SOME SIGNIFICANT RESULTS OF CRYSTAL STRUCTURE ANALYSIS

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The purpose of this article is to summarize what seem to be the most significant results of crystal structure studies by means of x-rays. Since a summary of organic crystal structure results was published in This Journal (1) not long ago, this paper will deal chiefly with inorganic crystals.[1]

CLASSIFICATION OF INTERATOMIC FORCES OF MOLECULES AND OF IONS

Attractive forces between atoms in crystals may be classified as follows: (*1*) *valence* forces, due to electron-pair bonds (or to one-electron or three-electron bonds (4)); (*2*) *ionic* forces, due to electrostatic forces between ions; (*3*) *metallic* forces,—those holding the atoms together in crystals of metals. (These probably are in part electrostatic attractions between the positively charged atom kernels and those valence electrons which are "free" or in other atoms, and in part attractions due to the interaction of valence forces similar to those producing electron-pair bonds in non-metallic crystals. Compare Slater (5)); (*4*) *residual* (or "van der Waals'") forces, not included in the above.

As examples of crystals in which the forces between all pairs of adjacent atoms are of one of these types exclusively (or practically so), the following may be mentioned:

(1) C (diamond), Si, SiC (figure 1)

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[1] Except as otherwise noted, the structures mentioned are described, with references to the x-ray work, by Ewald and Hermann (2). Most of them are also described by Wyckoff (3).

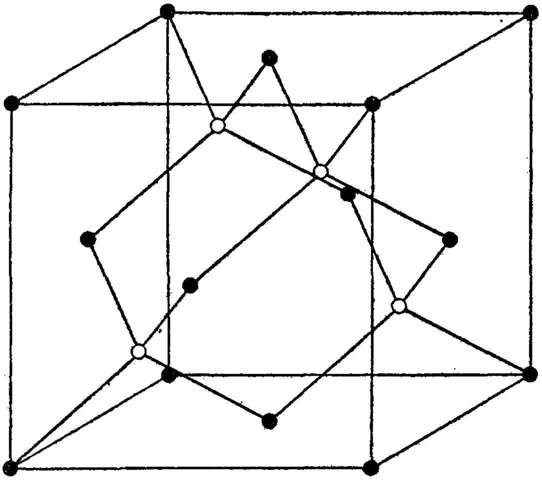


Fig. 1. The Unit Cube of the ZnS Structure

Each atom is tetrahedrally surrounded by four of the other kind. Like atoms (of either kind, considered separately) are in a face-centered cubic arrangement (cubic close-packing). The diamond has the same arrangement, all atoms being alike.

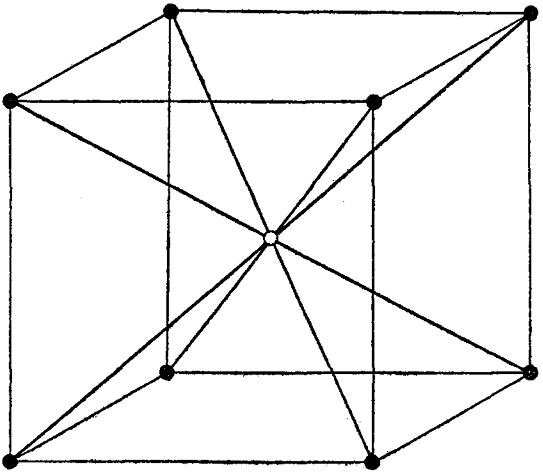


Fig. 2. The Unit Cube of the CiCl Structure

Each atom is cubically surrounded by eight of the other kind. With all atoms alike, this is the body-centered cubic arrangement possessed by a number of the metals (see table 4).

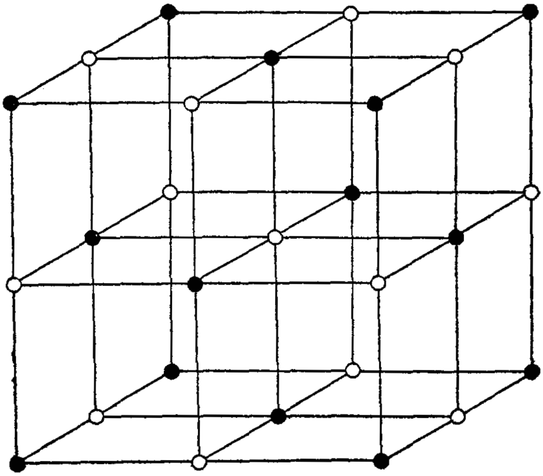


FIG. 3. THE UNIT CUBE OF THE NaCl STRUCTURE

Each atom is octahedrally surrounded by six of the other kind. Like atoms have the cubic close-packed arrangement possessed by many metals, by the rare gases, and by some molecules, such as HCl and H_2S.

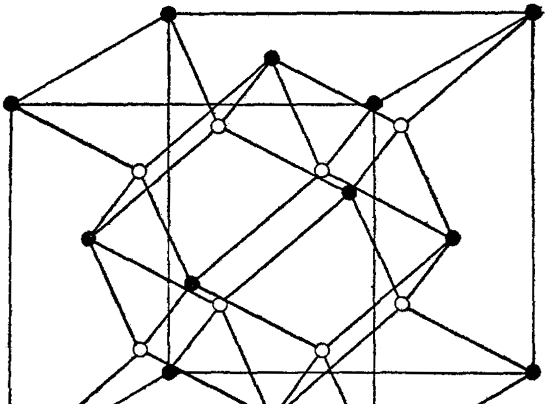


FIG. 4. THE UNIT CUBE OF THE CaF_2 AND Li_2O STRUCTURES

Each calcium or oxygen atom (represented by a dot) is cubically surrounded by eight fluorine or lithium atoms (open circles); each fluorine or lithium atom is tetrahedrally surrounded by four calcium or oxygen atoms. The calcium or oxygen atoms, considered separately, are in the cubic close-packed arrangement.

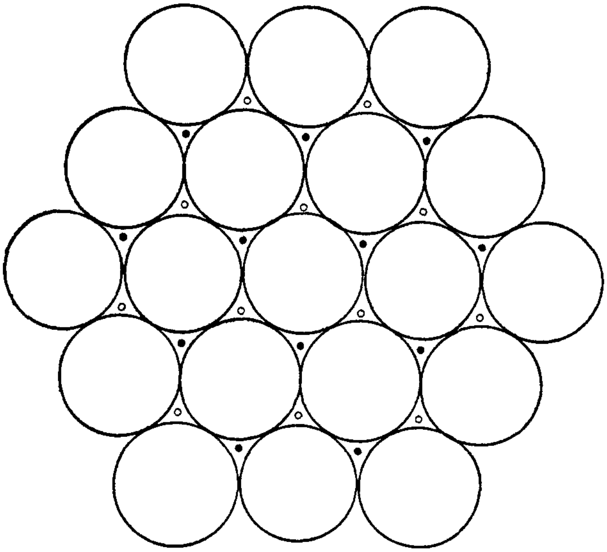


FIG. 5. A PORTION OF A LAYER OF "CLOSE-PACKED" SPHERES

The centers of the spheres in the second layer are over the dots. In "hexagonal close-packing" the third layer spheres are directly over those in the first layer; in "cubic close-packing" the third layer spheres are over the small open circles, the fourth layer spheres being over those in the first layer.

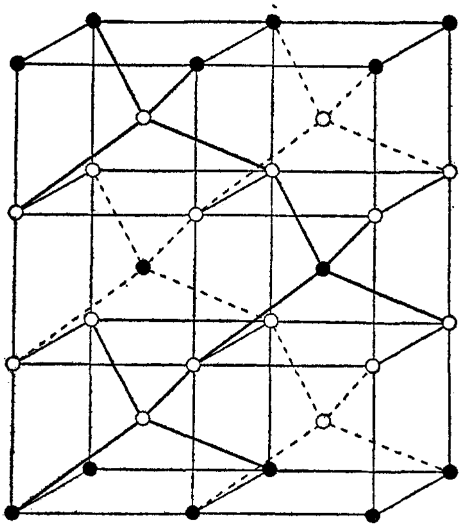


FIG. 6. A PORTION (TWO UNIT CELLS) OF THE $MoSi_2$ STRUCTURE

Each molybdenum atom (represented by a dot) is surrounded approximately cubically by eight silicon atoms (open circles); each silicon atom similarly by four molybdenum atoms and four other silicon atoms. Each atom may be tetrahedrally bonded to but four of its eight neighbors, in which case the whole crystal consists of two molecules. This is shown by representing the bonds in one molecule by full lines, those in the other molecule by dotted lines.

