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XVIII. *The Arrangement of Atoms in Crystals.* By W. LAWRENCE BRAGG, M.A., *Langworthy Professor of Physics, The University of Manchester*\*.

[Plate III.]

1. **I**N many simple crystalline structures the atoms are so arranged that their exact positions are determined by the symmetry of the crystal. In the diamond, for example, each carbon atom is at the centre of four other carbon atoms arranged at the corners of a regular tetrahedron. In the crystal of sodium chloride, the sodium atoms may be regarded as arranged at the corners and face-centres of the unit cube, the chlorine atoms being situated at the centres of the cube-edges and at the centre of the cube. Every sodium atom is surrounded symmetrically by six chlorine atoms, every chlorine atom by six sodium atoms. The atoms cannot be displaced from these positions without destroying the symmetry of the structure, and therefore their exact positions are defined by this symmetry.

In the case of a crystal such as iron pyrites,  $\text{FeS}_2$ , the positions of the sulphur atoms are not defined in this manner. The atoms of iron are at centres of symmetry of the structure, and so must be regarded as fixed in position. The sulphur atoms lie on axes of threefold symmetry, but they,

\* Communicated by the Author.

*Phil. Mag.* S. 6. Vol. 40. No. 236. Aug. 1920.

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on the other hand, may be anywhere along these axes, provided they all occupy similar positions, and yet be in accordance with the symmetry. The determination of their positions must be made by a quantitative examination of the diffraction of the X rays by the structure, since the parameter which fixes their positions may have any value between certain limits. The oxygen atom in the series of carbonates isomorphous with calcite has similarly an indeterminate position depending on the value of a certain parameter. In the case of the ruby,  $\text{Al}_2\text{O}_3$ , two parameters are necessary to define the crystal structure; in quartz,  $\text{SiO}_2$ , four parameters must be determined. The difficulty of analysing a crystal structure by the X rays is greatly increased by the necessity for defining these parameters, and it is this which has limited the types of crystals which have so far been fully worked out to the simpler forms where these parameters are few in number.

The first part of this paper deals with certain empirical relations, which hold between the distances separating atoms from their nearest neighbours in the simpler crystalline structures, and which the author has found to be of service in the analysis of complex crystal forms. In the latter part of the paper the physical significance of these relations will be discussed, particularly in relation to the theories of atomic structure proposed by Lewis\* and Langmuir†.

2. These relations may be expressed in a simple manner by regarding the atoms in a crystal as an assemblage of spheres packed tightly together, the centres of the spheres coinciding with those of the atoms. Each sphere is held in place by touching several neighbours. It will be shown that, within certain limits, it is possible to assign to the sphere representing an atom of any element a constant diameter characteristic of that element. The distance between the centres of two neighbouring atoms may be expressed as the sum of two constants, represented by the radii of the corresponding spheres. The molecular volume of a compound is in general very far from being equal to the sum of the molecular volumes of the elements composing it. On the other hand, if the distances between the atoms are considered, it will be shown that an additive law holds with considerable accuracy. The apparent variations in the contribution of any particular element to the molecular volume of compounds of which it forms a constituent are to be explained by differences

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

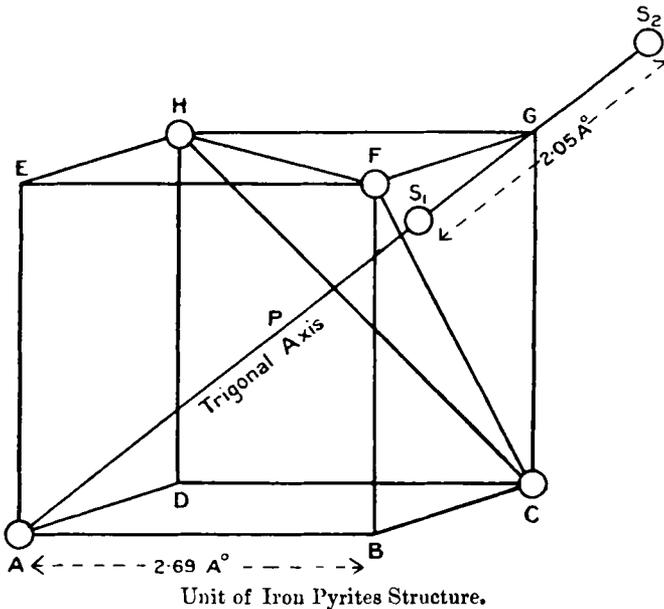
† I. Langmuir, *Journ. Amer. Chem. Soc.* xli, p. 868 (1919).

in crystalline structure, and not by variations in the space occupied by the atoms.

This additive law is only intended to be regarded as a working approximation, an aid to the analysis of complex structures. In analysing such a structure, various arrangements of the atoms have to be tried to explain the intensities of the reflected spectra. It will be shown that, when marshalling the atoms together, each atom must be given a certain space in the structure, so that two atoms may not be placed closer together than a distance equal to the sum of the radii of the spheres representing them. This greatly facilitates the determination of the parameters, which are confined to a much more limited range.

The diameter of the sphere representing an atom is, for the sake of brevity, called the diameter of the atom, and is expressed in Ångström units ( $\text{Å} = 10^{-8}$  cm.).

Fig. 1 a.



3. In the Iron Pyrites structure\*, the iron atoms are situated on a face-centred cubic lattice. If the unit cube of this lattice is divided into eight smaller cubes, each of these latter will have an iron atom situated at four of its eight corners. Figure.1a represents such a unit of the structure

\* W. L. Bragg, Proc. Roy. Soc. lxxxix. (Nov. 1913).

of iron pyrites, the iron atoms being at the corners A, C, H, and F. One diagonal of the cube, the diagonal AG in the figure, is an axis of threefold symmetry, and the sulphur atom lies at some position along this axis. Each corner of the cube is a centre of symmetry. If a sulphur atom is centred at the point  $S_1$ , there will be a corresponding atom at the point  $S_2$  where  $S_1G = S_2G$ . A pair of sulphur atoms is thus associated with each corner of the cube not occupied by an iron atom, since one threefold axis passes through every corner. On the conception of the atoms as a set of spheres packed together, it will be seen that there are two possible positions for the sulphur atom. It may lie at the centre of the cube, where it is symmetrically surrounded by four iron atoms at A, C, H, and F. Alternatively, it may move along the diagonal until it is at G, on the other side of the plane HFC, where it will be packed between the three atoms of iron at H, C, and F and the corresponding sulphur atom at  $S_2$ .

