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Bonding and crystal structures of average-valence- ⟨ 5 ⟩ compounds: A spectroscopic approach*

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A number of aspects of the Phillips-Van Vechten spectroscopic approach to covalent bonding are applied to average-valence- ⟨ 5 ⟩ compounds. An average energy gap E_g can be defined which is reasonably close to the energy of the single large peak that dominates the optical spectra of these compounds. The bond charge of As estimated from the dielectric constant as suggested by Phillips compares well with that determined from band-structure calculations. Covalent radii are determined and with these the Phillips electronegativities C and ionicities F_i are also found. Heats of formation are related to ionicities in the manner of Phillips and Van Vechten; however, their metallization factor is found not to be important here. A critical ionicity $f_i^c = 0.62 \pm 0.03$ appears to be the limit above which the rhombohedral α-GeTe and α-As structures do not exist under any conditions. The stability of the orthorhombic black P, SnS, and TlI structures relative to the cubic or rhombohedral ones is not yet understood; however, trends in the orthorhombic structures with ionicity are evident. Complications of metallic contributions to the bonding are considered. The relation of the Phillips approach to pseudopotential theory is reviewed. The expressions for the gap E_g in second-order pertubation theory show differences for average valences of ⟨ 4 ⟩ and ⟨ 5 ⟩. An examination of these differences suggests one more reason for why the group-V semimetals occur in the rhombohedrally distorted simple-cubic structure rather than the true simple-cubic or diamond structures. At the same time, the critical ionicity f_i^c of ⟨ 5 ⟩ compounds seems not surprisingly to have the same underlying explanation as the critical ionicity which separates tetrahedral from octahedral ⟨ 4 ⟩ compounds.

I. INTRODUCTION

In this paper we discuss the correlation of a number of properties of average-valence-⟨5⟩ compounds, using a number of ideas Phillips and Van Vechten[1-4] have had great success with in discussing average-valence-⟨4⟩ compounds. For convenience we shall refer to these as ⟨5⟩ compounds and ⟨4⟩ compounds, respectively.

We will discuss the definitions for ⟨5⟩ compounds of an average Phillips gap E_g between filled and unfilled states, the Phillips electronegativity difference C, ionicity f_i, and covalent radii. In this way, the optical spectra, the optical static dielectric constant $\epsilon_1(0)$,[5] heats of formation ΔH, and some trends in crystal structure stability can be related. Finally, in Sec. IX, the relation of the pseudopotential theory of metals and semiconductors to the spectroscopic approach is discussed, especially for α-As, Sb, Bi, and α-GeTe. Some extra insights are thus obtained.

Most of the concepts refined by Phillips and Van Vechten, such as ionicity or covalent radii, are certainly useful qualitatively and even semiquantitatively for describing a great many crystals for which an average valence has not been defined. Moreover, there is nothing in the development of Phillips's ideas that limits the use of his definitions of f_i, E_g, C to only ⟨4⟩ compounds. There are restrictions of course, to the compounds the Phillips theory can be applied to. For example, the optical absorption $\epsilon_2(\omega)$ should be dominated by a single band gap, but this is hardly a valence restriction. Stiles and Brodsky[6,7] have done preliminary calculations of the ionicities of some IV-VI compounds and obtain very reasonable results. Brodsky and Stiles[8] have pointed out that the rather large differences in the values of $\epsilon_1(0)$ between amorphous GeTe and rhombohedral α-GeTe can be understood in terms of the differences in their bonding with the aid of Phillips's scaling. Finally, Gillis[9] has assumed the dielectric bond charge model for calculations of the lattice dynamics of SnTe. It is therefore reasonable to look into the justification and internal consistency of the Phillips theory as applied to ⟨5⟩ compounds.

The experimental situation for ⟨5⟩ compounds is much worse than for ⟨4⟩ compounds. Not only have the ⟨5⟩ compounds been studied far less; many of them are much more difficult to study properly. The principal difficulty is achieving decent stoichiometry, particularly in Ge and Sn monochalcogenides. For example, the lattice constants of GeTe can change by 0.3% in going from $Ge_{0.50}Te_{0.50}$ to $Ge_{0.51}Te_{0.49}$.[10] Off-stoichiometry also results in a great many free carriers which make the determination of optical static dielectric constants difficult. The homogeneity region is entirely on the chalcogenide rich side of the phase diagram in SnS, SnSe, SnTe, and GeTe. The Pb chalcogenides are better behaved, and their narrow homogeneity regions straddle the perfectly stoichiometric composition.[10]

A further complication is that the ⟨5⟩ compounds are divided among a number of crystal structures, including the NaCl cubic, CsCl cubic, and a number of different distortions of the NaCl cubic.[10-12] Only a few highly ionic (in the Phillips sense) In and Tl monohalides have the CsCl structure, and the III-VII compounds which have the CsCl structure will not be extensively discussed here. The fact that many of the compounds of interest here have structures that are fairly large distortions of the NaCl structure seems, at first sight, to be much more frightening than it should be.

One last problem is that somewhere between a third and a half of the ⟨5⟩ compounds contain elements from the fifth, or Bi, row of the Periodic Table. Phillips and Van Vechten do not treat ⟨4⟩ compounds containing fifth-row elements in most of their work. There are several reasons for this.[3] The group-IV element of the fifth row is Pb, which does not occur in a tetrahedral structure. Few ⟨4⟩ tetrahedral binary compounds exist which contain one fifth-row element, and none exist where both elements are from that row. Besides, experimental values of the optical static dielectric constant $\epsilon_1(0)$ are not available for those tetrahedral compounds that do exist.

In this particular case, the situation is brighter for the ⟨5⟩ compounds than it is for the ⟨4⟩ compounds. The ⟨5⟩ compounds containing fifth-row atoms do not have radically different crystal structures. The structure of Bi is very similar to those of As and Sb, and the four lead salts all have the NaCl cubic structure. Moreover, the Pb chalcogenides have the best measured values of $\epsilon_1(0)$ among the ⟨5⟩ compounds. There is therefore no reason to leave out the ⟨5⟩ compounds containing fifth-row elements. In fact, they fit into a Phillips scheme quite well.

II. OPTICAL SPECTRA AND DIELECTRIC CONSTANTS

Optical spectra for PbS, PbSe, PbTe, SnTe, GeTe, As, Sb, and Bi are available, and all show one dominant peak just as the optical spectra of the ⟨4⟩ compounds do.[13,14] Calculations by Van Dyke[15] suggest that there will be a dominant peak for orthorhombic ϵ-As very near that for rhombohedral α-As. This peak, the E_2, in the NaCl cubic ⟨5⟩ compounds is somewhat wider than in the tetrahedral ⟨4⟩ compounds, and in the distorted NaCl cubic ⟨5⟩ compounds such as Sb or GeTe and probably in SnS it is wider still.[13,16,17] Nonetheless, a single large peak centered around 2–4 eV dominates all the ⟨5⟩ spectra known.

Thus we might expect that the Phillips theory for ⟨4⟩ compounds can be carried over to ⟨5⟩ compounds. In the ⟨4⟩ compounds good fortune provides us with a nearly constant energy gap around the entire Jones zone.[1] Thus it is possible in these compounds to define an average (Phillips) energy gap E_g which lies near the dominant E_2 peak in the optical-absorption spectrum.

In ⟨5⟩ compounds in NaCl structure, Onodera[18] finds that the Jones zone is dominated by the 24 (311) zone planes. They are not the only planes in the Jones zone; (200) faces are important in higher energy ($h\omega \approx 7$ eV) spectra. Thus, in the case of ⟨5⟩ compounds too, it is reasonable to expect a single low-energy peak which dominates the dielectric response. This is found as discussed below.[18]

The optical dielectric constant $\epsilon(\omega)$ can be written as the sum of a real refractive and an imaginary absorptive part $\epsilon(\omega)_2 = \epsilon_1(\omega) + i\epsilon_2(\omega)$. Phillips relates $\epsilon_1(0)$ to E_g by[1,]

$$\epsilon_1(0) = 1 + (\hbar\omega_p/E_g)^2 (1 - E_g/4E_f), \tag{1}$$

where

$$\hbar\omega_p = \hbar(4\pi Ne^2/m)^{1/2} \tag{2}$$

is the plasma energy of the N electrons per volume that contribute to the dielectric response, and E_f is the Fermi energy in the free-electron model. The values of E_g calculated from Eq. (1) with the measured dielectric constants $\epsilon_1(0)$[6,7,13,19,20] agree reasonably well with the values of E_2 obtained from $\epsilon_2(\omega)$ spectra.[13,21] Experimentally determined values[13] of $h\omega_p$ agree within experimental error with those calculated from the free-electron model of Eq. (2). Thus, the Phillips gap E_g is as closely related to the dominant peak in the optical spectra of ⟨5⟩ compounds as it is in ⟨4⟩ compounds.

