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Quantum Dielectric Theory of Electronegativity in Covalent Systems. III. Pressure-Temperature Phase Diagrams, Heats of Mixing, and Distribution Coefficients

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Electronegativity difference was redefined in Paper I of this series as a scaling parameter which combines the concepts of valence and size differences. A procedure has been developed for its evaluation in terms of a two-band model. In Paper II of this series it was shown that this model describes and predicts the ionization potentials and electronic interband gaps of binary $A^N B^{8-N}$ compounds and their alloys. Here the energy of this model semiconducting-insulating solid is evaluated relative to a free-electron gas, i.e., an idealized metal, as a function of composition, pressure, and temperature. Using this highly simplified scaling approach, we obtain suprisingly accurate predictions for the heat of fusion, melting point, and pressure-temperature phase diagrams of these materials. A revised method of calculating the excess heat of mixing of a substitutional alloy is presented. This calculation is extended to the case of an arbitrary dilute impurity in an arbitrary semiconducting host; the distribution coefficient at the melting point of the host is obtained.

I. INTRODUCTION

In the first two papers of this series,[1,2] hereafter referred to as I and II, the concept of electronegativity difference was defined as a scaling parameter which generalizes the concepts of valence and size differences in the manner proposed by Phillips.[3] The theory was formulated in terms of the low-frequency electronic dielectric constant of a semiconductor $\epsilon(0)=n^2$, where n is the index of refraction below the band gap.

The treatment was restricted to diatomic crystals of formula $A^N B^{8-N}$ which form in the diamond, zinc-blende, wurtzite, and rocksalt structures. Thus only the sp^3 hybridized, or tetrahedral covalent bond, and, by extension, the predominately ionic p^3 octahedral bonding in the rocksalt structure was described. However, other authors[4–8] have discussed the extension of this formulation to several other classes of semiconductors—primarily in connection with nonlinear optical susceptibilities.[9] Amorphous tetrahedral semiconductors have also been discussed.[10–12]

Unlike the electronegativity scales developed by Pauling[13] and by Mulliken,[14] the Phillips formulation[3] defines the electronegativity *difference* C between ions to be dependent upon their crystalline environment[1] rather than simply the difference of elemental electronegativities. (C is in fact the dielectrically screened potential difference[1] between the fields produced by the ion cores of the two atoms participating in a given bond measured at the point of contact of their covalent radii.[15] We refer to that point as the "bond site.")

It has already been demonstrated that the dielectrically defined scale of electronegativity differences has several advantages over previous formulations.[1,2,16] It will be shown here that the environmental dependence of the electronegativity difference and the scaling nature of the description of the sp^3 covalent bond allow one to estimate thermodynamic variables by calculating the effect of pressure, temperature, and composition (i.e., nature of distant atoms) on optical properties of the semiconductor and deducing their effects on the energy of the bonds. This possibility is totally absent in earlier empirical formulations, where "bond additivity" was assumed. (The bond-additivity assumption is that the energy of the whole is the sum of the energies of bonds between nearest neighbors and these depend only upon the nature of the atoms forming the bond—and perhaps their coordination number.[17])

The plan of this paper follows: In Sec. II, the dielectric two-band theory for determining the optical spectrum of a tetrahedral semiconducting compound[1,2] or alloy[18] is reviewed.

In Sec. III, simple but accurate methods of calculating the pressure and temperature dependence of the optical spectrum is described. In Sec. IV, we consider the energy difference ΔE^{19-21} for a given material between an idealization of the semiconducting phase, the Penn model,[22] and an idealization of a metallic phase (of the same composition), the free-electron gas. It is then proposed that ΔE may be identified with the difference in internal energy between the semiconducting, α, and high-pressure (β-tin) phases of the IV-IV and III-V semiconductors. The heat of fusion ΔH^F to melt a semiconductor to homogeneous liquid metal is also obtained from ΔE.

In Sec. V the possibility of predicting the changes in volume, $\Delta V_{\alpha\beta}$ and ΔV^F, concomitant with the phase transition to the β-tin and liquid phases is investigated. This is accomplished by resorting to the theory of covalent radii.[15]

In Sec. VI the entropy of fusion ΔS^F and the entropy of the α-β transition $\Delta S_{\alpha\beta}$ are estimated from simple quantum-mechanical arguments.

In Sec. VII the calculated pressure-temperature phase diagrams are presented and are compared with experiment. The theory introduces only two empirical constants for the entire family of semiconductors. These are used to estimate the heat of fusion and entropy of fusion of the metallic phase. All parameters specific to a given semiconductor are calculated self-consistently and are in good agreement with optical data. Agreement with experimental temperatures of fusion at 1 atm is generally within 5%. Agreement at high pressures is generally within experimental uncertainty. A pressure minimum is predicted for the α-β transition in most IV-IV and III-V crystals; this implies a metal-to-semiconductor transition with increasing temperature at constant pressure. This feature has not previously been reported but is consistent with published data[23] on InSb and with recent experiments[24] on Si and Ge.

In Sec. VIII the present theory is applied to calculate the distribution (or segregation) coefficients[25] of an arbitrary impurity in an arbitrary-host semiconductor. A revised calculation of the heat of mixing is also presented. All needed thermodynamic parameters specific to impurity or host are calculated without adjustment. Agreement with available data, principally for Si and Ge, is generally within a factor of 3 throughout the eight-orders-of-magnitude range covered by measured distribution coefficients.

II. REVIEW OF DIELECTRIC DEFINITION OF ELECTRONEGATIVITY DIFFERENCES AND THE TWO-BAND MODEL

We begin with the isotropic-Penn-model band structure (Fig. 1), a highly simplified approximation of a semiconductor which still gives a realistic wave-vector-dependent dielectric function.[22,26] For this model the low-frequency electronic dielectric constant (in the long-wavelength limit) is

$$\epsilon_1(0) = n^2 = 1 + [(\hbar\omega_p)^2/E_g^2](1 - B + \tfrac{1}{3}B^2) , \qquad (2.1)$$

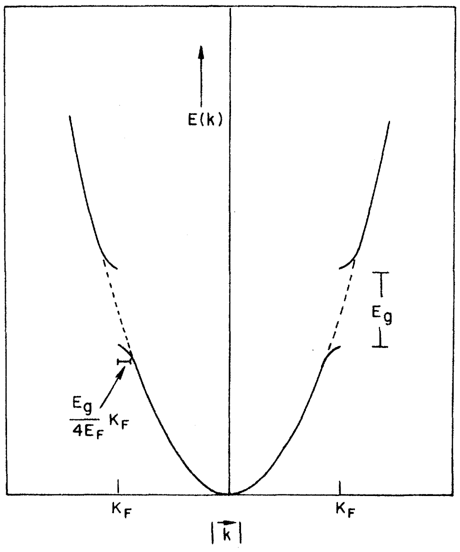

FIG. 1. Penn-model band structure (Ref. 22). The Jones zone, i.e., the first four Brillouin zones, which contains all eight valence electrons is approximated as a sphere. For the diamond/zinc-blende structure, the Jones zone is actually a regular duodecagon. The wave vectors of those free-electron states mixed by the crystal potential are related by $k' = k - 2k_F\hat{k}$. In the limit $E_g \to 0$, this Penn model reduces to the free-electron gas or jellium model of a metal.

where $B = E_g/4E_F$, ω_p is the plasma frequency of all the valence electrons (not just the free carriers, thus $\hbar\omega_p \approx 10-30$ eV), and E_F is the free-electron Fermi energy of all the valence electrons. E_g is the single band gap in the Penn model (Fig. 1) and corresponds to a weighted average of all the valence- to conduction-band gaps in the particular solid under consideration. The weighting of the average is proportional to the actual oscillator strength of the transition so that local field or excitonic effects[27] are automatically incorporated by resort to experimental values of $\epsilon_1(0)$. Values of the above parameters for the case of Si are $E_F = 12.5$ eV, $E_g = 4.8$ eV, $\hbar\omega_p = 16.6$ eV, $B = 0.1$.

In the dielectric theory,[28] E_g is decomposed into contributions due to the symmetric and antisymmetric parts of the potential within the unit cell[1-3];

$$E_g^2 = E_h^2 + C^2 \ . \qquad (2.2)$$

In (2.2), E_h is the contribution from the symmetric part or the "average homopolar band gap." C is the contribution from the antisymmetric part and is *defined* as the electronegativity difference for that bond under the prevailing condition. [In the diamond, zinc-blende, and rocksalt structures there is only one kind of bond so the single value of $\epsilon_1(0)$ suffices to determine C for all bonds once E_h has been fixed (see below). For structures containing more than one type of bond, one must make additional assumptions.] The form of Eq. (2.2) may be understood by noting that the symmetric and antisymmetric structure factors may be chosen to be pure real and pure imaginary, respectively.[29] Therefore, the symmetric and antisymmetric pseudopotential form factors add 90° out of phase. To first order, their effects, for each particular band gap, combine as in Eq. (2.2). (The justification of this equation has been further investigated by Heine and Jones.[30])

In the elemental crystals (C, Si, Ge, and Sn), $C = 0$ by definition so $E_g = E_h$. Thus the values for E_h in diamond and Si can be determined[1] from Eq. (2.1) using experimental values of $\epsilon_1(0)$ and the free-electron value of the plasma frequency, $\omega_p^2 = 4\pi Ne^2/m$, where N is the total number of valence electrons (four per atom or eight per unit cell) and m is the free-electron mass. The values obtained, 13.6 and 4.8 eV, respectively, may be used to determine the two parameters in a simple power-law formula for E_h as a function of nearest-neighbor distance r alone:

$$E_h(r) = E_h|_{\text{Si}}[(r/r)|_{\text{Si}}]^{-2.48} \ . \qquad (2.3)$$

The assumption that E_h is a function of r alone is supported by the observation[29] that the symmetric pseudopotential form factors are constant in sequences of compounds for which r is essentially constant, e.g., Ge-GaAs-ZnSe-CuBr.

When (2.3) is used to determine $E_h = E_g$ for Ge and Sn, one finds that use of the free-electron value of the plasma frequency in (2.1) will yield a value for $\epsilon_1(0)$ lower than experiment by 25 and 45%, respectively. The reason for this discrepancy is that the free-electron formula for ω_p presumes that the total oscillator strength connecting the valence and conduction band is equal to the number of valence electrons per unit volume. This is a good approximation for crystals formed of elements from the first two rows of the Periodic Table (C and Si rows), but not for elements containing a filled d-electron shell.[1,31,32] When d-core levels are present, the matrix elements and oscillator strength between them and the valence band are large, particularly for the s-like components of the sp^3 hybridized bands. These matrix elements make negative contributions to the f sum. As the total f sum is conserved, this results in an increase of the oscillator strength connecting the valence and conduction bands. This effect is described by defining N_{eff}, the effective number of valence electrons,

$$N_{\text{eff}} = \int_{\omega_0}^{\omega_c} n_{\text{eff}}(\omega) = \frac{m}{2\pi^2 e^2 N}\int_{\omega_0}^{\omega_c} \omega\epsilon_2(\omega)\, d\omega\text{-}, \qquad (2.4)$$

where ω_0 is a frequency below the band gap but above the reststrahl frequency, so that $\epsilon_2(\omega)$ is the imaginary part of the electronic dielectric function. ω_c is a cutoff frequency above the valence-to-conduction transitions but below the onset of excitations from the d-core levels. Thus, n_{eff} is the oscillator strength exhausted by all electronic transitions in the energy range $0-\hbar\omega$. There is a relatively limited amount of experimental data available on n_{eff}, but what there is[31,32] demonstrates that n_{eff}, i.e., the valence- to conduction-band f sum exceeds 4 electrons/atom well before the onset of d-core excitation (see Fig. 2).

The actual value of the plasma frequency is given by

$$\omega_p^2 = 4\pi N_{\text{eff}} e^2/m = (4\pi Ne^2/m)D \ , \qquad (2.5)$$

where D is defined by $D = N_{\text{eff}}/N$.

As the experiments required to determine N_{eff} are difficult, subject to large errors[31,32] (particularly from sample surface contamination), and affected by a somewhat arbitrary choice of ω_c, and as only limited data have been available, I have been forced to rely on a semiempirical prescription[1] to fix $D(AB)$ in AB crystals:

$$D(AB) = \Delta(A)\Delta(B) - [\delta(A)\delta(B) - 1](Z_A - Z_B)^2 \ . \qquad (2.6)$$

In (2.6), Z_A is the formal valence of element A. The parameters $\Delta(A)$ and $\delta(A)$ are functions of the covalent radius[15] of element A—at the prevailing

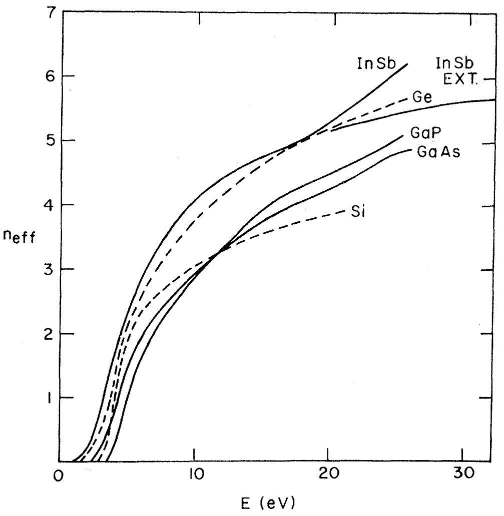

FIG. 2. Experimental $N_{\mathrm{eff}}(\omega)$ vs $\hbar\omega$ adapted from Philipp and Ehrenreich (Fig. 5 of Ref. 31). The oscillator strength connecting the valence and conduction levels with energy denominator less than or equal to $\hbar\omega$ saturates at four/atom or eight/unit cell for Si, but exceeds that value for crystals containing filled *d*-core levels at energies well below the onset of excitation out of the *d* levels. *d*-core excitation begins at 18 eV in InSb and produces a characteristic knee evident in the figure. The knee occurs at higher energies for the other compounds. A theoretical extrapolation of the valence-band oscillator strength is shown for InSb. The theoretical estimate, Eq. (2.6), was used to determine the plasma frequency.

pressure—alone. (I assume that the ratio of the covalent radii, r_A/r_B, remains constant as the crystal expands or contracts.) I use experimental values of $\epsilon_1(0)$ in Ge and Sn and the scaled values of E_h [Eq. (2.3)] to determine the two parameters in a simple power-law formula for Δ:

$$\Delta(A)=\Delta\,|_{\mathrm{Ge}}(r_A/r\,|_{\mathrm{Ge}})^{1.43}\ , \tag{2.7}$$

where $r|_{\mathrm{Ge}}$ is half the interatomic spacing in Ge at STP. These scaling hypotheses, Eqs. (2.3) and (2.7), may be tested by calculating the pressure dependence of $\epsilon_1(0)$, or the index of refraction, in C, Si, and Ge from these formulas and comparing with experiment.[1,33] The agreement is within experimental accuracy.

In I the parameters $\delta(A)$ were taken to be dependent only on the row of the Periodic Table to which element *A* belongs and were adjusted to fit $\epsilon_1(0)$ data. (The covalent radii of third-, fourth-, and fifth-row elements are constant across the row according to the Van Vechten–Phillips theory[15] used here.) For the first and second, C and Si, rows, $\Delta(A)=\delta(A)=1.0$ as these elements contain no *d* cores. The establishment of Δ and δ for fifth-, Pb, row elements is described elsewhere.[34] The three values of Δ and $\delta\neq1.0$ for the third, fourth, and fifth row at STP are given in Table I.