The structure of metallic iron has been determined by Hull\*. The iron atoms are situated on a cube-centred lattice, the side of the cube having a length of 2.86 Å, and the distance between the centres of neighbouring iron atoms is 2.47 Å. If this length is taken as a first approximation to the diameter of the sphere representing the iron atom, and spheres of corresponding radius are described with their centres at H, C, and F, the centre of the sulphur atom is thereby fixed. The atom must touch the three iron atoms and also the other sulphur atom at the point G, as shown in fig. 1*b*. The ratio  $S_1G/AG$  which determines the position of  $S_1$  can be calculated to be 0.22/1. This ratio was originally determined by the author as 0.20/1. A more exact determination by Ewald†, based on the Laue-photograph of Pyrites, gave the value of the parameter as 0.226/1.

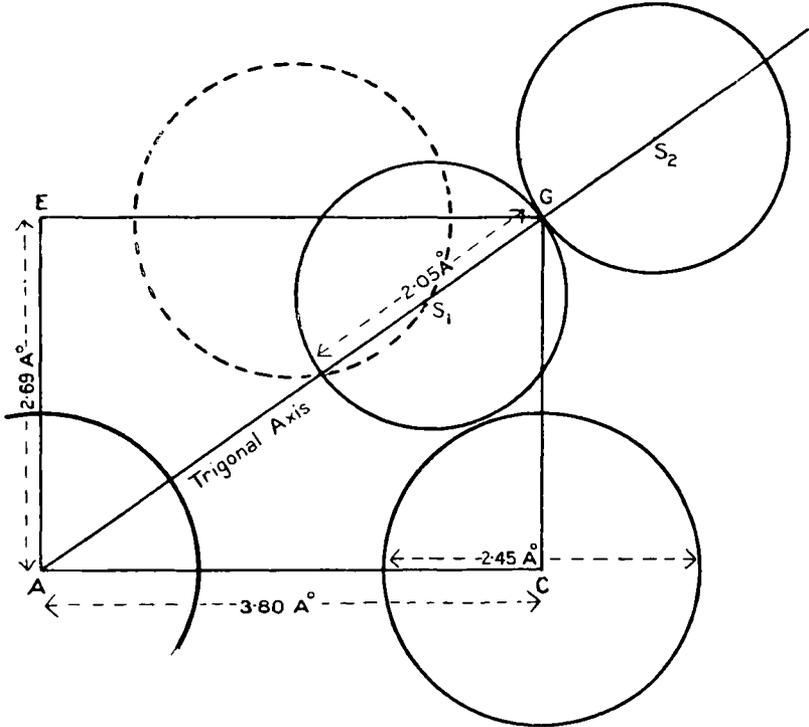
The exact correspondence of the position of the sulphur atom calculated in this way with that found by experiment is not to be expected, the diameters of the spheres representing the atoms cannot be regarded as absolutely fixed. It will be seen, however, that the conception of the atoms as spheres packed together does lead in this case to an approximate value for the parameter not far from the true one. The diameter of the sulphur atom is given by the distance  $S_1S_2$ , which is equal to 2.05 Å. Each sulphur atom is surrounded by three iron atoms and a sulphur atom, each iron atom by six sulphur atoms.

\* Hull, *Phys. Rev.*, 10 Dec. 1917.

† Ewald, *Phys. Zeit.* April 15, 1914.

4. In Zinc sulphide (Zinc-blende) the zinc atoms lie on a face-centred cubic lattice. The sulphur atoms lie on a similar lattice in such a way that every sulphur atom is surrounded by four zinc atoms arranged at the corners of a regular

Fig. 16.



Section through A C G E. The broken circle is the projection of the iron atoms centered at F and H.

tetrahedron, every zinc atom by four sulphur atoms similarly arranged. The distance between the centres of the zinc and sulphur atoms is 2.35 Å. Taking the diameter of the sulphur atom as 2.05 Å., this gives the diameter of the zinc atom as 2.65 Å.

In zinc oxide \* the zinc atoms have an arrangement which is that of hexagonal close-packing. The oxygen atoms have a similar arrangement, each oxygen atom being surrounded by four zinc atoms at the corners of a tetrahedron and each zinc atom by four oxygen atoms. The distance between

\* W. L. Bragg, *Phil. Mag.* vol. xxxix. p. 647, June 1920.

zinc and oxygen centres is 1.97 Å. The oxygen atom appears to occupy a smaller space than the sulphur atom, and the diameter 1.30 Å. must be assigned to the sphere representing it.

5. In comparing zinc oxide and zinc sulphide, the substitution of oxygen for sulphur decreases the distance between atomic centres by 0.38 Å. This holds true for a number of compounds, as will be seen by the following comparison. It is assumed that the compounds MgO, CaO, SrO, BaO and MgS, CaS, SrS, BaS, have the same structure as NaCl. This is known to be the case for MgO\*, and all these compounds fall into two isomorphous series of cubic crystals with cleavage parallel to the cube faces.

The distances given in the table are those between neighbouring atomic centres.

		Difference.
MgO .....	2.11	}
MgS .....	2.54	
CaO .....	2.40	}
CaS .....	2.77	
SiO .....	2.63	}
SiS .....	2.99	
BaO .....	2.81	}
BaS .....	3.20	
ZnO .....	1.97	}
ZnS .....	2.35	

6. Similar relationships are shown by the alkaline halides† the molecular volumes of which form a regular series. All these salts crystallize in the same form as NaCl. The following table gives the distances between atomic centres expressed in Ångström Units.