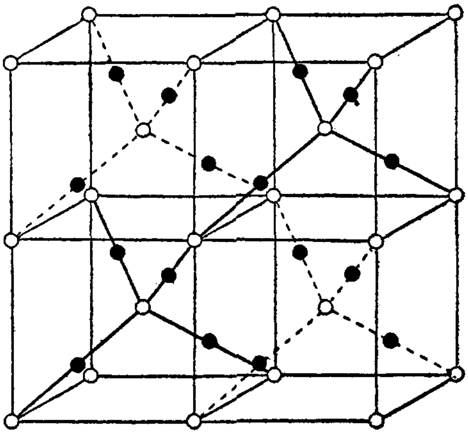


Fig. 7. A Portion (Four Unit Cubes) of the Cu_2O Structure

Each oxygen (open circle) is tetrahedrally surrounded by four copper atoms; each copper atom being midway between two oxygen atoms. The copper atoms, considered separately, are in cubic close-packing. The whole crystal can be considered as two molecules, the bonds in one being represented by full lines, those in the other by dotted lines.

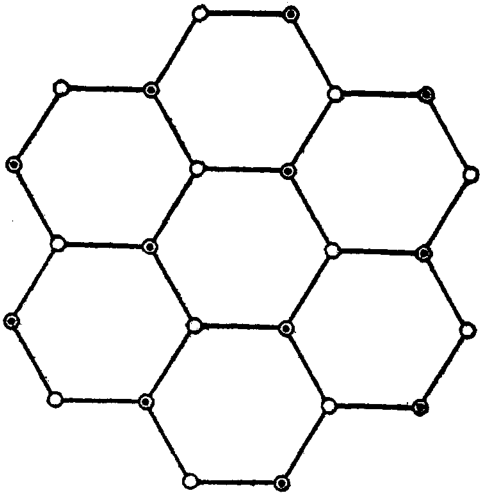


Fig. 8. A Portion of a Layer of the As Structure

The open circles represent atomic centers below the plane of the projection; the dotted circles those above the projection plane. The closest atoms in the next layers above and below this layer are directly over and under the centers of the hexagons.

This figure also represents a layer of silicon atoms in $CaSi_2$. The calcium ions are in parallel planes over and under the center of each hexagon.

This figure will also serve to represent a layer of the MoS_2 structure, the dotted circles denoting molybdenum atoms in the plane of the projection and each of the open circles two sulfur atoms, one below and one above the projection plane. Each molybdenum atom is bonded to six sulfur atoms, each sulfur atom to three molybdenum atoms. The nearest atoms (sulfur) in the next layers are over and under the molybdenum atoms in this layer.

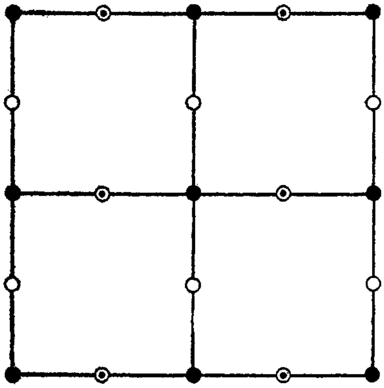


FIG. 9. A PORTION OF A LAYER OF THE HgI_2 STRUCTURE

Each mercury atom (dot) in the plane of the projection is tetrahedrally bonded to four iodine atoms, two above (dotted circles) and two below (open circles) the projection plane. The nearest atoms (iodine) in the adjacent layers are over and under the centers of the squares. The arrangement of iodine atoms approximates cubic close-packing.

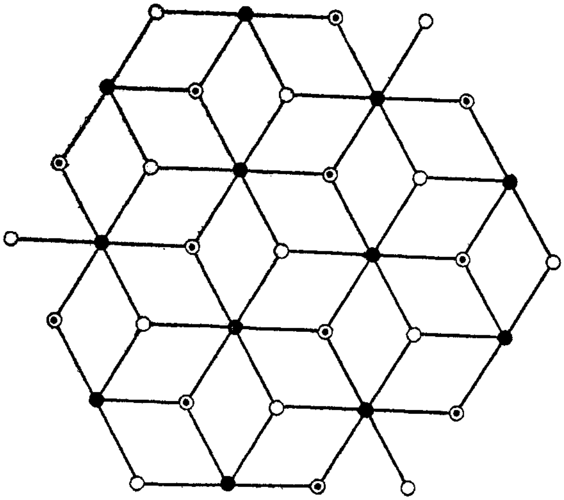


FIG. 10. A PORTION OF A LAYER OF THE $CdCl_2$ OR CdI_2 STRUCTURE

The cadmium atoms (dots) in the plane of the projection are equidistant from six chlorine or iodine atoms, three (dotted circles) above and three (open circles) below the projection plane. In $CdCl_2$ the nearest chlorine atoms in the adjacent layers are over and under the cadmium centers, the ensemble of chlorine atoms approximating cubic close-packing. In CdI_2 the lower iodine atoms in adjacent layers are over and under the lower iodine atoms in this layer; similarly for the upper iodine atoms and for the cadmium atoms. This gives an hexagonal close-packed arrangement of iodine atoms.

(2) CsCl, NaCl, CaF_2 (figures 2, 3, 4)
(3) Cu, Zn, Na (figures 2, 3, 5)
(4) Ne, A, Kr (figures 3, 5)

If we define a *molecule* as an assemblage of atoms all held together by valence forces, the whole crystal must be considered a single *giant molecule,* in such crystals as the diamond and SiC.

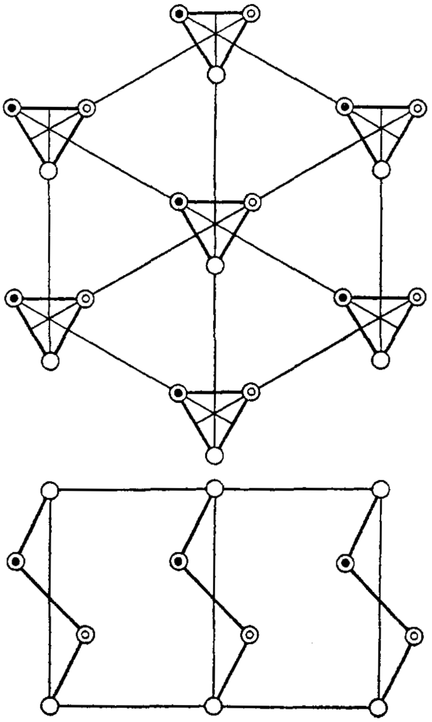


FIG. 11. A PORTION OF THE STRUCTURE OF Se, IN PLAN AND IN PROJECTION
Each selenium atom is bonded to two others in the same string

In $MoSi_2$ (figure 6) and in Cu_2O (figure 7) each single crystal is probably composed of two such molecules interlocking. Other giant molecules are merely *layers* (figures 8, 9, 10) or *strings* (figure 11) of bonded atoms, different layers or strings being held together by residual forces. Crystals containing small *formula molecules,* such as SnI_4, As_4O_6 (figure 12), and most organic compounds, are also mixtures of types 1 and 4. $CaSi_2$ consists of charged silicon layers, resembling the arsenic layers (figure 8) in metallic arsenic, separated by Ca^{++} ions; it is therefore a mixture of types 1 and 2. If we assume electron-pair bonds between the silicon and oxygen atoms in silicates (these atoms are no doubt held together in part by ionic forces), with ionic forces between the oxygen atoms and the other metal atoms, these are also mixtures of types 1 and 2 (see the later discussion), as are also crystals containing such polyatomic ions as NH_4^+, $N(CH_3)_4^+$, and $Fe(CN)_6^{---}$.

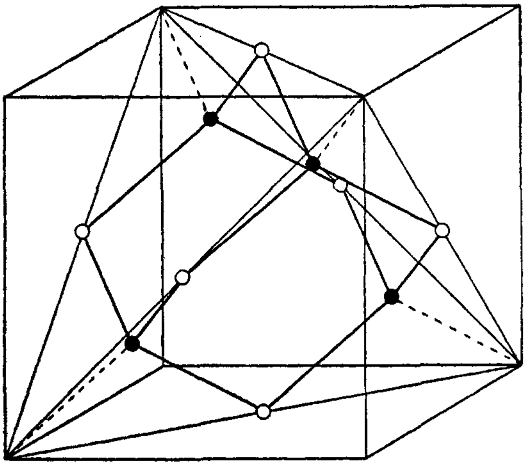


FIG. 12. A MOLECULE OF As_4O_6

Each arsenic atom (dot) is bonded to three oxygen atoms (open circles); each oxygen atom to two arsenic atoms. Light lines and dotted lines are merely to aid in visualization. In the crystal, molecules like this are arranged as are the carbon atoms in the diamond (figure 1). The arsenic centers are approximately in a cubic close-packed arrangement.