Having fixed the values of E_h and ω_p with Eqs. (2.3), (2.5), and (2.6), an experimental value of $\epsilon_1(0)$ suffices to fix the value of *C* from Eqs. (2.1) and (2.2) in partially ionic crystals, such as GaAs or SiC, where $C\neq0$. One can also estimate[1,3,16] *C* from its definition as the difference in the screened potentials due to the ion cores of the two atoms forming the bond at the bond site, i.e., point of contact of the covalent radii. In I, a simplified method of calculation is introduced:

$$C(A,B)=b(Z_A/r_A-Z_B/r_B)\,e^{-k_s r/2}\ . \tag{2.8}$$

In (2.8) we again have Z_A and r_A, the valence and covalent radii[15] (at prevailing pressure) of element *A*; k_s is the linearized Thomas–Fermi screening wave number, which may be expressed as

$$k_s=(4k_F/\pi a_0)^{1/2}\ , \tag{2.9}$$

where

$$k_F^3=3\pi^2N$$

is the Fermi wave number for all the valence electrons (*N* is eight per unit cell). In (2.8) *r* is the *A*-*B* bond length or nearest-neighbor distance. The parameter *b* in (2.8) is introduced to account for the fact that the linearized Thomas–Fermi screening factor, being a long-wavelength approximation, will overestimate the screening on the scale of the bond length considered here. Empirically, one finds[1]

$$b=1.5\pm10\%\ . \tag{2.10}$$

These scaling formulas have been tested by calculating the pressure dependence of $\epsilon_1(0)$ for various compounds and comparing with experiment[1,35]; agreement is generally within experimental error.

I shall now turn from the problem of estimating the average band gap and dielectric constant[1] to that of estimating particular features in the interband spectrum.[2] I cannot determine where in the Brillouin zone the Van Hove singularities[36] that produce the various optical features occur; these are delicate questions of symmetry that are deter-

TABLE I. Parameters used to calculate valence- to conduction-band oscillator strength and the effective plasma frequency. The deviation of Δ and of δ from 1.0 represents the effect of *d*-core levels which is to increase the valence- to conduction-band oscillator strength by adding negative terms to the *f* sum. See Eqs. (2.5)–(2.7), Fig. 2, and Ref. 31.

Row	Group-IV element	$\Delta-1.0$	$\delta-1.0$
3	Ge	0.12	0.0025
4	Sn	0.21	0.005
5	Pb	0.404	0.010

mined by the long-range order of the crystal and are therefore outside the scope of a nearest-neighbor bonding theory. Instead, I estimate the chemical trends in the energy of various critical-point features of the diamond/zinc-blende structure by fitting them with a formula analogous to Eq. (2.2). I adopt the Cardona notion[37] for the critical-point features—E_0, E_1, E_2, $E_{0'}$, and $E_{1'}$. I removed the spin-orbit splitting from the experimental data by taking weighted averages; thus $E_0 = \frac{1}{3}[2E_0 + (E_0 + \Delta_0)]$ and $E_1 = \frac{1}{2}[E_1 + (E_1 + \Delta_1)]$. Thus one is led[2] to

$$E^2_{g,i} = E^2_{h,i} + C^2$$

or

$$E_{g,i} = E_{h,i}(1 + C^2/E^2_{h,i})^{1/2} \, . \tag{2.11}$$

In (2.11), i ranges over the indices of the particular features, 0 to 1′, $E_{g,i}$ is the actual or composite value of the energy of the particular optical feature in the crystal with electronegativity difference C as determined—either experimentally or theoretically—from consideration of $\epsilon_i(0)$. (The same value[2] of C is used for all i.) The $E_{h,i}$ are the contributions to $E_{g,i}$ from the symmetric parts of the crystal potential and are determined by fitting the observed values in C and Si to simple power-law formulas like Eq. (2.3):

$$E_{h,i}(r) = E_{h,i}|_{\mathrm{Si}}(r/r|_{\mathrm{Si}})^{-s_i} \, , \tag{2.12}$$

where s_i is the scaling parameter for feature i. (Values of s_i range around 2.0–2.3; the empirical values are given in Ref. 2.)

Equation (2.11) must be modified in the case where the crystal contains filled d-core levels. As discussed in regard to N_{eff} and ω_p, d-core levels interact with the sp^3 hybridized valence and conduction bands. This interaction is nonlocal,[38] i.e., the interaction with s-like states is greater than with p-like states.[2] (s-like states feel no angular-momentum barrier and thus overlap the core d levels more than do p-like states. Alternatively, the s-like states penetrate the d core and feel more of the nuclear potential than do p-like states.) Therefore, s-like valence- and conduction-band states are lowered in energy relative to the p-like levels (and also relative to the vacuum level[2]). This splitting of the s- and p-like states weakens the energy of the sp^3 covalent bond.[39] It also reduces the energy of the particular band gap which corresponds to transitions from predominately p-like valence states to predominately s-like conduction-band states—in this case[2,37] E_0 and E_1. This may be verified directly by observing the trend of these features in alloys such as Si-Ge,[18,40,41] where there is no d core at one end of the composition range. In the Si-Ge case, E_0 varies by about 3 eV, while E_2, $E_{0'}$, and $E_{1'}$, which are predominately p-p transitions, vary only about 0.2 eV (see Fig. 3). I have taken account of this d-core interaction by modifying[2] Eq. (2.11) to

$$E_{g,i} = [E_{h,i} - \Delta E_i(D_{\mathrm{av}} - 1)]\,(1 + C^2/E^2_{h,i})^{1/2} \, , \tag{2.13}$$

where $i = 0$ or 1, and in analogy with (2.7),

$$\Delta E_i(r) = \Delta E_i|_{\mathrm{Ge}}(r/r|_{\mathrm{Ge}})^{t_i} \, , \tag{2.14}$$

and t_i is a scaling parameter fitted to experiment

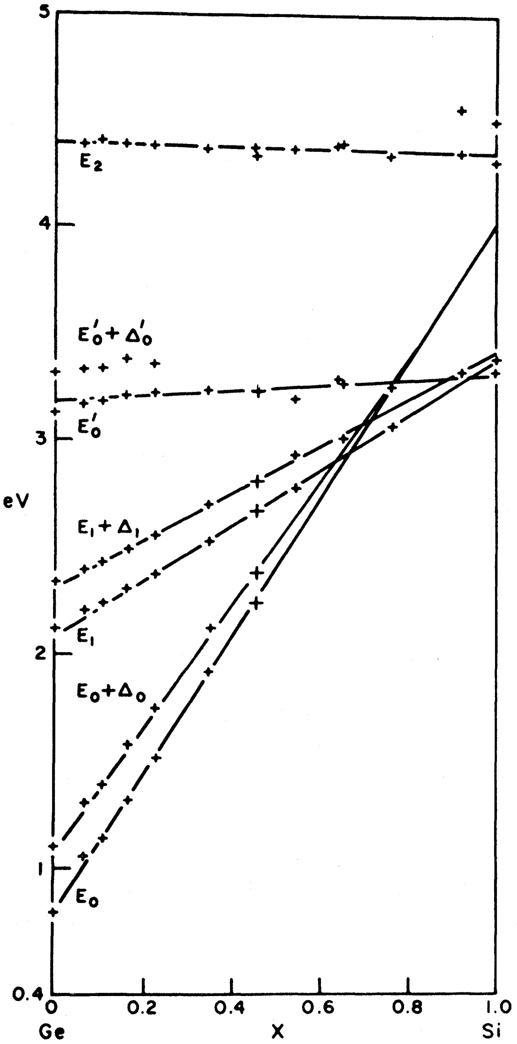

FIG. 3. Experimental variation of particular energy gaps or critical-point features in the optical spectrum of Si, Ge, and their alloys as determined by Klein, Pollak, and Cardona using electroreflectance, Ref. 40. The E_0 and E_1 band gaps are from predominantly p-like valence-band states to predominately s-like conduction-band states. The s-like states drop rapidly in energy when Ge is alloyed into Si due to interaction with the d-core states. Predominately p-p transitions E_2, E_0, and E_1 vary only slightly across the composition range as Si and Ge both have zero ionicity and have similar lattice constants.

for Sn and Ge. If elements A and B do not appear in the same row of the Periodic Table, i.e., if[15] $r_A \neq r_B$, then the average D value D_{av} in Eq. (2.13) differs from the factor D in Eq. (2.6) which specifies the d-core effect on the plasma frequency ω_p. The reader will recognize there is a distinction between the shift in energy of critical-point features, which may have different strength and may correspond to different regions in k space for different materials, and the enhancement of the valence- to conduction-band f sum. I have proposed[2]

$$D_{av}(AB) = \tfrac{1}{8}[(8 - Z_A)D(Z_A, r_A) + (8 - Z_B)D(Z_B, r_B)] . \quad (2.15)$$

In (2.15), Z_A is again the valence of A and $D(Z_A, r_A)$ is the value of D for the "horizontal compound"[42] containing element A. Thus, e.g., for InAs, $D_{av} = \frac{5}{8} D(\text{InSb}) + \frac{3}{8} D(\text{GaAs})$. Note that if elements A and B do come from the same row of the Periodic Table, (2.15) gives $D_{av} = D$. Otherwise, the weighted average, (2.15), is taken wherein the cation core has a greater effect on the conduction-band s-like states which terminate E_0 and E_1 (primarily Γ_1 and L_1) because the cations have the larger d cores and thus larger matrix elements with those states.[2]

Equations (2.11)–(2.15) are an extension and elaboration of the system of "λ^2 plots" proposed by Herman.[42] I do not propose that they can supersede the various methods that solve the Schrödinger equation in various approximations[43,44]; the dielectric two-band model (D2BM) provides no information on wave functions, matrix elements, or on symmetry questions. Instead of obtaining eigenvectors for a crystal potential which has been fitted to chemical trends, as in the empirical pseudopotential[29] (EPM) and empirically adjusted orthogonalized-plane-wave (OPW)[44] methods, and dealing with all the information contained in those eigenvectors, I have tried to establish the chemical trends in two of the moments of the optical spectrum of the sp^3 covalent bond:

$$\int_{\omega_0}^{\omega_c} (\epsilon_2(\omega)/\omega)\, d\omega \propto \epsilon_1(0) - 1$$

and

$$\int_{\omega_0}^{\omega_c} \omega\epsilon_2(\omega)\, d\omega \propto \omega_p^2 .$$

$\epsilon_2(\omega)$ may not contain as much information as the eigenvectors.[16,45] What I do maintain, however, is that many of the pertinent properties of the material, particularly the thermodynamic properties, can be deduced from just these two moments. (Wemple and DiDomenico[46] have shown that it is necessary to add only one other moment to describe optical-dispersion effects.) Recent studies of central cell corrections to impurity levels[47,48] have shown that the D2BM and EPM give essentially the same result (but the EPM requires more labor). In II and Ref. 19, I demonstrated that the accuracy with which Eqs. (2.11)–(2.15) predict the particular band gaps in 23 tetrahedral $A^N B^{8-N}$ crystals was equal to that of both the EPM and empirically refined OPW and that the D2BM used about $\frac{1}{3}$ as many empirically determined parameters to do this.

Finally, the D2BM provides an accurate and simple description of the variation of the various particular band gaps with composition in substitutional semiconductor alloys.[18] Whereas conventional band-structure calculations[29,43,44] rely on the translational invariance of ordered (pure compound) crystals to define their reciprocal-lattice vectors, and cannot easily be modified to describe the effects of disorder, as in alloys[18,49] or amorphous material,[10–12] the present real-space description of the chemical trends in the sp^3 covalent bond is ideally suited to interpolate its properties between the pure compounds.

In the description of the substitutional alloy $A_xB_{1-x}C$, the effects of disorder[18,49] are distinguished from the "virtual-crystal" variation of the optical spectrum that would obtain if the alloy had a perfect regular lattice with a compositionally averaged atomic potential at each lattice site. This virtual crystal variation is calculated by varying the bond length, C, and D_{av} parameters linearly between the values determined for the end-point pure compounds AC and BC. The result, $E_i^0(x)$, is *not* a linear variation,[18] as is sometimes supposed. To treat the effects of the fluctuations of the actual disordered crystal potential, the formulas

$$E_i(x) = E_i^0(x) - x(1 - x)c_e \quad (2.16)$$

and

$$c_e = C^2(AB)/\delta E > 0 \quad (2.17)$$

were suggested by an appeal to Fermi's "Golden rule."[18] Stroud has recently provided a more rigorous justification of the form of Eq. (2.16) in terms of coherent-potential-approximation theory.[49] In (2.16), $E_i(x)$ is the variation of the ith particular feature with composition x (the mole fraction of AC in the alloy). The energy denominator δE was assumed to be constant for all materials and all gaps i in Ref. 18. The value $\delta E = 0.98$ eV was fixed by observation of the variation of the E_0 gap in ZnS-Te alloys, where the maximum reported deviation from linearity is found.[50] The agreement between theory and experiment as regards the variation of E_0 is generally quite good[18,51] (see Fig. 4). Stroud argues[49] that δE should be larger for E_2, $E_{0'}$, and $E_{1'}$ at high photon energies than for the low-energy features E_0 and E_1. δE may even go through infinity (change sign) so that the highest features are driven slightly up in energy by the disorder. Some of the data tend to support Stroud's argument.[52, 53]

It is sometimes convenient to approximate the virtual-crystal variation with a parabola

$$E_i^0(x) = a_i + xb_i + x^2 c_i^0 , \tag{2.18}$$

where a_i and b_i are fixed by the values of E_i in AC and BC compounds. Therefore the total or observed variation of E_i with composition is approximated as a parabola[54, 55] as

$$E_i(x) = a_i + xb_i + x^2 c_i , \tag{2.19}$$

where

$$c_i = c_i^0 + c_e . \tag{2.20}$$

A table of calculated values of c_i appears in Ref. 18.

Table II provides a glossary of the symbols and terms introduced in the dielectric theory together with references to the equations of previously published work where they are introduced or discussed at length.

TABLE II. Glossary of symbols and terms introduced in the dielectric theory of electronegativity.

Symbol	Term	Ref. (Eq.)
C	Electronegativity difference, or average antisymmetric potential	1, (1.5); (4.5); 16, (5.6)
E_g	Average band gap	1, (2.7); 20, (2.2)
E_h	Average homopolar band gap	1, (1.5), (3.6)
$E_{g,i}$	ith particular band gap	2, (1.7) (3.1)
$E_{h,i}$	Homopolar contribution to ith particular band gap	2, (3.2)
B	Reduced band gap, $E_g/4E_F$	19, (2.4); 1, (2.8)
N_{eff}	Effective number of valence electrons	1, (3.10)
D	$\frac{1}{4} N_{\mathrm{eff}}$ per atom	1, (3.11)
$\mathfrak{D}$	d-core dehybridization factor, metalization factor	19, (4.1); 21 (3); 16, (10.9)
f_c	(Phillips) fraction of covalent character	16, (10.13)
f_i	(Phillips) fraction of ionic character	2, (5.2); 16, (10.11)
I	Ionization potential	2, (2.1)

III. TEMPERATURE AND PRESSURE DEPENDENCE OF OPTICAL SPECTRUM

The temperature dependence of $\epsilon_1(0)$ in the tetrahedral semiconductors has been treated by Yu and Cardona.[56] They separated the problem into two parts. The effect of thermal expansion was shown to account for less than 20% of the experimental (constant 1-atm pressure) values and was treated according to the theory of Sec. II—scaling on nearest-neighbor distance as with the pressure dependence[1] of $\epsilon_1(0)$. The explicit temperature dependence was calculated by adding Debye–Waller factors to pseudopotential form factors following the analysis of Heine and Jones[30]:

$$V_G(T) = e^{-B(T)|G|^2}\, V_G(0) . \tag{3.1}$$

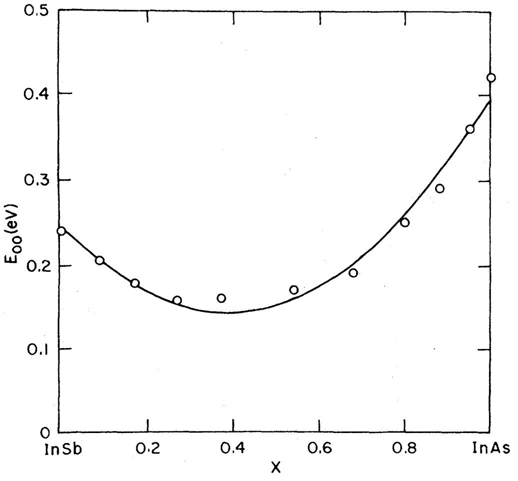

FIG. 4. Comparison of theory, Ref. 18 or Eq. (2.19), with experiment, Coderre and Woolley (Ref. 51), as to the variation of the E_0, or lowest direct band gap, in InSb-As alloys at $T=0$.