NaF ...	2.39	KF.....	2.73				
Diff.....	.41		.40				
NaCl ...	2.80	KCl ...	3.13	RbCl...	3.28	CsCl ..	3.26
Diff.....	.17		.15		.16		.14
NaBr ...	2.97	KBr ...	3.28	RbBr...	3.44	CsBr .	3.40
Diff.....	.26		.24		.22		.21
NaI ...	3.23	KI ...	3.52	RbI ...	3.66	CsI ...	3.61

The replacement of Fluorine by Chlorine, Chlorine by Bromine, and Bromine by Iodine, increases the dimensions of the structure by an approximately constant amount.

This series is peculiar in that the replacement of Rubidium by Cæsium appears to diminish the dimensions of the

\* Hull, Journ. Amer. Chem. Soc. August, 1919.

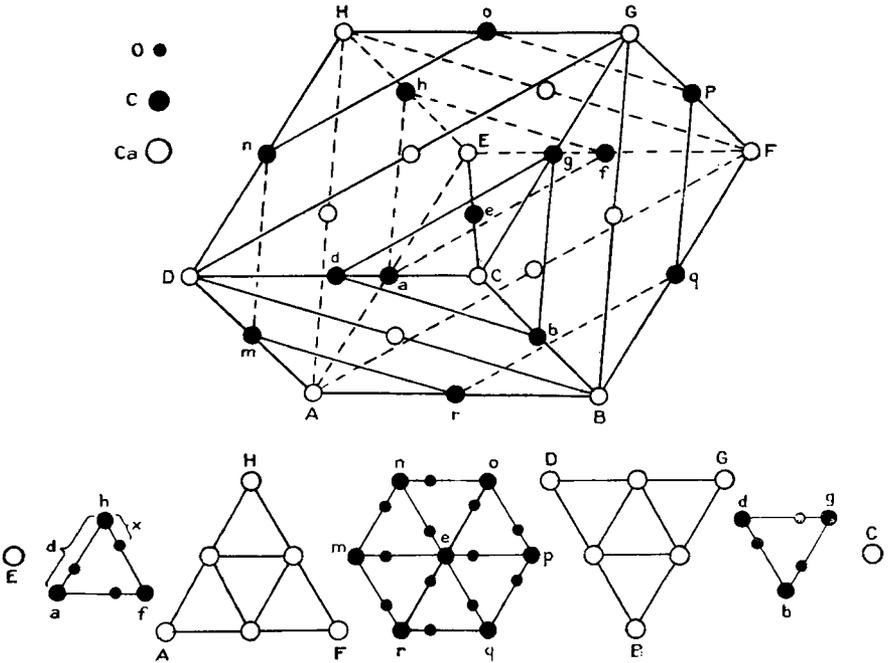
† The figures from which these results have been worked out are taken from Groth's *Chemische Krystallographie*.

structure. In most compounds the reverse is the case, as is illustrated by the following comparison of molecular volumes:—

$K_2SO_4$ ...	64.91	$K_2SeO_4$ ...	71.67	$KClO_4$ ...	54.91	$KMnO_4$ ...	58.53
$Rb_2SO_4$ .	73.34	$Rb_2SeO_4$ .	79.94	$RbClO_4$ .	61.33	$RbMnO_4$ .	63.23
$Cs_2SO_4$ .	84.58	$Cs_2SO_4$ .	91.09	$CsClO_4$ .	69.84	$CsMnO_4$ .	70.01

7. The structure of the isomorphous series of rhombohedral carbonates typified by Calcite,  $CaCO_3$ , is illustrated by fig. 2. In Calcite the calcium atoms lie on a face-centred

Fig. 2.



rhombohedral lattice, corresponding to a face-centred cubic lattice compressed parallel to a trigonal axis so that the angle of  $90^\circ$  between the edges of the cube becomes an angle of  $101^\circ 55'$ . The carbon atoms occupy the intermediate positions. Each carbon atom is surrounded by three oxygen atoms, as shown in the figure. The precise position of the oxygen atoms is not determined by the symmetry of the structure, they lie at some point along the line joining neighbouring carbon atoms in the planes parallel to the face (111) of the crystal. The ratio  $x/d$  in the figure, which fixes their

position, was found by the author to be approximately  $0.30/1$ , corresponding to a distance between oxygen and carbon centres of  $1.47 \text{ \AA}$ . This distance is the same for all compounds of the series.

In the diamond the distance between the centres of the carbon atoms is  $1.54 \text{ \AA}$ . Taking the diameter of the carbon atom as  $1.54 \text{ \AA}$ ., and that of the oxygen atom as  $1.30 \text{ \AA}$ ., the distance between oxygen and carbon centres should be  $1.42 \text{ \AA}$ . This is in agreement with the distance of  $1.47 \text{ \AA}$ . deduced from the X-ray measurements.

The distance between the centres of the metallic atom and the oxygen atom may be compared with the distance in the metallic oxide. In the carbonates the atom of the metal is surrounded by six oxygen atoms. In zinc carbonate the distance between zinc and oxygen centres is  $1.99 \text{ \AA}$ ., in zinc oxide it is  $1.97 \text{ \AA}$ . The agreement is not so good in other cases. The distance between calcium and oxygen centres is  $2.40 \text{ \AA}$ . in  $\text{CaO}$ ,  $2.30 \text{ \AA}$ . in  $\text{CaCO}_3$ . The corresponding figures for  $\text{MgO}$  and  $\text{MgCO}_3$  are  $2.10$  and  $2.00 \text{ \AA}$ . In  $\text{FeCO}_3$  the distance between the iron and oxygen centres is  $2.04 \text{ \AA}$ ., in  $\text{Fe}_3\text{O}_4^*$  (magnetite) it is  $2.00 \text{ \AA}$ . This leads to a value  $2.74 \text{ \AA}$  for the diameter of iron, greater than the value  $2.47 \text{ \AA}$  calculated from pyrites and metallic iron. Although this is the case, it will be seen that the conception of the crystal as a number of spheres packed tightly together leads to a determination of the parameter which is near the true one.

