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New Set of Tetrahedral Covalent Radii

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A table of additive covalent radii for tetrahedrally coordinated crystals is obtained by simple quantum-mechanical considerations using the bond lengths of the four diamond-type crystals and only two free parameters. The 39 bond lengths so obtained agree with experiment with an rms error of less than 1%. The extension of these considerations to other crystal structures and to molecules is considered. These radii should be useful for estimating lattice distortions produced by isoelectronic impurities.

1. INTRODUCTION

As soon as x-ray data on crystal structures began to accumulate,[1] various authors proposed that interatomic distances $d(AB)$ could be regarded as approximately the sums of atomic radii r_A and r_B,

$$d(AB) = r_A + r_B . \tag{1.1}$$

Relations such as (1.1) are consistent with the historical notion of atoms as indivisible particles which were presumed to be hard spheres independent of their environment. Theories of interatomic spacing have since attracted considerable interest and excellent reviews are available in the books by Pauling[2] and by Slater.[3]

Slater points out that if one is willing to tolerate errors as large as 10–20%, then any interatomic spacing can be calculated without employing any free parameters. One may take tabulated Hartree-Fock-Slater solutions for the electronic structure of the free neutral atoms[4] and assume that the atomic radii are the radii of the charge-density maxima of the outermost electrons. The assumption here[3] is that the covalent bond length is determined by the maximal overlap of the unperturbed valence wave functions and that ionic and other effects on interatomic distances may be neglected.

However, the opposite approach of introducing large numbers of free parameters in order to improve the accuracy of the calculated values has been the more popular. Typically, one introduces as a free parameter the atomic radius of each element and then varies these to give the best statistical fit to the class of materials under consideration. More sophisticated theories[2] take account of variations in environment associated with the covalent, ionic, or metallic nature of the bonding of each atom to its nearest neighbors as implied by coordination numbers and classical valence concepts. Such refinements introduce several free parameters for each element considered. While trends among these parameters are usually discernible, it is not always clear whether these arise because of necessity or convenience.

In this paper we attempt to clarify this situation somewhat by first restricting ourselves to the class of tetrahedrally coordinated crystals having the chemical formula $A^N B^{8-N}$. (These crystals have the diamond, zinc-blende, and wurtzite structures.) Within this restricted class, we develop explicit formulas for the interatomic spacings which produce rms errors of less than 1% Our formulas use a minimum number of free parameters and have a clear physical interpretation.

Many discussions of bond length have been carried out for molecules, where multiple π bonds and lone pairs produce large variations in bond lengths. In cubic crystals, on the other hand, these molec-

ular effects are largely absent. The tetrahedrally coordinated atoms we consider have no lone pairs or π bonds, and each atom is predominantly in an sp^3-hybridized state. Variations in bond length are therefore associated primarily with variations in core size. The latter can be treated either using Slater's rules for the radii of atomic shells[5] or by examining core wave functions derived in free-atom Hartree-Fock-Slater calculations.[4] Either way provides a quantum-mechanical basis for our theory, but we prefer using Slater's rules because of their algebraic simplicity as well as functional uniformity.

The plan of this paper follows. In Sec. 2 we review some empirical trends among atomic radii. In Sec. 3 we develop our explicit formulas for the tetrahedral covalent radii. In Sec. 4 a statistical comparison is made with Pauling's predictions and with experiment. In Sec. 5 we consider the relation of the tetrahedral radii to those obtaining in structures of higher coordination by treating the less ionic compounds which form crystals in the sixfold coordinated rock-salt structure. In Sec. 6 some recent experimental results on tetrahedral bond lengths in cage molecules are discussed. It is shown that crystalline tetrahedral radii are not simply related to molecular radii, because of lone-pair effects in the latter which are absent in the former.