In (3.1), G is a reciprocal-lattice vector and V_G is the corresponding pseudopotential form factor. In principle (3.1) should be applied to all G's in order to determine $(\partial E_g/\partial T)|_V$. Heine and Jones[30] relate E_g to the $G=(111)$, $G=(200)$, and $G=(220)$ form factors only. Yu and Cardona found that $(\partial E_g/\partial T)|_V$ and $[\partial\epsilon_1(0)/\partial T]|_V$ were evaluated within an accuracy of 10% using only $G=(111)$:

$$E_g(T) = \exp[-B(T)|\langle 111\rangle|^2]\, E_g(0) . \tag{3.2}$$

Presumably, this occurs because the V_{111} form factors are much larger than the V_{220} and other form factors for most semiconductors. [An exception is diamond[57] (C) for which the lack of p-core states and the concomitant weakness of the repulsive core psuedopotential introduces large form factors beyond (220).]

I shall be primarily interested in the effects of the Debye–Waller factor at high temperatures, i.e., from the Debye temperature Θ to the temperature of fusion (melting point) at 1 atm, $T^F \sim 3\Theta$. Therefore, for simplicity, I will adopt a high-temperature approximation[58] for $B(T)$;

$$B(T) = 3\hbar^2 T/2Mk\Theta^2 , \tag{3.3}$$

where M is the reduced atomic mass and k is Boltzmann's constant.

In order to use (3.3) we must determine the proper value of Θ. This is not straightforward because (a) experimental values vary over a range of up to 30%, presumably with the crystalline perfection of the material[59]; (b) experimental values are not available[59] for many of the semiconductors of interest; (c) Θ is, in principle, a temperature-dependent quantity because the elastic constants have an explicit temperature dependence (through the Debye–Waller factors acting on the form factors).

One is therefore forced to develop a theoretical prescription for the high-temperature Θ or equivalently $B(T)$. I adapt the Lindemann melting formula[60] for this purpose,

$$T^F = (x^2/9\hbar^2)\, Mk\Theta^2 r_s^2 \,, \tag{3.4}$$

where r_s is the Wigner–Seitz radius and x is a critical fraction of r_s such that melting occurs when rms displacement of an atom from its lattice site exceeds this value. Comparing with (3.3), we find

$$B(T)\, T^F = \text{const} \times r_s^2 T \,. \tag{3.5}$$

The factor r_s^2 in (3.5) cancels with that of $|\langle 111 \rangle|^2$ in (3.2), so that

$$E_g(V, T) = e^{-AT/T^F} E_g(V, 0) \,. \tag{3.6}$$

I fix the value of the constant A from Si data[59]: $e^{-A} = 0.91$. As I shall calculate T_F self-consistently in Sec. VII, (3.4) may be used to provide an *a priori* self-consistent calculation of Θ.

Regarding the specific temperature dependence of the particular band gaps, I shall assume that the predominantly p bonding to p-antibonding transitions E_2, $E_{0'}$, and $E_{1'}$ have the same dependence as E_g,[56] (3.6). (In Ref. 56, $\partial E_2/\partial T$ was calculated in this approximation.)

The predominantly p-bonding to s-antibonding transitions, E_0 and E_1, are known[61] to vary with temperature more rapidly than E_2. They also vary more rapidly with pressure. Again there is some difficulty because almost all data (known to the author) have been taken at constant 1-atm pressure near room temperature or below, whereas the desired quantities are the derivatives at constant volume and elevated temperature. For CdTe, data to 1000 °K are available[62]; these data indicate $(\partial E_0/\partial T)|_P$ is not independent of T. Another difficulty in interpreting experimental data is the question of the spin-orbit splitting. (Recall that I calculate the weighted average of E_0 and $E_0+\Delta_0$ and of E_1 and $E_1+\Delta_1$.) Brust and Liu concluded[63] that the splitting Δ_0 and Δ_1 should vary as $1/r^4$ at constant temperature. I expect they should also increase significantly with temperature at constant volume as the thermal vibration drives valence-charge density into the core region. However, when the experiment is done at constant pressure, this explicit temperature dependence should be partially canceled by the effect of lattice expansion. Thus experiments indicating that $(\partial\Delta/\partial T)|_P$ is small[64] do not exclude the possibility that both effects are large but nearly cancel in the (low-) temperature range examined.

I again resort to pseudopotential theory[29, 65] and observe that the values of $\partial E_0/\partial V_G$ and $\partial E_1/\partial V_G$ are large for $G = (220)$ and $G = (311)$ relative to $G = (111)$. To obtain the total temperature derivative, $\partial E_0/\partial V_G$ must be weighted by the Debye–Waller factor e^{-W}, for which $W \propto G^2$, times V_G. The "effective G^2 value" to be used in the analog of Eq. (3.6) for E_0 and E_1 is intermediate between 3 [(111)] and 11 [(311)]; I have chosen the value 6 for both E_0 and E_1. Thus,

$$\begin{aligned} E_0(V, T) &= e^{-2AT/T^F} E_0(V, 0) \,, \\ E_1(V, T) &= e^{-2AT/T^F} E_1(V, 0) \,. \end{aligned} \tag{3.7}$$

In view of the difficulties noted above in interpreting available data, a meaningful comparison between (3.7) and the experiment may not be possible at this time. However, I will note that for CdTe I calculate

$$\left(\frac{\partial[\frac{2}{3} E_0 + \frac{1}{3}(E_0+\Delta_0)]}{\partial T}\right)\bigg|_V = -1.9 \times 10^{-4}\ \text{eV}/\,^\circ\text{K}$$

over (0–1000) °K, whereas experimentally[62]

$$\left(\frac{\partial E_0}{\partial T}\right)\bigg|_P = -4.5 \times 10^{-4}\ \text{eV}/^\circ\text{K} \,;$$

for GaAs I calculate

$$\frac{\partial \frac{1}{2}(E_1 + E_1 + \Delta_1)}{\partial T} = -4.1 \times 10^{-4}\ \text{eV}/^\circ\text{K}$$

for (0–300) °K and experimentally[64]

$$\left(\frac{\partial E_1}{\partial T}\right)\bigg|_P = -4.0 \times 10^{-4}\ \text{eV}/^\circ\text{K} \,.$$

[I do not choose to fit the assumed G^2 values in (3.7) to a particular theoretical value obtained from pseudopotentials because the nonuniqueness of the pseudopotential implies a nonuniqueness in the calculated temperature variation.[65]]

The choice of effective G^2 values for (3.7) can undoubtedly be improved when the relevant data become available. For the purposes of this paper, i.e., thermodynamics, (3.7) will be important only for calculating the d-core dehybridization factor[19] $\mathfrak{D}$ [see Eq. (4.4)]. Thus we need only to have the average of E_0 and E_1 correctly described. Compensating errors between the two will not affect the result and a single value for G^2 suffices. As the total effect of the Debye–Waller factors is not large, little improvement in the over-all accuracy of this estimate of thermodynamic properties can be obtained by assumption of other possible average wave vectors.

Now we consider the pressure dependence of the optical spectrum. The variation of $\epsilon_1(0)$ and the various particular band gaps with nearest-neighbor distance as the material is compressed may easily be determined from the functional dependence of corresponding equations in Sec. II on nearest-neighbor distances; i.e., directly from the assumed nearest-neighbor scaling. The accuracy with which this method describes the experiment was demonstrated for $\epsilon_1(0)$ in I and for the particular band gaps by Camphausen, Connell, and Paul.[66]

All that remains to be done here is to establish the relations between pressure and nearest-neighbor distance. As we will be interested in pressures extending over 2000 kbar, we cannot simply use the 1-atm bulk modulus at all pressures. Thus we must consider the derivatives of the bulk modulus with nearest-neighbor distance, the third-order elastic constants,[67] as well as the ordinary (second-order) elastic constants and bulk modulus. Reliance on the 1-atm modulus[66] of Si up to the transformation to the β-tin form at about 150 kbar (at 300 °K)[68] would induce an error of 5.5% in the α-phase volume[69] at that pressure. We use this experimental datum together with an argument that the third-order elastic constants should scale[67] as $1/r^4$, just as the second-order constants scale[70] as $1/r^3$, to fix the pressure dependence of the bulk modulus κ. Thus

$$\kappa(P+1\text{ kbar})=\frac{\kappa(P)}{1+0.0067[a(0)/a(P)]^4}\,, \qquad (3.8)$$

where $a(P)$ is the lattice constant at pressure P.

In the calculations reported here I have relied on Ref. 66 for experimental values of the bulk modulus at 1 atm for the various semiconductors.

IV. HEAT OF FUSION, α-β TRANSFORMATION, AND PENN-MODEL SINGLE-PARTICLE ENERGY

Nature abhors a metal. Although any compound would be a metal if it assumed any of several feasible structures, $\frac{3}{4}$ of elements are metals in their standard state and a huge number of metallic compounds and alloys are known, the materials found in nature are invariably semiconducting or insulating. (Exception can be found in the core of the earth and in meteorites. At sufficient pressure any material should transform to a metallic state.) The reason for this circumstance must be that semiconductors and insulators are inherently lower states of free energy (at STP) than the corresponding metallic phases.

A simple explanation of this observation can be derived from the band gap that distinguishes nonmetals from metals.[20–22,71] To first order in the crystal potential, the energy of the occupied valence-band states is lowered by $\frac{1}{2}$ the band gap from the Fermi level; the unoccupied conduction-band states are raised in energy an equal amount from the Fermi level. One might thus conclude that the difference in energy between the metallic and semiconducting phases can be estimated as the difference between the total single-particle energy of a free-electron gas (idealization of the metallic phase) and that of the Penn-model idealization of the semiconducting phase[20,21] (see Fig. 5). For the idealized metal phase one has the total single-particle energy per valence electron,

$$E^m=\tfrac{3}{5}E_F+E_b^m\,, \qquad (4.1)$$

where E_F is again the Fermi energy of all the valence electrons and E_b^m is the "bottom-of-the-band" energy,[71] i.e., the zero point for the free-electron parabola. As we shall only be interested in the *difference* in energy between phases, we set $E_b^m=0$. For the idealized Penn-model semiconductor, a very good approximation to the exact total single-particle energy per valence electron is[20]

$$E_1=E_F\left[\tfrac{3}{5}+3B^2(1+\ln\tfrac{1}{2}B)-4B^3\right]+E_b\,. \qquad (4.2)$$

In (4.2) as in (2.1), $B=E_g/4E_F$, where E_g is the dielectrically defined average band gap. E_b is the bottom of the (eight-electron) valence-band energy relative to that of the metal E_b^m.

The immediate quantitative application of (4.2) seems unwarranted because I have not prescribed a method to calculate E_b. The assumption that E_b is zero or negligibly small, i.e., $E_b\approx E_b^m$, is very

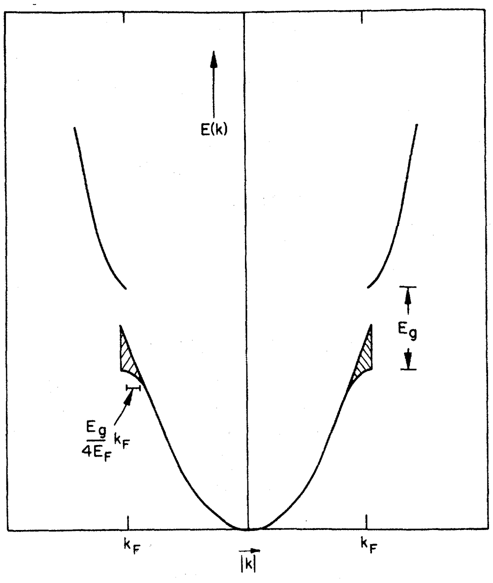

FIG. 5. Penn-model band structure showing the reduction in the single-particle energy of the idealized semiconductor relative to the idealized (jellium) metal as a function of wave vector k as the shaded area.

dubious. One might expect that the localization charge into covalent bonds[72] or ionic charges concomitant with formation of the band gap would increase the bottom of the band-gap energy relative to that in a (jellium) metal where the interaction charge density is rather constant.[73] (Obviously, the Fermi levels of the various phases will be equal when they are in contact.)

However, it has been observed[21,71] that to within experimental accuracy the difference in internal energy *per atom pair* between the semiconducting diamond (α) phase and the metallic tetragonal β-Sn phase of Si is equal to the difference of the total single-particle energies *per electron* between the free-electron gas and the Penn model when both models are evaluated at the critical pressure (volume) of the actual solid-solid phase transformation. Thus $\frac{7}{8}$ of the energy gained by opening the band gap in Si is lost forming the localized bond charges. The fact, as demonstrated in Ref. 21 and below, that this $\frac{7}{8}$ factor can be extended to the other tetrahedrally coordinated semiconductors is indicative of the power of a scaling approach to such problems. Therefore, the equation for the difference in internal energy between a metallic phase and a semiconducting phase that approximates the Penn isotropic two-band model is

$$\Delta E_m = -E_F[3B^2(1+\ln\tfrac{1}{2}B) - 4B^3] , \qquad (4.3)$$

where ΔE_m is energy per atom pair and E_F is per electron.

It has been noted repeatedly[1,2,16,19–21] that the simple Penn model is not adequate to describe Ge, Sn, or any material containing filled d-core levels. Just as one has to take account of the effects of the interaction between d-core levels and valence- or conduction-band s-like states when calculating the plasma frequency and the E_0 and E_1 critical-point band gaps in Sec. II, so one must take account of the concomitant weakening of the sp^3 hybridized covalent bond. As interaction with the d core lowers the energy of s-like states relative to p-like states, hybridization is diminished, and the stability of the semiconducting phase relative to possible metallic phases is reduced. [Recall that the value of E_g is independent of the presence of core d levels while the values of ω_p, $\epsilon_1(0)$, E_0, etc. clearly are not.] Mooser and Pearson have observed this "metallization" trend in a wide variety of materials and structures.[74]

In their analysis of the heats of formation[19] of tetrahedral semiconductors, Phillips and Van Vechten proposed an empirical formula for the "d-core dehybridization" of the sp^3 covalent bond which introduces a single adjustable parameter b:

$$\mathfrak{D} = 1 - b[2E_2/(E_0+E_1)]^2 , \qquad (4.4)$$

so that the difference in internal energy per atom pair between the semiconducting and metallic phases of compounds containing a filled d core, i.e., containing elements occurring after Ca in the Periodic Table, is

$$\Delta E = \mathfrak{D}\Delta E_m . \qquad (4.5)$$

In (4.4) E_0, E_1, and E_2 are, again, the energies of certain critical-point features of the optical spectrum which may be obtained from experiment or calculated for arbitrary composition, temperature, and pressure using the simple formulas of Secs. II and III. E_2, the strongest peak of the $\epsilon_2(\omega)$ spectrum which occurs near E_g, results from a predominately bonding-p to antibonding-p transition and shows very little explicit dependence on the presence of a d core[40,41] (see Fig. 3). E_0 and E_1 result from predominantly bonding-p to antibonding-s transitions; their energy is similar to that of E_2 in Si and other crystals lacking any filled d-core levels. As noted in Sec. II and Fig. 3, the E_0 and E_1 energies decrease with increasing d-core interaction. Thus the ratio $2E_2/(E_0+E_1)$ provides an easily calculable measure of the extent to which s-like states have been separated (dehybridized) from p-like states. In the case of grey or α-Sn, the $2E_2/(E_0+E_1)$ reaches the maximum value found for any tetrahedrally bonded material.