8. Two other examples will be taken as affording a cross-check on these measurements. In fluorspar,  $\text{CaF}_2$ , the distance between calcium and fluorine centres is  $2.34 \text{ \AA}$ . In sodium nitrate,  $\text{NaNO}_3$ , the arrangement of the sodium and nitrogen atoms is that of the calcium and carbon atoms in calcite. The ratio  $x/d$  determining the position of the oxygen atoms is approximately  $0.25$ . This gives the distance between oxygen and nitrogen centres as  $1.30 \text{ \AA}$ ., between oxygen and sodium centres as  $2.33 \text{ \AA}$ . We thus have the relations—

$\text{Na—O} \dots$	$2.33 \text{ \AA}.$	$(\text{NaNO}_3)$	$\text{Ca—O} \dots\dots$	$2.30 \text{ \AA}.$	$(\text{CaCO}_3).$
$\text{Na—F} \dots$	$2.39 \text{ \AA}.$	$(\text{NaF}).$	$\text{Ca—F} \dots\dots$	$2.34 \text{ \AA}.$	$(\text{CaF}_2).$

The space occupied by calcium in a crystal is much the same as that occupied by sodium; that occupied by oxygen is much the same as that occupied by fluorine.

9. These examples will indicate the manner in which the results shown in fig. 3 have been calculated. For instance, the diameter of oxygen has been taken to be  $1.30 \text{ \AA}$ ., and that

\* W. H. Bragg, *Phil. Mag.* vol xxx. (Aug. 1915).

of fluorine to be slightly greater, 1.35 Å. From a comparison of the alkaline halides, the diameters of the halogens are found to be :

Fluorine .....	1.35 Å.
Chlorine .....	2.10 Å.
Bromine .....	2.38 Å.
Iodine .....	2.80 Å.

Sulphur has been taken to have a diameter of 2.05 Å. The structure of Galena (PbS) corresponds to that of NaCl. The substitution of Selenium and Tellurium for Sulphur in the compounds PbSe and PbTe increases the distance between atomic centres by 0.15 Å. and 0.31 Å. respectively. We therefore get the values for the diameters :—

Oxygen .....	1.30 Å.
Sulphur .....	2.05 Å.
Selenium .....	2.35 Å.
Tellurium .....	2.66 Å.

The diameter of nitrogen is taken to be 1.30 Å. So far as the author is aware, no compounds containing phosphorus, arsenic, or antimony have yet been fully worked out, and the diameters of arsenic and antimony in the figure are the distances between atoms in crystals of the element.

The diameters of carbon and silicon\* are taken to be those separating the atoms of the element, 1.54 Å. and 2.35 Å. Gray tin† has a similar structure, with an inter-atomic distance of 2.80 Å.

Aluminium in its compounds occupies a volume slightly less than trivalent iron.

The divalent metals Nickel, Zinc, Magnesium, Copper, Cobalt, Iron, Manganese, Cadmium, and Calcium form several series of isomorphous compounds, which have been studied in detail by Tutton. The metals are arranged in the order of the molecular volumes of their compounds, those containing nickel having the least volume and those containing calcium the greatest.

The diameters of the spheres representing the monovalent alkali metals are calculated from the dimensions of the alkaline halides, diameters having been already fixed for fluorine, chlorine, bromine, and iodine.

\* Debye and Scherrer, *Phys. Zeit.* xvii. (1916).

† A. J. Bijl and N. H. Holkmeyer, *Proc. Roy. Soc. Ac. Amsterdam*, June-Sept. (1918).

These data have been used in calculating the diameters of fig. 3.

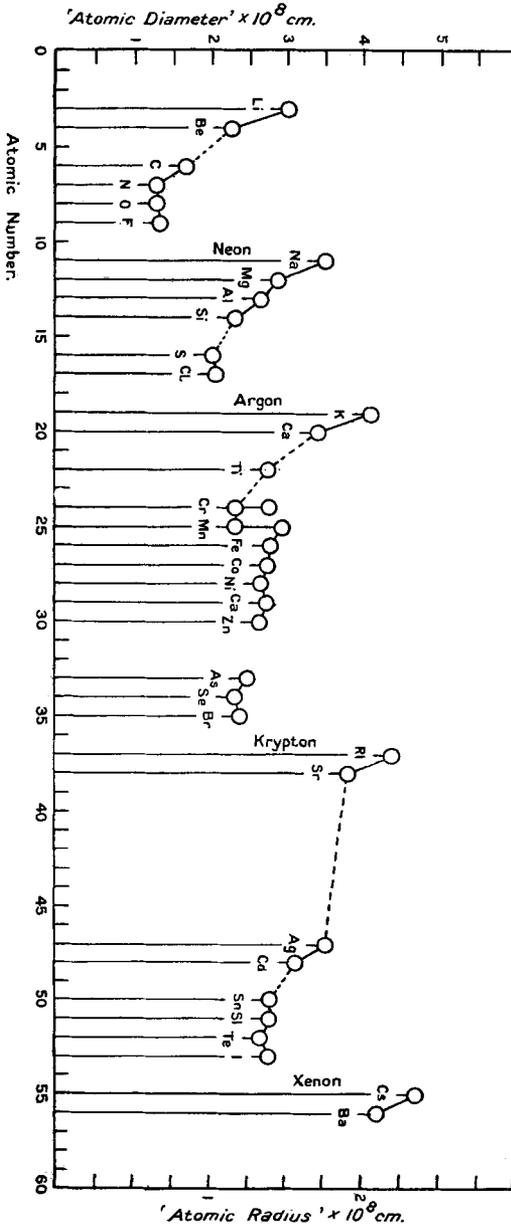


Fig. 3.

10. In fig. 3 the elements are arranged in the order of their Atomic Numbers. The ordinates represent the diameters of the "Atomic Domain" measured in Ångström Units. The figure summarizes the empirical relation which has been found to hold, namely, that the distance between neighbouring atomic centres in a crystal is the sum of two constants characteristic of the atoms. The crystal may be imagined as an assemblage of spheres packed together, the constants then representing the radii of the spheres.

The atomic diameters lie on a curve resembling Lothar Meyer's curve of atomic volumes. The alkali metals head each period with the greatest diameter, followed by the alkaline earths. The diameter diminishes steadily as the atomic weight is increased, reaching a minimum for the electronegative elements at the end of the period. In other words, when the atomic arrangement of compounds is taken into account, the periodic relation between the atomic volumes shown by Lothar Meyer's curve can be extended to the compounds of the atoms.

