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ATOMIC RADII. II[1]

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ABSTRACT

X-ray data show that *the two assumptions usually involved in previous calculations* of atomic radii from crystal structures—namely (1) that the distance between adjacent atomic centers in crystals equals the sum of the two atomic radii, and (2) that the radii of atoms of the same element in different crystals are equal—*in many cases cannot be correct.* Assuming that a valence electron pair can be assigned a definite position and *defining the atomic radius as the distance from the nucleus to a valence electron pair*, it is evident that (1) is only true when there is a valence pair on the straight line joining the centers of the adjacent atoms, and (2) should be true, or nearly so, only when the atoms of the given element are structurally similar and similarly surrounded in the two crystals. The probable arrangements of valence electrons in crystals, as deduced elsewhere by the author, are used in deciding as to the validity of the above assumptions in particular cases.

Comparable values of atomic radii have been calculated for a number of elements, in crystals in which atoms of these elements are each surrounded by *four* electronpairs at tetrahedron corners. Approximate radii of other elements similarly surrounded are obtained by interpolation and extrapolation. Radii are also calculated for certain elements in crystals in which each atom of these elements is surrounded by two, six, or eight electron pairs. The diameters of the hydrogen atom in six crystals are computed.

I. INTRODUCTION

IN 1920 W. L. Bragg[2] computed values for what he termed "atomic radii" and "atomic diameters" from crystal structure data. The chief assumptions underlying his calculations were: (1) that each atom of a given element is surrounded by a "sphere of influence" of the same size in different crystals; and (2) that the "spheres of influence" of adjacent atoms in crystals are tangent to one another.

Authors making similar calculations more recently,[3] realizing that these assumptions cannot both always be correct (Cf Table I), have assumed, in order to explain the x-ray data, atoms of irregular shapes or of different sizes (even though of the same element). They have, however, offered no criteria to use in determining when these assumptions are

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[1] This is a revision of a paper written in 1922–23, while the author was a National Research Fellow at the University of California and Harvard University. Cf. Phys. Rev. **21**, 205 (1923).

[2] W. L. Bragg, Phil. Mag. **40**, 169 (1920); W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," G. Bell and Sons, London (1924).

[3] For references to work in this field, see Lunnon, Proc. Phys. Soc. London **38**, 93 (1926) or Davey, Chem. Rev. **2**, 349 (1925); Gen. Elec. Rev. **29**, 274 (1926).

near enough correct to warrant their use in calculating radii. Some such criteria are obviously necessary if atomic radii calculations are to be of much value.

TABLE I

Interatomic distance differences (A) in crystals of certain metallic halides

M	Li[4]	Na[4]	Cs[4]	Cu[5]	Cu[6]	Ag[7]
(M-Cl) − (M-F)	.56	.50				
(M-Br) − (M-Cl)	.18	.15	.15	.14	.17	.11
(M-I) − (M-Br)	.26	.26	.23	.12	.14	-.07

It has been shown by the writer[8] that if the valence electrons in the diamond and similar crystals are in constant orbital motion, in all probability they do not enclose whole atoms or pairs of atoms within their orbits but are in rotation about the atomic center-lines. With this picture (or with a picture of stationary or vibrating electrons[9]) we can evidently speak of an electron "position" in space, meaning the center of the orbit or the point about which the electron is oscillating.

It is generally accepted now that the valence shells of electronegative atoms in most chemical compounds contain eight electrons. A careful analysis[10] of known crystal structures has verified this conclusion and has also shown, what had already been shown to be very probable from chemical considerations,[11] that in many of these crystals, at least, the valence electrons are distributed in pairs at tetrahedron corners rather than singly at cube corners.

In view of the above, it is obvious that the "atomic radius," at least in so far as applied to crystal structure calculations, may be defined[12] as "the distance between the nucleus and the position occupied by a valence electron pair" (which we may designate as a point midway between the "positions" of the single electrons constituting that pair). With this definition, the interatomic distance equals the sum of the two atomic radii only when there is a valence pair on the straight line joining their centers. So if we know the distribution of these pairs in the crystal we can determine whether or not a given interatomic distance is suitable for the calculation of the atomic radii.

[4] Davey, Chem. Rev. **2,** 349 (1925); Gen. Elec. Rev. **29,** 274 (1926).

[5] Wyckoff and Posnjak, J. Am. Chem. Soc. **44,** 30 (1922).

[6] Davey, Phys. Rev. **19,** 248 (1922).

[7] Wilsey, Phil. Mag. **46,** 487 (1923).

[8] Huggins, Phys. Rev. **21,** 379 (1923); **27,** 286 (1926).

[9] Cf. Urey, Phys. Rev. **27,** 216 (1926).

[10] Huggins, Ref. 8.

[11] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York (1923); Huggins, J. Phys. Chem. **26,** 601 (1922).

[12] Huggins, Phys. Rev. **19,** 346 (1922).

As regards the constancy of size of an atom of a given element in different crystals, it is evident from a consideration of the forces involved that the distance of a valence pair from the nucleus will depend on a number of factors[12]—the number of valence pairs around the kernel of the atom in question; the number and arrangement of electrons within the kernel; the number, kind or kinds, and arrangement of the surrounding atoms. In deciding whether the atoms of a given element are sufficiently similar in two crystals to make the assumption that the corresponding atomic radii in the two crystals are the same seem reasonable, use may again be made of the electron distributions shown elsewhere to be most probable, doubtful distributions being specifically mentioned as such. In general, these electron distributions depend on the following assumptions: (1) that the distribution of atomic centers as determined by x-rays is correct, (2) that the number of valence electrons per atom is as usually assumed by chemists and physicists, (3) that each electronegative atom (except in a very few crystals in which such an arrangement is impossible) has a valence shell consisting of four electron-pairs at tetrahedron corners, (4) that the valence tetrahedra are oriented, when possible, so as to place electron pairs on or near the centerlines between electropositive and electronegative atoms.

The author has shown[10] that in many cases the valence tetrahedra must be so oriented, while in all others (where the arrangement of atoms is known) the electron distribution around the kernels of the more positive atoms is at least as reasonable (usually more reasonable) with such an orientation as with any other orientation.

If we are to adhere to the limitations imposed by our definitions and the assumed structures, many crystal structure determinations are valueless for the calculation of accurate atomic dimensions. In fact, with no more data than are at present available, it is necessary, in order to get comparable values for more than a very few elements, to make approximations and assumptions which we know cannot be strictly true, but the attempt will be made, in this paper, to make these as few and as reasonable as possible, and to state definitely each assumption as it becomes involved in the calculations. Then, if later and better data show that some of these assumptions are in error, corrections can easily be made.

II. Radii of Atoms Having Four Electron Pairs in the Valence Shell

Our first calculations will deal only with crystals in which each atom of the element whose radius is being considered has a valence shell consisting of four electron pairs at tetrahedron corners, these bonding it to four other kernels, the net charge on each of which is $(8-n)$ where n is the charge on the kernel of the central atom.

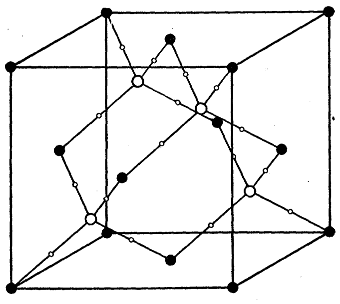

Fig. 1. The unit cube of the diamond—cubic ZnS type of structure. The large dots and circles represent the centers of Zn and S atoms respectively, or all C atoms. The small circles represent valence electron pairs. In crystals of the ZnS type these are closer to one kind of atom than to the other.