CuS is probably a mixture of types 1, 2, and 3, containing S_3^{--} and Cu^+ ions and metallic electrons (or neutral copper atoms).

CONFIRMATION OF THE LEWIS THEORY OF VALENCE

From G. N. Lewis' theory (6) of electron-pair sharing and the completion of tetrahedral valence shells for electronegative atoms, one can predict from the formula both the number of bonds between such atoms and their relative orientations.

The same conclusions, it has been shown (7), can be deduced from the wave mechanics. These predictions have been verified by the crystal structure results in many instances, the few exceptions ($CsICl_2$, $CaCO_3$, $NaNO_3$, to be discussed later) being reasonably explained. One would predict from the theory, for instance, that in iodine crystals each atom is bonded to but one other, in selenium and tellurium to two, in arsenic, antimony, and bismuth to three, and in carbon, silicon, and germanium to four, in agreement with the experimental results (figures 1, 8, 11). Likewise in As_2O_3 (or, better, As_4O_6) the prediction of three oxygen atoms around each arsenic atom and of two arsenic atoms adjacent to each oxygen atom is verified (figure 12). In each of these and many others which might be mentioned the arrangement around each atom of its neighbors is also in accord with the theory (compare references 8 and 9).

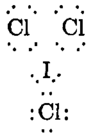
Electropositive atoms are sometimes bonded tetrahedrally but quite frequently octahedrally or in other ways to electronegative atoms. The arrangement adopted depends on various factors —namely, which arrangements are geometrically possible with the right relative numbers of atoms, whether the bonds are pure electron-pair bonds or wholly or partly ionic, relative sizes of the atoms, etc.—factors which have been discussed quite fully elsewhere and which will be briefly considered later in this paper.

ELECTRONEGATIVE ATOMS WITH MORE THAN FOUR VALENCE ELECTRON-PAIRS

A few instances are known of compounds in which an electronegative atom, when bonded to smaller and more electronegative atoms, has more than four electron-pairs in its valence shell. PCl_5 and SF_6 are the best known examples. $CsICl_2$ is another. It consists of Cs^+ and $(ClICl)^-$ ions in an arrangement similar to that in NaCl (figure 3). The three atoms in each negative ion are colinear (unless there is continuous rotation of the ion), as would be expected of this valence electron distribution:

$$:\overset{..}{\underset{..}{\mathrm{Cl}}}:\overset{\cdot\cdot\;\cdot\cdot}{\underset{..}{\mathrm{I}}}:\overset{..}{\underset{..}{\mathrm{Cl}}}:$$

The non-polar and polar valence numbers and the formal charge of the iodine, as defined in a later paragraph, are 3, +1, and −1, respectively. The I_3^- ion is undoubtedly similar, and ICl_3 would be expected to be



$$\begin{array}{c}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}\;\;\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}\\ \cdot\underset{\cdot\cdot}{\text{I}}\cdot\\ :\underset{\cdot\cdot}{\text{Cl}}:\end{array}$$

all the atoms having zero formal charge.

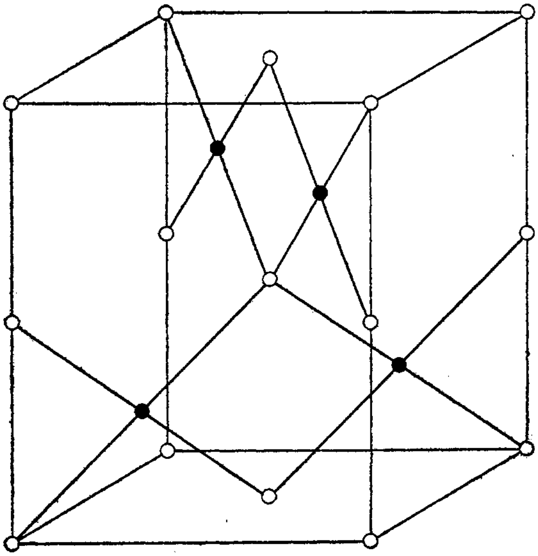


FIG. 13. A UNIT CELL (NOT THE SMALLEST) OF PdO
Each palladium atom (dot) is surrounded at equal distances by four coplanar oxygen atoms (open circles); each oxygen atom is surrounded tetrahedrally by four palladium atoms. The palladium atoms by themselves are approximately in cubic close-packing.

CONFIRMATION OF WAVE MECHANICS PREDICTIONS

An additional consideration of great importance has to do with the possible or favored electron *eigenfunctions* of the atoms involved. In certain cases the predictions of wave mechanics in this regard can be tested directly by crystal structure results. For instance Pauling (7) has shown that around bivalent nickel, palladium, or platinum an arrangement of four bonds at corners of a square is more stable than one of four bonds at tetrahedron corners. In agreement with this, a square arrangement of chlorine atoms around each platinum or palladium atom has been found in crystals of K_2PdCl_4, K_2PtCl_4, and $(NH_4)_2PdCl_4$. Similarly a nearly completed analysis of $N(CH_3)_4AuCl_4$ by the writer, seems to indicate a square $AuCl_4^-$ ion. Structure analyses of pentlandite, which has approximately the composition Ni_3FeS_4, and of millerite, NiS, place four coplanar sulfur atoms around each nickel atom. The observed x-ray data from PdO are in agreement with an arrangement (figure 13) in which each oxygen atom is tetrahedrally and each palladium atom (approximately) squarely surrounded by atoms of the other kind (10).

Another outcome of wave mechanics calculations is the conclusion that quadrivalent chromium, molybdenum, and tungsten can form six strong bonds at corners of a trigonal prism. This explains the previously anomalous structure possessed by MoS_2 and WS_2 (figure 8).

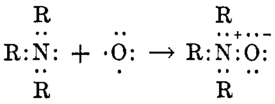
RELATIONSHIPS BETWEEN VALENCE AND STRUCTURE

Crystal structure studies have served to clarify considerably our ideas of the relationships between valences and structure and between the different kinds of valence. Lewis' shared electron-pair bond is interpreted (7), according to the new quantum mechanics, as due to the resonance or interchange phenomenon between two single electrons, one in each atom, with opposed spins.

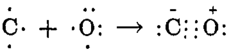
A valence number, as used in organic chemistry, is considered to be the number of bonds joining an atom to other atoms. It is evident that this equals for each atom the number of single (unpaired) electrons which are in the valence shells of the neutral atoms of which the structure can be considered to be composed: four for carbon, three for nitrogen or phosphorus, two for oxygen or sulfur, one for fluorine or chlorine, etc. If, however, the hypothetical formation of a compound from neutral atoms would necessarily involve the *transfer* of one or more electrons from one atom to another, either (a) in the production of ions

$$\text{(a)}\ \mathrm{Na}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \rightarrow \mathrm{Na}^+ + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:^-$$

or (b) in the process of bond formation,

(b) 

$$\mathrm{R}{:}\overset{\mathrm{R}}{\underset{\mathrm{R}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}}}{:} + \cdot\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{O}}}{:} \rightarrow \mathrm{R}{:}\overset{\mathrm{R}}{\underset{\mathrm{R}}{\overset{\cdot\cdot\,+}{\underset{\cdot\cdot}{\mathrm{N}}}}}{:}\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{\mathrm{O}}}{:}$$

(c) 

$$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{O}}}{:} \rightarrow {:}\overset{-}{\mathrm{C}}{:}{:}\overset{+}{\mathrm{O}}{:}$$

the non-polar valence number equals the sum of the number of bonds and the number of electrons added to or removed from the atom in question. Another way of stating the same relationship is to say that *the non-polar valence number equals the arithmetical sum of the number of shared electron-pairs and the formal charge,*—that is, the atomic charge calculated in a purely formal way by counting one electron of each shared pair (and of course both electrons of each unshared pair), regardless of any possible partial polarity of the bond.