The d-core dehybridization reaches a corresponding maximum, as grey α-Sn is well known to be in equilibrium with the metallic white or β-Sn phase near STP (292 °K at 1 atm). Thus the value of b in Eq. (4.4) was fitted[19] to this datum for Sn at STP. In Ref. 21 it was shown that (4.5) predicts the α-β transition energy of Ge, within experimental accuracy, although no experimental parameters specific to Ge are invoked.

It should be noted that the fact that α-Sn is a semimetal, i.e., the spin-orbit split $E_0 < 0$, is not the controlling parameter which heralds the instability of the tetrahedrally bonded structure against the metallic phase. α-Sn is the stable phase below 292 °K although it remains a semimetal at all temperatures. Moreover, HgTe, HgSe, and HgS are semimetals[19] and so are InSb and InAs at elevated temperatures,[75] yet all remain stable in the zincblende structure (at normal pressures). Thermodynamic properties are controlled by the total energy of the system so that the small amount of phase space around Γ responsible for E_0 cannot have a controlling effect. As E_0 goes through zero, the concomitant effect on material properties is slight.[76]

Another case in which Eq. (4.5) might be questioned is that of C where the "metallic" graphite phase[77] has slightly lower free energy, about 0.5 Kcal/mole lower, than the diamond phase at STP.[78] Actually, Eq. (4.5) gives a good value for the transition energy to the high-pressure metallic phase, which is presumably β-Sn,[79] as discussed in Sec. VII. I argue that there is a clear distinction between the β-Sn metal phase and graphite, because while the β-Sn is a three-dimensional more-or-less isotropic metal, graphite, one of the most anisotropic materials known, has only a tiny Fermi surface in the plane and has large band gaps around the rest of its Brillouin zone.[77] The effects of the small phase space in the plane associated with the Fermi surface are outweighed by the majority of phase space, wherein the sp^2 covalent bonding of that layer structure has lowered the energy of the valence-band states from the free-electron values. Thus graphite is essentially a strongly covalent insulator which could be treated by an extension of this theory that properly averaged the wave-vector-dependent dielectric tensor over all directions. [This contention is supported by the fact that the resistance of a graphite (carbon) resistor decreases with increasing temperature and that the optical spectrum of graphite shows characteristic σ and π bonding → antibonding peaks near 5 and 15 eV, respectively.]

In order to treat alloys and impurities which involve the introduction of elements which do contain d-core states into a host which does not, e.g., Si-Ge alloys or Au-doped SiC, I wish to modify Eq. (4.4) slightly. I wish to avoid a discontinuity in the value of $\Delta E = \Delta E_m$ by (4.3), to say, $Si_{1-x}Hg_x$ with $x \ll 1$, for which $\Delta E = \mathcal{D}\Delta E_m$ by (4.5). (I also want to retain ΔE_m as the calculated value for Si.) The modification here proposed is

$$\mathfrak{D} = 1 - b[2E_2/(E_0+E_1)]^2 + c[(E_0+E_1)/2E_2]^2 . \tag{4.6}$$

The constants b and c in (4.6) are fitted to experiment for the α-Sn → β-Sn equilibrium at 292 °K and 1 atm and to $\mathfrak{D} = 1.0$ for Si at STP; $b = 0.0467$, $c = 0.0875$ using my theoretical values for E_0, E_1, and E_2. As the ratio $2E_2/(E_0+E_1)$ is near 1.5 for crystals not containing d cores and generally large for those which do, this modification increases the value of $\mathfrak{D}$ that would be calculated for the former category of crystals by 3–4% and for the latter category only very slightly.

In conclusion, I propose here that the difference in internal energy between the metallic β-Sn or tetragonal or orthorhombic phases[24,79–82] and the semiconducting tetrahedral phases of the $A^N B^{8-N}$ semiconducting compounds and alloys is

$$\Delta E_{\alpha-\beta}(x, T, P) = \mathfrak{D}\Delta E_m = \Delta E , \tag{4.7}$$

where $\mathfrak{D}$ is defined by Eq. (4.6). The values of $\mathfrak{D}$ and ΔE_m are calculated for arbitrary conditions of composition, temperature, and pressure using the formulas of Secs. II and III. I shall show that this prescription is in good agreement with available data in Sec. VII.

In order to estimate the heat of fusion, i.e., the change in enthalpy upon melting, ΔH^F, I note that the more covalent $A^N B^{8-N}$ semiconductors are metallic in the liquid phase.[83] Therefore, I divide the heat of fusion ΔH^F of the semiconductor into the difference in internal energy between the metallic solid phase and the liquid ΔE_m^F, the pressure times change of volume at fusion term $P\Delta V^F$, and the difference in internal energy between the semiconducting and metallic solids ΔE from Eq. (4.7):

$$\Delta H^F = \Delta E + \Delta E_m^F + P\Delta V^F . \tag{4.8}$$

The problem of calculating ΔV^F is discussed in Sec. V; at pressures below several kilobar, the $P\Delta V^F$ term is quite negligible. I propose that ΔE_m^F scales with density as does the (free-electron) Fermi energy,

$$\Delta E_m^F(P) = 4.8455\,[a_{Si}(P=0)/a(P)]^2 \text{ kcal/g atom} . \tag{4.9}$$

(Note 1 g atom of Si contains an Avogadro's number of atoms, whereas a mole of any of the diatomic $A^N B^{8-N}$ crystals contain two Avogadro's number of atoms.) The constant of proportionality in (4.9) has been adjusted to experimental data[84] for ΔH^F in Si; experimentally $\Delta H^F = 12.082$ kcal/g atom for Si so that ΔE_m^F accounts for about 40% of the total heat of fusion.

The experimental data on ΔH^F are rather incomplete; by far the most accurate and complete compilation of data is that of the temperatures of fusion $T^F = \Delta H^F/\Delta S^F$. Therefore, we delay comparison with experiment to Sec. VII.

V. ESTIMATES OF $\Delta V_{\alpha\beta}$ AND ΔV^F

In principle, one could determine the density of a given material in a particular phase at a particular pressure by calculating its internal energy as a function of lattice constant. The minimum would be the predicted lattice constant at zero pressure; the curvature of the energy–vs–lattice-constant curve would yield the predicted bulk modulus. Results for the various competing phases would be required to determine the change in volume concomitant with the phase transformations.

There have been very few attempts to follow such a procedure. Goroff and Kleinman conducted an essentially *a priori* treatment of diamond[85]; Weaire and Heine have applied empirical pseudopotential theory to the case of group-IV elements[71] and some metal phases.[86] While these investigations have great academic value, they require an impractical amount of computation and have not achieved sufficient accuracy to be useful for our purposes.

Instead, I shall rely on the crystochemical concepts of fourfold- and sixfold-coordinated covalent radii $r_4(A)$ and $r_6(A)$ of the elements.[15,17] Van Vechten and Phillips have proposed a simple method of predicting $r_4(A)$'s which achieved an accuracy of 1% in the calculated nearest-neighbor distance between tetrahedrally coordinated atoms.[15] They also accurately estimated the interatomic spacing in rocksalt crystals of Mg, Ca, Sr, Cd, and Ag compounds by assuming that $r_6(A)$ is a constant multiple of their calculated value for $r_4(A)$. Here I shall refine that hypothesis by assuming

$$r_6(A) = 1.0925 r_4(A) \tag{5.1}$$

when the material is in equilibrium between a fourfold-coordinated phase and a sixfold-coordinated phase. I further assume that the covalent radius depends only on the coordination of the atom and not on the symmetry of the crystal structure. (Although difficult to justify, this is a common and fairly accurate chemical assumption.[17]) Therefore, I use the same estimate for $r_6(A)$ for the β-Sn structure[87] and similar sixfold-coordinated high-pressure phases[23,69,88,89] of the IV-IV and III-V semiconductor as for a simple cubic rocksalt structure. (However, the density will depend on structure.)

The value of the constant in (5.1), 1.0925, has been fitted to the empirical change in volume for the α-Sn to β-Sn transformation of Sn at 292 °K and 1 atm, $\Delta V_{\alpha\beta} = -0.209 V_\alpha$. This value is rather close to that used in Ref. 15, 1.0966, which was adjusted to fit the lattice constants of AgBr and AgCl in the rocksalt structure, using the theoretical values of r_4 for Ag, Br, and Cl. Although the experimental data are probably not sufficiently accurate to distinguish between the two evaluations empirically, I prefer to use the Sn $\Delta V_{\alpha\beta}$ value because the AgBr-AgCl value was not determined when the sixfold-coordinated structure was in equilibrium with a fourfold-coordinated phase. (The Mg, Ca, Sr, Cd, and Ag compounds are, however, within 10% of the critical ionicity needed to be stable in a tetrahedral structure.[2,16])

With the above assumptions one predicts that $\Delta V_{\alpha\beta} = -20.9\%\ V_\alpha(P)$ for any material that transforms from the diamond or zinc-blende structure to the β-Sn structure. The actual atomic positions of the III-V compounds in their high-pressure metallic phase have not been determined. However, one might expect them to assume structures tending toward the rocksalt structure as the ionicity and the repulsion between like ions increase. Using Eq. (5.1), the predicted change in volume for a transformation to the rocksalt structure, $-\Delta V_{\alpha R} = 15.3\%$ of $V_\alpha(P)$. Therefore, one might guess that the relation between transformation volume and ionicity is

$$-\Delta V_{\alpha\beta}/V_\alpha(P) = 0.209 - 0.056 f_i \ , \tag{5.2}$$

where f_i is the Phillips ionicity[16]

$$f_i = C^2/(E_h^2 + C^2) \ . \tag{5.3}$$

This hypothesis is compared with available data in Table III. I conclude that the theoretical estimate is accurate to within experimental accuracy. No correlation has been found between $\Delta V_{\alpha\beta}$ and $V_\alpha(P \doteq 0)$.

I note in passing that the above volume considerations give a simple explanation of the fact that the more covalent semiconductors transform to the β-Sn-like phases rather than to rocksalt structure under pressure. Namely, the β-Sn-like phases are denser than the rocksalt phase and, as demonstrated in II, these more covalent III-V and IV-IV materials would be metallic if they did assume the rocksalt structure. Therefore, the high-pressure rocksalt phase occurs only when the antisymmetric components of the crystal potential, and thus C, are large enough that a positive band gap results for that structure.[82,90] The lowering of the internal energy due to that band gap must be sufficient to compensate the increase in the free energy from the PV term.

Finally, I consider the change in volume on melting, ΔV^F. I have been able to obtain remarkably little data on this subject. However, it is well established that the slope of the liquid–high-pressure (β-Sn) solid-phase boundary is positive[23,81,82] for the $A^N B^{8-N}$ semiconductors, so that the liquid is less dense than the high-pressure solid at the same pressure. It is also well established that the slope of the liquid-diamond/zinc-blende phase boundary is negative for these semiconductors, so that liquid is more dense than the semiconductor at the same pressure. (That an sp^3 covalently bonded solid is less dense than its liquid phase should be expected from the directionality of the covalent bond; that property is not peculiar to water, as is sometimes asserted.) Although the

TABLE III. Comparison of theoretical and experimental values of the high-pressure solid-solid phase transformation volume. The calculated values are obtained from Eq. (5.2). Discrepancies between experimental values from different sources result primarily from hysteresis in the transformation, i.e., the transformation may not occur at equilibrium.

Crystal	$[\Delta V_{\alpha\beta}/V_\alpha(P)]_{\text{expt}}$ (Ref.) (%)	$[\Delta V_{\alpha\beta}/V_\alpha(P)]_{\text{calc}}$ (%)
Si	22.7 (69)	20.9
Ge	20.7 (69)	20.9
Sn	20.9 (69)	20.9
AlSb	16.5 (88)	18.5
GaSb	16.9 (88); 22.0 (89)	19.4
InSb	18.5 (88); 19.7 (23)	19.1

liquid lacks long-range order, the atoms are known to be nearly sixfold coordinated.[83,91] Therefore, I shall use Eq. (5.1) and assume the liquid has the same density as would a rocksalt phase:

$$\Delta V^F/V_\alpha(P) = -0.153\ . \qquad (5.4)$$

Published data for Si and Ge give significantly smaller values for ΔV^F, 10% and 5% of $V_\alpha(P)$, respectively.[83] However, the values of the entropy of fusion ΔS^F of these materials are accurately known[84] as are the positions of the triple points in the respective P-T-phase diagrams.[92] This information, together with the Clapeyron equation

$$\frac{dT^F}{dP} = \frac{\Delta V^F}{\Delta S^F}\ , \qquad (5.5)$$

suffices to fix ΔV^F. As can be seen in Fig. 6, excellent agreement for the α-liquid slope is obtained for Si and Ge when we assume $\Delta V^F = 15.3\%\ V_\alpha(P)$ as per Eq. (5.4).

VI. ESTIMATES OF ΔS^F AND $\Delta S_{\alpha\beta}$

I shall divide the entropy of fusion of an arbitrary semiconductor into four terms:

$$\Delta S^F = \Delta S_m^F + S_b^F + S_1 + \left(\frac{\partial \Delta E}{\partial T}\right)\bigg|_V\ . \qquad (6.1)$$

In (6.1), ΔS_m^F, S_b^F, and S_1 denote, respectively, the entropy of fusion of the solid metallic phase of the same material, the entropy of fusion (or dissociation) of the covalent bond which occurs when the semiconductor transforms to a metallic liquid, and the entropy of mixing of the liquid phase. The last term, $(\partial \Delta E/\partial T)|_V$, represents the contribution to the specific heat, and thus to the entropy, of the semiconducting phase resulting from the temperature dependence of the optical spectrum. According to the dielectric theory, a decrease in the various band gaps, as produced by increasing temperature, indicates an increase in the total energy of the material.

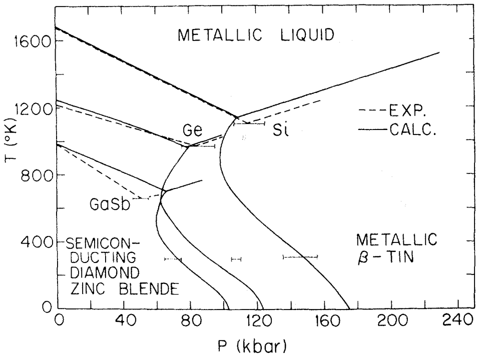

FIG. 6. Theoretical and experimental pressure-temperature phase diagrams for Si, Ge, and GaSb. Shaded triangle below experimental triple point of Si and Ge indicates that the slope of the α-β solid-solid equilibrium boundary is positive or vertical at that temperature (Ref. 24). The Debye temperature, $\Delta H^F(P=0)$, and $\Delta S^F(P=0)$ of Si were used to fix parameters in the theory. For all other substances, there is no empirical adjustment whatever.