In the diamond, silicon, germanium, and gray tin, (Fig. 1) each atom is surrounded by four others at corners of a regular tetrahedron. Each kernel has a charge of +4 and the four valence electrons per atom are in pairs,[8] midway between adjacent atomic centers. The atomic radius is therefore in each case just half the interatomic distance. The values calculated are given in the last column of Table II.

TABLE II

Crystal	Interatomic distance	Atomic radius
C (diamond)	1.54A[13]	0.77A
Si	2.34[14]; 2.35[15,16]; 2.36[17]	1.17; 1.18
Ge	2.43[18]; 2.44[19]	1.22
Sn (grey)	2.80[20]	1.40
SiC	1.90[21]	C = 0.77 (?); Si = 1.13 (?)

In crystals of silicon carbide, SiC, four silicon atoms are tetrahedrally distributed around each carbon, and four carbons are similarly disposed

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[13] W. H. and W. L. Bragg, Proc. Roy. Soc. **A89**, 277 (1914).

[14] Gerlach, Phys. Zeits. **22**, 557 (1921); **23**, 114 (1922).

[15] Hull, Phys. Rev. **9**, 564 (1917); **10**, 661 (1917).

[16] Küstner and Remy, Phys. Zeits. **24**, 25 (1923).

[17] Debye and Scherrer, Phys. Zeits. **17**, 277 (1916).

[18] Kolkmeijer, Verslag. Akad. Wetenschappen **31**, 155 (1922); Proc. Roy. Acad. Sci., Amsterdam **25**, 125 (1922).

[19] Hull, Phys. Rev. **20**, 113 (1922).

[20] Bijl and Kolkmeijer, Chem. Weekblad. **15**, 1077, 1264 (1918); Proc. Roy. Acad. Sci., Amsterdam **21**, 501 (1919).

[21] Ott, Naturwissenschaften **13**, 76, 319, 644 (1925); Zeits. f. Krist. **61**, 515 (1925); **62**, 201 (1925).

around each silicon. With valence electron pairs on the atomic centerlines, we should expect the Si-C distance (1.90A) to be equal to the sum of the carbon radius (0.77A) in the diamond and the silicon radius (1.17–1.18A) in elementary silicon, but we find this to be only approximately the case. Part of the difference may be due to experimental errors, but some of it must certainly be attributed to lack of constancy of the radii. As in many of the calculations to follow, we shall find it necessary to assume constant radii for a given element in different crystals when we have less reason to expect such constancy than in the substances just mentioned, we can obviously not expect our results to be in every case accurately correct. By means of various checks and calculations by different methods, however, we shall seek to make the errors as small as possible.

In proceeding to the calculation of atomic radii in other compounds, others have followed several different procedures; all of them, however, involve objectionable assumptions.

Pease[22] has assumed that all atoms having the same electronic arrangement (differing only in the charge on the nucleus) have practically the same radius. That this is not true is shown by a comparison of the interatomic distances in BeO (1.64–1.65A) and the diamond (1.54A), and in CuBr (2.49–2.52A) and Ge (2.43–2.44A), all of these substances having a similar arrangement around each atom in the crystal.

Davey[23] has assumed that Rb^+ and Br^- have the same radius, that being half of the interatomic distance in crystals of RbBr. Defining the atomic or ionic radius as the distance from nucleus to an electron pair in the outermost shell of each atom or ion, it is impossible for the electrons to be so disposed that the sum of the two radii, atomic or ionic, be equal to the interatomic distance in this crystal. Also, if the difference between the Cu and Ge radii is 0.05 to 0.09A greater or less than that between the Ge and Br radii, it would hardly seem likely that the Br^- and Rb^+ radii would be equal.

Wyckoff[24] prefers to start with the trihalides, such as $CsCl_2I$, in which three halogen atoms are on a straight line. Since the distance from the central halogen to each of the outer ones is obtained by intensity measurements, interpreted by means of assumptions which are known to be only qualitatively correct, it is not accurately known. A more important objection to transferring radii values calculated from these crystals to others, however, is that the number and arrangement of

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[22] Pease, J. Am. Chem. Soc. **43**, 991 (1921).

[23] Davey, Phys. Rev. **18**, 102 (1921); **22**, 211 (1923); Ref. 3.

[24] Wyckoff, Proc. Nat. Acad. Sci. **9**, 33 (1923).

valence electrons around the central halogen is unknown and cannot be the same as in ordinary halogen compounds; so even if the iodine radius in $CsCl_2I$ were calculable, it may be, and probably is, quite different from that in other iodine compounds.

Another suggested procedure is to subtract the carbon radius, obtained from the diamond, from the carbon-oxygen distance in $CaCO_3$ or $MnCO_3$, to get the oxygen radius. Each carbon kernel in these compounds, however, is surrounded by *three oxygen* atoms, to which it is probably bonded by six electron pairs, none of which are on the atomic centerlines.[12] The carbon radius is therefore probably quite different in $CaCO_3$ from what it is in the diamond, and the sum of the carbon and oxygen radii cannot equal the interatomic distance.

One might also consider subtracting half the interatomic distance in a crystal of one of the metals, say Zn or Fe, from the distance between atoms in a crystal such as ZnS, or FeS_2, to obtain the sulfur radius; but the atomic radius, as here defined, is only calculable in the few metals in which the valence pairs are on the atomic centerlines, and in the compounds of these elements with non-metals for which the structures are known, the arrangements of electrons and atoms around each metal atom are quite different from what they are in crystals of the elements.

Quartz (SiO_2) will not serve as a suitable basis for atomic radii calculations, because the positions of the atoms are not known with sufficient accuracy, and because each oxygen is surrounded by *two tetravalent* atoms (instead of *four divalent* atoms).

There is but one other alternative with the data now available. In FeS_2[25] each sulfur kernel we may assume to be surrounded[26] by four electron pairs, these serving to bond it to three adjacent iron atoms and one adjacent sulfur atom. The parameter defining the S-S distance has been determined[27] probably as accurately as is possible by present methods; although just how accurate that is we have no way of knowing; there are assumptions involved in the determination (e.g. that the atoms can be treated as point scattering centers) which are known to be only approximations to the truth. The best we can do under the circumstances is to assume the computed interatomic distance (2.088A) to be correct, and halve it to get the distance from each sulfur nucleus to the valence pair between sulfur atoms. Here we meet with another difficulty. This sulfur radius is certainly greater—how much greater we do not know—

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[25] W. L. Bragg, Proc. Roy. Soc. **A89**, 468 (1914).

[26] Huggins, Phys. Rev. **27**, 286 (1926); J. Am. Chem. Soc. **44**, 184 (1922).

[27] Ewald, Phys. Zeits. **15**, 399 (1914); Ewald and Friedrich, Ann. d. Physik **44**, 1183 (1914).

than the sulfur radius in a compound such as ZnS, where each sulfur is surrounded by four electropositive atoms. To emphasize the fact that it is necessary to make some assumption in regard to the magnitude of this difference, we shall arbitrarily assume it to be 0.024A in the calculations in this paper. This gives us the value 1.02A for the sulfur radius in ZnS and crystals similar to it. If this value is too low, then all the radii of electropositive atoms computed directly or indirectly from it in this paper are too high, and those of electronegative atoms are correspondingly too low, (provided the other assumptions involved are correct).