2. TRENDS IN EMPIRICAL COVALENT RADII

The most striking trend in the Pauling-Huggins table of covalent radii[2,6] and most other such tables is that the proposed radii of the elements *decrease* as one goes across the Periodic Table from left to right, i.e., with *increasing* core charge or valence number. Thus the radius of Mg is supposed to be 40% larger than that of Cl and that of Be 65% larger than F. *A priori*, this is rather surprising because the atoms of greater valence are usually considered to be larger than those of lesser valence in the same row. The crystal-structure diagrams of Wyckoff[7] and others follow this convention. Of course, the quantum-mechanical wave functions do not define a unique radius for the atoms. The Hartree-Fock-Slater calculations for the free atoms[4] do show that the charge-density maximum of the outermost electrons moves inwards with increasing valence, so that by the Slater criterion[3] for the covalent bond, this trend in the empirical radii is consistent with the quantum-mechanical calculations. However, one may note that by the Slater criterion, one calculates the nearest-neighbor distance in diamond to be 1.20 Å, whereas the observed value is 1.54 Å. Thus one has a 22% error in what is generally considered to be the prototypical covalent bond. Thus this bond length is fixed at a point substantially greater than the maximal overlap of the unperturbed wave functions. On the other hand, if we assume that the radius of the atom is determined by the point at which the total charge density falls to some fixed value, then the free-atom calculations show that the atoms get larger with increasing valence – not smaller.

We will thus seek some other explanation of the empirical trends in nearest-neighbor distances. When one considers the nearest-neighbor distance of all compounds in the diamond, zinc-blende, and wurtzite structures made up of elements from a given row or pair of rows of the Periodic Table, one finds[8] these to be nearly constant in most cases. The typical variation from the mean value is about 1% with larger deviations observed in a few cases (most notably the Be salts) for reasons to be discussed shortly. The deviations from the value observed in Ge for GaAs, ZnSe, and CuBr are -0.1, $+0.2$, and $+1.6$%, respectively, and the deviations from the (geometric) mean of the values for Ge and Sn for GaSb, InAs, ZnTe, CdSe, and CuI are $+1.0$, -0.4, $+0.5$, $+0.3$, and -0.3%, respectively. This observation was utilized to define a new set of covalent radii to be used to calculate electronegativity differences according to the dielectric definition.[8,9] There the radii were taken to be constant at the value observed in the group-IV element for the entire row; they were assumed to be independent of valence. The assumption there was that the bond length is determined by the eight valence electrons of the pair, independent of the atomic cores involved. This is, thus, the opposite extreme of the hard-sphere additive-radii picture.

To obtain more precise bond lengths we will now modify this valence-electron bonding model somewhat. We assume that as long as the core-electron radii are sufficiently small (this condition will be quantified shortly), the bond length will be determined by the sp^3-hybridized valence electrons, independent of the valence of the atoms involved. However, as Anderson[10] has noted, the wave functions of the valence electrons of a given atom must be orthogonalized, not only to the core states of that same atom, but also to the core states of neighboring atoms when brought together to form a crystal. The effective pseudopotential is thus repulsive in the region of the neighbor's core and a repulsive interaction between the atoms develops if they are brought so close together that substantial overlap between the valence electrons on atom A and the core electrons on atom B develops. If the lattice contraction is not stopped by the valence-bonding effects before this occurs, then the nearest-neighbor distance is limited by this core

repulsion to be larger than the value expected from valence-bonding effects alone. Thus the reason that empirical analysis of lattice constants implies that the additive radius of Mg is larger than that of Cl is *not* because the spatial extent of the valence wave functions of the free neutral Mg atom is greater than that of the free neutral Cl atom (this simply is not so), but because the spatial extent of the $2s$ and $2p$ cores of Mg is greater than those same cores in Cl.

Before we give an explicit formula for the interatomic distances based on the above considerations in Sec. 3, we note that another discernible trend in the empirical radii tables is that the values for a given atom tend to increase with coordination number. Pauling[2] treats this effect at length and proposes some quite plausible prescriptions for the trends. In this paper we shall avoid trying to calculate the relation of the additive radii from one environment to another. Instead we will consider all cases for which data are available for a given situation – such as the tetrahedrally coordinated $A^N B^{8-N}$ crystals – and fix the parameters of our model for each coordination class independently.