The effect is easily calculated using the formulas of Secs. III and IV:

$$\left(\frac{\partial \Delta E}{\partial T}\right)\bigg|_V = \left(\frac{\partial E_m}{\partial T}\right)\bigg|_V + E_m\left(\frac{\partial \mathfrak{D}}{\partial T}\right)\bigg|_V\ , \qquad (6.2)$$

$$\left(\frac{\partial E_m}{\partial T}\right)\bigg|_V = -E_F[6B(1.5+\ln\tfrac{1}{2}B) - 12B^2]\left(\frac{\partial B}{\partial T}\right)\bigg|_V\ , \qquad (6.3)$$

$$\left(\frac{\partial \mathfrak{D}}{\partial T}\right)\bigg|_V = 2\,\frac{(1-\mathfrak{D})}{B}\left(\frac{\partial B}{\partial T}\right)\bigg|_V\ , \qquad (6.4)$$

$$\left(\frac{\partial B}{\partial T}\right)\bigg|_V = -AE_g(V,0)e^{-AT/T^F}/4T^F E_F\ . \qquad (6.5)$$

The symbols in Eqs. (6.2)–(6.5) all have the meanings ascribed in Secs. II–IV. The melting point at zero pressure or temperature of fusion T^F is determined by $T^F = \Delta H^F/\Delta S^F$, so that the entire calculation must be iterated to achieve self-consistency. Thus one calculates the high-temperature Debye temperature using Lindemann's criterion[60] only to justify the use of a constant value for A in (3.6) and (6.5). That value was fixed using an experimental Debye temperature for Si.

One should recognize that both terms in Eq. (6.2) are negative, i.e., $\partial\Delta E/\partial T$ increases the entropy of the semiconducting phase relative to the metallic phase. It is the only term in (6.1) which does so. (One takes $\Delta S^F \equiv S_{1\text{iquid}} - S_{\text{solid}} > 0$.)

The entropy of mixing of the liquid phase, S_1, is assumed to be simply the entropy of mixing of an ideal solution. For an $A^N B^{8-N}$ compound with $A \neq B$, it is simply

$$S_1 = R\ln 4 \quad \text{if } A \neq B$$
$$= 2.75\ \text{cal/mole}\ ^\circ\text{K}\ , \qquad (6.6\text{a})$$

where R is the gas constant. For an elemental crystal,

$$S_1 = 0 \quad \text{if } A = B\ . \qquad (6.6\text{b})$$

This factor simply accounts for the fact that the A and B atoms, which are restricted to their respective sublattices in the solid, are free to mix and find like-atom nearest neighbors in the liquid phase.

Equation (6.6a) is not always a good approximation for the liquid phase of real semiconductors. It may happen, as in the case of III-As compounds,[93] that the constituent elements tend to phase separate in the liquid. If this occurs, then the true value of S_1 is less than $R\ln 4$. We shall return to this question when comparing calculated and observed values of T^F.

The first two terms in (6.1), $\Delta S_m^F + S_b^F$, represent a contribution to the entropy of fusion of an arbitrary tetrahedrally coordinated semiconductor which is constant independent of its chemical composition. I use one empirical parameter to fix the value of that constant,

$$\Delta S_m^F + S_b^F = 15.66 \text{ cal/mole °K} , \qquad (6.7)$$

where by 1 mole I mean two times Avogadro's number atoms. Thus for Si or Ge, I would have 2 g atom. The specific value in (6.7) was determined so that our calculated value of the total entropy of fusion would agree with experiment in the case for which we have the most accurate experimental datum. That material is Si for which we have[84] $\Delta S^F = 7.17 \pm 0.01$ cal/g atom °K or 14.34 cal/mole °K.

I have divided this constant contribution to ΔS^F into two terms, ΔS_m^F and S_b^F, because the sum is far larger than the entropy of fusion of common metals.[94] Indeed, ΔS^F for all the $A^N B^{8-N}$ semiconductors is two to three times the typical value for a metal, i.e., 2–3 cal/g atom °K. Moreover, if a semiconductor melts to a liquid which is also semiconducting, e.g., Se and SiO_2, then the observed ΔS^F is again small and comparable with values obtaining with metals. Thus I conclude that the dissociation of the covalent bond which occurs when the liquid phase is metallic, S_b^F, makes an important contribution to the total ΔS^F.

A simple explanation for the magnitude of S_b^F may be obtained from consideration of the correlation of the phase of the $4N$ sp^3 hybridized orbitals centered on N atoms (see Fig. 7.) In order to form the covalently bonded solid, the phases of orbitals on neighboring atoms must be correlated so that they add coherently to form the bonding states. When the crystal melts to a metallic liquid, the phases of the orbitals are randomized so that both bonding and antibonding states are equally likely to be occupied. As there are 2^{4N} choices of phase allowed in such a liquid, the contribution to the entropy of fusion is

$$S_b^F = k 4N \ln 2 = 11.04 \text{ cal/mole °K} , \qquad (6.8)$$

where k is Boltzmann's constant. For an elemental semiconductor, e.g., Si, one has $S_b^F = 5.52$ cal/g atom °K.

The bonding contribution (6.8) to ΔS^F can be obtained microscopically from any model of the electronic states of the semiconductor which contains two levels (bonding and antibonding). Models of this type have been discussed by Hall and more recently by Weaire and co-workers.[95]

Comparing (6.7) and (6.8), we find the entropy of fusion of the metallic phase must be

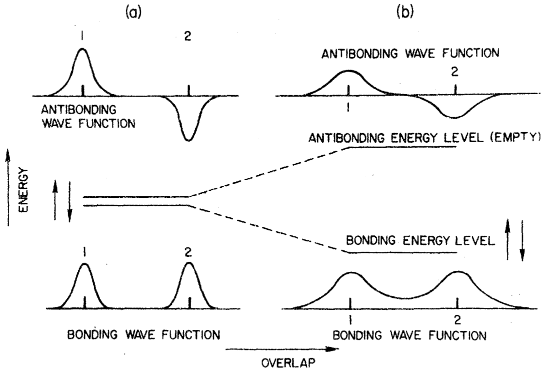

FIG. 7. The very large entropy of dissociation of the covalent bond, 5.52 cal/g atom °K, is explained in terms of the phase correlation of the valence electron. s-p^3 hybridized orbitals centered on the various atoms must be phase correlated in order that they interfere constructively with their nearest neighbors to form the (covalent) bonding states. This phase correlation is lost if the covalent solid melts to a liquid metal.

$$\Delta S_m^F = 4.62 \text{ cal/mole °K} , \qquad (6.9)$$

or for an elemental semiconductor, $\Delta S_m^F = 2.31$ cal/g atom °K. This value is in good agreement with experiment.[84]

Now we consider the change in entropy concomitant with the transformation from the diamond/zinc-blende/wurtzite or α phase to the high-pressure metallic solid or β phase, $\Delta S_{\alpha\beta}$. (If, as in InSb, several high-pressure metallic phases are possible, I do not distinguish between them.) I will assume $\Delta S_{\alpha\beta}$ to be the sum of two terms:

$$\Delta S_{\alpha\beta} = \Delta S_v + \left(\frac{\partial \Delta E}{\partial T}\right)\bigg|_V . \qquad (6.10)$$

$(\partial \Delta E/\partial T)|_V$ is the contribution from the temperature dependence of the semiconducting phase. It is fixed by Eq. (6.2) and is always less than or equal to zero according to my convention. ($\Delta S_{\alpha\beta} > 0$ implies greater entropy in the metallic phase.) ΔS_v denotes the vibrionic or phonon contribution to the entropy difference.

A rigorous calculation of ΔS_v, starting from a calculation of the phonon spectra of the two phases, promises much labor for little accuracy at this stage in the theory of solids. Instead, I shall rely on the scaling approach of our dielectric theory and introduce one constant of proportionality together with what is believed to be a reasonable approximation:

$$\Delta S_v(T) = 20.8 T (T^F - T)^2 / T^{F^3} \text{ cal/mole °K} . \qquad (6.11)$$

The form of ΔS_v in (6.11) assures that $\Delta S_v(T=0) = 0$ as required by the third law of thermodynamics. [Equation (6.2) will yield $\partial \Delta E/\partial T = 0$ at $T = 0$ if the low-temperature expression for the Debye–Waller factor is used; then $\partial B/\partial T=0$ at $T=0$. The error introduced by using Eq. (6.5) at all temperatures is slight.] Equation (6.11) also implies that $\Delta S_v=0$ at T^F. This corresponds to our assumption of the Lindemann criterion that the amplitude of atomic vibration is the same for both phases at their melting points. At all points between $T=0$ and T^F, ΔS_v is positive indicating that the metallic phase has a lower Debye temperature than the semiconducting phase at the same pressure. The factors $T(T^F-T)^2$ were chosen with reference to specific-heat data on Sn[84] and on InSb.[23] The value of the constant of proportionality was picked to agree with InSb data[23] for $T\Delta S_{\alpha\beta}$ at room temperature.

Because ΔS_v and $(\partial\Delta E/\partial T)|_V$ have opposite signs and ΔS_v decreases at high temperatures where $\partial\Delta E/\partial T$ is increasing in magnitude, Eq. (6.11) predicts that $\Delta S_{\alpha\beta}(T)=0$ for some T_c which is about $0.6T^F$ for most semiconductors. This is usually somewhat below the α-β-liquid triple point. $\Delta S_{\alpha\beta}$ is positive below T_c and negative above it. Therefore, a pressure minimum at T_c is predicted. By the Clapeyron equation, Eq. (5.4), the α-β-phase boundary should be positive as one approaches the triple point and negative at low (~ room) temperatures. While no explicit report of a pressure minimum has been published, the data of Hanneman, Banus, and Gatos[23] seem to clearly indicate one (see Fig. 8). Moreover Jamieson maintains[24] that for Si and Ge the slope is positive approaching the triple point. That the slope of the α-β boundary is negative at low temperatures is well established for Sn and is supported by comparison of the transition pressure at room temperature and at the triple point for several cases.[68,81,82]

VII. TEMPERATURE OF FUSION AND P-T PHASE DIAGRAM

We are finally in a position to compare our theory directly with experiment. We begin with that quantity which is most accurately known for the A^NB^{8-N} semiconductors, their melting points at 1 atm, T^F. These are calculated from

$$T^F=\Delta H^F/\Delta S^F\ , \tag{7.1}$$

where, under the assumption that the semiconductor melts to a stoichiometric homogeneous liquid metal, ΔH^F is given by Eq. (4.8) and ΔS^F by Eq. (6.1).

In Table IV we compare theory with experiment[79,84,96–99] for 16 IV-IV and III-V semiconductors. For the cases of Si, Ge, AlSb, GaSb, and InSb it is well established[91] that the observed liquid phase is a homogeneous stoichiometric metal. The III-As compounds were excluded from Table IV because As is believed to segregate in the liquid.[93] The II-VI and I-VII semiconductors are excluded because some of these may be semiconducting in their liquid phase. (Most II-VI and I-VII compounds would be semiconducting in the rocksalt structure at the liquid density[2] and are observed to be semiconducting in their high-pressure rocksalt phase.[82,90,100]) I shall discuss these excluded cases later.

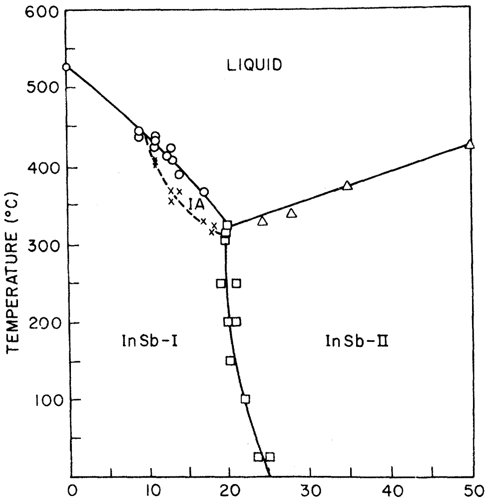

FIG. 8. Experimental P-T diagram of InSb obtained by Hanneman, Banus, and Gatos, Ref. 23. All transition pressures were obtained on the up stroke. Hysteresis is a problem and the metal phase is retained as a metastable solid on the down stroke. Other competing solid phases are shown which have not been characterized or considered. As the hysteresis must decrease with increasing temperature, we conclude that a pressure minimum is present and the α-β slope is positive at the triple point.

Of course, the agreement within experimental uncertainty for the case of Si was guaranteed by my use of the experimental values of ΔH^F and ΔS^F for Si to fix the two constants in Eqs. (4.9) and (6.7). [The Si Debye temperature was also used to fix the factor A in Eqs. (3.6) and (6.5).] However, the other cases, for which the discrepancy is never greater than 10%, should represent a fair test. Note that no information specific to the given semiconductor—except for the lattice constant—was assumed. Obviously, one could fit the data exactly by adjusting the optical-spectrum parameters E_g, E_0, E_1, and E_2 for T^F. This was not done: The theoretical values from I and II,[101] with temperature dependence as per Sec. III, were used.

As noted in Sec. III and Ref. 21, the large values of the C pseudopotential form factors at large wave numbers[27,57] imply that the actual temperature variation of the band gaps in diamond is more rapid than the present analysis—based on Si—assumes. Thus that I overestimate T^F for C (see

TABLE IV. Calculated and experimental melting points for semiconductors for which the liquid phase is known, or believed, to be a homogeneous liquid metal. These materials fulfill the assumptions of the theory. Much of the anomalously large error in the case of InN can be traced to an error in the calculated spectrum (see Ref. 2, p. 1014 and Ref. 101). The calculated value of $E_0 = 0.1$ eV, whereas the experimental value is 2.4 eV (Ref. 99).

Crystal	$\Delta S^F{}_{\text{calc}}$ (cal/mole °K)	$T^F{}_{\text{calc}}$ (°K)	$T^F{}_{\text{expt}}$ (°K)	Ref.
C	14.21	4859	~4400	79
Si	14.33	1683	1685 ± 2	84
Ge	13.92	1243	1210 ± 1	84
α-Sn	11.46	418	428 ± 24	96
SiC	16.70	2770	2810	97
AlSb	16.53	1344	1353	98
GaSb	16.17	983	985	98
InSb	15.57	745	809	98
BP	16.79	2250	~2300	94
AlP	16.69	1853		
GaP	16.52	1623	1740	99
InP	16.28	1357	1343	99
BN	16.64	4758		
AlN	16.61	3487	~3300	99
GaN	16.01	2791	>2000	99
InN	10.19	831	~1370	99

Table III) should have been expected; it is interesting that the error is only about 10%. A similar error probably appears in the BN value.

At this point I feel that some note should be made of the experimental difficulties and uncertainties encountered in the determination of T^F. Most impurities that may be present in a semiconductor will lower the apparent melting point.[102] Another difficulty is that sublimation may occur below the melting point at 1 atm. In that case, one must maintain an overpressure of the volatile component(s) such that a stoichiometric liquid is in equilibrium with the solid. For cases such as the III-N's, the requirements of pressure (several kilobar) and temperature [(2–5000) °K] are so severe that experimental melting points have not been reported. The effect of sublimation is also to lower the apparent melting point. Therefore, when selecting from among differing experimental values of T^F, I have chosen the highest value reported within the last 20 years. The case of CdS demonstrates that if the constituents are rather volatile, there may be substantial uncertainty in T^F even for a widely investigated material. Tiede and Schleede[103] first determined T^F to be 2020 °K with an S overpressure of 100 atm. Then Addamiano[104] found $T^F = (1748 \pm 15)$ °K with 2.5-atm overpressure. The current best estimate is probably that of Reynolds,[105] i.e., (1825 ± 30) °K with an equilibrium overpressure of 40 atm.