Recently, Stiles and Brodsky[6,7] have calculated Phillips ionicities f_i from the observed $\epsilon_1(0)$ and average nearest-neighbor distances d, scaled to the values of these quantities for Sb. These authors combine the Phillips–Van Vechten definition of ionicity

$$f_i \equiv \frac{C^2}{E_h^2 + C^2} = \frac{C^2}{E_g^2}, \tag{3}$$

where E_h is the Phillips homopolar energy gap and C is the Phillips electronegativity, with the Phillips scaling between the lattice constant a and E_h for ⟨4⟩ compounds

$$E_h^2 = E_h^2(\overline{\mathrm{IV}})(a^{\overline{\mathrm{IV}}}/a)^5$$

with Eq. (1) to obtain

$$f_i = 1 - \left(\frac{\epsilon - 1}{\epsilon_{\mathrm{Sb}} - 1}\right)\left(\frac{a_{\mathrm{Sb}}}{a}\right)^2, \tag{4}$$

where ϵ and ϵ_{Sb} are abbreviated notations for the real part of the optical static dielectric constants $\epsilon_1(0)$ of the compound of interest and of Sb. They obtain very reasonable results, especially given the uncertainty of the data. The trends in f_i are

TABLE I. Phillips-theory parameters for the group-V elements. Equation (2) is used to determine $(\hbar\omega_p)^2$ and E_g^2 is determined from Eq. (1). The effective cubic lattice constant a_{av} is calculated from $a_{av} = V^{1/3}$, where V is the volume of the eight-atom homopolar analog to the standard NaCl cubic unit cell.

Element	ϵ_1 (0)	E_g^2	$(\hbar\omega_p)^2$	a_{av}
α-As	52[a]	6.22	317	5.563[c]
Sb	80[b]	2.87	226	6.224[c]
Bi	100[b]	1.95	193	6.565[c]

[a] Reference 14.

[b] References 6 and 7.

[c] D. Schiferl and C. S. Barrett, J. Appl. Cryst. 2, 30 (1969).

generally what we would naively expect, except for SnTe compared to GeTe. Their ionicity value for SnTe seems too small. Cohen, Falicov, and Golin[22] have done band-structure calculations in which they investigate the stability of the NaCl structure for ⟨5⟩ compounds against the small distortions which transform it into the rhombohedral α-GeTe or α-As (in the case where the A and B atoms are identical) structures. They find that the NaCl structure is unstable when the antisymmetrical part of the pseudopotential is small enough. In the Phillips theory, rhombohedral structures should correlate with very low ionicity. Thus, the ionicity of SnTe, which has the NaCl structure, should be somewhat greater than that of GeTe, which has the rhombohedrally distorted NaCl structure, contrary to the calculations of Stiles and Brodsky. The discrepancy is not particularly surprising given the uncertainty in the values of $\epsilon_1(0)$. In SnTe experimental values of $\epsilon_1(0)$ vary between 38 and 64.[6,7,9,13,19] The error in $\epsilon_1(0)$ for GeTe is harder to judge since only one value is available.[6,7] However, the problems of free carriers resulting from off-stoichiometry are present in both materials so there is no reason to expect the situation to be any better for GeTe.

Dielectric constants $\epsilon_1(0)$ are available for rhombohedral α-As,[20] Sb,[6,7] and Bi.[6,7] These values along with the squares of the associated Phillips gaps E_g^2 and plasma frequencies $(\hbar\omega_p)^2$ are shown in Table I. For the group-⟨5⟩ elements, $E_h = E_g$, so that the values of E_h for the heteropolar ⟨5⟩ compounds can be determined if the scaling between E_h and some appropriate characteristic lattice dimension is known. The crystal structures of many of these materials are distorted NaCl structures, and consequently it is difficult to say how a nearest-neighbor distance or average nearest-neighbor distance ought to be defined and used. Several ⟨5⟩ compounds, such as As and SnSe, can exist under ordinary conditions in two crystal structures, and nearest-neighbor distances may differ by 8% to 20% between them.

In the NaCl structure $V = a^3$, where V is the volume of the unit cell and a is the cubic lattice constant. Thus we can define an average cubic lattice constant $a_{av} = V^{1/3}$ for distorted NaCl structures. In the two structures of As the respective values of a_{av} differ by less than a percent; the difference is even smaller in SnSe. Values of a_{av} are also listed in Table I. The empirical scaling formula of Phillips applied to ⟨5⟩ compounds is

$$E_h^2(1) = E_h^2(2)\,[a_{av}(2)/a_{av}(1)]^n \,, \qquad (5)$$

where the numbers in parentheses refer to the two different compounds in question. No correction is made for the different oscillator strengths of the d electrons; however, judging from the ⟨4⟩ compounds, this correction is small. In any case, there is no quantitative basis for estimating it here. The value $n = 7$ provides an excellent fit of Eq. (5) to the values of E_h^2 and a_{av} in Table I. Van Vechten has determined $n = 5$ for ⟨4⟩ compounds,[23] and this is the value Stiles and Brodsky[6,7] assume for ⟨5⟩ compounds. The values of ionicity are not strongly dependent on the choice of n, so their use of $n = 5$ rather than the better value $n = 7$ does not seriously alter their ionicities.

III. COVALENT BONDING CHARGE

The charge Q_a in units of electronic charge on an atom of valence z is $Q_a = z/\epsilon_1(0)$. Phillips[1] has suggested that charge neutrality then requires that the bond charge Q_b of each of y identical bonds be given by

$$Q_b = 2z/y\epsilon_1(0) \,, \qquad (6)$$

where the factor 2 results from two atoms contributing to the bond charge. This conjecture has since been verified by Heine and Jones[24] for diamond-type semiconductors.

In the group-V elements, Eq. (6) certainly produces the expected trends as we go from As to Sb and Bi. The bond charge should be greatest in As and least in Bi. From the dielectric constants of Table I, Eq. (6) can be seen to give the proper sequence of bond charges.

More interestingly, Golin and Stocco[25] have estimated the bonding charge of As from band-structure calculations and find that $Q_b \approx 0.03$. Within the accuracy of the calculation it does not matter whether we use $y = 3$ (the number of true nearest neighbors) or $y = 6$ (the number of nearest and next-nearest neighbors, all of which would be nearest neighbors in the undistorted simple-cubic structure) in Eq. (6). For $y = 6$, $Q_b = 0.03$, which is gratifying.

IV. COVALENT RADII

Van Vechten and Phillips have calculated covalent radii for ⟨4⟩ crystals for tetrahedral and octohedral coordinations.[4] These radii are additive and generally of the same value for a given row of the Periodic Table unless core effects are important. Deviations from ionic or metallic contributions to the bonding are neglected. Thermal expansion, which changes the cubic lattice constants by about 0.3% between 0 and 300 °K is also ignored.

Covalent bonding is known to be important in ⟨5⟩ compounds.[22,25] It is therefore natural to see if the Van Vechten–Phillips radii calculations can be extended to these compounds. The radii of ⟨5⟩ compounds, because they have an average of one more electron per atom. A major complication is the fact that many ⟨5⟩ compounds have distorted NaCl structures rather than the true NaCl cubic. None of the group-V elements has the simple-cubic structure which is the homopolar analog to the NaCl cubic.

The mean density of atoms is determined by the kinetic exchange and correlation energies and by the strength of the atomic pseudopotentials. Shifting the atoms about the unit cell somewhat, say 10% to 20%, need not change this volume much. A more detailed discussion of some of these points is contained in Sec. IX.

Many ⟨5⟩ compounds exist in more than one phase, depending on conditions. In all cases the volume per formula unit remains very nearly constant even though the atoms may shift positions considerably. The worst case is the transition between orthorhombic ϵ-As to rhombohedral α-As, and there the volume changes by less than 3%. More typical is SnSe which can exist in both the SnS orthorhombic form and in the NaCl cubic structure. SnSe changes its volume per formula unit by only 1% upon changing structures. This all suggests that the volume per formula unit is fixed by the species of atoms present; but that the atoms enjoy a certain amount of local freedom.

The average NaCl cubic lattice constant $a_{av} = V^{1/3}$ as defined in the previous section is very useful here. Here V will be taken to mean the volume per four formula unit, which is the volume of the standard NaCl cubic cell. A major goal is to understand why some ⟨5⟩ compounds have the true NaCl cubic, while others exist in various distorted NaCl structures. Thus, it is useful to put all the ⟨5⟩ compounds hypothetically in the true NaCl cubic, then look for criteria which make one distortion or another more stable for some compounds. The use of a_{av} to define covalent radii, as will be done below, also allows the consideration of crystals where the positions of the atoms in the unit cell are not well established. Finally, if we insist on defining covalent radii for all the ⟨5⟩ compounds, a_{av} is the best starting point we can come up with.