The polar valence numbers used in inorganic chemistry are the net charges on the atoms which are either actually present (in simple ions) or which would exist if both electrons of each shared pair were arbitrarily assigned to the more electronegative atom of the two which share that pair. (In cases of bonds between like atoms, as in HOOH or H_3CCH_3, or of bonds of doubtful polarity, the shared electron-pairs can be considered as being equally divided between the bonded atoms.) In other words, *the polar valence number equals the formal charge plus the number of electron-pairs shared with more negative atoms minus the number of electron-pairs shared with more positive atoms.*

It is obvious that the polar valence numbers, like the non-polar valence numbers, give the number of electron-pair bonds around an atom only if the structure could be built up from neutral atoms without the transfer of any electrons from atom to atom, as, for instance, in H_2O, SnI_4, and As_4O_6. We may define "secondary valence compounds" as those in which the number of bonds around each atom is not equal to either of its valence numbers, that is, as those in which some of the atoms have formal charges different from zero. All ionized compounds belong in this class, also all compounds whose formation solely from neutral atoms or from primary valence compounds would necessarily involve secondary valence *reactions* (b) as well as primary valence *reactions* (a),

$$\text{(a)}\quad A\cdot + \cdot B \rightarrow A:B$$

$$\text{(b)}\quad A + :B \rightarrow A:B$$

There is no difference whatever, as the writer has repeatedly pointed out (11, 12) between a primary valence *bond* and a secondary valence *bond*, once formed. To illustrate, there is good reason to believe that in a crystal of cuprous chloride (ZnS type, figure 1), each atom is bonded by electron-pair bonds to its four equidistant neighbors. A primary valence reaction could produce but one such bond per atom. Similarly $AuCl_3$ molecules could be formed from neutral atoms by primary valence reactions alone, but one of the four equivalent bonds in $AuCl_4^-$ must have been produced by a secondary valence reaction.

Although in many primary and secondary valence compounds and ions the atoms are thus held together by electron-pair bonds, in many others this is not the case, since atoms can be held in fixed relative positions with respect to each other by attractions due to their ionic charges or to polarization of the atoms or groups concerned. Crystal structure studies have shown the arrangement, usually tetrahedral or octahedral, of H_2O or NH_3 groups or Cl atoms, for instance, around a central positive atom in many cases, but other criteria, such as Pauling's magnetic criterion (7) or the interatomic distance criterion (see below) must be relied upon to determine whether or not there is electron-pair bonding.

INTERATOMIC DISTANCES

The equilibrium distance between two atoms in a crystal depends on many factors. By comparing distances between different pairs of atoms in the same or similar crystals and distances between like pairs of atoms in different crystals it has been possible to determine considerable in regard to the relative importance and magnitudes of these factors. Let us first divide interatomic distances into four classes, corresponding to the four classes of attractive forces listed at the start of this paper. For each of these classes we then choose one or more standard types of arrangement (those for which the most or best data are available) and deduce standard radii which, added together, will reproduce quite closely the observed distances between atoms in crystals of these types.

Table 1 and figure 14 give standard radii for "tetrahedral" crystals (13, 10), such as those of the ZnS type (figure 1), obtained on the assumption that the atoms are joined by electron-pair bonds. In such crystals, according to the new quantum mechanics, the binding can be partly ionic and partly non-ionic. Although there is reason to believe that in most of these crystals the ionic contribution to the bond is small, the method of derivation of these radii (starting with bonds of certain non-polar character and assuming additivity of radii and smooth curves for each row of the table) automatically takes care of corrections for partial ionic character, provided the absolute magnitude of the correction depends only on the columns of the table in which the elements concerned lie. The observed distances in BeO, AlN, and SiC indicate a decrease from the calculated values of about

TABLE 1

Standard radii for tetrahedral crystals containing electron-pair bonds

Li 1.35	Be 1.07	B 0.89	C 0.77	N 0.70	O 0.66	F 0.64
Na 1.70	Mg 1.40	Al 1.26	Si 1.17	P 1.10	S 1.04	Cl 0.99
Cu 1.35	Zn 1.31	Ga 1.26	Ge 1.22	As 1.18	Se 1.14	Br 1.11
Ag 1.53	Cd 1.48	In 1.44	Sn 1.40	Sb 1.36	Te 1.32	I 1.28
Au 1.50	Hg 1.48	Tl 1.47	Pb 1.46	Bi 1.46		

0.05 to 0.10 Å., due probably to small kernel repulsion, if the more negative atom is carbon, nitrogen, oxygen, or fluorine and the more positive atom is of an element in the first or second row of the Periodic Table. For a discussion of the factors producing variation in interatomic distances in different structure types the reader must refer elsewhere (10).

In table 2 and figure 15 are given standard ionic radii for NaCl type crystals (coördination number 6) obtained in a semi-theoretical manner by Pauling (14, 15). Zachariasen's empirical radii (16) are also given, in parentheses. An earlier empirical set (17) published by Goldschmidt differs but little from these two.

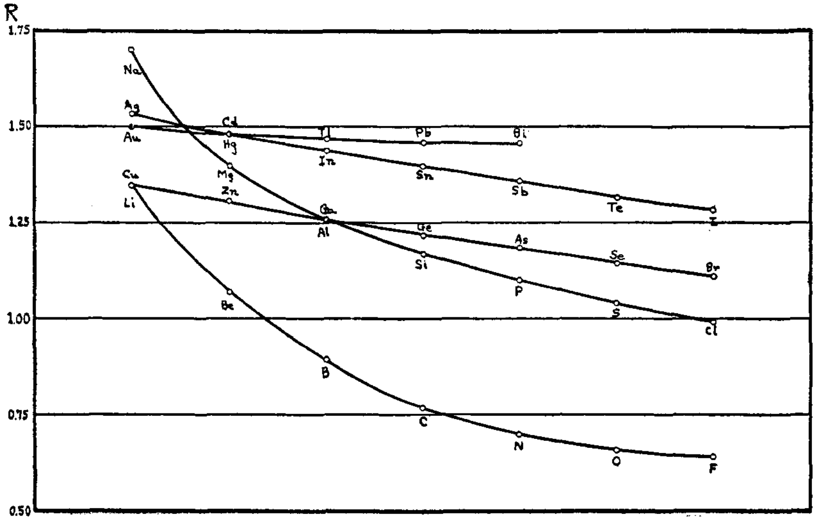


Fig. 14. Standard Radii for Electron-pair Bonded Atoms in Tetrahedral Crystals

Interatomic distances in CsCl type crystals (coördination number 8) are about 3 per cent larger than the sum of these radii. A similar but probably slightly larger correction in the opposite direction must be made to obtain distances between ions in tetrahedral crystals (coördination number 4). Zachariasen (16) has calculated it to be 4.3 per cent, from theoretical considerations. (The data for testing this directly are very meager. See, however, the following paragraph.) Other corrections are necessary for other structure types, for polarization, and for other factors.

If we compare interatomic distances calculated on the assumption of pure ionic binding (table 2) with those calculated on the assumption of electron-pair binding (table 1), using appropriate corrections for structure type, etc., it appears that in all or nearly all cases where other evidence indicates that the bonding is

TABLE 2

Standard ionic radii for sodium chloride type crystals

CHARGE −4	CHARGE −3	CHARGE −2	CHARGE −1	CHARGE +1	CHARGE +2	CHARGE +3	CHARGE +4	CHARGE +5	CHARGE +6	CHARGE +7
			H 2.08 (1.36)[*]	Li 0.60 (0.68)	Be 0.31 (0.39)	B 0.20 (0.24)	C 0.15 (0.19)	N 0.11	O 0.09	F 0.07
C 2.60	N 1.71	O 1.40 (1.40)	F 1.36 (1.33)	Na 0.95 (0.98	Mg 0.65 (0.71)	Al 0.50 (0.55)	Si 0.41 (0.44)	P 0.34	S 0.29	Cl 0.26
Si 2.71	P 2.12	S 1.84 (1.85)	Cl 1.81 (1.81)	K 1.33 (1.33)	Ca 0.99 (0.98)	Sc 0.81 (0.78)	Ti 0.68 (0.62)	V 0.59	Cr 0.52	Mn 0.46
				Cu 0.96	Zn 0.74	Ga 0.62	Ge 0.53	As 0.47	Se 0.42	Br 0.39
Ge 2.72	As 2.22	Se 1.98 (1.96)	Br 1.95 (1.96)	Rb 1.48 (1.48)	Sr 1.13 (1.15)	Y 0.93 (0.93)	Zr 0.80 (0.79)	Cb 0.70	Mo 0.62	
				Ag 1.26	Cd 0.97	In 0.81	Sn 0.71	Sb 0.62	Te 0.56	I 0.50
Sn 2.94	Sb 2.45	Te 2.21 (2.18)	I 2.16 (2.19)	Cs 1.69 (1.67)	Ba 1.35 (1.31)	La 1.15 (1.06)	Ce 1.01 (0.89)			
				Au 1.37	Hg 1.10	Tl 0.95	Pb 0.84	Bi 0.74		

[*] The values in parentheses are those of Zachariasen (16); the others are those given by Pauling (14, 15).

chiefly of one type or the other, the distance calculated on the basis of that assumption is the smaller. To illustrate this, in table 3 have been listed the ratios of the sums of radii from tables 1 and 2, without correction for structure type or other factors, for pairs of atoms whose kernel charge sum equals 8. The lowest values of this ratio are found for the undoubtedly electron-pair bonded CC (diamond), SiC, etc., while the highest values are those for the alkali halides and alkaline earth oxides and sulfides,