There are two simple types of crystal structure which binary compounds can possess in which each atom of one kind is surrounded by four of the other at tetrahedron corners. One of these is like the diamond structure, except that there are two kinds of atoms; the other has hexagonal symmetry and is usually known as the "zinc oxide type." X-ray analysis has shown that AlN, AlSb, ZnO, ZnS, ZnSe, CdS, HgS, BeO, CuCl, CuBr, CuI and AgI have one or the other (or both) of these structures.[28] The electrons in all of the above crystals may, on the basis of evidence previously presented,[8] be assumed to be in pairs on the centerlines between atoms, forming a tetrahedron of four pairs around each.

Comparisons of the interatomic distances in the sulfides, selenides and tellurides of zinc, cadmium and mercury (Table III) give us fairly concordant values (Table IV) for the radii of the component atoms. Too much faith must not be placed in the accuracy of these values, both because of the lack of satisfactory data and because the assumption that the radius of an atom is practically the same in different crystals may perhaps be incorrect. The checks obtained, on comparing the zinc and mercury compounds for instance, merely show that *if* the sulfur radius differs in ZnS and HgS, then the Se and Te radii in their compounds with Zn and Hg differ in the same way and about the same amount, and *if* the Zn radius changes in the series, sulfide, selenide, telluride, then the Hg radius changes similarly in the corresponding series of mercury compounds.

In the spinels, the general formula for which is $R''R'''_2O_4$ (R'' being an electropositive divalent element and R''' a positive trivalent element), each R'' atom is surrounded by four oxygen atoms at corners of

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[28] Crystallographic data and interatomic distance comparisons (Huggins, Phys. Rev. **21**, 211 (1923)) make it seem very probable that ZnTe, CdSe, CdTe, HgSe and HgTe also have one or both of these two types of structure. The interatomic distances in these compounds, calculated from the densities on this assumption, have been included in Table III.

a regular tetrahedron, each R‴ by six oxygen atoms at corners of an octahedron, and each oxygen atom by one R″ and three R‴ atoms at tetrahedron corners. The valence electrons are in all probability in pairs on or very near the centerlines between adjacent atoms.[36] In the zinc spinels the arrangement of electrons and other atoms around each zinc kernel is precisely the same, and that of electrons and other atoms around each oxygen kernel is very nearly the same, as in ZnO. The Zn–O dis-

TABLE III

Crystal	Interatomic distance	Sum of radii (Table IV)
ZnO	1.96[29, 30]; 1.98A[31]	1.98A
ZnS	2.33[32]; 2.34[33]; 2.35[25]	2.35
ZnSe	2.45[34]	2.45
ZnTe	2.54[35]	2.56
$CdCr_2O_4$	(Cd-O) = 2.16; 2.18[36]	2.17
CdS	2.52[37]; 2.54[38]	2.54
CdSe	2.61[39]	2.64
CdTe	2.75[40]	2.75
HgS	2.53[41]; 2.54[42]	2.53
HgSe	2.63[43]	2.63
HgTe	2.73[44]	2.74
BeO	1.64[45]; 1.65[46]	1.64
$MgCr_2O_4$	(Mg-O) = 1.94; 1.96[36]	1.95
$MnCr_2O_4$	(Mn″-O) = 2.04; 2.06[36]	2.06
$FeFe_2O_4$	(Fe″-O) = 1.92; 1.94[36]	1.94
$CuFeS_2$	(Cu″-S) = 2.23–2.25[47]	2.23

[29] W. L. Bragg, Phil. Mag. **39,** 647 (1920).

[30] Aminoff, Zeits. f. Krist. **56,** 495 (1921); **57,** 204 (1922).

[31] Weber, ibid. **57,** 398 (1922).

[32] Aminoff, ibid. **58,** 203 (1923).

[33] Gerlach, Phys. Zeits. **23,** 114 (1922).

[34] Davey, Phys. Rev. **21,** 380 (1923).

[35] From density = 6.34 (Groth, "Chemische Krystallographie," Engelmann, Leipzig).

[36] Huggins, Phys. Rev. **21,** 509 (1923). The first of the two figures given for Cd-O, Mg-O, Mn″-O, and Fe″-O is in each case that calculated on the assumption that Zn-O in corresponding zinc compounds = 1.96A; in calculating the other it was assumed that Zn-O = 1.98A. The other assumptions involved are that the densities given by Groth (Ref. 35) are correct and that the R‴-O distance in different spinels is the same if the R‴ atom is the same.

[37] Ulrich and Zachariasen, Zeits. f. Krist. **62,** 260 (1925).

[38] Davey, Phys. Rev. **19,** 248 (1922).

[39] From density = 5.80 (Groth, Ref. 35).

[40] From density = 6.20 (Margottet, Comptes Rendus **84,** 1293 (1877)).

[41] Kolkmeijer, Bijvoet and Karssen, Proc. Acad. Sci. Amsterdam **27,** 390, 847 (1924); Lehman, Zeits. f. Krist. **60,** 379 (1924); Olshausen, ibid. **61,** 463 (1925).

[42] Buckley and Vernon, Mineralog. Mag. **20,** 382 (1925).

[43] From density = 8.20 (Groth, Ref. 35).

[44] From density = 8.07 (Spencer, Mineralog. Mag. **13,** 268 (1904)).

[45] Aminoff, Zeits. f. Krist. **62,** 113 (1925).

[46] Zachariasen, Norsk geol. tidsskrift **8,** 189 (1925).

[47] From density = 4.196 and c/a = 0.9853 (Groth, Ref. 35), assuming (Fe″-S) = 2.29 – 2.31A.

tances should therefore be practically equal in the two cases. If we assume this, the oxygen atoms can be more accurately located in these crystals with reference to the other atoms than directly by x-ray means, and we can calculate the R$'''$–O distances. Then by transferring these to the Mg, Mn, Cd, and Fe spinels it is possible to obtain the R$''$–O distances and so the radii of these divalent atoms. The Cd–O distance obtained by this roundabout route (involving two possibly inaccurate density determinations) checks well with the sum of the radii calculated from CdS and ZnO.

TABLE IV

Li	Be	B	C	N	O	F	Ne	Na$^+$
1.16	0.99	0.86	0.77	0.70	0.65	0.61	0.58	0.56
Na	Mg	Al	Si	P	S	Cl	A	K$^+$
1.41	1.30	1.22	1.14	1.08	1.02	0.97	0.93	0.91
Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb$^+$
1.42	1.33	1.26	1.21	1.16	1.12	1.09	1.06	1.05
Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs$^+$
1.62	1.52	1.43	1.36	1.29	1.23	1.19	1.16	1.14
Au	Hg	Tl	Pb	Bi				
1.60	1.51	1.42	1.36	1.3				

Mn$''$, 1.41; Fe$''$, 1.29; Cu$''$, 1.21.

Chalcopyrite, $CuFeS_2$, has been assigned a structure[48] similar to that of cubic zinc sulfide except for the replacement of half of the zinc atoms by copper and half by iron. From chemical considerations we should expect both copper and iron atoms to be divalent. Calculating the dimensions of the unit from the published density and axial ratio and assuming the iron-sulfur distance to be equal to the sum of the radii already computed (Table IV), we can calculate the copper-sulfur distance and from that obtain a value for the radius of the divalent copper atom.