Van Vechten and Phillips[4] devote considerable space to the changes in covalent radii of ⟨4⟩ compounds due to core effects. A repulsive interaction between neighboring atoms develops if they are brought so close that there is substantial overlap between the valence electrons on atom A and the core electrons on atom B. If valence bonding effects do not stop the lattice contraction before this occurs, then the nearest-neighbor distance is limited by this core repulsion. Core effects enter in the ⟨4⟩ compounds containing alkaline earths and the elements in the first two rows of the Periodic Table except F, S and Cl. The only elements in ⟨5⟩ compounds in which core effects might play a role are O and P. However, the extra valence electron per atom expands the lattice considerably and core effects are apparently not important, even for ⟨5⟩ compounds containing these two elements.

The actual calculation of covalent radii for ⟨5⟩ compounds is very simple. The equivalent NaCl cubic lattice constant a_{av} is found from the volume V of the standard NaCl cubic four formula unit cell of binary compounds. In the case of the group-V elements, V is the volume of the eight-atom homopolar analog to the NaCl cubic. In the case of ternary compounds such as $TlSbS_2$ or solid solution series, the four-"molecule" cell is assumed to consist of four cations and four anions, though these each may be of several different atomic species. In the NaCl cubic the interatomic distance $d_{av} = \frac{1}{2}a_{av}$. The covalent radii r_A and r_B for the compound AB must add so that

$$d_{av} = r_A + r_B \,.$$

Following Van Vechten and Phillips,[4] the covalent radii for all elements of the same row are assumed equal. Core effects, contributions from ionic or metallic contributions to bonding, and thermal expansion are all ignored. Preliminary radii are found from the group-V elements P, As, Sb, Bi and from those IV-VI compounds which have both elements from the same row, GeSe, SnTe, PbPo. The best fit to d_{av} is obtained for all the IV-VI compounds and group-V elements. The III-VII compounds which are much more ionic, are not considered in the calculation. Finally, the covalent radius of Tl is checked from ternary compounds of the form III-V-VI$_2$. The results are shown in Table II. The interatomic distances d_{calc} can be calculated from Table II and compared with the observed values d_{av}. The results are shown in Table III and in Fig. 1. The agreement is excellent. The maximum error in d_{calc} is 1.86% (for $TlAsS_2$, a monoclinic crystal) and the rms error is 0.74%. Thus, the effective lattice constants a_{av}, or perhaps persuasively the volumes per formula unit V_{av}, can be fitted for 25 compounds and alloys, containing 13 different elements, with only 5 adjustable parameters, namely, the covalent radii for each row.

TABLE II. Covalent radii for elements in compounds with an average valence of ⟨5⟩. These have been adjusted to give the best fit for the compounds of Table III.

	III	IV	V	VI
Element				O
Covalent radius (Å)				1.039
			P	S
			1.320	1.320
		Ge	As	Se
		1.416	1.416	1.416
		Sn	Sb	Te
		1.578	1.578	1.578
	Tl	Pb	Bi	Po
	1.648	1.648	1.648	1.648

The values of d_{calc} for As, Sb, Bi are consistently greater than d_{av} in these elements. Van Vechten and Phillips[4] note that empirical values of covalent radii for a given species of atom tend to increase with increasing coordination number. The coordination number for each atom in the NaCl structure is six. In the rhombohedrally distorted structures of As, Sb, Bi the coordination number should be considered somewhat less than 6, but more than 3, which is the number of nearest neighbors. No attempt will be made to define a continuously varying coordination number here. However, it should be noted that as the rhombohedral angle $\alpha \rightarrow 90°$, the next nearest distances in the rhombohedral arsenic structure approach the nearest-neighbor distances, and so the coordination number, in some sense, increases upon going along the sequence: As, Sb, Bi, GeTe. Likewise, the difference $(d_{calc} - d_{av})$ decreases as $\alpha \rightarrow 90°$ in this sequence as can be seen from Table III.

TABLE III. Comparison of observed average interatomic distances $d_{av} = a_{av}/2$ with the value d_{calc} calculated from the covalent radii of Table II. The rms error is 0.74% for 13 elements in 25 crystals with only 5 radii as variable parameters.

Compound	d_{av}	d_{calc}	% difference	structure
P	2.668	2.640	−1.05	ortho
ϵ-As	2.807	2.832	+0.89	″
GeS	2.737	2.736	−0.04	″
GeSe	2.842	2.832	−0.35	″
SnS	2.888	2.898	+0.35	″
SnSe	3.001	2.994	−0.23	″
SnSe	3.010	2.994	−0.53	cubic
SnTe	3.160	3.156	−0.01	″
PbS	2.968	2.968	0.00	″
PbSe	3.062	3.054	−0.26	″
PbTe	3.227	3.226	−0.03	″
PbPo	3.295	3.296	−0.03	″
GeTe	3.008	2.994	−0.46	rhomb.
Bi	3.283	3.296	+0.13	″
Sb	3.112	3.156	+1.41	″
α-As	2.782	2.832	+1.80	″
$PbSnS_2$	2.922	2.933	+0.38	misc.
$Sb_2Tl_2Se_4$	3.0445	3.029	−0.51	″
$SbTlTe_2$	3.202	3.191	−0.34	″
$BiTlSe_2$	3.071	3.064	−0.23	″
$BiTlTe_2$	3.236	3.226	−0.29	″
$AsTlS_2$	2.955	2.900	−1.86	″
Red PbO	2.682	2.687	−0.99	″
Yellow PbO	2.714	2.687	+0.02	″
SnO	2.596	2.617	+0.81	″

V. ELECTRONEGATIVITY AND IONICITY

The Phillips electronegativity C is defined by[1,2]

$$C = b\,|Z_A/r_A - Z_B/r_B|\,e^{-k_s R}, \qquad (7)$$

where Z_A and Z_B are the valences of the A and B atoms and r_A and r_B are their covalent radii as calculated above, R is half the average interatomic spacing, b is an adjustable parameter, and k_s is the Thomas-Fermi screening length. The value of

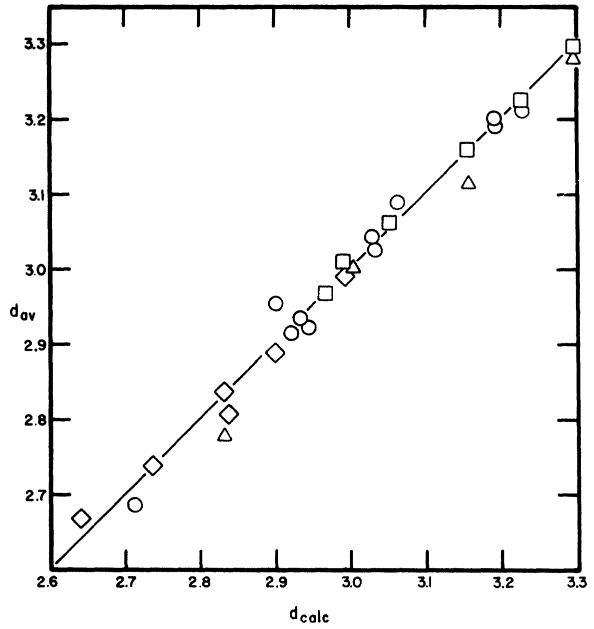

FIG. 1. Comparison of observed NaCl equivalent interatomic spacings d_{av} with d_{calc} calculated from the covalent radii of Table II. A number of the most important compounds are indicated. Compounds with the NaCl cubic structure are denoted by □, those with the As and GeTe rhombohedral structures by △, those with the black P or SnS orthorhombic by ◇, and those with various miscellaneous structures, including ternary compounds with the formula III-V-VI_2, are denoted by ○. All the points would lie on the straight diagonal line if there were perfect agreement.

k_s, is found from $k_s^2 = 4k_F/\pi a_0$, where a_0 is the Bohr radius and k_F is the wave number on the surface of the Fermi sphere in the free-electron approximation. If there are N_i atoms of species i in the volume V, with each contributing Z_i valence electrons, then

$$k_F = V^{-1/3}\left[3\pi^2\left(\sum_i Z_i N_i\right)\right]^{1/3} .$$

If $R = \frac{1}{2} d_{av} = V^{1/3}/4$, then

$$k_s R = \frac{1}{2}\left(\frac{1}{\pi a_0}\right)^{1/2}\left[3\pi^2\left(\sum_i Z_i N_i\right)\right]^{1/6} V^{1/6}$$
$$= 1.2614 V^{1/6} \tag{8}$$

for the standard NaCl cubic cell containing four formula units where V is in Å^3.