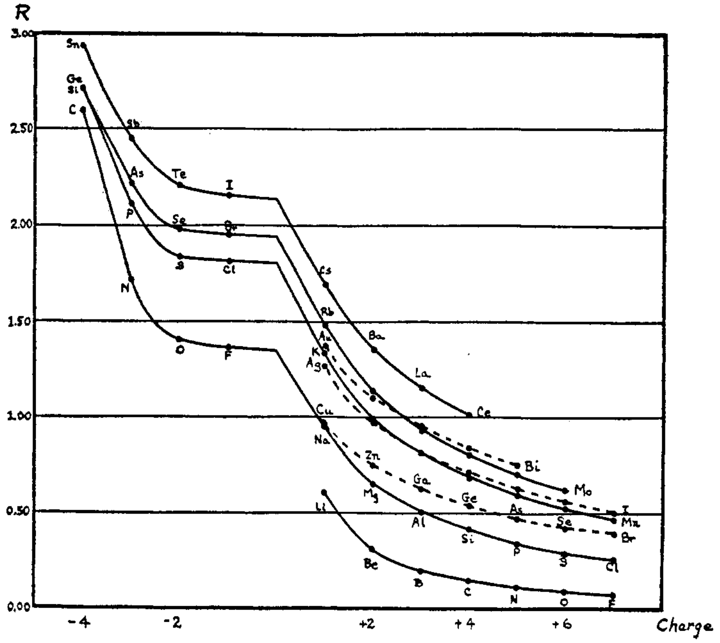


FIG. 15. STANDARD IONIC RADII FOR NaCl TYPE CRYSTALS

which are surely ionic. The ratios for the copper, silver, and gold halides are probably low, partly on account of assumed ionic radii for these metal atoms which are too high (see footnote to table 3) and partly on account of the neglect of polarization corrections. (Cf. Pauling (14), especially pages 772 and 779.) In general, it appears that if we can assume interatomic distances in tetrahedral crystals to be about 95 per cent of their values calculated for NaCl type crystals, the relative values of the calcu-

TABLE 3*

Ratios of interatomic distances calculated from tables 1 and 2

CC	BN	BeO	LiF	BP	BeS	LiCl	BAs	BeSe	LiBr	BSb	BeTe	LiI
0.56	0.83	1.01	1.02	0.86	0.98	0.97	0.86	0.97	0.97	0.85	0.95	0.95
SiC	AlN	MgO	NaF	AlP	MgS	NaCl	AlAs	MgSe	NaBr	AlSb	MgTe	NaI
0.64	0.89	1.00	1.01	0.90	0.98	0.98	0.90	0.97	0.97	0.89	0.96	0.96
GeC	GaN	ZnO	CuF	GaP	ZnS	CuCl	GaAs	ZnSe	CuBr	GaSb	ZnTe	CuI
0.64	0.84	0.92	0.86	0.86	0.91	0.85	0.86	0.90	0.85	0.85	0.89	0.84
SnC	InN	CdO	AgF	InP	CdS	AgCl	InAs	CdSe	AgBr	InSb	CdTe	AgI
0.66	0.85	0.90	0.83	0.87	0.90	0.82	0.87	0.89	0.82	0.86	0.88	0.82
PbC	TlN	HgO	AuF	TlP	HgS	AuCl	TlAs	HgSe	AuBr	TlSb	HgTe	AuI
0.65	0.82	0.86	0.78	0.84	0.86	0.78	0.84	0.85	0.79	0.83	0.85	0.79

---

* The ratios calculated using Goldschmidt's or Zachariasen's radii in general do not differ by more than 0.02 from those given. The values obtained for AgF, AgCl, AgBr, and AgI, using Goldschmidt's radii, are however 0.88, 0.86, 0.85, and 0.84. (Goldschmidt gives no values for the Cu^+ and Au^+ radii.)

TABLE 4*

Radii for metallic crystals

Coördination number																	
	Li	Be															
12		1.11															
8	1.50																
	Na	Mg	Al														
12		1.59	1.43														
8	1.83																
	K	Ca	Sc			Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	
12		1.96				1.45	1.30	1.35	1.36	1.27	1.26	1.24	1.28	1.37		1.39	
8	2.31							1.25		1.24							
	Rb	Sr	Y			Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
12		2.15				1.58				1.32	1.34	1.37	1.44	1.52	1.57	1.58	1.61
8	2.43						1.43	1.36									
	Cs	Ba	La	Ce-----	Er-------	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
12			1.86	1.81	1.86	1.57			1.37	1.34	1.35	1.38	1.44	1.55	1.71	1.75	1.82
8	2.62	2.17					1.42	1.37									
						Th		U									
12						1.79											
8								1.49									

* The figures for the elements Mn–Ge, Ru–Sb and Os–Bi are from Goldschmidt (18); the others from Neuberger (19).

lated interatomic distances are at least a rough criterion as to the type of bond.

It would be desirable, if possible, to have a standard set of radii for atoms in metallic crystals obtained only from crystals containing atoms similarly surrounded (as by twelve others in the close-packed types, figure 5) and either having the same number of valence electrons per atom (the electron distribution in the atomic kernel changing regularly from atom to atom) or

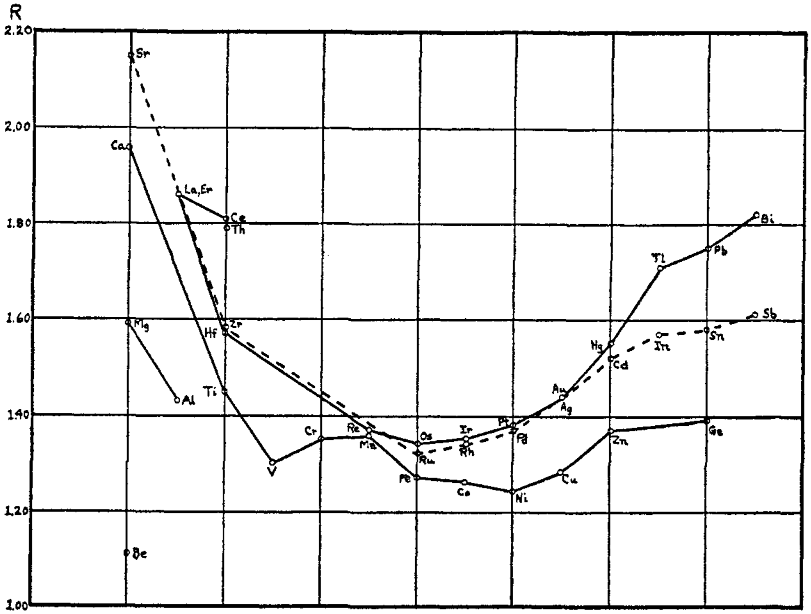


FIG. 16. RADII FOR ATOMS IN CLOSE-PACKED METALLIC STRUCTURES

having a regularly increasing number of valence electrons (the kernel maintaining the same electronic distribution) as one proceeds along a row of the Periodic Table. Unfortunately, however, our present knowledge of electron distributions in metals is very inadequate for this purpose. The best we can do is to list together and plot together radii for atoms in similar structure types (e.g., the "close-packed" types), disregarding differences in electron distribution. (See table 4 and figure 16.) These differences are no doubt responsible for the breaks in the curves connecting the radii in each row, but we shall for the present forego speculation as to their more specific interpretation.

A metal atom radius is ordinarily about 2 or 3 per cent smaller if it is surrounded by only eight neighbors than if it is surrounded by twelve (18, 54). If the data on chromium are correct, however, the difference in that case is about 8 per cent. This discrepancy may perhaps be attributable to the existence of strong electron-pair bonds between the atoms in the body-centered cubic form. If four valence electrons per atom are used for these bonds, each atom can be bonded tetrahedrally to four of its eight nearest neighbors. Such a structure can be described as consisting of two interpenetrating diamond type giant molecules (Cf. Cu_2O, figure 7).

TABLE 5

Radii for non-bonded atoms with twelve like neighbors

			Ne 1.60
P 1.65	S 1.75	Cl 1.85	A 1.92
As 1.7	Se 1.8	Br 1.9	Kr 1.98
Sb 1.8	Te 1.95	I 2.1	Xe 2.19
Bi 1.85			

Interatomic distances between non-bonded electronegative atoms, having complete valence shells, in crystals give us a measure of the distances at which the repulsions between them start to become appreciable. Rough values of radii obtained from such distances in crystals of the rare gases and of the layer molecule types, such as HgI_2 (figure 9) and CdI_2 (figure 10),—there being twelve approximately equidistant like atoms surrounding each negative atom—are listed in table 5 and plotted in figure 17. Similar data from crystals, such as As (figure 8) and Se (figure 11), in which each negative atom is surrounded by six others, show distances about 90–95 per cent of those given.