Because of the marked disagreement between different observers in regard to the distances between atoms in the cuprous halides (Table V), the probable inaccuracy of the data on gray tin, and the disagreement between the values for the silicon radius calculated from silicon carbide and from elementary silicon, we cannot safely calculate directly the magnitudes of the atomic radii in these crystals and expect the results to be accurate and comparable with those already obtained. The values given for these radii in Table IV have been chosen so as to give smooth

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[48] Burdick and Ellis, J. Am. Chem. Soc. **39**, 2518 (1917); Huggins, ibid. **44**, 1841 (1922).

curves when radii are plotted against atomic numbers (Fig. 2) and at the same time give Cu–X distances in fair agreement with the observed values. The silicon radius obtained from these curves agrees well with that from silicon carbide. The tin radius obtained by interpolation is not in good agreement with the experimental value. A discussion of possible reasons for this will be postponed until the experimental results have been checked.

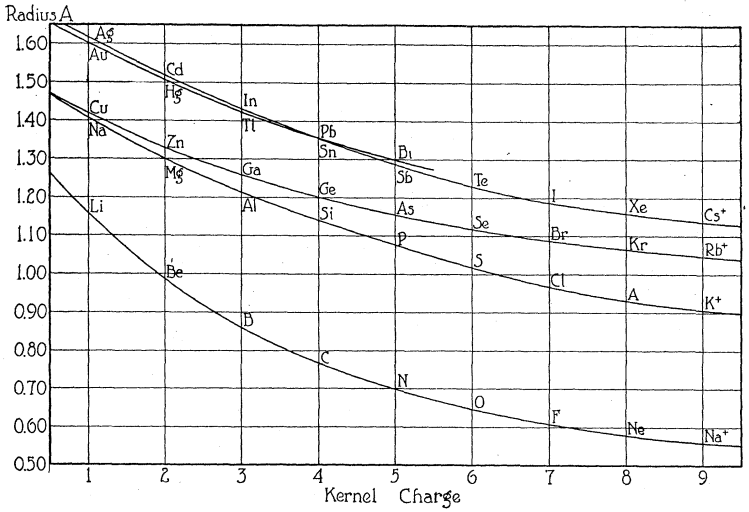

Fig. 2. Atomic radius—atomic number curves for atoms of kernel charge n bonded to four others of kernel charge $8-n$.

Subtracting our assumed iodine radius from what is probably the most accurately determined Ag–I distance in silver iodide, a figure is obtained for the silver radius which fits in well on the atomic radius—atomic number curve.

The radii of the elements in columns 3 and 5 of the periodic table can probably best be obtained from the curves of Fig. 2. Adding the appropriate radii, however, we get only a rough check with the experimental value for the interatomic distance in aluminum nitride and still poorer agreement in the case of aluminum antimonide (Table VI). The experimental results should be checked in order to determine whether there is actually as much variation of the radii as is indicated by these figures.

We can also obtain by extrapolation approximate values for the radii of the lithium, sodium, and fluorine atoms, in crystals comparable with the others discussed, as well as estimates of the distance from nucleus

TABLE V

Crystal	Interatomic distance	Sum of radii (Table IV)
CuCl	2.32[6]; 2.38A[5]	2.39A
CuBr	2.49[6]; 2.52[5]	2.51
CuI	2.61[49]; 2.63[6]; 2.64[5]	2.61
AgI	2.81[7,50]; 2.83[6]	2.81
AuCl	2.56[51]	2.57

TABLE VI

Crystal	Interatomic distance	Sum of radii (Table IV)
AlN	1.89 A[52]	1.92 A
AlSb	2.65[53]	2.51

to outer shell in neon, argon, krypton and xenon. By further extrapolation we can very roughly estimate the magnitudes of the radii of certain of the electropositive *ions* (Table IV).[54]

Let us now turn to the study of crystals in which we can reasonably assume that the distance between atoms equals the sum of the atomic radii (i.e. in which the valence electron pairs are probably on or near the atomic centerlines) but in which we should expect radii differing from those already computed.

In Table VII are listed such interatomic distance data as are at present available for crystals of this kind. These data (as well as the data in Table VIII) all depend on the evaluation of one or more parameters. In general we should place less faith in their accuracy than in the accuracy of the interatomic distance determinations in crystals in which the atomic positions are fixed entirely by symmetry considerations and the dimensions of the unit cell.

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[49] Aminoff, Geol. Fören. Förh. **44,** 197 (1922).

[50] Aminoff, Zeits. f. Krist. **57,** 180 (1922).

[51] From density = 7.4 [Rose, J. Chem. Soc. **67,** 905 (1895)]. There are available neither x-ray nor crystallographic data on the halides of monovalent gold. But if we assume this substance to possess one of the two structures possessed by ZnS, (or any other structure in which each ion is surrounded by four of the other kind at corners of a regular tetrahedron) the interatomic distance may be calculated from the density, and from this a tentative value for the Au radius. This comes out to be nearly the same as the Ag radius, just as the Hg radius was found to be practically equal to that of Cd. Such a result would seem to be quite improbable if the assumption in regard to the AuCl structure were incorrect. If a similar assumption were made regarding AgBr (which actually has the NaCl type of structure) for instance, the computed Ag radius would have been 1.44A, just 0.18A less than the value obtained from AgI.

[52] Ott, Zeits. f. Phys. **22,** 201 (1924).

[53] Owen and Preston, Proc. Phys. Soc. London **36,** 341 (1924).

[54] In this connection it may be noted that if we define the radius of an atom or ion as the distance from the nucleus to an electron pair in the outermost shell of that atom or ion, the *atomic* radius is the same as the *ionic* radius in the case of an electronegative ion, but not in the case of an electropositive ion.

TABLE VII

Crystal	Interatomic Distance	Sum of radii (Table IV)
As	2.51 A[55]	2.32A
Sb	2.87[56]; 2.92[57]	2.58
Bi	3.10[58]	2.6
Se	2.32[59]	2.24
Te	2.86[59]	2.46
As_4O_6	2.01[60]	1.81
Sb_4O_6	2.22[60]	1.94
SnI_4	2.63[61]	2.55
HgI_2	2.78[62]	2.70
SiO_2 (β-quartz)	1.62[63]	1.79
$C_6H_{12}N_4$	(C–N) = 1.44[64]	1.47
$BaSO_4$	(S–O) = 1.5[65]	1.67
$LiKSO_4$	(S–O) = 1.5–1.6[66]	1.67
$N_2H_6Cl_2$	(N–N) = 0.55–1.7[67]	1.40
C_2H_6	(C–C) = 1.5–1.6[68]	1.54
Ag_2MoO_4	(Mo–O) = 2.00[69]	——

It might be expected that the distance from nucleus to valence pair would be greater, other things being equal, the greater the kernel charge of the other atom holding to the valence pair in question; also that this distance would be greater the fewer other atoms surround the given atom, provided the number of electron pairs in the valence shell remains the same. So we should expect the radii of arsenic, antimony and bismuth, in crystals of the elements, in which each atom (having a kernel charge of +5) is bonded to three others of the same kind, to be greater than the radii obtained from the curves of Fig. 2. That this is the case is indicated by the experimental data (Table VII). Similarly in crystals of selenium and tellurium, in which each atom (having a kernel charge of +6) has a complete valence shell of four pairs, using two of them to bond it to other like atoms, the observed interatomic distances are considerably greater than twice the Se or Te radius in a crystal such as ZnSe or ZnTe. A similar situation exists in As_4O_6 and Sb_4O_6, in which all the atoms have

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[55] Bradley, Phil. Mag. **47**, 657 (1924).