In ⟨4⟩ compounds, Van Vechten[26] finds empirically that $1.4 \leq b \leq 1.6$ and b is usually approximated at $b = 1.5$. To determine b, E_h was found for a number of IV-VI compounds from Eq. (5) and E_g was determined from the optical spectra.[13,14,16] The value of C was determined from the relation $C^2 = E_g^2 - E_h^2$. Comparing these values of C with the results obtained from Eq. (7) yielded values for b. In ⟨5⟩ compounds, $2.44 \leq b \leq 3.18$ and b is taken here to have the value $b = 2.77$.

Several pseudobinary alloys such as $(\mathrm{Ge}_x\mathrm{Sn}_{1-x})\mathrm{Te}$ are included in the calculations of C. In these cases, the two species of cation (or anion) are disordered, and the electronegativity difference between the different cation (or anion) species is ignored. If there are two kinds of cations $A(1)$ and $A(2)$ with fractions x and $1-x$, respectively, then the valence ratio of Eq. (7) becomes

$$\frac{Z_A}{r_A} \equiv x\left(\frac{Z_{A(1)}}{r_{A(1)}}\right) + (1-x)\left(\frac{Z_{A(2)}}{r_{A(2)}}\right) .$$

Alloys of group-V elements with IV-VI compounds in which the group-V element randomly replaces either the IV or VI element are treated in the following manner. If proportion of the IV-VI compound AB is x and that of the group-V element is $1-x$, then

$$|Z_A/r_A - Z_B/r_B|_{\text{alloy}} = x\,|Z_A/r_A - Z_B/r_B|_{\text{pure } AB} .$$

Electronegativities are also calculated for a number of III-VII compounds. In this case, the covalent radii are assumed to be those of the row to which each atom belongs. The volumes used in Eq. (8) are the actual volumes per four formula unit.

The Phillips ionicities are found from Eq. (3) with C calculated as described above and E_h found from Eq. (5) with $n = 7$.

TABLE IV. Phillips ionicities f_i calculated from Eq. (3). The electronegativity C is found from Eq. (7) with the covalent radii of Table II. E_h is found from the data of Table I with the use of Eq. (5) with $n = 7$. The values of f_i as calculated by Stiles and Brodsky (Refs. 6 and 7) are also included. There is only one free parameter, b in Eq. (7), in this calculation; the value of b is 2.77. The two sets of ionicities are in reasonable agreement.

Compound	C^2	E_h^2	f_i	(Stiles and Brodsky) f_i
GeS	12.90	7.1	0.65	•••
GeSe	7.78	5.4	0.59	0.68
SnS	14.89	4.8	0.76	0.8
SnSe (ortho)	9.56	3.7	0.72	0.7
SnSe (cubic)	9.47	3.6	0.72	•••
GeTe	3.13	3.6	0.46	0.52
SnTe	4.51	2.5	0.64	0.49
PbS	15.31	4.0	0.79	0.77
PbSe	10.16	3.2	0.76	0.72
PbTe	4.97	2.2	0.65	0.63
PbPo	3.62	1.9	0.66	•••
PbO (yellow)	51.82	8.2	0.86	•••
SnO	53.41	10.0	0.84	•••
InBr	25.04	2.4	0.91	•••
InI	15.12	1.7	0.90	•••
TlF	99.91	6.2	0.94	•••
TlCl	38.34	3.3	0.92	•••
TlBr	27.63	2.6	0.92	•••
α-TlI	15.35	1.5	0.91	•••
$\mathrm{Ge_3Sn_7Te}$	4.09	2.8	0.60	•••
$\mathrm{Ge_{10}Sn_{90}Te}$	4.37	2.6	0.62	•••
$\mathrm{(GeTe)_{0.06}(GeSe)_{0.94}}$	7.40	5.2	0.59	•••
$\mathrm{(GeTe)_{0.60}(SnSe)_{0.40}}$	5.27	3.6	0.60	•••
$\mathrm{As_{0.7}(GeSe)_{0.3}}$	0.72	5.7	0.11	•••

Table IV presents the calculated values of C^2, E_h^2, and f_i along with the values of f_i obtained by Stiles and Brodsky.[6,7] The two sets of ionicities are in reasonable agreement. Moreover, we now have a method of estimating f_i with reasonable accuracy even where $\epsilon_1(0)$ values are unknown, such as in ternary alloys or many III-VII compounds. Trends in the ionicities f_i(calc) of this work are particularly reasonable. TlF has the highest ionicity as we might naively expect; and GeTe has the lowest ionicity in agreement with the work of Cohen, Falicov and Golin[22] as discussed in Sec. II. The fact that GeTe is the only IV-VI compound to be in a heteropolar analog to the rhombohedral α-As structure at room temperature has a natural explanation in terms of the Phillips theory. The low ionicity is due to the "accident" that in Eq. (7), the quantity $(4/r_{\mathrm{Ge}} - 6/r_{\mathrm{Te}})$ happens to be a relatively small number. The connection between ionicity and the rhombohedral α-GeTe structure is discussed further in Sec. VII.

VI. HEATS OF FORMATION

The heat of formation $\Delta H(T)$ of a compound is the difference in the enthalpy at a given temperature T, usually 298 °K, between the compound and the constituent elements in their usual state at that temperature. Thus, $\Delta H(T)$ is a measure of bond energies in the compound.

Tetrahedral $\langle 4 \rangle$ compounds are found with ΔH (298 °K) values ranging over nearly two orders of magnitude. The various contributions to ΔH for these compounds have been analyzed by Phillips and Van Vechten.[3] First, there is the ionic ordering energy which causes the A and B atoms to form interpenetrating sublattices in the compound. This is taken into account by assuming ΔH is proportional to f_i^t, where f_i is the Phillips ionicity. The tetrahedral $\langle 4 \rangle$ compounds can be described with great success by assuming $t=1$, but there is no physical reason that the author knows of to govern the choice of t. Thus t will be considered an adjustable parameter to be found empirically.

Dehybridization effects are taken into account in two ways. The fraction of covalent energy which is not lost due to dehybridization depends on the extent of mixing between the valence and conduction bands. This mixing in turn depends on the lattice constant through the competition between potential and kinetic energies. Thus, it is assumed that $\Delta H(T) \sim a^{-s}$, where s is determined from experiment, Phillips and Van Vechten[3] find s from BN, BeO, and ZnO. If they make corrections suggested by Pauling[27] for the double and triple bonds of O_2 and N_2, respectively, then $s=4$. If these corrections are not made then they find $s=3$. In the present work on $\langle 5 \rangle$ compounds, the Pauling[27] corrections are not used and s is set arbitrarily to $s=3$ as a tentative estimate.

The other contribution to dehybridization in $\langle 4 \rangle$ compounds is termed "metallization" from the trend in column IV of the Periodic Table from covalent structures to metallic ones as we pass from C, Si and Ge to Sn and Pb. The reason for this is that the s-antibonding conduction band is lowered due to increased spin-orbit splitting as we go down column IV. It finally touches the valence band in Sn and drops below it in Pb. Thus the electron configuration is sp^3 in the lighter fourth-column elements and s^2p^2 in Pb. Phillips and Van Vechten[3] introduce a spectroscopically defined correction factor for metallization, which is responsible for lowering the heat of formation of heavy element $\langle 4 \rangle$ compounds.

Metallization is not as important for $\langle 5 \rangle$ compounds. Both the predominantly s-bonding and s-antibonding bands are filled, so that the lowering of the s-antibonding levels with respect to the p-bonding levels due to spin-orbit effects does not have the same dramatic consequences in $\langle 5 \rangle$ compounds that it does in $\langle 4 \rangle$ compounds. Indeed, the bonding properties of Bi are very similar to those of As, and Sb, while those of PbPo are apparently similar to SnTe. For this reason, the metallization factor which is so important in the discussion by Phillips and Van Vechten[3] of $\langle 4 \rangle$ compounds, is set equal to unity here and ignored in our considerations of ΔH in $\langle 5 \rangle$ compounds.

The expression for $\Delta H(T)$ to be expected is therefore similar to that proposed by Phillips and Van Vechten[3] for $\langle 4 \rangle$ compounds

$$\Delta H(T) = \Delta H_0 f_i^t / a_{av}^3 = \Delta H_0 f_i^t / V \ . \tag{9}$$

In Fig. 2, $V\Delta H(298\ ^\circ\mathrm{K})$[10,28] vs f_i is plotted on a log-log scale as suggested by Eq. (9). Since the scatter is fairly large, the line is fitted only visually. The line corresponds to $\Delta H_0 = 1.4\times 10^4$ Å^3 kcal/mole and $t=3.0$. The scatter, particularly for the IV-VI compounds, has several causes. The relative uncertainties of f_i(calc) are about 5%, which corresponds to an error in $V\Delta H(298\ ^\circ\mathrm{K})$ of 16%. The error in the measured value of ΔH is certainly large, as can be seen from the comparison of the data from Wagman *et al.*[28] with those of Abrikosov *et al.*[10] For several compounds the differences between the two sets of values is on the order of 25%, and this casts some doubt on the accuracy of ΔH in the remaining compounds, particularly the IV-VI compounds. These two sources of error can account for most of the departures of the data points from the relation given in Eq. (9). Other contributions to bonding not considered here cannot be ruled out, but the dominant effects appear to be contained in Eq. (9). As expected from the discussion above, a spectroscopically defined metallization parameter does not improve matters significantly.