We return now to consider the III-As compounds. In Table V, I compare experimental values[99] of T^F with those calculated, as in Table IV, under the assumption that the liquid phase is homogeneous—i.e., assuming As does not segregate[93]—so that $S_1 = R \ln 4$. We note that all experimental values are about 15% higher than the corresponding calculated values. Either the calculated ΔH^F is too small or the assumed ΔS^F is too large. As I can see no reason why the calculation of ΔH^F should consistently underestimate true values for III-As compounds, as no anomaly was found when the heats of formation of these compounds were calculated[19] in a similar manner, and as there is evidence that As segregates in the liquid phase,[93] I conclude that the assumed ΔS^F is too large because S_1 is less than $R \ln 4$. Arthur estimated the As aggregations at between 10 and 15 atoms.[93] If I assume that $S_1 = 0$, i.e., that there is no more mixing of the metal and the As in the liquid than in the solid, I calculate the alternate values shown in Table V. The alternate calculation tends to overestimate T^F slightly.

Let us begin our consideration of II-VI compounds with those which are most likely to be metallic in their liquid phase—HgSe and HgTe. These are semimetallic in their zinc-blende phase. In Table VI, I compare experimental values[107,108] with those calculated as in Table IV for InSb, etc. The calculated T^F is seen to be about 20% less than the experimental melting point (but above the sublimation temperatures). In this case the discrepancy is most likely due to the anomalous temperature dependence of the band gaps[109] in HgSe and HgTe. Whereas the various particular band gaps in InSb

TABLE V. Calculated and experimental melting points for As compounds. As is believed to phase separate in the liquid phase of GaAs (see Ref. 93). Such phase separation is expected to reduce the entropy of fusion and increase the melting point. Therefore, two calculations are presented. In columns 2 and 3 values are calculated exactly as in Table IV, assuming the full atomic-mixing term $S_1 = R \ln 4$ in ΔS^F. Note that these values of T^F underestimate the experiment rather badly. In columns 5 and 6 values are calculated under the assumption that phase separation is complete so that $S_1 = 0$. The same ΔH^F is used. Note that these values of T^F overestimate the experiment slightly.

	$S_1 = R \ln 4$			$S_1 = 0$	
Crystal	ΔS^F_{calc} (cal/mole °K)	T^F_{calc} (°K)	T^F_{expt} (Ref.) (°K)	T^F_{calc} (°K)	ΔS^F_{calc} (cal/mole °K)
BAs	16.68	1865		2235	13.92
AlAs	16.59	1719	2013 ± 20 (106)	2062	13.83
GaAs	16.31	1340	1511 (99)	1612	13.56
InAs	15.76	993	1216 (99)	1203	13.01

and the other semiconductors listed in Tables IV–VI decrease with rising temperatures, as described in Eq. (3.7) and assumed in the calculation, the lowest, E_0, band gaps in HgSe and HgTe increase.

This anomalous temperature variation is concomitant with anomalous amplitudes of thermal vibration; although heavier, the Hg atoms vibrate with greater amplitude than the anions.[110] These effects may be explained qualitatively by noting that E_0 and E_1 are so much lower than E_2 (~9 eV) because of the strong interaction between the s-like conduction-band states (Γ_1 and L_1) and the d core about the Hg nucleus. The vibration of the Hg nucleus reduces this interaction so that E_0 experiences a net increase. Because an increase in E_0 affects an increase in $\mathfrak{D}$ [Eq. (4.6)] and thus a decrease in the total energy, the energetic motivation for this anomaly is clear.

Lacking specific information as to the temperature variation of the particular gaps other than E_0, I recalculate $\mathfrak{D}$, H^F, and T^F assuming $dE_i/dT=0$. The important effect is to apply the value of $\mathfrak{D}$ calculated [Eq. (4.6)] for $T=0$ at $T=T^F$; the same value of $\mathfrak{D}$ could arise from a variety of possible variations of E_0, E_1, and E_2. The resulting values of T^F, shown in Table VI, exceed the experimental values for HgSe and HgTe by 8 and 3%, respectively.

Table VII shows the values of T^F for the remaining II-VI elements calculated, as in Table IV for Si, etc., under the assumption that the liquid phase is metallic. We also show experimental values[98,105,111–116] for T^F and available values for the conductivity of the liquid phase.[83] This calculation consistently overestimates the melting point of the II-VI elements but, in many cases, the error is only 10–20%. Those errors are small because the band gaps in the liquid phase, and thus its energy relative to a metal phase, are small in those cases. (It may also happen that, as the liquid becomes semiconducting, I overestimate ΔS^F as well as ΔH^F but the estimate of their ratio T^F remains fairly accurate.)

TABLE VI. Calculated and experimental melting points for HgSe and HgTe. The thermal vibrations and temperature dependence of the band gaps in these materials are known to be anomalous (see Ref. 110). In columns 2 and 3, values are calculated exactly as in Table IV, assuming that the temperature variation of the various band gaps were normal. Note that these values of T^F underestimate the experiment rather badly. This occurs because the calculated high-temperature values of E_1, in particular, are too low. In column 5, values are calculated under the assumption that the band gaps at high temperature are all the same as those (calculated) at $T=0$. Note that these values overestimate the experiment somewhat. Therefore, as seems resonable, the true situation is intermediate between these extreme hypotheses.

Crystal	ΔS^F_{calc} (cal/mole °K)	T^F_{calc} $\frac{dE_i}{dT}>0$ (°K)	T^F_{expt} (Ref.) (°K)	T^F_{calc} $\frac{dE_i}{dT}=0$ (°K)
HgSe	12.92	836	1072 (107)	1161
HgTe	13.62	750	943 (108)	967

As the band gap in the liquid phase increases, the error introduced in assuming it to be metallic increases. For the I-VII compounds, that error is a factor of 3 and the band gaps are so large (~3 eV) that electronic conduction is negligible compared to ionic conduction.[117]

I have not, as yet, attempted to analyze the spectrum of these liquid phases in order to account for their true free energy and thus to correct the estimate of T^F.

The calculation of the full P-T-phase diagram is now straightforward. I calculate the liquid-α boundary as a function of pressure P using (5.4) to estimate ΔV^F and the theory of Sec. III to determine the variation of the theoretical optical spectrum[2] of the α phase with P and T. Thus,

$$T^F(P,\,T)=\Delta H^F(P,\,T)/\Delta S^F(P,\,T)\ . \qquad (7.2)$$

The α-β solid-solid phase transition is calculated, as a function of T, using the requirement that the difference in Gibbs free energy of the two phases be zero at the α-β boundary,

$$\Delta G_{\alpha\beta}=\Delta E(P,\,T)+P\Delta V_{\alpha\beta}(P,\,T) - T\Delta S_{\alpha\beta}(P,\,T)=0\ . \qquad (7.3)$$

I use the calculated values of $\Delta V_{\alpha\beta}$ obtained from Eq. (5.2). The intersection of these two phase boundaries determines the α-β-liquid triple point. The slope of the β-liquid phase boundary is determined at the triple point from the requirements that volume, entropy, and energy be conserved in a circuit around the triple point. The calculation is compared with experimental values for the α-β transition pressure at room temperature[68,69,80–82] $P_\tau(300\ ^\circ\mathrm{K})$ in Table VIII and with data[23,24,118] for the triple point in Table IX. Calculated phase diagrams are presented in Figs. 6 and 9–15. Only IV-IV and III-V cases are considered because II-VI and I-VII crystals transform into a semiconducting rocksalt phase instead of a metallic β-Sn phase under pressure. The reason for this difference was discussed in Sec. V.

The reader should be cautioned that there are substantial uncertainties in the experimental data. These arise chiefly from problems of calibration, of pressure inhomogeneities, and of metastability. The standard Drickamer high-pressure resistance cell, which is commonly used to gauge pressure, has recently been recalibrated.[68] This recalibra-

TABLE VII. Calculated and experimental melting points for II-VI and I-VII semiconductors for which the liquid phase may not be metallic. The values in columns 2 and 3 are calculated under the (doubtful) assumption that the liquid phase is metallic in all cases. In column 5 measured values of the conductivity of the liquid phase appear. These conductivity values should be compared with those of materials in Table IV, e.g., for Ge, $\sigma = 16\,000$ $(\Omega\ \mathrm{cm})^{-1}$. Where the liquid phase is not metallic, one will overestimate ΔH^F and thus also T^F. (However, there may be a compensating effect from an overestimate of ΔS^F.) As might be expected, the calculated T^F overestimates the experiment by a relativity small amount in materials, such as ZnS, which are small-band-gap semiconductors in their rocksalt phase. The overestimate becomes progressively worse as one goes to more ionic materials and the band gap increases.

Crystal	$\Delta S^F_{\mathrm{calc}}$ (cal/mole °K)	T^F_{calc} (°K)	T^F_{expt} (Ref.) (°K)	σ Liq. $(\Omega\ \mathrm{cm})^{-1}$
BeTe	16.73	1452	< 1570 (111)	
MgTe	16.60	1471	> 1300 (111)	
ZnTe	16.34	1657	1563 (112)	80
CdTe	16.10	1631	1365 (98)	90
BeSe	16.68	1964		
MgSe	16.48	2484	~ 1560 (113)	
ZnSe	16.29	2059	1788 ± 20 (114)	
CdSe	16.07	1835	1512 (115)	
BeS	16.71	2292		
MgS	16.49	2783		
ZnS	16.29	2294	2196 (114)	
CdS	16.21	2077	1825 ± 30 (105)	
BeO	16.52	6058		
ZnO	16.10	3621	1975 (97)	
CuCl	16.32	3094	703 (116)	
CuBr	16.27	2453	761 (116)	
CuI	16.40	2055	861 (116)	3.5
AgI	15.98	1847	831 (116)	

tion lowered the estimated $P_T(300\ ^\circ\mathrm{K})$ of Si, for example, by 33%. (The correction is nonlinear, increasing with pressure.) This revised calibration, which has been applied to all experimental pressures reported in the present tables and figures, is probably accurate to about 10% for pressures below 160 kbar. Estimates of the accuracy of the

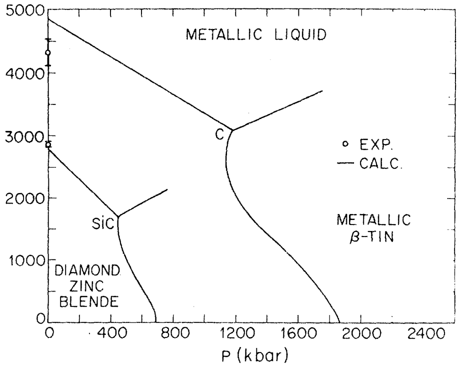

FIG. 9. Theoretical P-T diagram for C (diamond) and SiC. The graphite phase is not considered. The experimental values of $T^F(P=0)$ with their estimated uncertainties are indicated.

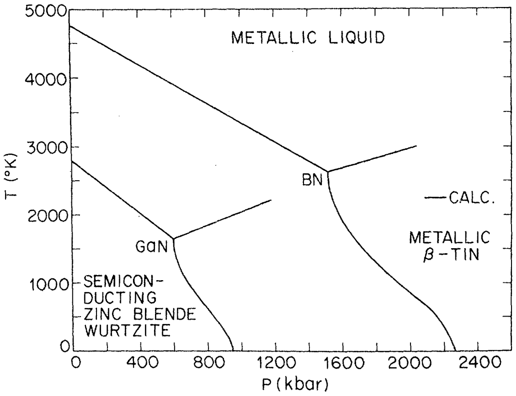

FIG. 10. Theoretical P-T diagram of GaN and BN.

TABLE VIII. Calculated values for the critical pressure for transformation to the metallic ("β-Sn") high-pressure phase compared with reported values. For InP, the reported transition is to the rocksalt structure, where the material is a small-band-gap semiconductor, rather than to the metallic structure. The rocksalt phase has not been considered in the calculation because an accurate estimate of its optical properties is not avialable. Note that experimental uncertainties are large due to the hysteresis and calibration problems. The theory relies on Eq. (5.2) to predict $\Delta V_{\alpha\beta}$. (The fundamental quantity is $P_T \Delta V_{\alpha\beta}$.) Equation (5.2) may not be an accurate formula in all cases.

Crystal	$P_T(300\ ^\circ\mathrm{K})_{\mathrm{calc}}$ (kbar)	$P_T(300\ ^\circ\mathrm{K})_{\mathrm{expt}}$ (Ref.) (kbar)
C	1680	
Si	148	150 ± 5 (68)
Ge	92	105–110 (68)
Sn	0	0
SiC	640	
AlSb	122	100–115 (68)
GaSb	73	65–75 (68)
InSb	43	22 (23)
BAs	305	
AlAs	220	
GaAs	153	175–185 (68)
InAs	92	85–90 (68)
BP	401	
AlP	269	
GaP	216	
InP[a]	141	105–115[a] (68)
BN	2110	
AlN	900	
GaN	870	
InN	260	

[a] Transition observed is to rocksalt phase rather than "β-Sn."

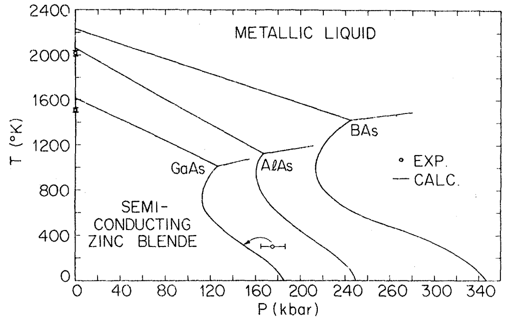

FIG. 11. Theoretical P-T diagram of GaAs, AlAs, and BAs. Experimental values of $T^F(P=0)$ and of $P_T(T=300\ °\mathrm{K})$ are indicated.

thermal couples used to measure temperature at high pressure vary from ± 2 to ± 50 °K.[119] The problem of pressure inhomogeneity must be analyzed according to the particular experiment. Pressure inhomogeneity generally decreases the apparent α-β transition pressure whereas metastability problems cause an overestimate.

The author has neither found nor developed a comprehensive analysis of the effect on experiment of metastability, i.e., the persistence of a phase when the condition of pressure and temperature changes so that it is no longer the state of lowest free energy. However, some qualitative comments are in order. The transition pressures reported in Table VIII were all obtained on the "up stroke," i.e., when pressure was increasing. (Both phases were present when the measurement was made.) If the pressure is raised so that all the material transforms into the high-pressure metal phase and is then reduced, the material will generally not return to the diamond or zinc-blende phase at the "up-stroke" transition pressure. InSb and GaSb can be retained in their metallic phases at 1 atm and low temperatures[120]; Si and Ge can persist in distorted tetrahedral structures which are denser than the diamond phases but also semiconducting.[121–124] Despite this hysteresis, I believe that the equilibrium pressure is near (~10%) the "up-stroke" pressure because the α semiconducting phase, which has lower entropy and density, exists in contact with the β metallic phase there. The conditions of the experiment tend to inhibit the ~20% volume expansion which occurs in the β to α transformation. Moreover, a state of greater en-

TABLE IX. Calculated semiconductor-solid–metal-liquid–metal triple point. Also shown is the calculated slope of the phase boundary between the solid metal and the liquid at the triple point. A few experimental values have been reported and are shown in columns 5 and 6. (The pressure recalibration suggested by Drickhamer has been applied to previously reported estimates.)