We further note that in the tetrahedrally coordinated crystals which are our primary interest, the ratio of the second-nearest-neighbor distance to the nearest-neighbor distance is $2\sqrt{2}/\sqrt{3} = 1.63$. This ratio is large enough so that the covalent radii (by either Pauling's table or the one we shall propose) of the second-nearest neighbors never overlap. Thus, in contrast to the situation in some other structures, such as the more ionic oxides, [3] we will neglect to consider any second-nearest-neighbor interaction for this class.

3. CALCULATION OF ADDITIVE RADII

Although we emphatically reject the hard-sphere model as an explanation for the observed interatomic distances, we will continue to use the additive-radii notation with the explicit understanding that their only significance is that by (1.1) they give the nearest-neighbor distances in the crystal. We do this solely for simplicity and convenience.

First let us note that the radius of the core electronic shells is no better defined by quantum-mechanical calculations than is the radius of the valence electrons. Therefore, in order to quantify our notion of the size of the core shell, we may fall back to the Bohr orbit model of the atom and use Slater's rules[5] for the effective charge seen by electrons in the various shells.

Therefore, the effective radius of the outermost core s or p shell as seen by the sp^3-hybridized bonding electrons is assumed to be

$$r_c = R(n)/Z_{\text{eff}} . \tag{3.1}$$

Here Z_{eff} is the effective charge for this outermost s or p core state as given by Slater. Henceforth all mention of Z_{eff} will be with the understanding that we refer to that shell. (Note that sp^3 electrons do not feel a repulsive pseudopotential due to d-core shells.) n is the principal quantum number of that shell and $R(n)$ is a parameter. We shall fix $R(n)$ for one particular n and then assume it varies according to the Bohr formula

$$R(n) = n^2 \left[Z_{\text{eff}}(C)/Z_{\text{eff}}(\text{IV}) \right] 4.0a_0 . \tag{3.2}$$

Here $Z_{\text{eff}}(C)$ denotes the effective charge for C, 5.7 electrons, and $Z_{\text{eff}}(\text{IV})$ denotes the effective charge for the group-IV element in whichever row of the Periodic Table the element in question belongs. Z_{eff} is 9.85 for Si, 20.75 for Ge, and 22.25 for Sn. The constant $4.0a_0$ is our choice for the one adjustable parameter introduced so far.

In terms of r_c the covalent radius of an atom from row n of valence Z_{eff} is

$$r(n, Z) = r_v(n), \qquad r_c \leq 0.4 r_v \tag{3.3}$$

$$r(n, Z) = r_v(n) + (r_c - 0.4 r_v), \qquad 0.4 r_v < r_c . \tag{3.4}$$

According to (3.3) and (3.4), there are two regimes to be considered. When r_c is sufficiently small, the covalent radius is a function of n alone, and is therefore constant in each row when Z_{eff} exceeds a certain minimum value which makes $r_c \leq 0.4 r_v$. Larger values of r_c increase r, as described by (3.4). The coefficient 0.4 is our second adjustable parameter. It has been estimated by consideration of compounds containing elements of the first two rows of the Periodic Table. There is no expansion in the elements belonging to the third and fourth rows. In Sec. 5, we will discuss evidence that this parameter should be 0.25 instead of 0.4 for the $3d$ transition-metal elements, as well as Ca. This would not affect the values in Tables I and II.

To complete our model we utilize the observed values of the nearest-neighbor distance in the diamond-type crystals of the group-IV elements C, Si, Ge, and Sn to determine the values of the effective additive radii in the absence of any core effect. We denote these four parameters by $r_v(n)$, $n = 1-4$ f the four rows from C to Sn. The values thus determined are 0.672, 1.127, 1.225, and $1.405a_0$, respectively. Note that for C and Si, the additive radii (equal to one-half the nearest-neighbor distance), 0.772 and 1.176 Å, are greater than $r_v(1)$ and $r_v(2)$ because of the effect of the size of their cores, while for Ge and Sn the cores are much smaller due to the filled d levels, and r is equal to r_v. In Table I we show the values of Z_{eff}, r_c, and r for $Z = 1-7$ and $n = 1-4$.