General trends in Fig. 2 are very encouraging despite the large scatter. The largest f_i(calc) belongs to TlF, which also has the largest $V\Delta H$ (298 °K). The heat of formation and consequently $V\Delta H(298\ ^\circ\mathrm{K})$ for GeTe is abnormally small, as expected from Eq. (9) and the work of Cohen, Falicov, and Golin.[22]

VII. RHOMBOHEDRAL STRUCTURES OF As, Sb, Bi AND α-GeTe

The rhombohedral structure of As, Sb, Bi and α-GeTe is stable only when the ionicity f_i is low enough, as discussed in Secs. II and V. We will now look into this matter further. Ionicity is not the only factor determining the stability of the rhombohedral structure; pressure, temperature, and stoichiometry enter as well. The high-temperature β-phase of GeTe has the NaCl structure, and the rhombohedral-NaCl-cubic transition temperature T_c is[29]

$$T_c = 460\ ^\circ\mathrm{C} \quad (\text{Ge rich})$$

$$T_c = 390\ ^\circ\mathrm{C} \quad (\text{Te rich}) \ .$$

Also at about 43 kbar, α-GeTe transforms at room temperature to the NaCl cubic phase.[30] Compressibility data for GeTe are not available, but the change in f_i due to thermal expansion through the dependence of E_h^2 and C^2 on volume is not significant.

Moreover, the rhombohedral angle α, which is 90° in the NaCl cubic and slightly less in the rhombohedral, does not necessarily increase with increasing f_i. In $As_{1-x}(GeSe)_x$, $As_{1-x}(GeTe)_x$, $Sb_{1-x}(SnTe)_x$ alloys, f_i is obviously increasing with x, but α in fact decreases.[31] In $(GeTe)_{1-x}(SnSe)_x$ alloys, α first decreases to a minimum at about $x = 0.12$, then increases with x and therefore f_i.[31] In $Ge_{1-x}Sn_xTe$ alloys at constant temperature α increases with x and f_i until $\alpha = 90°$.[31] There is no simple relation between f_i and α.

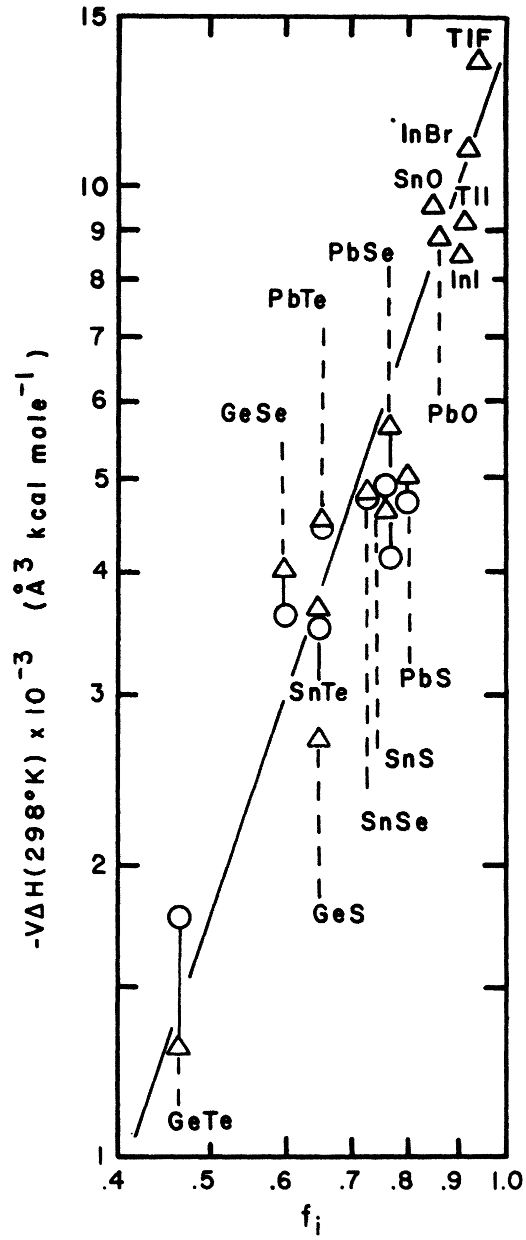

FIG. 2. Log-log plot or $V\Delta H$(298 °K) vs. f_i. The points obtained with ΔH(298 °K) values from Ref. 10 are denoted by ○, and those from Ref. 28 are denoted by △. The straight line represents a fit of the points with Eq. (9) with $\Delta H_0 = 1.4 \times 10^4$ $Å^3$ kcal/mole and $t = 3.0$.

There does appear to be a critical ionicity f_i^c above which the rhombohedral structure is not stable under any conditions with respect to either the NaCl cubic or the SnS orthorhombic structure. This is a somewhat tentative statement which is consistent with the results of Cohen, Falicov, and Golin,[22] who point out that the NaCl or simple-cubic structures may not be stable against the rhombohedral distortions leading to the α As or α-GeTe structures. It should be noted that the rhombohedral structure does not necessarily occur if f_i is low, orthorhombic black P is evidence of this.

Phase diagrams without complications such as solid solubility limits are available for only three systems: GeTe-SnTe, GeSe-GeTe, GeTe-SnSe. Of these only the GeTe-SnTe system forms a continuous series of solid solutions. In both the remaining systems there is a mixture of two phases over most of the composition range. One of these phases is based on the rhombohedral GeTe structure and the other on orthorhombic GeSe or SnSe. In Table V, the range of compositions of these systems which do not include the rhombohedral structure, even as one component of a two-phase region, and critical ionicity f_i^c are presented. From Table V, f_i^c apparently is well defined lying in the range $0.59 \le f_i^c \le 0.64$. The spread of f_i^c values is within the error of calculation of f_i. Above this value of f_i^c the rhombohedral structure does not exist, and below it, the rhombohedral structure often (but not always; for example, black P) appears either alone or as one component of a mixed-phase region. Incidentally, the low value of ionicity in GeSe ($f_i = 0.63$) plus the comments in Table V suggest the possibility of a low-temperature transformation from orthorhombic to rhombohedral. This transformation does not have to take place because of the low f_i of GeSe, of course; but it would be interesting if it did. Such a transformation would probably require cold-working by the methods of Barrett.[32]

VIII. TRENDS IN ORTHORHOMBIC STRUCTURES: BLACK P, SnS, AND TlI STRUCTURES

Consistent trends in the orthorhombic GeS, GeSe, SnS, and SnSe structures are very difficult to find. It is useful to examine not only the structure of the IV-VI compounds but also those of black P, and has been suggested by Klement and Cohen[33] and Bienenstock,[34] and TlI as well. The

TABLE V. Critical ionicities f_i^c above which the rhombohedral α-GeTe structure does not exist under any conditions. For these three solid solution series f_i^c is remarkably consistent with $f_i^c = 0.615 \pm 0.025$.

System	Nonrhombohedral Range of x	Nonrhombohedral Range of f_i	f_i^c	Temp (°K)	Comments
$(GeTe)_{1-x}(SnTe)_x$	$0.9 \leq x \leq 1.0$	$0.62 \leq f_i \leq 0.64$	0.62	0	a
$(GeTe)_{1-x}(GeSe)_x$	$0.94 \leq x \leq 1.0$	$0.59 \leq f_i \leq 0.59$	0.59	615 to 640	b
$(GeTe)_{1-x}(SnSe)_x$	$0.40 \leq x \leq 1.0$	$0.60 \leq f_i \leq 0.72$	0.60	298	c

[a] Rhombohedral SnTe has recently been found by Muldawer (G. Lucovsky, private communication relating the results of Muldawer). Cubic SnTe is stabilized by large enough numbers of vacancies, which are in turn caused by offstoichiometry.

[b] The value of x separating the mixed-phase region from the pure orthorhombic region is nearly temperature independent in this temperature range. No data are available at lower temperatures, as $T \rightarrow 0$, x may increase slightly.