	Calc. triple pt.			Expt. triple pt.	
Crystal	P (kbar)	T (°K)	β-liquid slope (°K/kbar)	P (kbar)	T (°K)
C	1180	3080	1.1		
Si	108	1140	3.1	115±10	1100
Ge	78	960	3.0	85±10	970
Sn	<0	418	...	...	...
SiC	445	1680	1.3		
AlSb	95	780	2.7		
GaSb	66	700	2.7	50	660
InSb	46	585	2.8	19	600
BAs	245	1420	1.6		
AlAs	167	1120	1.8		
GaAs	125	1010	2.3		
InAs	91	825	2.6		
BP	385	1430	1.7		
AlP	190	1050	2.0		
GaP	158	1010	2.0		
InP	107	845	2.3		
BN	1520	2625	0.7		
AlN	620	1800	1.1		
GaN	600	1650	1.0		

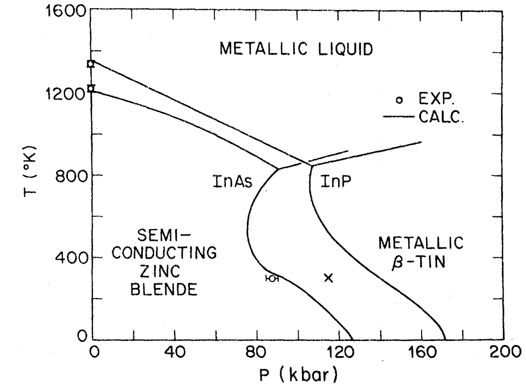

FIG. 12. Theoretical P-T diagram for InP and InAs. The x indicates the pressure at which InP transforms to the rocksalt structure. InP is semiconducting in this phase also. However, the dielectric constant and spectrum of InP in the rocksalt phase has not been determined. Therefore, one is unable to calculate the conditions of equilibrium between these phases.

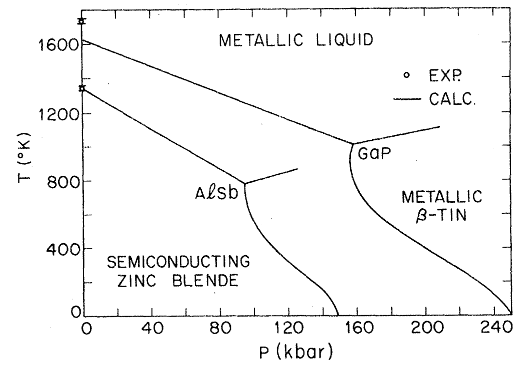

FIG. 13. Theoretical P-T diagram of AlSb and GaP.

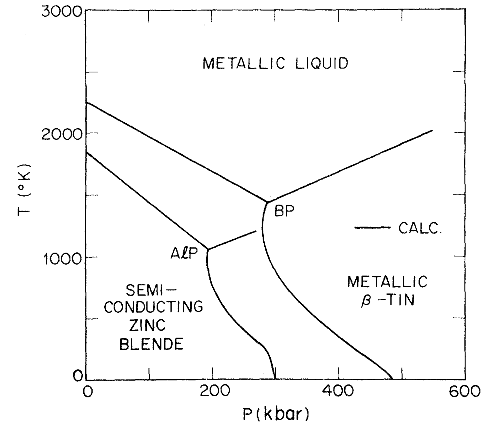

FIG. 14. Theoretical P-T diagram of AlP and BP.

tropy tends to be metastable because some sort of nucleation process is required to establish the more ordered phase; no such nucleation process is required to disorder the α phase. Note that many liquids may be supercooled to a significant extent, but very little superheating of a solid is ever observed. (The case of the metastability of diamond relative to graphite can be explained by noting that both phases are covalently bonded so they probably have comparable entropy, and that diamond is denser.)

The reader should also be cautioned that the results of the calculation are very sensitive to the values assumed for ΔV and for ΔS. The theory of Secs. V and VI used to predict these values is rather speculative. For example, if one were to use Skelton's experimental value[89] for $\Delta V_{\alpha-\beta}$(300 °K) for GaSb, 22.0%, instead of the calculated 19.4%, the calculated transition pressure would be 60 kbar instead of 73 kbar. If Jamieson's value[88] of 16.9% were used, the calculated pressure would be 83 kbar.

The calculation is also sensitive to errors induced by use of the theoretical values for the optical spectrum. (In II the rms error was found to be about 0.2 eV.) This is particularly significant for small-band-gap semiconductors because $\mathfrak{D}$ is a rapidly varying function of E_0 ($P=0$, $T=0$), E_1 ($P=0$, $T=0$), P, and T in these cases. This is illustrated by the glaring discrepancy between calculation and experiment which occurs in the case of InSb (Fig. 15). This error can be traced to the assumed temperature dependence of E_0 and E_1. Whereas the theory[2] is in reasonable agreement with experiment at $T=0$, the semiconductor becomes a semimetal as T increases; Eq. (3.7) cannot reproduce this behavior. If the true values of E_0 and E_1 near the triple point were used to calculate $\mathfrak{D}$, the calculated pressure would undoubtedly be in better agreement with experiment. To illustrate the sensitivity of the calculated transition pressure to $P=0$, T, I note that the calculated transition pressure for α-Sn drops from 23 kbar at $T=0$ to 1 kbar at $T=70$ °K.

However, it is obvious that the phase diagrams could be fitted perfectly if one were allowed the freedom to adjust the assumed optical spectrum. As there does not at this time appear to be adequate high-temperature data, I will not try to improve or empirically refine the rough estimates made in this paper. We must be content with the level of accuracy achieved using only the calculated values.

In closing this section I note that previous prescriptions for estimating α-β transition pressures have been advanced by Jamieson[88] and by Musgrave.[125] Both these approaches assumed that the transition involved the promotion of electrons from a Fermi level in the middle of the forbidden gap to the conduction-band minimum of the semiconductor. (This promotion would make the semiconductor metallic.) However, Adler[126] has

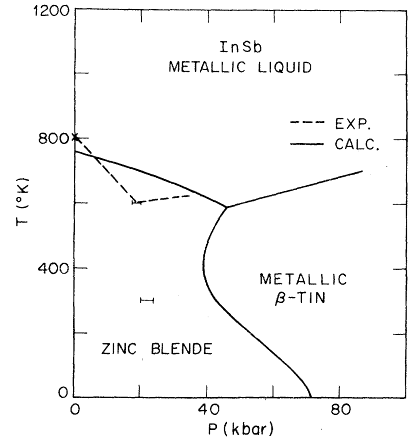

FIG. 15. Worst-case analyses. The discrepancy between the calculated P-T diagram of InSb and experiment (see Fig. 8 and Ref. 23) may be traced to errors in the calculated optical spectrum of InSb at high temperatures. The theory of Ref. 2 achieved agreement within 0.2 eV with experimental values at $T=0$. However, for a narrow band-gap semiconductor, $\mathfrak{D}$ and ΔE are very sensitive to errors in E_0 and E_1 [see Eqs. (4.6) and (4.7)]. As T increases, the calculated E_0, and probably also E_1, gaps do not decrease as rapidly as do the observed values. Above 500 °K the experimental E_0 becomes negative, while the values calculated from Eq. (3.7) clearly cannot go to zero. The calculated E_0 is always greater than 0.3 eV. The dependence of the error in P_T on the error in E_0 is highly superlinear at low pressure because E_0 increases rapidly with pressure so that ΔE also increases rapidly. Note that the error in the temperature variation of E_0 increases the calculated ΔS^F. This error compensates that in ΔE so that the calculated T_F is 6% less than experiment.

noted that the increase of the forbidden band gap of the semiconductor with pressure does not stabilize that phase nor does the doping of the material have a significant effect on the transition pressure. I add to these criticisms that the zero band gap in HgTe, HgSe, and, at high temperatures, in InSb and InAs does not imply that they transform to the β phase at zero pressure. I conclude that although these prescriptions achieve a surprisingly good empirical correlation, they have little fundamental content.

VIII. DISTRIBUTION COEFFICIENTS

The distribution coefficient K_{IH} of an impurity I in a semiconductor host H is defined as the equilibrium ratio of the concentration of I in the solid phase to its concentration in the liquid phase when the two phases are in contact.[25] K_{IH} is sometimes also called the "segregation coefficient." It has great technological importance as the controlling parameter in the zone refining and in the doping of semiconducting materials.

The evaluation of K_{IH} poses a rigorous test for any theory of covalent bonding. To be successful one must accurately determine bond energies both in the perfect pure-host-semiconductor and in the impurity-host-semiconductor systems. Thus, one must understand both the ideal state and the perturbation.

As the melting point of a solid is dependent upon its composition, K_{IH} may be regarded as a function of temperature, $K_{IH}(T)$. In this paper I shall consider only the limit of infinite dilution of an impurity element in a pure semiconducting compound. In this limit the equilibrium temperature tends to the melting point of the pure host, T^F. This restriction to $K_{IH}(T^F)$ is indicated not by the theory, but by the availability of experimental data. Extensive compilations are available only for $K_{I\,\mathrm{Si}}(T^F)$ and $K_{I\,\mathrm{Ge}}(T^F)$. Hereafter, I shall denote $K_{IH}(T^F)$ as simply K_{IH}.

The thermodynamic relations relevant to K_{IH} were advanced by Thurmond and Struthers.[25] Their method was to determine chemical potential of the impurity in both the liquid and the solid phase relative to a fixed reference state and to equate the two.

I treat the problem only within the regular-solution approximation,[127] i.e., I will assume that, although H and I atoms interact with different potentials and the presence of I atoms perturbs the enthalpy of the system in a nonlinear manner, the disorder of the system is negligibly affected by the difference between H and I. The partial molar entropy of I in a regular solution is the "ideal-entropy-of-mixing" value

$$\Delta \bar{S}_I = -R \ln x_I , \tag{8.1}$$

where R is the gas constant and x_I is the mole fraction of I in the solution. This is a common and apparently an accurate approximation.[91,127,128]

In this regular-solution approximation, with the pure elemental solids at their respective melting points chosen as the reference states, the Thurmond–Struthers result is

$$K_{IH} = \exp\{[\Delta \bar{H}_I^L - \Delta \bar{H}_I^S + \Delta S_I^F(T_I^F - T)]/RT\} . \tag{8.2}$$

In (8.2), ΔS_I^F and T_I^F are the entropy and temperature of fusion of the (elemental solid) impurity species; $T = T^F$ of the host semiconductor in the present case (dilute limit of I). $\Delta \bar{H}_I^L$ and $\Delta \bar{H}_I^S$ are the differential heats of solution of I in the liquid phase and in the solid phase, respectively. $\Delta \bar{H}_I$ may be defined in terms of the heat of mixing $\Delta H_m(x_I)$:

$$\Delta H_m(x_i) \equiv H(x_I) - x_I H(I) - (1 - x_I) H(H) , \tag{8.3}$$

where $H(x_I)$, $H(I)$, and $H(H)$ are, respectively, the enthalpies of the solution containing a mole fraction χ_I of I, of the pure I species, and of the pure-host species. $\Delta \bar{H}_I$ is then given by

$$\Delta \bar{H}_I = \left(\frac{\partial [(n_I + n_H) \Delta H_m(x_I)]}{\partial n_I} \right) \Bigg|_{n_H} , \tag{8.4}$$

where n_I and n_H denote the number of moles of I and of H, respectively, present in the system. (The motivation for casting this definition in terms of n_I and n_H is that x_I and x_H cannot be taken as independent variables.) In terms of $\Delta \bar{H}_I$, the heat of mixing $\Delta H_m(x_I)$ is given by

$$\Delta H_m(x_I) = x_I \Delta \bar{H}_I + (1 - x_I) \Delta \bar{H}_H .$$

Therefore, one must be able to determine the excess heat (enthalpy) of mixing $\Delta H_m(x_I)$. As all the data[129–131] available to me were obtained at low pressure (< 1 kbar) and as volumetric effects are small, I may neglect the PV term and consider only the internal energy.

Furthermore, I shall only attempt to calculate $\Delta H_m^S(x_I)$ because I have not developed a theory of liquid-phase interactions. Therefore, I shall first assume $\Delta \bar{H}_I^L = 0$ and later attempt to analyze experimental data.[132] A solution for which $\Delta \bar{H}_I^L = 0$ and with entropy given by Eq. (8.1) is said to be an ideal solution.[127] Thus, in an ideal solution the different atoms I and H interact with the same potentials. It is generally found that liquid-phase interactions affect the value of K_{IH} relatively little when H is the liquid phase of a semiconductor. The largest empirical correction known to the author[132,133] is a factor of 5.6 for In in Si; in most cases the correction is a factor of 3 or less. This magnitude is to be compared with the eight orders-of-magnitude range of experimental values,[129–131] e.g., $K_{\mathrm{B,Ge}} = 17$ while $K_{\mathrm{Tl,Si}} = 10^{-7}$. In many cases the experimental value is uncertain within a factor of 3. Thus I conclude that the approximation of the liquid phase as an ideal solution, in the absence of experimental data, is reasonable.[91]

In my view, the reason that the liquid phases of these doped semiconductors are effectively ideal is that they are metallic. In contrast with the covalent bonding of the semiconducting phase, metallic bonding, in, for example, the jellium idealization, is nonspecific and primarily dependent on average charge density.[134] The difference in valence between I and the host atom for which it substitutes, H,

$$\Delta Z = | Z_I - Z_H | , \tag{8.5}$$

has little effect on the metal phase because there is no band gap at the Fermi level. We shall see that ΔZ has a dominant effect on the semiconducting phase (provided the forbidden band gap is larger than about 0.2 eV.[12])

For a limited class of solutions, namely, the substitutional alloys such as GaAs-P or GaP-ZnS, for which the (effective) $\Delta Z = 0$, the author has already presented one method for calculating the heat of mixing.[135] This was to calculate the composition dependence of the heat of formation, using the Phillips–Van Vechten spectroscopic theory,[19] from the theoretical[18] variation of the optical spectrum with composition—Eqs. (2.16)–(2.20):

$$\Delta H_F = \Delta H_0 f_i \mathfrak{D}/a^3 , \tag{8.6}$$

where ΔH_0 is an empirical constant and a is the virtual-lattice constant. By the definition of ΔH_F, this method uses the standard chemical states of the pure elemental constituents as the reference states for the enthalpy of the solution. This is the same choice as was made by Thurmond and Struther and in Eq. (8.2).

In Ref. 135 the author showed that the range of miscibility of the substitutional alloys could be explained and predicted by calculating the heat of mixing using Eq. (8.6). More recently, Stringfellow[136,137] has used the same method to calculate the liquidus-solidus-phase diagram of the III-V substitutional alloys with good success. As the ratio of the solidus to liquidus composition at a particular temperature is the distribution coefficient at that temperature, the problem is effectively solved for isovalent ($\Delta Z = 0$) cases, such as P on the N site in GaN.[137]

However, to treat the more difficult cases where $\Delta Z \neq 0$, such as In in Ge, I wish to avoid the use of Eq. (8.6) and to change the reference states to the (hypothetical) metallic phase of the same composition—just as was done to calculate T^F and P_T. This is because to use (8.6), one would have to determine the value of f_i and of a for each bond[6] within the range of the perturbation caused by I. As that range usually includes many shells of atoms,[47,48] this would be an unappealingly complicated task and the accuracy of the result would probably not be acceptable. Moreover, I have not developed a method to calculate ΔS_I^F and T_I^F for the various metallic, gaseous, etc., standard states of the impurity elements.

Therefore, instead of considering the mixing of elemental I into the host semiconductor H, I shall consider the mixing of a hypothetical compound HI into the HH host. (If the host is a compound semiconductor, one would have $H_A - H_B$ with ΔZ dependent upon which site I occupied. However, as the available data are for Si and Ge, I will denote the host species simply as H.) I calculate the optical spectrum of HI that would obtain if one could remove the excess or deficit electrons contributed by I without perturbing the spectrum. Given this spectrum I calculate ΔS_{HI}^F and T_{HI}^F. Then I calculate the composition dependence of the substitutional alloy of HI with HH under the same assumption.