A list is given below of the "atomic diameters" assigned to the elements, and for convenience the "atomic radii" are added. The second table is a comparison of the observed distance between atoms in crystals with those obtained by adding together the radii of the two atoms concerned. It will be seen that the difference between observed and calculated values is never large, the average difference being  $0.06 \times 10^{-8}$  cm.

It is not intended to assign any physical significance to these "diameters" other than that discussed below. Sodium, for instance, has been given a diameter much larger than that of chlorine, yet it will be seen that there is every reason for supposing that the group of electrons surrounding the sodium nucleus in sodium chloride has smaller dimensions than that surrounding the chlorine nucleus in the same crystal.

The way of regarding the atoms as spheres packed tightly together is useful in constructing models of crystalline structures. Such models are illustrated in Plate III., the crystalline structures being those of sodium chloride, calcium carbonate, and zinc-blende.



Compound.	Atomic centres.	Sums of radii, in Å.	Observed Distance, in Å.	Difference, in Å.
Element Na.		3.55	3.72	+0.17
NaF.	Na, F.	1.77 + 0.67 = 2.44	2.39	-0.05
NaCl.	Na, Cl.	1.77 + 1.05 = 2.82	2.80	+0.02
NaBr.	Na, Br.	1.77 + 1.19 = 2.96	2.97	+0.01
NaI.	Na, I.	1.77 + 1.40 = 3.37	3.23	-0.14
NaNO <sub>3</sub> .	Na, O.	1.77 + 0.65 = 2.42	2.33	-0.09
Element Mg.		2.85	3.22	+0.37
MgO.	Mg, O.	1.42 + 0.65 = 2.07	2.10	+0.03
MgCO <sub>3</sub> .	Mg, O.	1.42 + 0.65 = 2.07	2.00	-0.07
MgS.	Mg, S.	1.42 + 1.02 = 2.44	2.54	+0.10
Element Al.		2.70	2.87	+0.17
Al <sub>2</sub> O <sub>3</sub> .	Al, O.	1.35 + 0.65 = 2.00	2.02	+0.02
KF.	K, F.	2.07 + 0.67 = 2.74	2.78	+0.04
KCl.	K, Cl.	2.07 + 1.05 = 3.12	3.13	+0.01
KBr.	K, Br.	2.07 + 1.19 = 3.26	3.28	+0.02
KI.	K, I.	2.07 + 1.40 = 3.47	3.52	+0.05
CaO.	Ca, O.	1.70 + 0.65 = 2.35	2.40	+0.05
CaCO <sub>3</sub> .	Ca, O.	1.70 + 0.65 = 2.35	2.30	-0.05
CaS.	Ca, S.	1.70 + 1.02 = 2.72	2.77	+0.05
CaF <sub>2</sub> .	Ca, F.	1.70 + 0.65 = 2.35	2.34	-0.01
MnCO <sub>3</sub> .	Mn, O.	1.47 + 0.65 = 2.11	2.10	-0.01
MnS <sub>2</sub> .	Mn, S.	1.47 + 1.02 = 2.49	2.59	+0.10
Element Fe.		2.80	2.47	-0.33
FeCO <sub>3</sub> .	Fe, O.	1.40 + 0.65 = 2.05	2.04	-0.01
Fe <sub>2</sub> O <sub>3</sub> .	Fe, O.	1.40 + 0.65 = 2.05	2.10 app.	+0.05
Fe <sub>3</sub> O <sub>4</sub> .	Fe, O.	1.40 + 0.65 = 2.05	2.00	-0.05
FeS <sub>2</sub> .	Fe, S.	1.40 + 1.02 = 2.42	2.28	-0.14
Element Cu.		2.75	2.55	-0.20
Cu <sub>2</sub> O.	Cu, O.	1.37 + 0.65 = 2.02	1.87	-0.15
ZnO.	Zn, O.	1.32 + 0.65 = 1.97	1.97	0.00
ZnCO <sub>3</sub> .	Zn, O.	1.32 + 0.65 = 1.97	1.99	+0.02
ZnS.	Zn, S.	1.32 + 1.02 = 2.32	2.35	+0.03
RbCl.	Rb, Cl.	2.25 + 1.05 = 3.30	3.28	-0.02
RbBr.	Rb, Br.	2.25 + 1.19 = 3.44	3.44	0.00
RbI.	Rb, I.	2.25 + 1.40 = 3.65	3.66	+0.01
SrO.	Sr, O.	1.95 + 0.65 = 2.60	2.63	+0.03
SrS.	Sr, S.	1.95 + 1.02 = 2.97	2.99	+0.02
CdCO <sub>3</sub> .	Cd, O.	1.60 + 0.65 = 2.25	2.21	-0.04
CdS.	Cd, S.	1.60 + 1.02 = 2.62	2.67	+0.05
CsCl.	Cs, Cl.	2.37 + 1.05 = 3.42	3.26	-0.14
CsBr.	Cs, Br.	2.37 + 1.19 = 3.56	3.40	-0.16
CsI.	Cs, I.	2.37 + 1.40 = 3.77	3.61	-0.16
BaO.	Ba, O.	2.15 + 0.65 = 2.80	2.81	+0.01
BaS.	Ba, S.	2.15 + 1.02 = 3.17	3.20	+0.03

11. These empirical relations will now be considered with reference to the theory of atomic structure proposed by Lewis\*, which has been greatly extended by Langmuir†. Briefly stated, some of the principal features of the theory in the form in which Langmuir presents it are the following:—

- (a) The electrons surrounding the positively charged nucleus of an atom are either stationary, or oscillate about certain fixed positions.
- (b) The electrons are distributed in a series of approximately spherical shells surrounding the nucleus.
- (c) Certain arrangements of electrons around a nucleus, those of the atoms of the inert gases, are very stable. These arrangements are:—Helium, where a nucleus with two unit positive charges is surrounded by a shell containing two electrons. Neon, nuclear charge 10, surrounded by an inner shell containing two electrons and an outer shell containing eight electrons. Argon, nuclear charge 18, surrounded by three shells containing two, eight, and eight electrons. Krypton, nuclear charge 36, shells containing two, eight, eight, and eighteen electrons. Xenon, nuclear charge 54, shells containing two, eight, eight, eighteen, and eighteen electrons. Niton, nuclear charge 86, shells containing two, eight, eight, eighteen, eighteen, and thirty-two electrons.
- (d) The chemical properties of the elements depend primarily on the tendency of the atom to surround itself with a more stable arrangement of electrons. The most simple chemical properties are exhibited by those atoms which revert most easily to the inert gas form, *i. e.*, the atoms nearest the inert gases in the periodic table. An electropositive element is one which tends to give up electrons in doing this, an electronegative element one which tends to take up electrons.