[c] Data at lower temperatures are not available.

black P, SnS, and TlI structures are presented in Fig. 3. The drawings are taken from Wycoff[12] with the origins changed to show the similarities between the three structures better. From Fig. 3, it is clear that increasing the ionicity f_i upon going from black P, to SnS, to TlI does not move the structure back to the NaCl cubic. However, if we look at only the right-hand or left-hand halves of the unit cells of Fig. 3, we can see that the NaCl arrangement is more nearly achieved with increasing ionicity. The distortion of each half of the unit cell from the NaCl cubic is very small in TlI. This trend is only roughly true, however, and it is not followed consistently in the IV-VI compounds when they are considered alone.

The most curious aspect of these structures is that the atoms of the left half of the unit cell are shifted from their NaCl cubic positions by a half-lattice-spacing along the a axis relative to those of the right half.[35] The atoms of each half-unit-cell tend to form a double layer perpendicular to the b axis. The bonding within each such double layer appears to be considerably stronger than bonding between layers. This shift is obviously unaffected by ionicity since it occurs in homopolar black P as well as in TlI which has $f_i = 0.91$.

There appear to be two contributions to this shift. In black P each atom has three nearest neighbors, which are very nearly equidistant from the given atom, and two other next neighbors within the same double layer, as can be seen in Fig. 3. These five atoms would all be nearest neighbors in the simple-cubic structures. The sixth simple-cubic nearest neighbor is "broken off" and found on an adjacent double layer. Given that covalent bonding links atoms within each double layer in this manner, and that the interlayer bonding is very weak, it is easy to see that this shift of alternate double layers from their simple-cubic positions allows the ion cores on different double layers to be further apart without requiring an increase in the volume per atom. In a sense, the double layers can be said to "nest" better after the shift.

The existence of A-A homopolar bonding in the heteropolar AB compounds also encourages the same shift by roughly a half-lattice-spacing because this shift allows the two A atoms to be closer together. NMR studies by Novoselov, Baidakov, and Strakhov of α-TlI (orthorhombic) indicate that the Tl-I bonds are "strongly" covalent and the Tl-Tl bonds are "weakly" covalent.[36] Apparently the covalent Tl-I bonds serve to define the double layers, and the Tl-Tl covalent bonding is partly responsible for the shift. The A-A bonding apparently manifests itself in the crystal structures, too. The A-A distances between atoms on double layers are shorter than the corresponding B-B distances regardless of covalent or ionic sizes.[37] It would be interesting to do NMR studies on the remaining orthorhombic $\langle 5 \rangle$ compounds to look for evidence of cation-cation homopolar bonding.

The competition between ionicity and covalency seems to have a clear effect only within each double layer, with increasing ionicity tending to bring the bond angles closer to 90°. Certainly, increasing the ionicity will also tend to oppose the shift of adjacent double layers, but it is difficult to assess the relative strengths of the "nesting" and A-A homopolar bonding contributions. A further complication that should be pointed out is that InS and InSe both occur in the SnS structure. This is especially curious since these are average-valence-$\langle 4.5 \rangle$ compounds. In view of the complexity of the situation it is not surprising that these structures are so difficult to understand. Some parameter in ad-

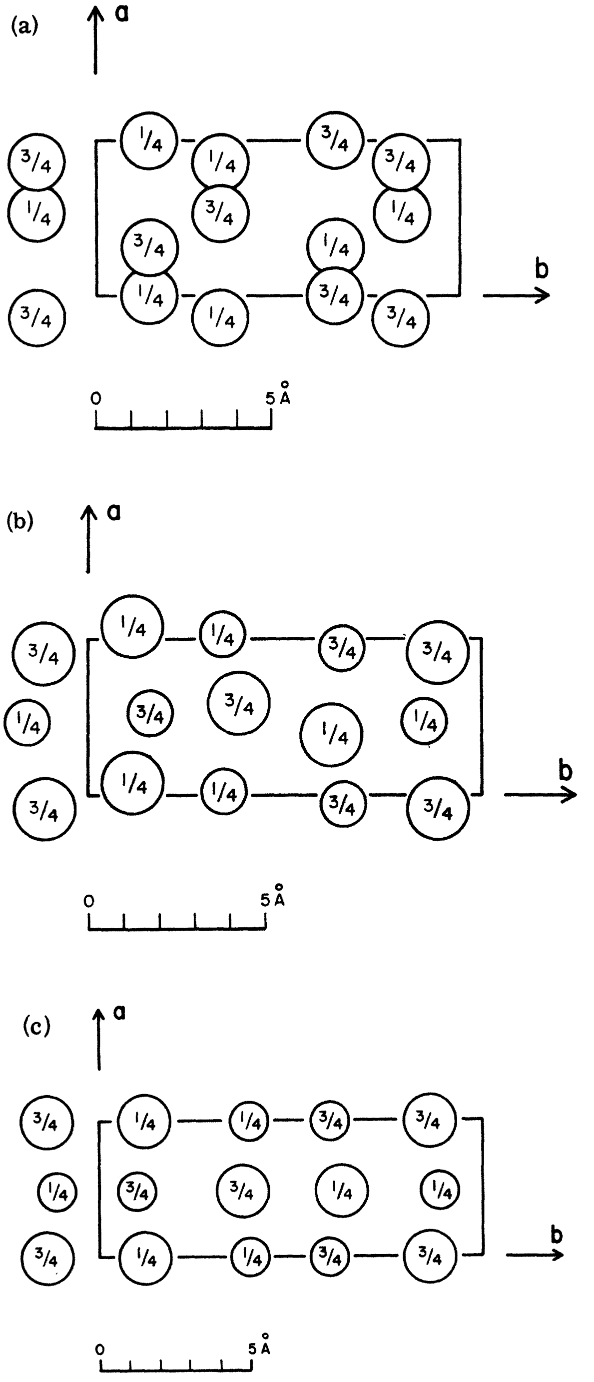

FIG. 3. Comparison of the orthorhombic crystal structures of black P, SnS, and TlI. The drawings are taken from Wycoff (Ref. 11) with the origins changed to better show the similarities. The fractions denote the distance in units of the lattice constant c of the atoms in the direction perpendicular to the plane of the drawings. Figure 3(a) shows the structure of black P, Figure 3(b) shows the structure of SnS, where the small circles represent S atoms and the large circles Sn atoms. Figure 3(c) shows the structure of TlI. The small circles represent Tl atoms and the large circles represent I atoms.

dition to ionicity is probably required, but none has been found yet. However, Eqs. (10)–(12) in Sec. IX below at least appear to provide a basis for a quantitative understanding of the black P structure.

IX. COVALENT VERSUS METALLIC CONTRIBUTIONS TO BONDING

The character of the bonding in the $\langle 5\rangle$ compounds appears to be a mixture of metallic as well as covalent and ionic character, particularly in As, Sb, Bi, and α-GeTe. There are two topics to be discussed in this regard. These are the relation of the screening properties of metals and semiconductors to the existence of bond charges and well-defined covalent radii; and a comparison of the approach of Heine and co-workers[24,38,39] to metals and semiconductors to the spectroscopic one.

In simple metals, it is not possible to have a bonding charge buildup between atoms or well-defined metallic radii. In a typical metal, the electrostatic screening of the electron gas is very effective; a representative screening length is 0.5 Å. As a result, the electronic charge localized around each ion core exactly cancels the ion core charge; thus no extra bonding charge can exist between neighboring atoms.[40] The screening also causes the radius of a metal atom to depend considerably on the nature of the alloy or host metal in which it finds itself. However, in alloys of metals from the same column of the Periodic Table or alloys in which the number of electrons per atom is fixed, the electron density remains approximately constant across the solid solution series. In this case metallic radii can be defined to within about 3% for each average valence as can be seen from the data of Pearson.[11] In semiconductors the dielectric constant $\epsilon(q)$ at small q may be considerably less sensitive to these changes in electron density than it is for metals. Thus, the change in volume on going, for example, from GeSe to PbSe does not affect the screening of the Se atom much.

The great majority of $\langle 5\rangle$ compounds are semiconductors. For these, as discussed in Secs. III and IV, we find a pileup of charge between nearest neighbors above the overlap of spherical atomic distributions, and covalent radii defined to roughly 1% accuracy. These properties, which we normally associate with covalent bonding, are also exhibited by As, Sb, Bi, and α-GeTe, which are semimetals with nonvanishing Fermi surfaces. This is because the Fermi surface area in these semimetals is quite small, and the screening length is consequently very large.[41,42] The radius of the neutralizing electron cloud of As, Sb, or Bi is on the order of 100 interatomic spacings. Within this distance it is possible to have a net charge at a covalent bond site localized on an atomic scale.[40] Thus, there is a greater resemblance of the semimetals to semiconductors as regards bonding character.

The relation between covalent and metallic bonding is made clearer by considering the work of Heine,[38] Heine and Jones,[24] and Heine and Weaire.[39] What is meant by covalent as opposed to metallic bonding is partly a matter of definition. The definition of Heine[38] and Heine and Jones[24] discussed below is implicit in the Phillips theory. In fact, Heine and Weaire[39] have indicated the sort of connection between the Phillips theory and the pseudopotential theory of metals.