[56] James and Tunstall, ibid. **40**, 233 (1920).

[57] Ogg, ibid. **42**, 163 (1921).

[58] James, ibid. **42**, 193 (1921). Recalculated by McKeehan, J. Frank. Inst. **195**, 59 (1923).

[59] Bradley, Phil. Mag. **48**, 477 (1924).

[60] Bozorth, J. Am. Chem. Soc. **45**, 1621 (1923).

[61] Dickinson, ibid. **45**, 958 (1923).

[62] Huggins and Magill, from unpublished data.

[63] Wyckoff, Science **62**, 496 (1925); Am. J. Sci. **11**, 101 (1926).

[64] Dickinson and Raymond, J. Am. Chem. Soc. **45**, 22 (1923).

[65] James and Wood, Proc. Roy. Soc. **A109**, 598 (1925).

[66] Bradley, Phil. Mag. **49**, 1225 (1925).

[67] Wyckoff, Am. J. Sci. **5**, 15 (1923).

[68] Mark and Pohland, Zeits. f. Krist. **62**, 103 (1925).

[69] Wyckoff, J. Am. Chem. Soc. **44**, 1994 (1922).

tetrahedral valence shells, the arsenic or antimony atoms (kernel charge +5) being bonded each to three oxygen atoms (kernel charge +6) and the oxygen atoms each to two arsenic or antimony atoms. In the same category are SnI_4, in which each tin atom (kernel charge +4) is bonded to four iodines (kernel charge +7) and each iodine to but one tin, and HgI_2, in which each mercury atom (kernel charge +2) is bonded to four iodine atoms (kernel charge +7) and each iodine to two mercury atoms.

In β-quartz (SiO_2) each silicon is tetrahedrally surrounded by four oxygens and each oxygen is equidistant from two silicon atoms, two of the four oxygen valence electron pairs being presumably near the Si–O centerlines. We might here also expect the Si–O distance to be a little greater than the sum of the radii from Table IV, but according to Wyckoff's determination the reverse is the case. Possibly the valence pairs are far enough from the atomic centerlines to account for this.

A similar but smaller discrepancy exists in the case of hexamethylene tetramine, $C_6H_{12}N_4$, in which each carbon is bonded to one nitrogen and three hydrogen atoms and each nitrogen to three carbon atoms. The parameter determinations may perhaps be inaccurate enough to account for these results.

Accurate determinations of the distances between adjacent atoms in $BaSO_4$, $LiKSO_4$, $N_2H_6Cl_2$, and C_2H_6 have not been made.

The structure of silver molybdate, Ag_2MoO_4, is one in which each molybdenum atom is bonded to four oxygens and each oxygen to one molybdenum and three silver atoms. From the Mo–O distance, assuming the oxygen radius to be 0.65A, we get the value 1.35A for the radius of hexavalent molybdenum in this compound.

III. Radii of Atoms having Six Electron Pairs in the Valence Shell

Data for calculating radii of atoms having six electron pairs in their valence shells are fairly numerous but usually quite inaccurate. They are collected in Table VIII, together with the radii calculated therefrom on the assumption that the more negative atoms (to which the atoms in question are bonded) have the radii given in Table IV. This assumption is undoubtedly not strictly true, but the resulting errors are probably much less than the errors in the measurement of the distances between atoms, and some such assumption is necessary if we are to calculate these radii at all.

The figures in column 3 of Table VIII have been obtained directly by x-ray analysis, except in a few cases of which special mention is made in the footnotes. In many of the crystals listed the valence pairs are

TABLE VIII

	Crystal	Interatomic distance (observed)	Radii Assumed	 Calculated
Na–F	$NaHF_2$	2.36A[70]	F=0.61A	Na=1.75A
Na–O	$NaNO_3$	2.41[71]	O=0.65	Na=1.76
Mg–O	$Mg(OH)_2$	2.09[72]	O=0.65	Mg=1.44
Mg–O	$MgCO_3$	2.10[73]	O=0.65	Mg=1.45
Al–F	$(NH_4)_3AlF_6$	1.66[74]	F=0.61	Al=1.01
Al–O	$ZnAl_2O_4$	1.90; 1.92[75]	O=0.65	Al=1.25; 1.27
Al–O	Al_2O_3	1.84–1.99[76]	O=0.65	Al=1.19–1.34
Si–F	$(NH_4)_2SiF_6$	1.72[77]	F=0.61	Si=1.11
Ca–O	$CaCO_3$	2.37[78]	O=0.65	Ca=1.72
Cr'''–O	$ZnCr_2O_4$	1.99; 2.00[75]	O=0.65	Cr'''=1.34; 1.35
Mn''–O	$MnCO_3$	2.17[79]	O=0.65	Mn''=1.52
Mn''–O	$Mn(OH)_2$	2.19[80]	O=0.65	Mn''=1.54
Mn''–S	MnS_2	2.59[81]	S=1.02	Mn''=1.57
Fe''–O	$FeCO_3$	2.17[82]	O=0.65	Fe''=1.52
Fe''–S	FeS_2	2.25[83]	S=1.02	Fe''=1.23
Fe'''–F	$(NH_4)_3FeF_6$	1.9[74]	F=0.6	Fe'''=1.3
Fe'''–O	$ZnFe_2O_4$	2.02; 2.03[75]	O=0.65	Fe'''=1.37, 1.38
Ni''–N	$Ni(NH_3)_6Cl_2$	2.29–2.47[84]	N=0.70	Ni''=1.59–1.77
Ni''–N	$Ni(NH_3)_6I_2$	<2.64[84]	N=0.70	Ni''<1.94
Zn–O	$ZnCO_3$	2.12[73]	O=0.65	Zn=1.47
Zr–F	$(NH_4)_3ZrF_7$	1.77[85]	F=0.61	Zr=1.16
Mo^{IV}–S	MoS_2	2.41[86]	S=1.02	Mo^{IV}=1.39
Mo^{VI}–(O,F)	$(NH_4)_3MoO_3F_3$	1.9[74]	(O,F)=0.63	Mo^{VI}=1.27
Ag'–O	Ag_2MoO_4	2.31[87]	O=0.65	Ag'=1.66
Cd–O	$CdCO_3$	2.31[73]	O=0.65	Cd=1.66
Cd–I	CdI_2	3.00[88]	I=1.19	Cd=1.81
Sn^{IV}–Cl	K_2SnCl_6	2.44[89]	Cl=0.97	Sn=1.47
Sn^{IV}–Cl	$(NH_4)_2SnCl_6$	2.46[89]	Cl=0.97	Sn=1.49
Cs–Cl	$CsCl_2I$	3.65[90]	Cl=0.97	Cs=2.68
Pt^{IV}–Cl	$(NH_4)_2PtCl_6$	2.16–2.36[91]	Cl=0.97	Pt=1.19–1.39

[70] Rinne, Hentschel and Leonhardt, Zeits. f. Krist. **58,** 629 (1923).

[71] From $a=6.320$, $\alpha=48°6'$, $u=0.25$; Wyckoff, "The Structure of Crystals," p 349, Chemical Catalog Co., New York (1924).

[72] Aminoff, Geol. Fören. Förh. **41,** 405 (1919); Zeits. f. Krist. **56,** 506 (1921).