12. Broadly speaking, the theory distinguishes between two different types of combination in chemical compounds. The first type is represented by a compound such as KCl. The potassium atom has a nuclear charge of 19 units, and is surrounded by 18 electrons arranged in the same way as those of the argon atom, with in addition an electron which finds

\* G. N. Lewis, *loc. cit.*

† I. Langmuir, *loc. cit.*

no place in the stable argon arrangement. Chlorine has a nuclear charge of 17, and is surrounded by 17 electrons, one less than the number required to form the stable argon arrangement. When an atom of potassium combines with one of chlorine, the chlorine atom absorbs into its system the additional electron from the potassium atom. Both atoms are now surrounded by the argon shells, but as the nuclear charges are 19 and 17, and each atom is surrounded by 18 electrons, there will be a resultant positive charge of one unit on the potassium atom and a negative charge of one unit on the chlorine atom. The electrostatic attraction of these charges holds the molecule together. The nuclei, surrounded by the stable argon shells, compose the mono-valent cations and anions of potassium and chlorine.

The other type of combination is represented by a compound of two electronegative elements. In this case both atoms have fewer electrons than correspond to a stable system. They complete the required number of electrons in their outer shells by holding one or more pairs of electrons in common. In such compounds as  $\text{SO}_2$ ,  $\text{CO}_2$ , the atoms complete their outer shells of eight electrons by sharing them with their neighbours.

The crystalline structure of a compound such as  $\text{KCl}$  is very simply explained by this theory. As has been pointed out by Langmuir, the crystal is to be regarded as an assemblage of potassium and chlorine ions arranged on a cubic lattice\*. The ions consist of the stable argon shells, but as the nuclear charges are 19 and 17 the ions have resultant unit positive and negative charges. Each ion tends to surround itself with as many ions of the opposite sign as possible. This is realised in the  $\text{KCl}$  structure, where each ion is surrounded by six ions of the opposite sign. There are no individual molecules in the crystal structure, the potassium ion has exactly the same relation to the six chlorine ions surrounding it, and *vice versa*. Some repulsive force must exist between the outer shells, which holds the atoms apart against the electrostatic attraction.

In the structure of calcium sulphide, the calcium atom loses two electrons, and the sulphur atom gains two, in reverting to the argon form. The resultant charges on the ions are twice as great as those in the  $\text{KCl}$  structure, and as a result of the increased attraction between the ions the structure, while being similar to that of  $\text{KCl}$ , has all its dimensions reduced.

\* Cp. Debye and Scherrer, *Phys. Zeit.* xix. (1918), where evidence is given that an electron has passed from the Li atom to the F atom in  $\text{LiF}$ .

In the diamond, each carbon has a nuclear charge of six units. The atom has two electrons in its inner shell and four in the outer shell. In order to complete the number of electrons, eight, which would make its outer shell correspond to the stable neon form, it shares its electrons with the four carbon atoms surrounding it in the diamond structure. Each pair of atoms holds two electrons in common. The forces binding the atoms together are of a different type, the atoms are united because they share electrons, not as a result of opposite charges on ions as in KCl.

A crystal of an electropositive element, such as sodium, consists of an assemblage of the stable "inert gas" shells with an additional electron associated with each in order to neutralize completely the nuclear charge. These electrons have no fixed positions in the structure, they move under the action of an electromotive force and convey a current of electricity through the metal. On the other hand, a crystal in which the atoms are bound together by sharing electrons, so that there are no free electrons, is a non-conductor. This is the case for the typical electronegative element.

13. The empirical relations of fig. 3 are readily explained by this theory. In each period, the alkali metal which follows one of the inert gases has been assigned a large "diameter." This expresses the fact that it appears to occupy a large space in any crystal structure; the centre of the atom is separated by a considerable distance from the centres of the neighbouring atoms. Successive elements are assigned smaller diameters, and at the end of the period the electronegative elements immediately preceding the next inert gas have diameters which approximate closely to a limiting minimum value for that period.

The small diameters have been assigned to the electronegative elements on account of their proximity in a crystal structure. In sodium nitrate, for example, the distance between the oxygen and nitrogen centres is 1.30 Å., that between the oxygen and sodium centres 2.38 Å. In all these atoms the nuclei are surrounded by the stable neon arrangement of electrons, and presumably these electrons are approximately the same distance from the nucleus in sodium, nitrogen, and oxygen. The oxygen and nitrogen atoms have realized the stable arrangement, however, by sharing electrons, and their centres are correspondingly close together. The sodium atom is already surrounded by a stable shell and is isolated in the structure. In sodium nitrate there is the same arrangement of positive and negative ions as in sodium chloride, except that the negative ion in this case is the

complex  $\text{NO}_3$  group. In order to complete a stable arrangement around the four nuclei, the  $\text{NO}_3$  group has borrowed an electron from the sodium atom, leaving it a positively charged ion. These ions are arranged in the same way in  $\text{NaNO}_3$  and  $\text{NaCl}$ , each ion being surrounded by six of the opposite sign. The form of the  $\text{NO}_3$  group has, however, distorted the structure so that the crystal is rhombohedral instead of cubic.

In  $\text{MgCO}_3$  the arrangement of the atoms is the same as in  $\text{NaNO}_3$ . The magnesium ion has a double positive charge, the  $\text{CO}_3$  ion a double negative charge. As a result of the greater electrostatic forces, the dimensions of the structure are reduced, the distance between magnesium and oxygen centres being  $2.00 \text{ \AA}$ ., as compared with  $2.38 \text{ \AA}$ . in the case of sodium nitrate. This will make it clear why the divalent element appears to occupy a smaller space in a crystalline structure than the monovalent element preceding it in the periodic series.