The total energy U of a metal may be written, to second order in the pseudopotential, in the notation of Heine,[38] as

$$U = U_0 + U_E + U_{bs}, \tag{10}$$

where U_0 is the structure-independent contribution determined by the kinetic, exchange, and correlation energies of a free-electron gas, and by the strength of the pseudopotential, U_E is the structure-dependent or Ewald energy of point ions in a uniform electron sea, and U_{bs} is the change in the energy of the electron gas due to the crystal potential. In a simple metal, U_{bs} is given by

$$U_{bs} = \sum_{\vec{g}} |S(g)|^2 [v(g)]^2 \chi(g) \epsilon_1(g), \tag{11}$$

where $S(g)$ is the structure factor, $v(g)$ is the spherically symmetric pseudopotential, $\chi(g)$ is the perturbation characteristic, and $\epsilon_1(g)$ is the dielectric function, all as functions of the reciprocal lattice vectors $\vec{g}$ with moduli g.

For a given volume per atom, Eqs. (10) and (11) can be used to predict the stable crystal structures quite successfully for a large number of nontransition metals.[39] The relative stability of two structures depends on the balance between U_E, which always favors highly symmetric arrangements of the ion cores, and U_{bs}, which may favor certain distorted structures depending on the shape of the $v(g)$ curve.

In a semiconductor or semimetal this picture breaks down, although not necessarily irretrievably.[39] In this case, the form of the dielectric function $\epsilon_1(g)$ is changed; and at least one the pseudopotential coefficients $V(g) \equiv S(g)v(g)$ is now on the order of the Fermi energy. The perturbation theory used in the derivation of Eqs. (10) and (11) becomes invalid as a consequence. The appearance of strong pseudopotential coefficients $V(g)$ is associated with such covalent bonding properties as a pileup of charge between nearest neighbors above the overlap of spherical atomic distributions, and preferred bond angles or correlations between three or more atoms.

The Jones zone of the NaCl cubic ⟨5⟩ compounds is dominated by the (311) faces.[18] Reasonably strong pseudopotential coefficients $V(g)$, where $\vec{g} = [311]$ in this case, are sufficient to cause a band gap. To some extent this can already be considered covalent bonding; but, following Heine and co-workers,[24,38,39] we will not do so here. According to Heine and Jones[24] and Heine,[38] the extra pileup of charge between nearest neighbors and preferred bond angles arise only when there are reciprocal-lattice vectors $\vec{g}_1$, $\vec{g}_2$ such that $\vec{g}_1 + \vec{g}_2 = \vec{g}$ and $V(g_1)$ and $V(g_2)$ are large enough to contribute in second order as much as $V(g)$ in first order.[24,36] Only in cases in which this is satisfied will we say we have covalent bonding.

Onodera[18] has shown that higher orders in the pseudopotential must be considered in SnTe. The second-order perturbation expansion for the effective pseudopotential coefficient $V_{\text{eff}}(311)$ at the point W on the Jones zone yields

$$V_{\text{eff}}(311) = V(311) + \frac{2m}{\hbar}\left(\frac{a}{2\pi}\right)^2 \times V(111)\,[V(200) + V(220)] \tag{12}$$

From the pseudopotentials of Lin and Kleinman[43] we can see by inspection that $V(111)$, $V(200)$, and $V(220)$ are also very strong in PbS, PbSe, and PbTe, and the energy gap around the Jones zone is therefore also determined by Eq. (12). From Table III of Cohen, Falicov, and Golin,[22] it can be seen that $V(111)$ and $V(200)$ are quite strong in the rhombohedral α-As structure also. Actually, the secular determinant used to derive (12) was too small to yield quantitatively correct results; however, Eq. (12) provides some useful qualitative insights.

In the ⟨4⟩ compounds with the diamond or zincblende structures, the $V(111)$ is exceptionally strong.[24] This reflects the fact that the potential midway between nearest neighbors is low, in contrast to the typical metallic case. This low potential attracts the extra bonding charge, so that the charge distribution in the crystal is no longer simply the sum of spherical atomic distributions.[39] Second-order effects of $V(111)$ cause the Fourier coefficient $\rho(222)$ to be nonzero and cause the "forbidden" (222) x-ray reflection.[44] The Jones zone of these ⟨4⟩ compounds is covered by the twelve (220) planes; and the $V(111)$ is strong enough to contribute as much to the band gap in second order as the $V(220)$ does in first order. Heine and Jones[24] find, after evaluating structure factors, etc., that

$$V_{\text{eff}}(220) = v(220) + \frac{2m}{\hbar}\left(\frac{a}{2\pi}\right)^2 v(111)\,v(111)\,. \tag{13}$$

For both ⟨4⟩ and ⟨5⟩ compounds, the band gap is of course given by $E_g = |2V_{\text{eff}}|$, where V_{eff} is given by Eqs. (12) or (13) as appropriate. In Eq. (12) the $V(111)$ and $V(200)$, and, to a much lesser extent, the $V(220)$, play the same role in widening the Jones zone gap E_g of ⟨5⟩ compounds that the $V(111)$ does in opening the gap in ⟨4⟩ compounds. Here, the strongest pseudopotential coefficient is the $V(200)$, corresponding to a low potential midway between nearest neighbors of the NaCl-cubic structure. The enhancement of the $\rho(311)$ coefficient of the charge density by the second-order effects of $V(200)$ and $V(111)$ is similar to the enhancement of $\rho(222)$ in the tetrahedral ⟨4⟩ compounds by higher-order effects of $V(111)$.

Equations (10)–(12) provide a basis for understanding the stability of a number of crystal structures assumed by the group-V elements under various conditions.[45] For the present we will note a few interesting consequences of Eq. (12). In the NaCl cubic where the A and B atoms are identical (equivalent to the simple cubic with twice the normal simple-cubic lattice constant), $V(111) = 0$; there is no covalent bonding, only metallic bondings. If the A and B atoms are different, then $V(111)$ is no longer zero and in addition to the ionic contribution, covalent bonding is also possible by Eq. (12). $V(200)$ and $V(220)$ remain large since they are symmetric combinations of the potentials of the A and B atoms. In a sense we have ionicity generating covalency!

If the A and B atoms are identical, it is possible to have $V(111) \neq 0$ if the atoms shift their positions to change the structure factors. The α-As and black P structures both satisfy this condition. In the case of α-As, the structure may be considered as two interpenetrating face-centered rhombohedral sublattices. The B sublattice has its origin at a point (u, u, u) along the cubic diagonal relative to the origin of the A sublattice. In the NaCl structure both sublattices are face centered cubic and $u = \frac{1}{2}$. In the diamond structure $u = \frac{1}{4}$; and in the α-As structure u is slightly less than $\frac{1}{2}$. In the ⟨4⟩ compounds, the band gap $E_g = |2V_{\text{eff}}(220)|$ is largest for $u = \frac{1}{4}$. For the ⟨5⟩ compounds, in contrast, the band gap $E_g = |2V_{\text{eff}}(311)|$ is a maximum for $\frac{1}{4} < u < \frac{1}{2}$, since $V(111) = 0$ at $u = \frac{1}{2}$ and $V(200) = 0$ at $u = \frac{1}{4}$. The cohesive energy contribution from the gap goes as E_g^2 according to Heine and Jones.[24] This is part of the reason that the group-IV elements C, Si, Ge, and Sn assume the diamond structure with $u = \frac{1}{4}$, while the group-V elements As, Sb and Bi are found in structures with $u \lesssim \frac{1}{2}$.[46]

It is not surprising to find that a critical ionicity f_i^c exists in both ⟨4⟩ and ⟨5⟩ compounds above which neither the tetrahedral nor α-As structures may exist, respectively. High ionicity is associated with a large difference in the pseudopotential strengths of the A and B atoms. This large difference has two consequences. First, $V(111)$ will also be large even when $u = \frac{1}{2}$ because it is formed from an antisymmetric combination of the A and B pseudopotentials. This in turn causes both Eqs. (12) and (13) to yield large band gaps without reducing u below $\frac{1}{2}$. Second, the electronic charge distribution will shift to be more localized around the atom, say B, with the stronger pseudopotential at the expense of the A atom and bond sites. The result is that net charges form on the A and B sites. The electrostatic interaction clearly favors the more closely packed NaCl structure over the tetrahedral structures, but the cohesive energy $\sim E_g^2$ due to the band gaps is greatest for $u < \frac{1}{2}$. As the ionicity f_i is increased, the balance shifts from favoring the diamond and zinc-blende or α-As structures toward favoring the NaCl cubic for ⟨4⟩ and ⟨5⟩ compounds, respectively. These arguments are naive, but the similarities and differences between Eqs. (12) and (13) appear to provide some understanding of the role of ionicity in determining crystal structures in ⟨4⟩ and ⟨5⟩ compounds.

