58] MgO,[50,51,59] NiO,[88] CaS,[51] ZnS,[60] $CaCO_3$ (calcite),[40,61,62,63] $BaSO_4$[40] and Rochelle salt.[40] The scattering curve for an ion is found closely to resemble that of the corresponding inert gas: Na^+, Ne[39]; KCl, A[45,50]; NaF, Ne[48,50,55,56]; MgO, Ne[48,50]. The effect of temperature has been widely studied. It is found, for example, that the Debye-Waller law holds for KCl from liquid air temperature to 400° absolute, above which it becomes less applicable.[42] The F curves are such that F equals the atomic number Z for zero incident angle.

Atomic F curves have been determined for Ag,[64,65,66,69] Al,[67,68,69,70,71,72,75,76,77] Au,[69,72] Be,[71,73,74] C,[72,75,78] (diamond)[79,80,81,82] (graphite),[71,76,77] Cu,[83,64,68,69,70,84,85,86] Fe,[83,86,87,72] Ni,[86,88] O,[84,88] Pb,[68,70] Pt,[69] Si,[89] and Sn.[72] An Al single crystal[67] gave intensities of reflection at liquid air and laboratory temperatures in agreement with the Debye-Waller theory. The atomic scattering power of Al, corrected for temperature, and including zero-point energy, agreed with that calculated by the Schrödinger-Hartree method. Whilst the atomic structure factor of Be[73] showed no appreciable change on annealing, that of Cu[85] is reduced by filing, which causes distortion of the Cu lattice.

The scattering of X-rays by solid paraffins[68,70] and the structure factors of anthracene[90] have been determined. For further work on organic compounds, see [71].

Liquids have been examined in the cases of water,[71] mercury,[91] gallium,[91] CCl_4[91] and benzene.[92]

The X-ray scattering by gases is considered in Vol. 3: 37C, in connection with Debye's method of determination of interatomic distances in gaseous molecules. An account of the scattering of X-rays by gases from the standpoint of structure factors is due to Wollan.[93] The following have been examined: A,[94,95,96,97] CCl_4,[98] Cl_2,[99] H_2,[94] He,[94,95,97,100] Ne,[94,95,97] O_2[94] and Hg vapour.[101] The theory is largely the work of Woo[102,103,104,106,107,108] and Jauncey[105]. Woo's contribution has mainly consisted in clearly separating the coherent and incoherent parts of the scattered radiation. Barrett's results on He and A[103] were shown to be in

satisfactory agreement with calculation by the Thomas-Fermi method. Yu[109] has applied Woo's work to argon.

It is known that anomalous dispersion of X-rays occurs in the neighbourhood of an " absorption edge." The anomalous scattering of X-rays by Au,[110] Cu,[112] Fe,[110] W[110] and Zn[111] has been examined. The theory of the effect is mainly due to Hönl,[113] Schäfer,[114] Williams[115] and Coster and Knol.[116]

A summary of work on atomic structure factors and values of F for a large number of atoms and ions obtained by the Hartree and Thomas-Fermi methods is due to James and Brindley.[117]

Further convenient summaries of recent work are due to Wollan,[93] Blake,[118] Ehrenberg and Schäfer[119] and James.[120]

The theory of X-ray scattering by matter appears to be in a satisfactory state from the following consideration. It is possible to calculate F values by four independent methods : (1) Reflection from crystals ; (2) Scattering by gases ; (3) Diffuse scattering of X-rays ; (4) Hartree and Dirac-Fermi theoretical method. It is found that the values calculated by the four methods are in agreement for A and KCl/2 (see [93]).

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Chapters { I to IX: Part I; X to XIV: Part II; XV to XVIII: Part III } of Volume II.

Notes.—Roman numerals refer to reference lists, other numbers to references in lists. The symbol H denotes Head of list, where a book is cited. "App." refers to the reference list to the Appendix to Part I on page 214. In cases where two or more authors have the same name and initials, separate classification is not adopted. Where the same author gives different initials in different papers, he may appear more than once in this list. A complete list of names in the subjects treated in this volume is obtained by combining the list below with the names in the three works mentioned in the Preface to Volume II (page xxi).

SUBJECT INDEX

Sections { **1 to 25 : Part I** / **26 to 47 : Part II** / **47 to 67 : Part III** } **of Volume II**

Notes.—The numbers refer to sections ; letters and further numbers indicate sub-sections. The section numbers are not repeated where more than one reference is made to the same section ; thus 33Ca, 33Cb is abbreviated to 33Ca,b and 28B, 28Gc to 28B,Gc. In general, the classification is not the same as that of the Table of Contents, which may be used for general reference to specific physical properties. The present index refers mainly to individual substances or types of substance, and to subjects which do not appear in the earlier Table. It is suggested that the two lists may be conveniently used in conjunction with each other.

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