TABLE I. Tetrahedral covalent radii. For each element the effective charge Z_{eff} seen by electrons in the outermost s or p core shell as calculated according to Slater's rules (Ref. 5) is shown together with the corresponding core radius r_c and the tetrahedral covalent radius. The underlined values of the tetrahedral radii are those which have been affected by the core. (See Secs. 3 and 4.)

Be	Element		B	C	N	O	F
3.70	Z_{eff}		4.70	5.70	6.70	7.70	8.70
0.572	r_c Å		0.450	0.371	0.316	0.275	0.243
0.975	r Å		0.853	0.774	0.719	0.678	0.672
Mg			Al	Si	P	S	Cl
7.85			8.85	9.85	10.85	11.85	12.85
0.625			0.554	0.497	0.452	0.413	0.381
1.301			1.230	1.173	1.128	1.127	1.127
Ca	Cu	Zn	Ga	Ge	As	Se	Br
8.75	17.75	18.75	19.75	20.75	21.75	22.75	23.75
0.598	0.295	0.279	0.265	0.252	0.241	0.230	0.220
1.333	1.225	1.225	1.225	1.225	1.225	1.225	1.225
Sr	Ag	Cd	In	Sn	Sb	Te	I
10.25	19.25	20.25	21.25	22.25	23.25	24.25	25.25
0.846	0.451	0.428	0.408	0.390	0.373	0.358	0.344
1.689	1.405	1.405	1.405	1.405	1.405	1.405	1.405

It is interesting to note that because $r_v(n)$ is fixed by the bond lengths of group-IV crystals, our model, in effect, replaces the 24 parameters used by Pauling to describe $n=1-4$ and $Z=1-3$ and 5—7 by just two parameters. If these two parameters can reproduce the bond lengths of 35 zinc-blende and wurtzite crystals with high accuracy, then one can conclude that the core model is not inconsistent with a quantum description of the nature of crystalline covalent radii.

4. COMPARISON WITH EXPERIMENT AND WITH PAULING-HUGGINS'S VALUES

In Table II we compare the observed values of the nearest-neighbor distances in the tetrahedrally coordinated AB crystals with the values predicted according to (1.1) using the Pauling-Huggins tetrahedral covalent radii[6] and using the radii we calculate (Table I). However, special note must be taken of cases such as SiC. The radii of Si and C are uniquely determined by observation of diamond-type C and Si crystals. However, the nearest-neighbor distance in SiC, 1.8827 Å, is significantly less than the sum of these radii, 1.9480 Å. Pauling's explanation of this and several similar cases is that the difference between the sum of the radii and the nearest-neighbor distance must be due to the partial ionic character of the bond.[11,12]

Although an appeal to ionic character would be useful for SiC, more ionic crystals such as ZnS do not exhibit such an effect. We therefore propose a different explanation. In our model, both Si and C have radii which are larger than the values that would obtain in the absence of the core-valence electron repulsion discussed in Sec. 3. We assume that this effect is diminished when the valence electrons of the atoms forming the crystal have different principal quantum numbers.

We know of no quantum-mechanical explanation for this diminution. The following mechanism has some appeal, however. Consider the specific case of SiC, where bonds are formed between $2s2p^3$-hybridized C orbitals and $3s3p^3$-hybridized Si orbitals. When the bonding electron is centered on C it avoids the C core, which increases the C radius by approximately 0.10 Å (Table I). Suppose when it moves to the neighborhood of Si the bonding orbital "remembers" that it has already increased its natural "size" by 0.1 Å. Then it may require little extra kinetic energy to avoid the Si core, which in pure Si increases its radius by only 0.05 Å. Another possible explanation for this "memory" effect is that the core energies are quite different, being about three times as great for the $1s$ electrons of C as for the $2s$ and $2p$ electrons of Si.