X. SUMMARY

It is shown that a number of aspects of the Phillips–Van Vechten dielectric theory of covalent bonding can be adapted to include ⟨5⟩ compounds. The distorted NaCl structure of most ⟨5⟩ compounds requires appropriate averaging which was done by defining an effective NaCl cubic cell volume from which effective lattice constants and interatomic distances can be derived. The expressions for E_h and C can be carried over to ⟨5⟩ compounds with only minor changes in the adjustable parameters. The ionicity trends can thus be followed without the difficulty of depending on the measured dielectric constants of each compound, which are sometimes subject to large experimental errors and which have not been determined in many cases. The bond charges of As estimated with Phillips's approach are in reasonable agreement with that calculated from band structures.

Heats of formation can be related to the ionicity and cell volume in a manner very similar to that used by Phillips and Van Vechten for ⟨4⟩ compounds. The correlation between the low values of C_{calc} and f_i with the unusually low value of $\Delta H(298\,^\circ\text{K})$ for GeTe is still particularly striking. In fact, an early recognition of this correlation spurred much of the present work. The adjustable parameters assume somewhat different values, while the metallization factor is apparently unimportant in ⟨5⟩ compounds. The general trends in Fig. 2 were very encouraging, although the scatter is greater than Phillips and Van Vechten obtained with ⟨4⟩ compounds.

There appears to be a critical ionicity $f_i^c \approx 0.62$ above which the rhombohedral α-As or α-GeTe structures are unstable. Curiously, there is no simple relation between f_i and the rhombohedral angle α, even though the rhombohedral structure can be described as a continuous deformation of the NaCl cubic. Certain general structural trends with ionicity are evident in the orthorhombic ⟨5⟩ compounds such as black P, SnS, and TlI. However, ionicity alone does not determine the stability of the orthorhombic over the cubic or rhombohedral structures. Another parameter, as yet unfound, seems to be required.

The relation of pseudopotential theory to the Phillips approach was reviewed. The Jones zone gaps E_g of ⟨5⟩ compounds and ⟨4⟩ compounds are found to have different forms, approximated by Eqs. (12) and (13), respectively. The comparison of these two equations suggests one more reason that some ⟨5⟩ compounds "choose" between the NaCl or simple cubics and the rhombohedral distortions of these structures, in contrast to ⟨4⟩ compounds which "choose" between the NaCl cubic and tetrahedral structures. At the same time it suggests why a critical ionicity exists in both these cases.

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[1] J. C. Phillips, *Covalent Bonding in Crystals, Molecules and Polymers* (University of Chicago Press, Chicago, 1969).

[2] J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).

[3] J. C. Phillips and J. A. Van Vechten, Phys. Rev. B 2, 2147 (1970).

[4] J. A. Van Vechten and J. C. Phillips, Phys. Rev. B 2, 2160 (1970).

[5] We are speaking here only of the *optical* dielectric constant, that is, the electronic contribution to the dielectric response. We have excluded the phonon contribution $\epsilon_{ph}(0)$. This phonon contribution is also of great interest in ⟨5⟩ compounds. Often $\epsilon_{ph}(0)$ becomes very large, presaging ferroelectric or antiferroelectric transitions in these compounds.

[6] P. J. Stiles(*sic*), Solid State Commun. 11, 1063 (1972).

[7] P. J. Stiles and M. H. Brodsky, Solid State Commun. 12, xiii (1973).

[8] M. H. Brodsky and P. J. Stiles, Phys. Rev. Lett. 25, 798 (1970).

[9] N. S. Gillis, Phys. Rev. Lett. 22, 1251 (1969).

[10] N. K. Abrikosov *et al. Semiconducting II-IV, IV-VI and V-VI Compounds* (Plenum, New York, 1969).

[11] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals* (Pergamon, Oxford, 1967), Vol. 2.

[12] R. W. G. Wycoff, *Crystal Structures, Vol. I* (Wiley, New York, 1963).

[13] M. Cardona and D. L. Greenaway, Phys. Rev. 133, A1685 (1964).

[14] P. J. Lin and J. C. Phillips, Phys. Rev. 147, 469 (1966).

[15] J. P. Van Dyke, J. Non-Cryst. Solids 12, 263 (1973).

[16] Y. Mochida, Sci. Light 17, 57 (1968).

[17] The dominant peak has the label E_2 in the notation of Ref. 9. However, these are not the same transitions; the E_5 for ⟨5⟩ compounds corresponds to the E_2 of ⟨4⟩ compounds. No simple analog exists for the E_2 of ⟨5⟩ compounds.

[18] Y. Onodera, Solid State Commun. 11, 1397 (1972).

[19] D. M. Korn and R. Braunstein, Phys. Rev. B 5, 4837 (1972).

[20] H. D. Riccius, in *Proceedings of the Ninth International Conference on the Physics of Semiconductors* (Nauka Publishing House, Leningrad, 1968), Vol. 1.

[21] V. V. Sobolev and V. I. Dometskikh, Zh. Eksp. Teor. Fiz. 59, 3 (1970) [Sov. Phys.-JETP 32, 1 (1971)].

[22] M. H. Cohen, L. M. Falicov and S. Golin, IBM J. Res. Develop. 8, 215 (1964).

[23] J. A. Van Vechten, Phys. Rev. 182, 891 (1969).

[24] V. Heine and R. O. Jones, J. Phys. C 2, 719 (1969).

[25] S. Golin and J. A. Stocco, Phys. Rev. B 1, 390 (1970).

[26] J. A. Van Vechten, Phys. Rev. 182, 891 (1969).

[27] L. Pauling, *The Nature of the Chemical Bond* (Cornell U. P., Ithaca, N.Y., 1960).

[28] D. D. Wagman *et al.*, *National Bureau of Standards Technical Note No.* 270 (U. S. GPO, Washington, D.C., 1968).

[29] J. N. Bierly, L. Muldawer, and O. Beckman, Acta Met. 11, 447 (1963).

[30] S. S. Kabalkina, L. F. Vereschchagin, and N. R. Serebryanaya, Fiz. Tverd. Tela 9, 3208 (1967) [Sov. Phys.-Solid State 9, 2527 (1966)].

[31] H. Krebs, K. Grun, D. Kallen, and W. Lippert, Z. Anorg. Chem. 308, 200 (1961).

[32] C. S. Barrett, Acta Cryst. 9, 671 (1956).

[33] W. Klement and L. H. Cohen, Science 154, 1176 (1966).

[34] A. Bienenstock, Bull. Am. Phys. Soc. Ser. II, 18, 307 (1973).

[35] The $\vec{a}$, $\vec{b}$, and $\vec{c}$ directions in the orthorhombic structures correspond to the [101], [010], and [10$\bar{1}$] directions in the NaCl cubic. By the simple-cubic structure is meant the standard eight-atom NaCl cubic in which the A and B atoms are indistinguishable.

[36] S. K. Novoselov, L. A. Baidakov, and L. P. Strakhov, Fiz. Tverd. Tela 12, 1173 (1970) [Sov. Phys.-Solid State 12, 915 (1970)].

[37] C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1967).

[38] V. Heine, J. Phys. C 1, 222 (1968).

[39] V. Heine and D. Weaire, Solid State Phys. 24, 249 (1970).

[40] M. H. Cohen, J. Phys. Radium 23, 643 (1962).

[41] The dielectric constant defined in Sec. II and referred to in Ref. 5, excludes the free-carrier contribution $\epsilon_{fc}(\omega)$, which can be taken as the usual Lindhard (Ref. 42) dielectric function for a free-electron gas, but with a smaller number of carriers corresponding to the reduced Fermi surface area. Each ion core is completely screened at large distances since $\epsilon_{fc}(\omega) \to \infty$ as $\omega \to 0$ for any nonvanishing Fermi surface.

[42] J. Ziman, *Principles of the Theory of Solids* (Cambridge U. P., Cambridge, England, 1964).

[43] P. J. Lin and L. Kleinman, Phys. Rev. 142, 478 (1966).

[44] L. Kleinman and J. C. Phillips, Phys. Rev. 125, 819 (1962).

[45] D. Schiferl (unpublished).

[46] It should be noted, however, that the pseudopotential theory for metals expressed in Eq. (10) and (11) apparently yields the correct structures for black P (Ref. 45), α-As (Refs. 45 and 47) and Sb (Refs. 45 and 47) without considering any higher effects such as described by Eq. (12).

[47] A. R. Williams and D. Weair, in *The Physics of Semimetals and Narrow Gap Semiconductors* (Pergamon, Oxford and New York, 1971).