[73] In $MgCO_3$, $ZnCO_3$ and $CdCO_3$, the metal-oxygen distances have been computed from the densities and axial ratios given in Groth, Ref. 35, assuming the carbon-oxygen distance to be 1.26A.

[74] Pauling, J. Am. Chem. Soc. **46,** 2738 (1924).

[75] The two figures given are based on assumed values of the Zn-O distance of 1.98 and 1.96A, respectively. It is also assumed that the density given in Groth, Ref. 35, is correct.

[76] Pauling and Hendricks, J. Am. Chem. Soc. **47,** 781 (1925).

[77] Bozorth, ibid. **44,** 1066 (1922).

[78] From $a=6.360$A, $\alpha=46°6'$, $u=0.25$ (Wyckoff, Ref. 71, p. 357).

[79] From $a=5.836$A, $\alpha=47°45'$, $u=0.27$ (Wyckoff, Ref. 71, p. 358).

[80] Aminoff, Geol. Fören. Förh. **41,** 405 (1919).

[81] Calculated from density = 3.463 (Gmelin-Kraut, "Handbuch der anorg. Chem.," (Winter, Heidelberg), **3** (2), 278) and $u=0.400$ (Ref. 27).

[82] From $a=5.822$A, $\alpha=47°45'$, $u=0.27$ (Wyckoff, Ref. 71, p. 358).

[83] From $a=5.38$A (Ref. 25) and $u=0.388$ (Ref. 27).

[84] Wyckoff, J. Am. Chem. Soc. **44,** 1239 (1922).

[85] Hassel and Mark, Zeits. f. Physik **27,** 89 (1924).

[86] Dickinson and Pauling, J. Am. Chem. Soc. **45,** 1466 (1923); Hassel, Zeits. f. Krist. **61,** 92 (1925).

probably not accurately on the centerlines between atoms, but the structures are such as to make it seem likely that the errors introduced on this account are small.

Comparing the metal-oxygen distance in crystals in which each metal atom is surrounded by (and bonded by single bonds to) four oxygens with its value in crystals in which there are six oxygens bonded to each metal atom, we find the latter to be the larger, as would be expected. (Compare the Mg, Mn″, Zn, and Cd radii in Tables IV and VIII.)

The Na, Mg and Al radii, in crystals in which each is bonded to six oxygens, form a gradually decreasing series, due no doubt to the changing kernel charge. (The 1.01A, 1.11A and 1.16A values for Al, Si and Zr, respectively, are probably considerably too low.)

Under corresponding circumstances we find the Ca radius considerably larger than that of Mg, and that of Cd larger than that of Zn. The Cs radius, in $CsICl_2$ is considerably larger than any of the others. These relationships are again as predicted from atomic theory.

Whether the two radii obtained for Fe″ are due to incorrect values of the interatomic distances, or to the difference between the arrangement around each Fe in FeS_2 and $FeCO_3$, or are the result of two types of kernel structure must be left to the future to decide.

The cadmium atom apparently has a greater radius when surrounded by six iodine atoms than when surrounded by six oxygens, probably chiefly because of the difference in the kernel charges of the iodine and oxygen.

Hexavalent molybdenum seems to have a smaller radius than tetravalent molybdenum, the larger kernel charge pulling the valence shell closer in. The data by themselves however are insufficient to make this certain. Similar reasoning in the case of the ferrous and ferric compounds would lead us to assume the larger value for the Fe″ radius to be more nearly correct than the other, unless there are two kinds of Fe″ atoms.

IV. COMPOUNDS HAVING THE CALCIUM FLUORIDE TYPE OF STRUCTURE

The calcium fluoride structure is pictured in Fig. 3. If we assume the fluorine valence tetrahedra to be oriented so as to point toward the calcium atoms, then each of the latter is bonded to eight fluorines and

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[87] Wyckoff, J. Am. Chem. Soc. **44,** 1994 (1922).

[88] Bozorth, ibid. **44,** 2232 (1922).

[89] Dickinson, ibid. **44,** 276 (1922).

[90] Wyckoff, ibid. **42,** 1100 (1920).

[91] Wyckoff and Posnjak, ibid. **43,** 2292 (1921).

each fluorine to four calciums. In Table IX have been listed the distances between adjacent atoms in this and other crystals of like structure, as well as the radii of the electropositive atoms, calculated on the assumption that the electronegative atoms have the radii given in Table IV.

The substances listed in Table X also have the calcium fluoride type of atomic arrangement, but in these each of the more negative atoms,

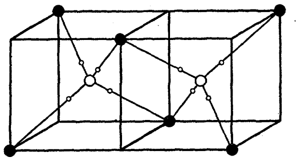

Fig. 3. Two adjacent eighth-unit cubes in the CaF_2 structure. The dots represent the centers of Ca atoms, the large circles F atoms, and the small circles valence electron-pairs.

TABLE IX

		Radii	
Crystal	Interatomic Distance	Assumed	Calculated
CaF_2	2.34[25]; 2.36[14]; 2.37[14]; 2.38A[6]	F = 0.61A	Ca = 1.73–1.77A
SrF_2	2.53[6]	F = 0.61	Sr = 1.92
$SrCl_2$	3.03[92]	Cl = 0.97	Sr = 2.06
BaF_2	2.69[6]	F = 0.61	Ba = 2.08
CeO_2	2.34[93]	O = 0.65	Ce = 1.69
ThO_2	2.41[93]	O = 0.65	Th = 1.76

TABLE X

		Radii	
Crystal	Interatomic Distance	Assumed	Calculated
Li_2O	2.00A[94]	O = 0.65A	Li = 1.35A
Li_2S	2.47[95]	S = 1.02	Li = 1.45
Na_2S	2.83[95]	S = 1.02	Na = 1.81
Cu_2S	2.45[96]	S = 1.02	Cu = 1.43
Cu_2Se	2.49[34]	Se = 1.12	Cu = 1.37
Ag_2S	2.63[97]	S = 1.02	Ag = 1.61
Ag_2Se	2.70[98]	Se = 1.12	Ag = 1.58
Ag_2Te	2.81[99]	Te = 1.23	Ag = 1.58
Mg_2Si	2.77[53]	Si = 1.14	Mg = 1.63
Mg_2Sn	2.92[100]; 2.94[101]	Sn = 1.36	Mg = 1.56; 1.58
Mg_2Pb	2.93[100]	Pb = 1.36	Mg = 1.57

[92] Mark and Tolksdorf, Zeits, f. Physik **33,** 681 (1925).

[93] Goldschmidt and Thomassen, Vidensk. Skrifter (1923) No. 2; Goldschmidt, Ulrich and Barth, ibid. (1925), No. 5.

[94] Bijvoet and Karssen, Rec. trav. chim. **43,** 680 (1924).

[95] Claasen, ibid. **44,** 790 (1925).

[96] From density = 5.8 (Mellor, "Comprehensive Treatise on Theoretical and Inorganic Chemistry," Vol. III, Longmans, London (1923)).

[97] From density = 7.27–7.32 (Groth, Ref. 35).

[98] From density = 8.00 (Groth, Ref. 35).

[99] From density = 8.32 (Groth, Ref. 35).

[100] Sacklovski, Ann. Physik **77,** 241 (1925).