Whatever the microscopic mechanism, we find that when atoms belonging to *different* rows are combined, we can calculate bond lengths quite well by simply deleting the smaller of the two core-effect expansion parameters $r_c - 0.4r_v$. That is, we have

$$d(A,B) = r_v(A) + r_v(B) + \delta r_c \,, \tag{4.1}$$

where

TABLE II. Comparison of predicted nearest-neighbor distances to experiment. All experimental values are taken from Wyckoff (Ref. 7), except for MgS, MgSe, and ZnO. The MgS and MgSe values are due to Mittendorf (Ref. 13). The ZnO value is due to S. C. Abrahams and and J. L. Bernstein [Acta Cryst. (to be published)]. When a compound occurs in both the zinc-blende and wurtzite forms, the value shown is that of the more stable low-temperature form.

Compound	d_{obs} (Å)	d_{calc} (Å)	$d_{Pauling-Huggins}$
Bn	1.565	1.572	1.58
BeO	1.649	1.653	1.72
AlP	2.360	2.358	2.36
MgS	2.410	2.428	2.44
GaAs	2.441	2.450	2.45
ZnSe	2.454	2.450	2.45
CuBr	2.464	2.450	2.46
InSb	2.805	2.810	2.80
CdTe	2.806	2.810	2.80
AgI	2.807	2.810	2.80
SiC	1.883	1.901	1.94
BP	1.965	1.980	1.98
BeS	2.100	2.102	2.10
AlN	1.892	1.902	1.96
GaN	1.944	1.944	1.96
ZnO	1.973	1.903	1.97
CuF	1.843	1.897	1.99
BAs	2.069	2.078	2.06
BeSe	2.195	2.200	2.20
InN	2.154	2.124	2.14
BeTe	2.399	2.380	2.38
AlAs	2.451[a]	2.455	2.44
MgSe	2.533	2.526	2.54
GaP	2.360	2.353	2.32
ZnS	2.342	2.352	2.35
CuCl	2.341	2.352	2.34
InP	2.541	2.533	2.54
CdS	2.532	2.532	2.52
AlSb	2.656	2.635	2.62
MgTe	2.762	2.706	2.72
GaSb	2.649	2.630	2.62
ZnTe	2.637	2.630	2.63
CuI	2.617	2.630	2.63
InAs	2.614	2.630	2.62
CdSe	2.633	2.630	2.62

[a]J. F. Black and S. M. Ku, J. Electrochem. Soc. 113, 249 (1966); J. Whittaker, Solid State Electron. 8, 644 (1965).

$$\delta r_c = \text{greater of}$$
$$[r_c(A) - 0.4 r_v(A),\ r_c(B) - 0.4 r_v(B)].$$

Thus for SiC, we add the radius of C, including the effect of the core, to the r_v for the Si row, $r_v(2)$, to obtain 1.901 Å, in reasonable agreement with the observed value 1.883 Å for the zinc-blende form. This prescription has been used to correct all our predicted bond lengths for which both radii are expanded by core effects (Table II).

The rms error in our predictions of the bond lengths of all the tetrahedrally coordinated AB crystals is 0.96%, as compared to 1.75% for the predictions according to the Pauling-Huggins covalent radii. The fact that the Pauling-Huggins radii give a larger rms error results from several facts. Pauling and Huggins did not restrict themselves to these crystals, and included large numbers of molecules when fixing their parameters. They also did not have as accurate data when they made their survey. With one parameter for each atom at their disposal they could not do worse than we do in fitting the same class of bond lengths. Indeed we could improve our predictions by introducing a few more parameters, e.g., a scaling factor for the core correction for the first row of the Periodic Table 10% smaller than that used for the other rows. In view of the good agreement already achieved we regard such refinements as marginal, and they will not be analyzed here.

5. ADDITIVE RADII FOR COORDINATION GREATER THAN FOUR

We shall now consider the relationship between our tetravalent radii and the interatomic spacing that obtain in crystals having some coordination number greater than four. Let us consider the case that the coordination number is six. As before, we restrict our considerations to $A^N B^{8-N}$ type crystals so as to eliminate spurious effects. Thus we investigate the rock-salt crystals.