It is usually assumed, apparently justifiably, that the repulsion between two negative ions becomes of importance at a distance equal to the sum of their ionic radii. A comparison of tables 2 and 5 or of figures 15 and 17 shows that although the ionic radii (for negative ions) and the non-bonded atom radii are of the same order of magnitude, they change oppositely as one proceeds along a row of the Periodic Table.

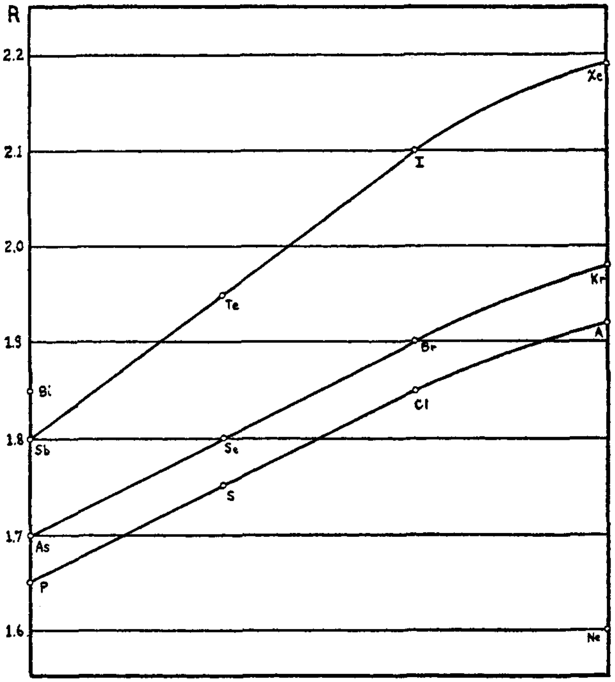


FIG. 17. STANDARD RADII FOR NON-BONDED ATOMS WITH TWELVE LIKE NEIGHBORS

STRUCTURE PRINCIPLES IN IONIC CRYSTALS (14, 15, 17, 20, 21)

Insofar as is permitted by structural limitations (depending on the relative numbers of the different kinds of atoms necessary for neutrality and their relative radii) it has been found, as would be expected from potential theory, that ions with unlike charges tend to be close together, at distances approximating the sum of their ionic radii, while ions with like charges tend to be as far apart as possible. Thus one always finds positive ions surrounded by negative and vice versa; moreover, other requirements permitting, a structure in which two positive ions are mutually bonded to but one negative ion (A, figure 18) is preferred to one in which the two positive ions are mutually bonded to two or three negative ions (B and C, figure 18). This relationship is similar to that between single, double, and triple bonds in organic molecules.

In crystals containing positive ions with different charges, one finds, in agreement with calculations of potentials, arrangements in which each negative ion is bonded to both kinds of cations rather than some exclusively to one and others exclusively to the other kind. Thus in Mg_2SiO_4, which we may for this purpose consider as a purely ionic crystal, each oxygen atom is surrounded by one silicon and three magnesium atoms, rather than some only by magnesium atoms and some only by silicon atoms.

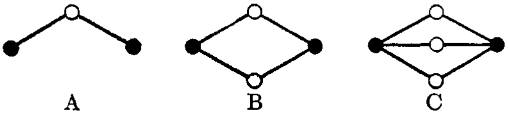


FIG. 18. ILLUSTRATING THE SHARING OF ONE, TWO, OR THREE ANIONS BY TWO CATIONS, CORRESPONDING TO THE SHARING OF CORNERS, EDGES, AND FACES OF THE ANION POLYHEDRA (Pauling)

A further deduction from potential theory, necessarily correct if all anions in a crystal have like charges and are similarly surrounded, and usually so in other ionic crystals, is Pauling's "electrostatic valence principle" (20), which states that the charge of an anion tends to be equalled by the sum of the $\left(\frac{\text{charge}}{\text{coördination number}}\right)$ ratios for the surrounding cations.

Although of most importance in ionic crystals, these same considerations, limited by the requirements of bond formation, are also applicable to other crystals containing more than one kind of atom, due to differences in degree of "electropositivity" or "electronegativity" and in many cases, as probably in the Mg_2SiO_4 example given in the second paragraph above, to a mixed ionic and non-ionic character of the bonds.

THE RADIUS-RATIO EFFECT. CLOSE-PACKING

The ratios AB/BB for cubic, octahedral, and tetrahedral arrangements of B atoms around an A atom are 0.866, 0.707, and 0.613 respectively. If the ratio of the distance between A and B atoms for stable bonding (e.g., the sum of the A and B radii from table 1 for electron-pair binding or from table 2 for ionic binding, in appropriate structures) to the distance between two B atoms at which repulsion between them begins to be considerable (e.g., twice the B radius from table 2 if B is a negative ion or twice that from table 5 if B is an uncharged atom) is less than 0.866, the cubic arrangement is less stable than the octahedral, provided other factors can be neglected. If this ratio is less than 0.707, the octahedral arrangement is less stable than the tetrahedral. This idea, first expressed by Cuy (22), has been used by him and others (14, 15, 17, 23) to account for the coördination numbers of different ions, the relative stabilities of different types of structure for simple salts, and certain relationships between structure and properties such as melting and boiling points, heats of fusion, etc. It ought to be mentioned, however, that some of the phenomena which have been attributed to the radius-ratio effect are probably, in part at least, due to other influences. For instance, the tetrahedral structures found for many compounds may be attributed either to this effect or to the possibility of four tetrahedral bonds around each atom in such structures but not in arrangements like that in NaCl. Similarly the existence of four oxygen atoms arranged tetrahedrally around each silicon atom in the silicates can be the result either of electron-pair bonding or of a small radius-ratio, with ionic bonding. Probably both factors are of importance, there being some ionic and some electron-pair character to each bond. Another point often neglected is that in the ZnS, ZnO, and NaCl structures, like atoms are in a close-packed array, each equidistant from twelve, whereas in the CsCl type each atom has but six atoms of the same kind surrounding it. This is a further reason for the fact that very few AB compounds have the last arrangement.

Partly, no doubt, because the mutual repulsions between electronegative atoms or ions become great at distances which are relatively large compared with the usual distances between atoms of opposite electrochemical nature, a great many compounds whose crystal structures are known (for instance, those of the NaCl, ZnS, ZnO, NiAs, Li_2O, CdI_2, $CdCl_2$, HgI_2, SnI_4, Al_2O_3, and $MgAl_2O_4$ types and many silicates) have arrangements of these negative atoms or ions which at least approximate a close-packed assemblage. The more positive atoms or ions then fit into the interstices in such a way as to satisfy best the various other requirements and tendencies which have been mentioned.

Similar reasoning accounts for the fact that most metals crystallize in a close-packed structure, whether the electrons be considered as small mobile negative ions in a regular lattice arrangement or as forming some sort of weak bonds between the atoms. (The valence forces must be so distributed as to play only a minor rôle in determining the atomic arrangement (cf. reference 5).)

THE STRUCTURES OF SILICATES (24)

The close-packing generalization mentioned above has proved to be of great value in working out structures of complicated crystals, especially the silicates. These substances, whose chemistry and structural relationships a few years ago were probably the least well understood of all large classes of inorganic compounds, are now among those best understood, at least as far as their structures and the reasons for them are concerned, thanks to the work of W. L. Bragg, Pauling, and others. The strongest attractive forces are undoubtedly those between silicon and oxygen atoms. The latter are always found tetrahedrally around the former, satisfying both radius-ratio requirements and the requirements for tetrahedral bonds. (As already stated, the bonds are probably only partially ionic.) In orthosilicates, with an oxygen to silicon ratio of 4, these SiO_4^{-4} groups are linked together only through other metals. If the oxygen/silicon ratio is 3.5, two such groups have one oxygen in common, producing $Si_2O_7^{-6}$ groups; if the ratio is 3, two oxygens of each SiO_4 must be shared with others, giving $Si_3O_9^{-6}$ or $Si_6O_{18}^{-12}$ rings or $(SiO_3^{-2})_x$ strings, extending completely through the crystal. If the ratio is 2.75, half of the SiO_4 groups contain two shared oxygens and half three, a more complex chain having the composition $(Si_4O_{11}^{-6})_x$, giving this result. Layer molecules (or rather ions) of composition $(Si_4O_{10}^{-4})_x$, in which three of each four SiO_4 oxygens are shared, are found in the micas, with a ratio of oxygen to silicon of 2.5. In the various forms of SiO_2 all of the oxygen atoms are shared by two silicon atoms, producing a three-dimensional network filling the entire crystal. The charges on silicon-oxygen groups, chains, and layers are neutralized by other positive ions, placed, usually in the centers of octahedra or tetrahedra of oxygens, in accordance with the principles already outlined.