[101] Pauling, J. Am. Chem. Soc. **45,** 2777 (1923).

if it has but four electron pairs in its valence shell, can be bonded to but four of the eight surrounding positive atoms (Fig. 4). The structure is like that of cubic ZnS or CuCl with the insertion of a number of positive atoms equal to the number already present in such a way as to surround each by four of the more negative atoms. From Table X it may be seen that in the copper and silver compounds listed the distance between atoms is probably slightly less than the sum of the radii in Table IV, while in the similar lithium, sodium, and magnesium compounds the observed interatomic distances are considerably the greater.

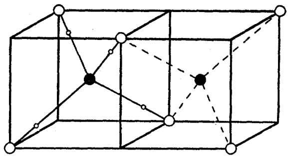

Fig. 4. Two adjacent eighth-unit cubes in the Li_2O structure. The dots represent the centers of Li atoms, the large circles O atoms, and the small circles electronpairs, in their most probable arrangement.

V. Compounds having the Caesium Chloride Type of Structure

The caesium chloride structure (Fig. 5) may be thought of as being composed of two interlocking networks of the cubic ZnS type. Each atom, although surrounded at equal distances by eight others of opposite kind, is bonded by ordinary single bonds to but four of them. The interatomic distances and approximate radii of the component atoms are given in Table XI.

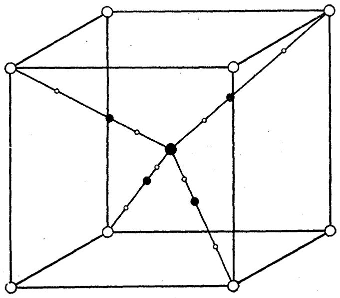

Fig. 5. The unit cube of the low temperature form of NH_4Cl. The large dot represents the center of an N atom; the smaller dots denote H atoms, the large circles Cl atoms, and the small circles electronpairs. This figure will also serve to represent the CsCl structure, the large dot and large circles denoting centers of Cs and Cl atoms, respectively.

Ammonium chloride and bromide crystallize similarly. From the interatomic distances and the halogen radii from Table IV we can calculate "radii" for the NH_4 group (*d*, Fig. 6) comparable with the atomic radii calculated for thallium and caesium.

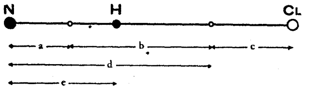

Fig. 6. The distribution of atomic centers and electronpairs along a N-Cl centerline in a crystal of NH_4Cl (low temperature form).

TABLE XI

Crystal	Interatomic Distance	Radii Assumed	 Calculated
CsCl	3.56[102]; 3.57A[103]	Cl=0.97A	Cs=2.59; 2.60A
CsBr	3.71[104]; 3.72[105]	Br=1.09	Cs=2.62; 2.63
CsI	3.94[105]; 3.95[106]; 3.97[107]	I=1.19	Cs=2.75; 2.76; 2.78
TlCl	3.32[108]; 3.33[109]	Cl=0.97	Tl=2.35; 2.36
TlBr	3.44[108]; 3.45[110]	Br=1.09	Tl=2.35; 2.36
NH_4Cl	3.34[111]; 3.35[102]; 3.36[112]	Cl=0.97	NH_4=2.37; 2.38; 2.39
NH_4Br	3.45[111]; 3.50[102]; 3.52[112]	Br=1.09	NH_4=2.36; 2.41; 2.43

VI. THE DIMENSIONS OF THE HYDROGEN ATOM IN CRYSTALS

Subtracting the nitrogen radius (*a*, Fig. 6) obtained from Table IV, from the NH_4 radii (*d*) in NH_4Cl and NH_4Br, we obtain what we might call the diameters (*b*) of hydrogen in these compounds. Since we do not know in either case the position of the hydrogen nucleus relative to the two nearest electron pairs we obviously cannot calculate the hydrogen "radii," nor can we calculate the radii (*e*) of the ammonium *ion*.

The probable structure of ice, according to W. H. Bragg, is like that of ZnO, with zinc atoms replaced by more oxygen and with a hydrogen midway between each pair of adjacent oxygens. The oxygen valence tetrahedra in such a structure we should expect to be oriented so as to place a corner (an electron pair) on each O–H centerline. The hydrogen

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[102] Havighurst, Mack and Blake, ibid. **46,** 2368 (1924).

[103] Davey, Phys. Rev. **21,** 143 (1923).

[104] Davey, ibid. **19,** 538 (1922).

[105] Wyckoff, J. Wash. Acad. Sci. **11,** 429 (1921).

[106] Clark and Duane, Phys. Rev. **21,** 380 (1923).

[107] Davey, ibid. **18,** 102 (1921).

[108] Lunde, Zeits. f. Phys. Chem. **117,** 51 (1925).

[109] Davey and Wick, Phys. Rev. **17,** 403 (1921).

[110] Van Arkel, Physica **4,** 33 (1924).

[111] Bartlett and Langmuir, J. Am. Chem. Soc. **43,** 84 (1921).

[112] Vegard, Zeits. f. Physik **5,** 17 (1921).

diameter may then be obtained by subtraction, and from it the hydrogen radius in this substance. It is not surprising to find that in ice, which consists of but a single network of atoms (if the assumed structure is correct), the hydrogen diameter is somewhat less than in the ammonium halides, which are composed of two such networks interlocking with each other.

TABLE XII

Crystal	Interatomic distance	Assumed radii	Calculated hydrogen diameter
NH_4Cl	N–H–Cl = 3.34[111]; 3.35[102]; 3.36A[112]	N = 0.70; Cl = 0.97A	1.67; 1.68; 1.69A
$(H_3N–NH_3)Cl_2$	N–H–Cl = 3.14[67]	N = 0.70; Cl = 0.97	1.47
NH_4Br	N–H–Br = 3.45[111]; 3.50[102]; 3.52[112]	N = 0.70; Br = 1.09	1.66; 1.71; 1.73
H_2O	O–H–O = 2.76[113]	O = 0.65	1.46
KHF_2	F–H–F = 2.24 ± .16[114]	F = 0.61	1.02 ± .16
$NaHF_2$	F–H–F = 2.42[70]	F = 0.61	1.20

Another approximate value for the hydrogen diameter can be obtained from hydrazine dihydrochloride $(H_3N–NH_3)Cl_2$. The most probable hydrogen positions are near the N–Cl centerlines, each nitrogen being then surrounded tetrahedrally by four atoms. The N–Cl distance in Table XII has been calculated on the assumption that the N–N distance is 1.40A and that the parameter defining the chlorine positions has been correctly determined. If we postulate further that the N, H and Cl nuclei and the valence pairs between them are colinear (Fig. 6) and that the nitrogen and chlorine radii are as given in Table IV, we obtain a value (possibly quite inaccurate) for the hydrogen diameter which is practically the same as that calculated for ice.

In the structures which have been proposed for KHF_2 and $NaHF_2$ there is a hydrogen midway between each pair of fluorine atoms. Assuming again the correctness of the parameter determinations we obtain two more values of the diameter of hydrogen.

Some of the variability in the values calculated for this distance from different crystals results no doubt from inaccurate data and incorrect assumptions, but part of it must probably be attributed to a real difference in size in different types of compounds. Surely we should expect such variation.

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[113] W. H. Bragg, Proc. Phys. Soc. **34,** 98 (1922).
[114] Bozorth, J. Am. Chem. Soc. **45,** 2128 (1923).