Now our radii are covalent radii and the prototypical rock-salt crystals are the ionic alkali halides, which are quite different in their physical properties, binding, etc., so we would not expect our investigations of covalent bonding to be applicable to the study of these crystals. However, it has recently been noted[8] that the transition from "covalent" to "ionic" behavior of many crystalline properties does not occur at the point where the crystal structure changes from wurtzite or zinc blende to rock salt, 78% Phillips ionicity, but at a much higher ionicity. For instance, the index of refraction of the rock-salt crystal MgO decreases when subjected to hydrostatic pressure, as is the case with all diamond, zinc-blende, and wurtzite compounds, whereas in the alkali halides the index of refraction increases with pressure.[8] MgS and MgSe are found to be metastable in the wurtzite structure[13] as well as stable in the rock salt. Furthermore, Kunz[14] has shown that only for those alkali halides which are 94% or more ionic (on the Phillips scale) are the free-ion wave functions acceptable basis functions for the va-

lence-bond states of the crystal. Thus full ionic behavior is only achieved in crystals of the Rb and K halides and their alloys. The less ionic, rock-salt crystals share some of the properties of wurtzite and zinc-blende crystals. The Li and Na halides are intermediate between covalent and ionic in their behavior.

We begin by considering AgBr and AgCl. Because both of these are crystals involving atoms of comparable covalent radii, which have no core-expansion effect, and both have a relatively low ionicity (85 and 86%) for rock-salt-type crystals, we feel they are the proper place to begin. The average of the ratio of the observed nearest-neighbor distance to the sum of the tetrahedral covalent radii is 1.0966. Thus we assume that, for all cases, the octahedral covalent radii are 9.66% larger than the tetrahedral radii. We keep our calculation of the core sizes exactly as before and continue to assume that the radius is extended by an amount $(r_c - 0.4r_v)$ when the $r_c > 0.4r_v$. The octahedral covalent radii thus obtained are shown in Table III. In Table IV we compare the nearest-neighbor distances predicted using these radii with experiment.

We note in Table IV that many bond lengths are predicted with surprisingly great accuracy – for the Mg salts we have a 0.34% rms error. However, several discrepancies are also evident. We first note that while the value of MgO is very accurate, those for CaO, SrO, and CdO are all much too low. We recall from Table II that a similar occurrence obtains with the tetrahedral radius of O; BeO is predicted very accurately in our model, but the value for ZnO is much too low. We suspect that this discrepancy is due to an interaction between the 2*s* O electron and the *d* states in Zn, Ca, Cd, and Sr. In any event, if we increase the assumed tetravalent radius of O so as to obtain a nearest-neighbor distance of 1.97 Å in ZnO, the corresponding octahedral radius of O would be 0.811 Å instead of 0.737 Å. We would then predict the values shown in parentheses in Table IV. The new values for CdO and SrO agree very well with experiment, but the value for CaO is still about 0.2 Å too small. However, we note that the values for CaS, CaSe, and CaTe are also all 0.2 Å too small. Clearly, our octahedral covalent radius for Ca is approximately 0.2 Å too small. It is not clear to us why Ca deviates from our model while Sr does not, but it seems to have a consis-

TABLE IV. Comparison of predicted nearest-neighbor distances to experiment. All experimental values are taken from Wyckoff (Ref. 7). In the column headed d_{calc}, we show our calculated values and, in parentheses, our calculated values corrected for spurious effects in O and Ca compounds as described in Sec. 5. In the column headed $d_{Zachariasen}$, we show the values calculated using Zachariasen's table of ionic radii.