HYDROGEN BONDS

The structure of ice is one in which each oxygen atom is surrounded by four others at tetrahedron corners. Various considerations lead to the conclusion that the hydrogen nuclei are on the centerlines between adjacent oxygen atoms and midway between them. According to the new quantum mechanics each hydrogen can be bonded by electron-pair bonds to but one other atom at any given instant; there would however be ionic or polarization forces of considerable magnitude between a hydrogen so bonded and another neighboring oxygen, and one might expect frequent or continuous interchange of the ionic and electron-pair bonds (resonance). Such a pair of bonds, in which a hydrogen atom serves to hold two electronegative atoms together, was postulated some years ago by the writer (25) and by Latimer and Rodebush (26) in order to account for various physical and chemical facts. Essentially this same idea, expressed in terms of Werner's theory of secondary valence rather than in terms of electron-pairs, was previously employed by Moore and Winmill (55) and by Pfeiffer (56) to explain the experimental behavior of certain organic compounds. Crystal structure studies point definitely to the existence of such "hydrogen bonds" not only in ice but also in crystals of $NaHF_2$, KHF_2, KH_2PO_4, $FeHO_2$(7), $H_4Mg_3Si_2O_9$ (50), $H_2FeAl_4Si_2O_{12}$ (51), and a number of other compounds. Similar bonds are probably of quite common occurrence outside of crystals, in NH_4OH and in liquid water, for instance, being in part responsible for the peculiar solvent and dissociating properties of the latter (cf. reference 52). They might also be expected to be formed temporarily during the progress of many reactions, such as those between acids and organic or inorganic bases.

ROTATION OF MOLECULES, IONS, AND OTHER ATOMIC GROUPS IN CRYSTALS AND GLASSES

It has been suggested that in such crystals as those of solid H_2S and HCl (figure 3) the hydrogen atoms or ions are symmetrically situated with respect to four or more of the negative atoms or ions. It is more likely, however, that these crystals are composed of molecular units in free rotation with respect to each other.

This idea of molecular rotation in the solid state (27, 28) has proven useful in accounting for an apparent symmetry higher than that to be expected of any reasonable arrangement of atoms in such crystals as NH_4Cl, in which the NH_4^+ ion rotates, $Ni(NH_3)_6Cl_2$ and $KAl(SO_4)_2 \cdot 12H_2O$, in which the NH_3 and H_2O groups (six around each metal ion) rotate, and in $C_5H_{11}NH_3Cl$, in which zigzag C_5H_{11} groups rotate about the chain axis (29). It is to be expected that many more examples of this phenomenon will be found among molecules or atomic groups in organic crystals. (Cf. reference 27, footnote 25.)

The rather sharp changes of specific heat and some other properties of glasses at temperatures somewhat below their softening ranges (30) are probably also to be explained as due to the start of rotational motion of the molecules or of atomic groups, while the relative arrangement of these molecules or groups as a whole remains fixed. Although this arrangement is in one sense "random," intermolecular forces at the time of solidification must be such as to make the immediate surroundings of all or most of the molecules or of like atomic groups very similar, in many cases probably reproducing the crystalline arrangement in small regions of the glass (31). As a result the forces tending to prevent rotation of the molecules or atomic groups are nearly the same throughout the mass and so their individual "melting points," corresponding to the start of rotation for each molecule or group of atoms, do not differ much and the transition takes place within a fairly narrow temperature interval.

The gradual transition (32) in sodium nitrate crystals at about 275°C. is probably due to rotation of the NO_3^- ions about the trigonal axes. A somewhat similar transition might also be expected at much lower temperatures, if Pauling's suggestion (7) of a pyramidal nitrate group is correct, the nitrogen remaining on one side of the O_3 plane at temperatures below the transition but oscillating through that plane at higher temperatures. Similar transitions would of course be expected in calcite, $CaCO_3$, which has the same type of structure.

A comparable state of affairs may exist in the benzene ring (33). It would seem likely that the most stable static arrangement of carbon atoms is a slightly puckered one. Except at very low temperatures, however, one would expect rapid reversal of the puckering at a rate corresponding to a natural oscillation frequency of the molecule. A plane ring would thus be simulated, accounting for the conclusions reached by various observers from comparisons of predicted and observed isomers and from x-ray data.

PREFERRED ORIENTATIONS. RESIDUAL AFFINITIES

Studies of crystal structures, especially those of organic compounds, are providing much new knowledge of the "residual" forces between atoms and molecules,—those forces other than attractions and repulsions between charged ions and the forces which produce electron-pair bonds. From the arrangements of atoms within molecules in crystals can be deduced certain facts regarding which of various relative orientations, all satisfying primary valence requirements, is the *preferred* one. From the relations between the orientations of different molecules certain conclusions can be drawn relative to intermolecular forces. It must be realized of course that the arrangements observed are those which satisfy best both inter- and intramolecular forces, and both must be considered in making deductions from experimentally determined structures.

In 1922 Pauly (34) and the writer (35) independently arrived at the conclusion that the alternation in melting points and other properties shown by long chain compounds was due not to an alternation in polarity of the carbon atoms, as had previously been suggested, but to the repulsion between the hydrogen nuclei of adjacent CH_2 groups, this repulsion making a zigzag arrangement a preferred one. In other words, even through the rotation about each single bond is sufficiently "free" in the liquid or gaseous state to prevent the isolation of isomers, the *residual* forces between atoms make certain orientations slightly more stable than others. On the average, a liquid composed of long CH_2 chains would be expected to have the hydrogens of one CH_2 group on the opposite side of the chain from the hydrogens of the adjacent CH_2 groups more often than on the same side, and the same forces might be expected to maintain zigzag arrangements of this sort in crystals. A molecule having an odd number of carbon atoms would then have the end carbons on the same side of the chain axis, while one having an even number of carbon atoms would have the end carbons on opposite sides of the axis. This should result in differences between the intermolecular forces for the two types and so different crystal properties. Such conclusions have been completely verified by the structure analyses. (See, for instance, references 36 and 37.)

With respect to the way in which molecules pack together in crystals, only two points will be mentioned: (*1*) they tend to pack as closely as possible, leaving no large spaces between; and (*2*) electronegative parts of one molecule tend to be close to electropositive parts of others. This is due usually to the attractions of hydrogen nuclei, especially those attached to the more negative elements nitrogen and oxygen rather than those bonded to carbon, for the electronegative portions (the lone electron-pairs) of nitrogen, oxygen, chlorine, etc. In some instances, as probably in the carboxylic acids, in which the carboxyl groups of different molecules are adjacent, in quinol, $p\text{-}C_6H_4(OH)_2$ (38), in which the hydroxyl groups of different molecules are adjacent, and in $(C_6H_5CH_2)_3NHCl$ (38), in which hydrogens are between neighboring nitrogen and chlorine atoms, hydrogen bonds are probably formed; in others the C-H or N-H or O-H bonds may be merely "pointing" toward neighboring electronegative atoms.

DOUBLE AND TRIPLE BONDS AND BONDS OF MIXED TYPES

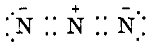
Crystal structure studies of carbon, nitrogen, and oxygen compounds supposed to contain double or triple bonds are in agreement with the supposition that they consist of two or three electron-pairs shared between two atoms, with interatomic distances somewhat less than distances for single bonds between the same kinds of atoms (10, 13, 57). Thus in complex cyanides such as $K_2Zn(CN)_4$ the carbon and nitrogen centers are all on axes going through the centers of the zinc atoms, as would be expected of the electron distribution

$$\mathrm{Zn} : \mathrm{C} \vdots\vdots \mathrm{N} :$$

Incidentally, in KCN the units are K^+ and $(CN)^-$, each ion being surrounded by six of the other kind as in NaCl (figure 3). (The tautomerism of HCN involves merely the removal of a proton, H^+, from one end of the ion and the addition of one to the other end, without any making or breaking of bonds between carbon and nitrogen.) Metal carbides such as CaC_2 have similarly been found (39) to contain C_2^{--} ions, presumably having the structure

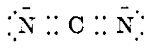
$$: \mathrm{C} \vdots\vdots \mathrm{C} :$$

In KN_3, NaN_3, KNCO, and $CaCN_2$ the three atoms composing each negative ion are all in a straight line, the two end atoms being equivalent, insofar as could be determined by the x-ray methods used. The electron structures in best agreement with these facts[2] are



$$\vdots\overset{-}{\mathrm{N}} :: \overset{+}{\mathrm{N}} :: \overset{-}{\mathrm{N}}\vdots$$

$$\vdots\overset{-}{\mathrm{N}} :: \mathrm{C} :: \mathrm{O}\vdots$$



$$\vdots\overset{-}{\mathrm{N}} :: \mathrm{C} :: \overset{-}{\mathrm{N}}\vdots$$

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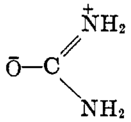
[2] Calculations from band spectra (53) show that the N_2O molecule is linear and slightly unsymmetrical, in agreement with an electron distribution like that given above for the N_3^-, NCO^- and NCN^{--} ions.

but it appears likely that there is resonance between these structures and the corresponding structures containing single and triple bonds (57). (In these formulas the + and − signs indicate the formal charges.)