VII. COMPOUNDS HAVING THE CUPROUS OXIDE ARRANGEMENT

Cu_2O and Ag_2O crystallize with a structure (Fig. 7) in which each oxygen atom is surrounded tetrahedrally by four metal atoms and each metal atom is midway between two oxygen atoms. If the oxygen valence tetrahedra have their corners oriented toward the neighboring Cu or Ag atoms, we can calculate the radii of Cu and Ag atoms containing but two electron pairs in the valence shell. As would be expected, these (Table XIII) are much less than the corresponding radii in Table IV.

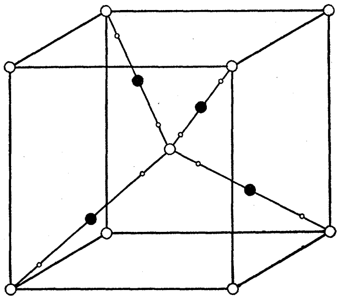

Fig. 7. The unit cube of Cu_2O. The large dots and circles represent the centers of Cu and O atoms respectively. One of the possible distributions of valence electron pairs (small circles) is shown.

VIII. ELEMENTS HAVING THE BODY-CENTERED CUBIC STRUCTURE

The probable structure of chromium, molybdenum and tungsten (Fig. 8) is one consisting of two interpenetrating simple cubic networks

TABLE XIII

Crystal	Interatomic distance	Radii	
		Assumed	Calculated
Cu_2O	1.84[6, 115]; 1.86 A[116]	O=0.65A	Cu=1.19; 1.21A
Ag_2O	2.03[6]; 2.04[115]; 2.06[117]	O=0.65	Ag=1.38; 1.39; 1.41

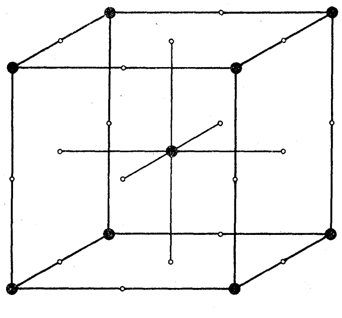

Fig. 8. Unit cube of the Cr, Mo or W crystal.

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[115] Niggli, Zeits. f. Krist. **57,** 253 (1922).

[116] W. H. Bragg and W. L. Bragg, Ref. 2; Greenwood, Phil. Mag. **48,** 654 (1924).

[117] Wyckoff, Am. J. Sci. **3,** 184 (1922).

of atoms, each atom being bonded by single bonds not to the eight nearest atoms but to the six others at a slightly greater distance. The radii obtained from such crystals (Table XIV) are comparable with each other but cannot reasonably be expected to agree with corresponding radii in other types of structure.

TABLE XIV

Crystal	Interatomic distance	Radius
Cr	2.88A[118]	1.44A
Mo	3.08[119]; 3.14[120]	1.54; 1.57
W	3.15[121]; 3.18[122]	1.58; 1.59

IX. LEAD MONOXIDE

In lead monoxide, PbO, each oxygen is tetrahedrally surrounded by four lead atoms and each lead atom is at the apex of a pyramid having four oxygen atoms at its base. The Pb–O distance has been given[123] as 2.33A. If the valence pairs are on the atomic centerlines the Pb'' radius is then about 1.68A, considerably greater (as might be expected) than that extrapolated for Pb^{IV} from Fig. 2.

TABLE XV

Crystal	Interatomic distance
CO_2	$(C=O)=1.05$[124]; 1.25[125]; 1.59[126]
$CaCO_3$	$(C=O)=1.25$[127]
$MnCO_3$	$(C=O)=1.27$[128]
$NaNO_3$	$(N=O)=1.29$[129]
N_2O	$(N=O)$ or $(N=N)=1.15$[130]
NaN_3	$(N=N)=1.17$[131]
KN_3	$(N=N)=1.16$[131]
KCN	$(C\equiv N)=1.15$[132]

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[118] Patterson, Phys. Rev. **26,** 56 (1925); Davey and Wilson, ibid. **27,** 105 (1926).

[119] Stoll, Arch. Sci. Phys. Nat. **3,** 546 (1921).

[120] Davey, Phys. Rev. **25,** 753 (1925); Fischvoigt and Koref, Zeits. f.Techn. Phys. **6,** 296 (1925).

[121] Davey, Ref. 120. Davey and Wilson, Ref. 118.

[122] Debye, Phys. Zeits. **18,** 483 (1917); Fischvoigt and Koref. Ref. 120.

[123] Dickinson and Friauf, J. Am. Chem. Soc. **46,** 2457 (1924).

[124] DeSmedt and Keesom, Proc. Acad. Sci. Amsterdam **27,** 839 (1924); Zeits. f. Krist. **62,** 312 (1925).

[125] McLennan and Wilhelm, Trans. Roy. Soc. Can., Sec. III (3), **19,** 51 (1925).

[126] Mark and Pohland, Zeits. f. Krist. **61,** 293 (1925).

[127] From $a=6.360$A, $\alpha=46°6'$, $u=0.25$ (Wyckoff, Ref. 71, p. 357).

[128] From $a=5.836$A, $\alpha=47°45'$, $u=0.27$ (Wyckoff, Ref. 71, p. 358).

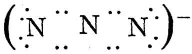
[129] From $a=6.320$A, $\alpha=48°6'$, $u=0.25$ (Wyckoff, Ref. 71, p. 349).

[130] DeSmedt and Keesom, Proc. Acad. Sci. Amsterdam **27,** 839 (1924).

[131] Hendricks and Pauling, J. Am. Chem. Soc. **47,** 2904 (1925).

[132] Bozorth, ibid. **44,** 317 (1922).

IX. Double and Triple Bonds

Table XV contains the various values calculated from x-ray data for the distances between atoms which are probably connected by double or triple bonds. These are all very approximate except perhaps the $C=O$ and $N=O$ distances in $CaCO_3$, $MnCO_3$ and $NaNO_3$. In these compounds each C or N is probably joined by double bonds to three surrounding oxygen atoms.[12] In CO_2 and N_2O the central atom is probably connected by double bonds to the other two, atoms. In KCN the CN groups (or "ions") are related to the potassium "ions" in the crystal only as the "ions" of chlorine are related to those of sodium in crystals of NaCl. So also in KN_3 and NaN_3 the structural units are the K^+, Na^+ and N_3^- ions. The two end nitrogens of the N_3^- ion seem to be equivalent; if each of the three has a valence shell containing eight electrons the structure must then be  $\left(\overset{\cdot}{\underset{\cdot}{:\mathrm{N}}}\ \overset{\cdot\cdot}{\underset{\cdot\cdot}{}}\ \mathrm{N}\ \overset{\cdot\cdot}{\underset{\cdot\cdot}{}}\ \overset{\cdot}{\underset{\cdot}{\mathrm{N}:}}\right)^{-}$.[133]

Theory would lead one to expect smaller distances, in general, between two atoms joined by a double or triple bond than between the same atoms joined by a single bond. This seems to be the case.

In conclusion the author wishes to point out again the tentative nature of the results given in this paper and their limited applicability. It is believed, however, that when properly used they will prove of greater value than atomic and ionic "radii" calculated without regard to the electronic structures of the crystals concerned. Helpful suggestions from Professor Wm. C. Bray of the University of California are gratefully acknowledged.

Stanford University,
March 19, 1926.

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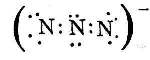
[133] Hendricks and Pauling, Ref. 131, prefer the structure  $\left(\overset{\cdot}{\underset{\cdot}{:\mathrm{N}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\overset{\cdot}{\underset{\cdot}{\mathrm{N}:}}\right)^{-}$ for the trinitride ion.