Compound	d_{obs} (Å)	d_{calc} (Å)		$d_{Zachariasen}$ (Å)
MgS	2.602	2.603		2.55
CaSe	2.950	2.747	(2.947)	2.96
SrTe	3.235	3.312		3.32
MgO	2.106	2.104		2.11
CaO	2.405	2.141	(2.215) (2.415)	2.40
CdO	2.346	2.278	(2.352)	•••
SnO	2.580	2.508	(2.582)	2.56
AgF	2.460	2.278		•••
MgSe	2.726	2.710		2.67
CaSe	2.845	2.640	(2.840)	2.84
SnS	3.010	3.007		3.00
AgCl	2.774	2.777		•••
CaTe	3.173	2.945	(3.145)	3.16
SnSe	3.115	3.114		3.12
AgBr	2.887	2.884		•••

TABLE III. Octahedral covalent radii. Values calculated as described in Sec. 5. As in Table I, the underlined radii have been affected by the core. The value for O shown in parentheses is that which seems to obtain due to *d*-state effects when O is bonded to a 3rd or 4th row element (see Sec. 5). The value for Ca shown in parentheses is what we find to be the correct value (Sec. 5).

Element r (Å)						
Be			B	C	N	O	F
1.014			0.892	0.813	0.758	0.737 (0.811)	0.737
Mg			Al	Si	P	S	C
1.367			1.296	1.239	1.236	1.236	1.236
Ca	Cu	Zn	Ga	Ge	As	Se	Br
1.404 (1.604)	1.343	1.343	1.343	1.343	1.343	1.343	1.343
Sr	Ag	Cd	In	Sn	Sb	Te	I
1.771	1.541	1.541	1.541	1.541	1.541	1.541	1.541

tent octahedral radius of about 1.604 Å as opposed to the predicted value of 1.404 Å.

We suspect that the fault lies with our assumption that the scaling factor for the core correction (3.3) is a constant (40%), independent of the row of the Periodic Table to which the element belongs. We have already noted that we could improve the agreement between theory and experiment for the tetrahedral radii (Table II), if we used slightly different values for the scaling factor for the first and second rows. (Of course, one would expect that we could fit data better with three free parameters than with two.) If we assume that the scaling factor for the $3d$ transition-metal elements, to which we add Ca, is 25% instead of 40%, then we would calculate the observed octahedral covalent radius for Ca. As Ca does not occur in a wurtzite or zinc-blende structure, this speculation can not be investigated directly. The 25% scaling factor would not affect the radii listed in Table I. It would, however, change the predicted value of tetrahedral radius of Mn from 1.225 to 1.299 Å. MnS and MnSe occur in the zinc-blende structure, but were not included in Table II because Mn is a transition metal and we wished to avoid the spurious effects of a partially filled d band. However, because the d band in Mn is exactly one-half filled and symmetric, one would expect Mn to exhibit the simplest behavior of all transition metals. With a radius 1.299 Å we would calculate for MnS and MnSe $d = 2.426$ and 2.524 Å, respectively, in excellent agreement with the observed values 2.425 and 2.520 Å.[7]

Finally, we note that the value for AgF is also too small. Presumably the same effect that occurs in the oxides occurs in the fluorides also.

The nearest-neighbor distances we would calculate using our octahedral covalent radii for the intermediate and ionic rock-salt crystals are all substantially smaller than the observed values. In order to treat these crystals accurately one must consider ionic effects or use tables of ionic radii. One can conclude, however, that in the ionicity range $0.78 < f_i < 0.89$, modified covalent radii may predict the lattice constants as accurately as conventional ionic radii. For the purpose of comparison we include in Table IV the values calculated using Zachariasen's table of ionic radii.[15]

6. APPLICATIONS AND CONCLUSIONS

The covalent radii described here are suitable for discussing bond lengths in A^NB^{8-N} crystals. Probably the reader is already aware of the fact that even tetrahedrally coordinated atoms exhibit different apparent radii in molecules than in crystals because of lone-pair effects.

A good illustration of this fact is contained in some recent molecular work. Studies[16] of the molecules P_4O_9 and P_4O_{10}, which have tetrahedral cage structures, have produced an estimate of the P-O single bond length of 1.66 Å, compared to the value 1.76 Å predicted by Pauling's tetrahedral radii and the value 1.80 Å predicted by our radii. Note, however, that these molecules contain an average of 5.7 electrons per atom, and less than four bonds per atom, leaving more than three unbonded electrons per atom in "lone-pair" states. These lead to appreciable shortening of the molecular bond lengths compared to crystal bond lengths where there are no lone pairs.