In urea, $O{=}C(NH_2)_2$, all of the atoms except hydrogen lie on one plane of symmetry, the carbon and oxygen centers being on the line of intersection of two planes. This symmetry and the interatomic distances deduced are in agreement with the structure represented by the usual formula, with or without resonance between that and the structure



Crystals of carbon oxysulfide (40) contain molecular units in which the three atoms are colinear. The parameters as determined favor the electron distribution

$$:\overset{+}{\mathrm{O}}\;\vdots\vdots\;\mathrm{C}:\overset{-}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{S}}}}:$$

rather than

$$\vdots\mathrm{O}::\mathrm{C}::\mathrm{S}\vdots$$

in agreement with Lewis' generalization that elements other than those in the first row of the Periodic Table rarely form true double bonds (reference 6, p. 94). The evidence, however, is certainly not conclusive and there may be resonance between the two structures.

The writer for a long time considered that in calcite the threefold axis of symmetry passing through each carbon atom and the twofold axis passing through each oxygen and its carbon neighbor is evidence for the existence of three double bonds joining each carbon atom to the surrounding oxygen atoms. Since, however, the wave mechanics does not permit more than four electron-pairs in the L shell of an atom, that possibility seems to be eliminated. Let us list the alternatives:[3]

---

[3] The last two alternatives (3 and 4) were suggested to the writer by Pauling. The pyramidal character of the second alternative is also due to him (7).

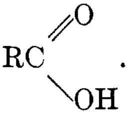
(*1*) The bonds are all ionic. In view of the non-polarity of other carbon compounds and the small (C-O) distance (about 1.25Å.), this does not seem likely.

(*2*) The bonds are all single bonds involving three *p* eigenfunctions of the carbon atom. This would give a pyramidal group. The observed symmetry would not disagree with this if the carbon atoms oscillated back and forth through the oxygen plane, as already mentioned.

(*3*) One oxygen is held by a double bond and the others by single bonds, these bonds frequently or continuously becoming interchanged owing to the resonance phenomenon.

(*4*) Combinations of the above, the actual state of affairs being describable as a mixture of all three.[3] This seems to be the best solution of the problem.

All that has been said above about CO_3^{--} applies equally to NO_3^-, $NaNO_3$ having the same structure as $CaCO_3$ (calcite), as previously mentioned. The nature of the bonds in solution and in other crystals containing these ions remains undetermined.

The $CaCO_3$ and $NaNO_3$, structures, together with certain other considerations, led the writer to consider for some time that in a $—CO_2^-$ or $—NO_2$ group both carbon-oxygen or nitrogen-oxygen linkages are double bonds, the carbon and nitrogen atoms then having five electron-pairs in their valence shells. It now seems more probable that these are further examples of the sort of resonance, involving an interchange between single and double bonds, just suggested for the carbonate and nitrate ions. The interchange would of course be stopped if the environment became sufficiently unsymmetrical, perhaps, for instance, by the addition of a proton to RCO_2^- to give  $RC\begin{matrix}\diagup\!\!\diagup O\\ \diagdown OH\end{matrix}$. On the other hand, the hydrogen may be held jointly by the two oxygen atoms or may frequently pass from one to the other with an interchange of the single and double bonds. In such cases as these it looks very much as if we must give up the idea that a molecule can be represented adequately by a single structural formula of the usual type. The new quantum mechanics teaches us that the atomic interactions may be such as to give a single structure the characteristics represented by two or more formulas at one and the same time.

SOLID SOLUTIONS. INTERMETALLIC COMPOUNDS

Atoms or ions in a crystal can frequently be in part replaced, in a random manner, by atoms or ions of another kind, without altering the structure except for slight changes, approximately proportional to the amount of replacement, in dimensions. (See, for instance, reference 41.) The chief requirements seem to be that the replaced and replacing atoms or ions have the same valence and nearly the same size. The former requirement is sometimes waived (42) if other replacements, in equivalent amount, involving valence changes in the opposite direction take place at the same time; also in metallic crystals the valence seems to be of secondary importance.

Many examples are known of a complete series of solid solutions, all with the same type of structure, extending from one pure compound to another. There are also many cases of stability of a particular structure type over only a limited range of composition. By extrapolation of the dimensions-composition curves however, the dimensions of unstable phases can sometimes be obtained. For example, the dimensions which pure silver iodide would have if it could be obtained with a sodium chloride type of structure can be calculated from the dimensions of a series of AgBr–AgI solid solutions having that structure (43).

Additional atoms, usually of a "foreign" element, or sometimes even groups, as of H_2O in the zeolites, can sometimes occupy places ("holes") in a crystal structure, the lattice being thereby expanded. A classical example is that of hydrogen in palladium. Carbon and nitrogen also seem to be small enough to enter spaces in metal crystals in this way, with or without the formation of definite compounds (44). Whether or not definite chemical bonds are produced, it is probable that each carbon or nitrogen completes an eight electron valence shell, the required extra electrons being obtained from the valence electrons of the other atoms present.

Although we shall not enter into a detailed discussion of the structures of intermetallic compounds, one very interesting relationship may be mentioned (45, 46). The ratio of the number of valence electrons to the number of metal atoms is found to be the same (3:2) for a number of intermetallic compounds having a body-centered cubic arrangement of atomic centers (figure 2), neglecting differences in kind. Similarly for some other structure types, constant ratios of this sort have been discovered. This ratio therefore seems to be an important factor in determining both the compositions of intermetallic compounds and the types of structure assumed by them. Its existence has been taken as evidence in favor of the "electron lattice" theory of metals (47, 48). Alternative explanations are, however, possible. For instance, the stability of the body-centered structure when the valence electron to atom ratio is 3 to 2 may be attributed to the possibility of each atom being joined by three single-electron bonds (cf. Pauling, reference 4), making 90° angles with each other, to three of its six neighbors (not the nearest) at a distance a (equal to the edge of the cube) away.

Similar considerations, either of electron lattices or of weak interatomic bonding, are without doubt also of importance in determining the structure types assumed by pure metals. It may be noted that Slater (5) has concluded from quantum mechanical considerations that in metals "the forces in general are of the same nature as those met in ordinary homopolar binding . . . . except that the purely electrostatic force from penetration of one atom by another is relatively more important, the valence effect from the exchange of electrons relatively less important, than in diatomic molecules." He further concludes that the number of "free" electrons "is rather small compared with the number of atoms." (Cf. also Bernal, reference 49.)

SUMMARY

Attractive forces between atoms in crystals may be classified as valence, ionic, metallic, or residual forces. Considering as belonging to a single molecule all atoms which are linked together by valence forces, the whole crystal may be a single giant molecule or it may consist of two interlocking molecules, of many parallel layer molecules (held together by non-valence forces), of many parallel string molecules, or of small formula molecules. Ions may be similarly classified.

Lewis' theory of electron-pair sharing and the completion of tetrahedral valence shells for electronegative atoms has received abundant confirmation from crystal structure results, as have the deductions of Pauling from wave mechanics regarding favored bond directions around certain metal atoms, producing, for instance, a square arrangement around bivalent nickel, palladium, or platinum atoms.

Relationships between non-polar valence numbers, polar valence numbers, numbers of shared electron-pairs, and formal charges, holding equally for molecules, ions, and crystals, have been stated. The nature of secondary valence, no longer a mystery, has been discussed. The nature of the forces between atoms—whether valence or ionic (including polarization)—can in many cases be definitely determined, Pauling's magnetic criterion and one proposed by the writer, based on calculated interatomic distances, being of use in this connection.

Standard radii, for use where the atoms are held together principally by one or another of the types of force mentioned above, have been listed and plotted.

The more important principles determining the structure types assumed by different substances have been briefly discussed.

The structures of silicates, hydrogen bonds, the rotation of molecules, ions, and atomic groups in crystals and glasses, preferred orientations and residual affinities of organic molecules, double and triple bonds, bonds of mixed types, solid solutions, and intermetallic compounds are among the special topics discussed.

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