The large diameters assigned to the electropositive elements as compared with the electronegative elements do not imply a corresponding difference in the dimensions of the atomic structure. They are an expression of the fact that the electropositive element does not share electrons with neighbouring atoms, it is always surrounded by a complete stable shell. The repulsion between this outer shell and the shells of neighbouring atoms keeps the atom at a distance from its neighbours, so that it appears to occupy a large space in the crystal structure.

It is interesting to compare the structure of graphite with that of diamond from this point of view. The graphite crystal has been analysed by Debye and Scherrer\*. It corresponds to a diamond structure in which, firstly, the dimensions of the whole structures parallel to a trigonal axis have been lengthened in the ratio  $0.598 : 1$ , and, secondly, the carbon atoms in the pairs of (111) planes of the diamond have been so displaced that they lie very nearly in the same plane. The atoms in a (111) plane are therefore very much closer to each other than they are to the atoms in the next planes. This may be explained by supposing that they are sharing electrons with their neighbours in the (111) planes but not with the other atoms, the very ready cleavage parallel to (111) lending support to this view (cp. Debye's paper). In such a case as this, the analogy of the crystal structure to a set of spheres packed together obviously

\* Debye and Scherrer, *Phys. Zeit.* xviii. (June 1917).

breaks down. The distance between neighbouring carbon atoms in graphite is  $1.45 \text{ \AA}$ .

14. It has been seen that in each period the diameters of the electronegative atoms appear to approach a lower limit. If it is true that these atoms share electrons when combined together in the crystal, the diameters which have been assigned to them should give an estimate of the diameters of the outer shells in which the electrons are situated.

In the first short period the diameters assigned to the atoms of carbon, nitrogen, oxygen, and fluorine are  $1.54 \text{ \AA}$ .,  $1.30 \text{ \AA}$ .,  $1.30 \text{ \AA}$ .,  $1.35 \text{ \AA}$ .. The first three of these have been calculated from compounds in which the atoms share electrons, the nitrates, carbonates, and diamond. No compound in which fluorine shares electrons has been analysed, but evidence has been given that it occupies the same volume as oxygen. The outer electron shell which these atoms tend to complete is that of Neon. We may therefore estimate the diameter of the outer neon shell as being  $1.30 \text{ \AA}$ . Since two electrons at least are held in common by the elements this estimate may be somewhat too large.

In the second short period the diameters of silicon, sulphur, and chlorine are  $2.35 \text{ \AA}$ .,  $2.05 \text{ \AA}$ .,  $2.10 \text{ \AA}$ .. The structure of phosphorus has not yet been analysed. The diameter of the outer Argon shell appears to be  $2.05 \text{ \AA}$ .

In the first long period, the lower limit to which the diameters tend is  $2.35 \text{ \AA}$ .. The structure of arsenic has not been analysed, but it crystallizes in a form isomorphous with antimony, the structure of which has been recently determined by James and Tunstall. If its structure is that of antimony, the distance between the nearest atoms is  $2.52 \text{ \AA}$ .. Selenium has been assigned a diameter of  $2.35 \text{ \AA}$ ., bromine a diameter of  $2.38 \text{ \AA}$ .. Other elements in the same period tend to approach this limit. When manganese and chromium act as acid-forming elements and so share electrons with other atoms, they enter into compounds isomorphous with the sulphates and selenates, and the molecular volumes of the compounds are very nearly those of the selenates, so that the atoms appear to have dimensions identical with those of selenium. The distances between atomic centres in iron, nickel, and copper are  $2.47 \text{ \AA}$ .,  $2.39 \text{ \AA}$ .,  $2.55 \text{ \AA}$ .. These figures confirm the estimate of  $2.35 \text{ \AA}$ . as the lower limit to which the diameter tends.

In the second long period, the distance between atomic centres in gray tin is  $2.80 \text{ \AA}$ ., in antimony  $2.80 \text{ \AA}$ .. Tellurium

and iodine have been assigned diameters of 2.66 Å. and 2.80 Å. The evidence for the lower limit is imperfect, but it may be estimated as 2.70 Å.

The diameters of the outer electron shells of the inert gases therefore appear to be—

Neon	.....	1.30 Å.
Argon	.....	2.05 Å.
Krypton	.....	2.35 Å.
Xenon	.....	2.70 Å.

On Langmuir's theory, the crystal of an electropositive element consists of an assemblage of positively charged ions held together by electrons which are free to move in the structure. The empirical relation between inter-atomic distances in compounds is less accurate when applied to the metals, perhaps as a result of the different nature of the forces in this latter case. For instance, in a number of isomorphous series the substitution of magnesium for iron decreases the molecular volume, yet the distances between atomic centres in metallic magnesium and iron are 3.22 Å.\* and 2.47 Å, respectively. Silver and sodium form many isomorphous salts of nearly identical molecular volume. The distances between atomic centres in crystalline silver and sodium are 2.87 Å. and 3.72 Å. Isomorphous salts of the same molecular volume are formed by rubidium and thallium, by strontium and lead, substances whose atomic volumes differ widely. The relations shown in fig. 3 hold most accurately for compounds and for the electronegative elements.

The electropositive elements crystallize in the cubic or hexagonal systems. This was pointed out by Barlow and Pope, and used as a basis for the theory of close-packing in crystalline structures, since an assemblage of equal spheres packed together in the closest manner has either cubic or hexagonal symmetry. It is now known that the atoms of some metals are not arranged in a close-packed manner. Nevertheless, the idea of a metal as an assemblage of positive ions held together by electrons indicates a reason for the simple crystalline structure. Each atom has the same relation to its neighbours, it is not bound in any way to one rather than another of them, and the assemblages will take a form like the arrangement of a set of equal spheres. The crystal of an electronegative element, on the other hand, where atoms are linked by holding electrons in common, will have a more complicated structure, as is the

\* A. W. Hull, Phys. Rev., July 1917.

case for sulphur, selenium, tellurium, iodine, arsenic, antimony, bismuth.