While the present radii have no obvious molecular applications, we believe that the radii should be useful for estimating lattice distortions produced by neutral substitutional impurities (isoelectronic impurities) such as N in GaP.

From our point of view, the most significant aspect of the present work is the high precision obtained with two free parameters in fitting the bond lengths of 39 tetrahedrally coordinated crystals. We believe that our 1% accuracy implies that the "core-expansion" mechanism is genuinely important in determining lattice constants for this family of crystals.

7. POSTSCRIPT

After completion of this paper, two additional developments occurred that appear to indicate that the present analysis of atomic radii from a quantum-mechanical viewpoint is justified: (a) In analyzing the heats of formation of tetrahedrally coordinated A^NB^{8-N} crystals we found[17] an explanation for the anomalously small lattice constant of the Hg salts. This explanation is of interest because it exhibits an explicit effect of the *details* of the energy band structure on the lattice constant. Conversely, one can conclude from that analysis that band-structure effects are negligible for compounds of lighter elements considered here, which apparently leaves our explanation of core effects as the only one available. (b) We have explicitly restricted our analysis to atom pairs sharing eight valence electrons. Suppose a pair of atoms share $8 + Q$ valence electrons in a tetrahedrally coordinated structure, with $Q = \pm 1$. An example of such a structure is $ZnSiP_2$, with SiP bonds with $Q = +1$ and ZnP bonds corresponding to $Q = -1$.

One can imagine expanding Eq. (1.1) in powers of Q, retaining terms only to first order in Q. These turn out to be small and the magnitude of the coefficient should be about the same in ZnP and SiP bonds. This means that $D = d(\mathrm{SiP}) + d(\mathrm{ZnP})$ should be given fairly accurately by our radii formulas. In fact, we predict $D = 4.654$ Å, Pauling and Huggins[2] predict 4.68 Å, and the experimen-

tal value[18] is 4.639 Å. While our results show a marked improvement over the older values, there are still significant discrepancies with experiment, and revisions of our table may prove desirable after more data is obtained on $A^{II}B^{IV}C^{V}_2$ compounds. It is worth noting that the cases $Q = \pm 1$ correspond to donor or acceptor impurities, so that further study of this question may supply valuable insight into the strain fields surrounding electrically active impurities in semiconductors.

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Lattice Dynamics, Mode Grüneisen Parameters, and Coefficient of Thermal Expansion of CsCl, CsBr, and CsI†

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The phonon dispersion curves for CsCl, CsBr, and CsI have been obtained using a rigid-ion model with an appropriate effective ionic charge. The five model parameters for each crystal are obtained from three elastic constants and the two long-wavelength optic-mode frequencies, reliable data for which exist for all three crystals. Our results are in agreement with those of more elaborate models. The phonon density of states and the Debye characteristic temperatures are also calculated. A Born-Mayer-type potential is used to calculate long-wavelength LO and TO mode frequencies as functions of pressure from pressure dependence of bulk modulus. The result for TO of CsBr agrees well with a recent experimental determination. Next, using the values of the elastic constants and LO and TO frequencies at various pressures, ω-versus-$\vec{k}$ curves in selected directions are generated as functions of pressure. Mode Grüneisen parameters are then calculated as functions of $\vec{k}$. Finally, the Grüneisen constant and the volume coefficient of thermal expansion are obtained as functions of temperature. They agree very well with available experimental data.

I. INTRODUCTION

The lattice dynamics of crystals having the CsCl structure was first worked out by Ganesan and Srinivasan.[1] They used the results from the lattice dynamics to predict the temperature variation of the Grüneisen constant. Their calculations were based on a Born-Mayer-type potential incorporating an r^{-n}-type repulsive term and a formal ionic charge of unity. This treatment is thus essentially similar to the one first introduced by Keller-