15. In order to obtain a more complete knowledge of the distances between atoms which hold electrons in common, the examination of salts such as the nitrates, chlorates, bromates, sulphates, and selenates would be desirable. The investigation of these salts presents some difficulty, since their crystalline forms are complex. The symmetry of the crystal is of less assistance in determining the arrangement of the atoms than it is for the simple crystals, as it is of a much lower type. It is hoped that the empirical relations formulated in this paper will help in this investigation. The conception of the atoms as a set of spheres of appropriate diameters packed tightly together limits the number of possible arrangements and aids in deciding the correct disposition of the atoms. The scheme may be of assistance in analysing the structure of crystals such as quartz\*, sulphur\*, and the alkaline sulphates†, crystals for which the dimensions of the lattice are known, but which have so far proved too complicated for complete analysis.

#### *Summary.*

1. An examination of the distances between neighbouring atoms in a crystal leads to an empirical relation determining these distances. The distance between the centres of two atoms may be expressed as the sum of two constants characteristic of the atoms. The arrangement of the atoms in a crystalline structure may therefore be pictured as that of an assemblage of spheres of appropriate diameters, each sphere being held in place by contact with its neighbours.

2. This empirical law is summarized by the curve of fig. 3, where the constants for a number of elements, arranged in the order of their atomic numbers, are plotted. The curve is periodic and resembles Lothar Meyer's curve of Atomic Volumes. Each atom occupies a constant space in any crystalline structure of which it forms part. The space occupied by the alkaline metals and alkaline earths is greatest, that occupied by the electronegative elements least.

3. The accuracy of the relation is discussed. Variations of the order of 10 per cent. between the calculated and observed distances occur, so that the law is only approximately true. Nevertheless, it is of considerable assistance

\* W. H. Bragg, Proc. Roy. Soc. A. vol. lxxxix. (Jan. 1914).

† Ogg and Hopwood, Phil. Mag. [6] xxxii. p. 518 (1916).

in the analysis of the more complex crystal structures, since the conception of the atoms as an assemblage of spheres of known diameters packed tightly together limits the number of possible arrangements which have to be tried in interpreting the diffraction of X rays by the crystal.

4. The physical significance of the relation is examined with reference to Langmuir's theory of atomic structure. From this point of view, it follows that two electronegative atoms are situated close together in a crystalline structure because they share electrons, and the spheres representing them are therefore assigned small diameters. On the other hand, an electropositive element does not share the electrons in its outer shell with the neighbouring atoms, and is therefore situated at a distance from other atoms so that it appears to occupy a greater space in the structure.

5. It is shown that the relation is less accurate when applied to the crystals of metals, which, on Langmuir's theory, consist of an assemblage of positive ions held together by electrons which have no fixed positions in the structure.

6. From the distance between electronegative atoms holding electrons in common, an estimate is made of the diameter of the outer electron shell in the inert gases.

Manchester University,  
April 1920.

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XIX. *The Dissociation of Iodine Vapour and its Fluorescence.* By ST. LANDAU, B.Sc., Lecturer in Physics at the Governmental Technical School, Warsaw, and ED. STENZ\*.

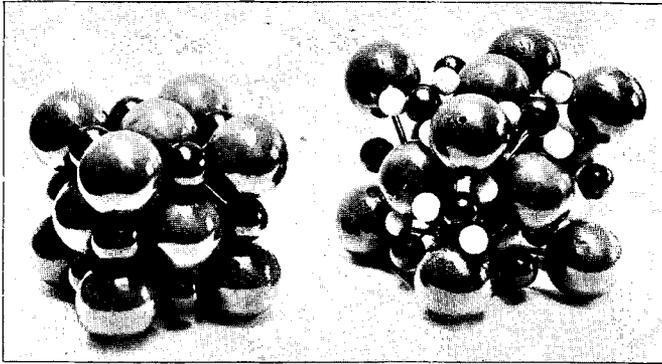
I. *The aim of this work.*

THE researches of R. W. Wood on the fluorescence of the vapours of sodium, mercury, and iodine are generally known; he discovered the remarkable phenomenon of optical resonance in these vapours. The most complicated relations were found by Wood † in the case of iodine vapour; the number of lines in the absorption spectrum of iodine is estimated by Wood to be 40,000–50,000. Different "resonance spectra" may be obtained, when the exciting line covers different absorption lines.

We put the following question: Is the complicated vibrating system, which corresponds to these various resonance

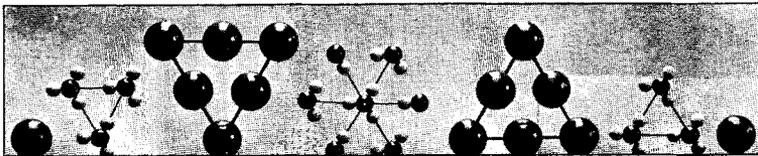
\* Communicated by the Authors. Presented by Prof. L. Natanson to the Polish Academy of Sciences (Cracow) 18th Nov. 1919.

† Phil. Mag. March 1918, p. 236.

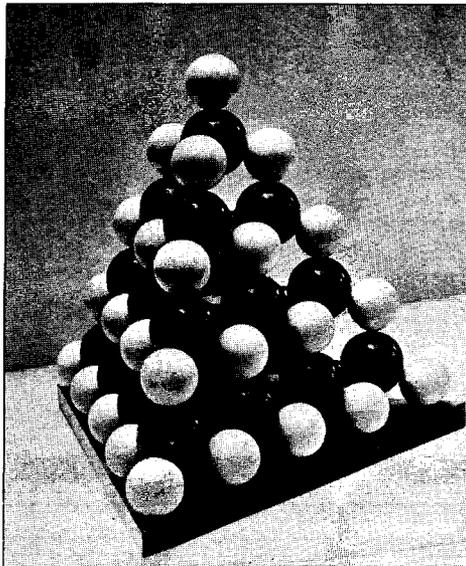


Sodium chloride.

Calcium carbonate (Calcite).



Planes (III) of Calcite.



Zinc sulphide (Zinc-blende).