To determine the excess heat of mixing, I consider two contributions:

$$\Delta H(x_{HI}) = \Delta H_0(x_{HI}) + \Delta H_e(x_{HI}) . \tag{8.7}$$

ΔH_0 results from the variation of the optical spectrum in a manner analogous to that of Ref. 135 except that the (hypothetical) metallic phase is used as the reference state, rather than the standard states of the elemental constituents, and Eq. (4.5) is used instead of Eq. (8.6). Thus,

$$\Delta H_0(x_{HI}) = \Delta E(x_{HI}) - x_{HI}\Delta E(HI) - (1 - x_{HI})\Delta E(HH) . \tag{8.8}$$

The contribution ΔH_e results from the effect of excess or deficit electron contributed to the crystal due to the difference in valence between I and the H atom it replaces, ΔZ. In the present dilute limit, and *assuming that the impurity does not complex or cluster so as to be nonionized*—as happens, e.g., with As,[138] P,[139] and B[140] in Si—the magnitude of this effect should be

$$\Delta H_e(x_{HI}) = \tfrac{1}{2} x_{Hi} \Delta E_{\mathrm{frbd}} \Delta Z e , \tag{8.9}$$

where ΔE_{frbd} is the forbidden band gap of the host semiconductor and e is the magnitude of the charge of the electron. Equation (8.9) results from the assumptions that the Fermi level of the intrinsic semiconductor is at the center of the forbidden gap and that the excess electrons (or holes) must occupy the lowest conduction-band (highest valence band) states at an energy $\frac{1}{2}\Delta E_{\mathrm{frbd}}$ from the Fermi level. When complexing and nonionization are believed to occur,[138–140] we shall take

$$\Delta H_e(x_{HI}) = 0 \tag{8.10}$$

on the pressumption that the complex allows the electron or hole to be accommodated at or near the Fermi level. (The complex would not form were it not energetically favorable to do so.)

For practical reasons (computer precision), ΔH_0 was not calculated for an infinitely dilute concentration of I. Instead it was calculated for a 5% solution of I in H—or rather 10% HI in HH. The resultant value of $\Delta H(x_{HI})$ was fitted to the formula

$$\Delta H(x_{HI}) = x_{HI}\, x_{HH} \Omega_{IH} \; . \tag{8.11}$$

Then this value of Ω_{IH} was assumed for the differential heat of solution $\Delta \bar{H}^{S}_{IH}$ in the analog of Eq. (8.2), i.e.,

$$K_{IH} = \exp\{[-\Omega_{IH} + S^{F}_{HI}(T^{F}_{HI} - T^{F}_{HH})]/RT^{F}_{HH}\} \; . \tag{8.12}$$

A solution A-B for which the differential heat of solution $\Delta \bar{H}_A = \text{const}, x^2_B$, i.e., for which Ω is constant, across the entire composition range is called "strictly regular."[127] The strictly regular solution approximation is often made[91,133,136] for the semiconductor-dopant solutions under consideration. While a few exceptions are noted,[135,137] it is generally found to be acceptable. In order to test whether or not the present calculation would predict the same value of Ω_{HI} if it were performed in the limit of very dilute concentration of I as was obtained with 5% I, the calculation was repeated

TABLE X. Comparison of calculated and observed distribution coefficients of nontransition-metal impurities in Si and in Ge. For this table the theory assumes that the liquid phase is an ideal solution (see Table XI). In each case a value is presented, in column labeled w/o comp., calculated under the assumption of Eq. (8.9), that the impurity does not form a complex which accommodates the excess or deficit ΔZ electrons at the Fermi level. Where the experiment indicates otherwise, e.g., Refs. 138–140, a second value is calculated for the contrary assumption, Eq. (8.10).

	Si			Ge		
Impurity	K_{expt}	K_{calc} w/o comp.	K_{calc} w comp.	K_{expt}	K_{calc} w/o comp.	K_{calc} w comp.
C	0.1–1.0	1.81			1.01	
Si	1.0	1.0		5.5	2.42	
Ge	0.33	0.21		1.0	1.0	
Sn	0.016	0.074		0.020	0.084	
Pb		0.062		1.7×10^{-4}	3.3×10^{-4}	
B	0.8	0.096	1.38	17	0.044	1.63
Al	2×10^{-3}	8.0×10^{-3}		0.073	0.065	
Ga	8×10^{-3}	1.4×10^{-2}		0.087	0.0070	
In	4×10^{-4}	4.9×10^{-3}		1×10^{-3}	1.4×10^{-3}	
Tl	$(4-8)\times10^{-5}$	3.3×10^{-3}		4×10^{-5}	8.0×10^{-7}	3.0×10^{-5}
N		0.14	1.98		8.4×10^{-3}	0.31
P	0.35	0.029	0.41	0.080	0.055	
As	0.3	0.016	0.22	0.02	0.016	
Sb	0.023	0.0057	0.082	3×10^{-3}	6.3×10^{-3}	
Bi	7×10^{-4}	3.7×10^{-3}		4.5×10^{-5}	4.9×10^{-4}	
Be		3.9×10^{-3}			1.2×10^{-3}	
Mg		8.7×10^{-4}			1.5×10^{-3}	
Zn	4×10^{-4}	9.8×10^{-4}		4×10^{-4}	1.9×10^{-4}	
Cd		3.8×10^{-4}		$>1\times10^{-5}$	1.1×10^{-4}	
Hg		2.9×10^{-4}		$2\times10\times10^{-7}$	1.4×10^{-7}	
O	0.5	9.0×10^{-3}	1.84		2.4×10^{-5}	0.034
S	10^{-5}	1.9×10^{-3}			1.1×10^{-3}	
Se		1.2×10^{-3}			7.2×10^{-4}	
Te		4.9×10^{-4}		$>10^{-4}$	8.0×10^{-4}	
Po		3.0×10^{-4}			1.5×10^{-4}	
F		5.0×10^{-4}			4×10^{-8}	
Cl		1.3×10^{-4}			2.0×10^{-5}	
Br		8.2×10^{-5}			2.2×10^{-5}	
I		3.7×10^{-5}			3.8×10^{-5}	
Cu^{+2}	4×10^{-4}	10×10^{-4}		1.5×10^{-5}	2.4×10^{-4}	
Cu^{+1}		6.7×10^{-5}			4.6×10^{-6}	
Ag^{+2}		4.8×10^{-4}			7.9×10^{-4}	
Ag^{+1}	4×10^{-5}	3.2×10^{-5}		4×10^{-7}	1.6×10^{-5}	
Au^{+2}	2.5×10^{-4}	2.6×10^{-4}		1.3×10^{-5}	4.7×10^{-5}	
Au^{+1}		1.7×10^{-5}			9×10^{-7}	

with a concentration of 25% I (or rather 50% HI) assumed, and the corresponding values of Ω_{IH} were obtained. The variation in these calculated values was usually such as to produce a change in the calculated $K_{IH}(T^F)$ of less than 25%. Therefore, I conclude that the use of the value of Ω_{IH} fitted at 5% introduces a negligible error in most cases.

In Table X we compare experimental values of $K_{IH}(T^F)$ for $H=$Si and Ge with those calculated under the assumption that the liquid phase is an ideal solution. Where there is reason to believe that the impurity forms a complex, the calculation was repeated using Eq. (8.10) and both results are shown.

I also show two calculated values for the noble metals Cu, Ag, and Au in Table X. These may assume a valence of either[1,16,17,141] +1 or +2. Experimentally it is not clear which state they assume as an impurity in a given host semiconductor. Therefore, I calculate K_{IH} for both possible valences and compare them with the single experimental value. If the energies of the two states of the atom are roughly the same, one would expect the +2 species to dominate as an impurity due to the energy required to produce the additional hole concomitant with a +1 valence. We see that for Cu and Au in both Si and Ge, the $Z_I=2$ calculation is indeed in good agreement with experiment. For Ag the $Z_I=1$ calculation agrees with experiment for Si and is rather *larger* than the experimental value for Ge. The chemical experience is that the polyvalent state of Cu and Au is quite stable, while Ag^{+2} is "very unstable."[141] Therefore, except for the anomalously small experimental value of $K_{\mathrm{Ag,Ge}}$, the agreement between experiment and theory guided by chemical evidence is excellent.

It should be noted that the present calculation only considers substitutional impurities. Interstitial impurities are also known. These could have the effect of making the experimental value larger than expected but not smaller. In some cases, such as O, the interstitial impurity forms bonds with the host (SiO_2). In such cases I feel justified in classing the interstitial as a "complex" and applying Eq. (8.10).

It is also important to note that Eq. (8.12) is not simply equivalent to Eq. (8.2). The distinction between the assumptions of monatomic and of diatomic species affects both the entropies of the solution and the heats of mixing. The magnitude of the effects of this distinction may be illustrated by the case of Si in Ge. The calculation, considering GeSi in GeGe, finds $\Omega=0$, i.e., the solid phase is predicted to be an ideal solution. If one were to assume an ideal solution of Si in Ge, almost exact agreement with experiment would be obtained using Eq. (8.2). However, as I use (8.12), I find

$$S^F_{\mathrm{GeSi}}(T^F_{\mathrm{GeSi}}-T^F_{\mathrm{GeGe}})\simeq\tfrac{1}{2}S^F_{\mathrm{Si}}(T^F_{\mathrm{Si}}-T^F_{\mathrm{Ge}})\ .$$

Therefore, the calculated value differs from the experimental value by a factor of about 2.4, i.e., $(K_{\mathrm{calc}})^2\approx K_{\mathrm{expt}}$ for this particular case.

Experimental values for the liquid-phase interaction[132] provide some indication as to which assumption is appropriate for a particular case. When the experimental liquidus curve is analyzed from the monatomic point of view, both positive and negative values for the differential heat-of-mixing constant $\Delta\bar{H}^L_I$ or Ω^L_{IH}, which is also denoted as "b" in Refs. 132 and 133, are found. A negative value implies an attractive interaction between H and I so that the HI species tends to form in those cases. Therefore, the factor

$$e^{b/RT}$$

in Eq. (8.2) may be viewed as an empirical correction to cancel the error induced by the assumption of a monatomic (ideal) solution for the case $b<0$. Then my assumption that the liquid is a di-

TABLE XI. Analysis of the effects of nonideality in the liquid phase. Experimental values for b parameter (the differential heat of mixing in the liquid) have been obtained (Ref. 132) for the impurity-host systems represented. This experimental analysis proceeded on the assumption that both phases contained only monatomic species. The present theory, in contrast, assumes diatomic species. In cases where b is negative, those listed first in the table, the experiment indicates formation of diatomic species so that the assumptions of the present theory are approximately correct. Note that the discrepancy between theory and experiment is generally small in these cases. Where b is positive, opposite species repel each other so that no diatomic species will form in either phase. However, a rigorous treatment of the correction to theory appears to be very complex. However, a simple approximate correction $e^{-b/RT}$ is suggested and compared with experiment. Note that the experimental correction is never larger than a factor of 5.6, whereas experimental values range over eight of magnitude.

Impurity	Host	$e^{b/RT}$	K_{expt}	K_{calc} ideal liq.	$(Ke^{-b/RT})_{\mathrm{calc}}$
As	Si	0.35	0.3	0.22	...
Al	Si	0.5	2×10^{-3}	8.0×10^{-3}	...
As	Ge	0.54	0.02	0.016	...
Al	Ge	0.36	0.073	0.065	...
Ga	Ge	0.80	0.087	0.0070	...
Sn	Si	4.5	0.016	0.074	0.016
Sb	Si	4.1	0.023	0.083	0.020
Ga	Si	1.6	8×10^{-3}	1.4×10^{-2}	8.6×10^{-3}
In	Si	5.6	4×10^{-4}	4.9×10^{-3}	8.7×10^{-4}
Sn	Ge	1.4	0.020	0.084	0.062
In	Ge	1.4	1×10^{-3}	1.4×10^{-3}	1.0×10^{-3}
Sb	Ge	1.4	3×10^{-3}	6.3×10^{-3}	4.4×10^{-3}
Bi	Ge	2.9	4.5×10^{-5}	4.9×10^{-4}	1.7×10^{-4}
Pb	Ge	5.2	1.7×10^{-4}	3.3×10^{-4}	6.4×10^{-5}
Tl	Ge	4.4	4×10^{-5}	3.0×10^{-5}	6.8×10^{-6}

atomic ideal solution should be appropriate and my calculated values should not need adjustment. In Table XI we see that this is correct.

The case that $b > 0$, i.e., that H and I repel each other in the liquid, is more difficult to analyze. Surely my assumption that only diatomic HI and HH species are present in both phases is in error. However, it would not be correct to apply the empirical correction $e^{b/RT}$, deduced from the assumption of monatomic species, to the presumed ideal diatomic solution. Such a correction would only affect the free energy of the liquid and would clearly overestimate the effect there. It seems probable that the error in the solid phase is greater than that in the liquid.

It appears that no rigorous treatment of this problem is available and that any accurate correction will be quite involved.[142] However, one can make the simple observation that the factor $e^{-b/RT}$ suffices to reconcile calculation with experiment in eight of ten cases for which values of $b > 0$ are available (see Table XI). Moreover, the two cases where this factor does not seem to be appropriate, Pb in Ge and Tl in Ge, both involve values of K_{calc} less than 4×10^{-4} and then $K_{\mathrm{calc}} \simeq K_{\mathrm{expt}}$. For six values of K_{calc} greater than 2×10^{-4} the proposed correction always works well. Thus one may distinguish those cases where the proposed correction factor will suffice from those where it probably should not be applied.

Finally, I wish to compare the present method of calculating the distribution coefficients with one well-known previous method—that proposed by Weiser.[132] This is probably the most successful treatment previous to the present work. Weiser used the elements as reference states and thus used Eq. (8.2). He also used experimental values for ΔS^F and T^F for all species as well as for $\Delta \bar{H}_I^L$ (which he denotes as b). Thus he only proposed a method for calculating $\Delta \bar{H}_I^S$ in the regular solution approximation. Weiser considered two contributions,

$$\Delta \bar{H}_I^S = E^s + E^b , \tag{8.13}$$

where E^b is a "bond-strength" term, i.e., a function of only the elements forming the bond independent of their nearest-neighbor distance. The term E^s is the "strain energy" derived from the mismatch of the atomic radius of the impurity atom and of the host lattice. Weiser assumed that the excess or deficit electrons contributed to the lattice had no effect on the energy of the system. Thus he assumed $\Delta \bar{H}^s$ was independent of ΔZ_I. This is in sharp contrast to the present theory where ΔZ_I makes a very important contribution as indicated in Eq. (8.9). The present work also calculates the total band energy as a function of both composition and interatomic spacing without resort to the artificial separation into two constructs E^s and E^b.

In order to estimate the value of E^b, Weiser made use of an interesting empirical rule suggested by Allen[143] relating the cohesive energy of compounds to those of the constituent elements,

$$E^b = (H_I^v - H_H^v)^2/(H_I^v + H_H^v) , \tag{8.14}$$

where H_I^v and H_H^v are the heats of vaporization of the elemental I and H solids. It should be noted that Allen's rule applies to the energy of bonds with unstrained bond lengths. These energies are clearly dependent upon the interatomic distance. Weiser used empirical values for all the H^v's.

The remaining problem was to determine the "strain-energy" term E^s. To do this Weiser replaced the diamond lattice with a simple cubic monatomic lattice and treated the region outside the nearest-neighbor shell as a continuous medium. He ignored the bond-bending force constants[144] which stabilize the lattice. He introduced the empirical bulk modulus and one adjustable parameter which was fitted to K_{IH} data. His final result was

$$\begin{aligned} E^s &= 170(\Delta R/\text{Å})^2 \quad \text{kcal/g atom for Ge} , \\ E^s &= 220(\Delta R/\text{Å})^2 \quad \text{kcal/g atom for Si} , \end{aligned} \tag{8.15}$$

where ΔR is the difference in tetrahedral covalent radii between H and I. (Weiser used the Pauling–Huggins table[145] of tetrahedral covalent radii.)

Although considerable criticism can be leveled against the assumptions in Weiser's model, it must be admitted that he achieved an impressive degree of success accounting for the distribution coefficients of some group III–V impurities in Si and Ge.[132] Here I wish to determine how well his method can be extended to other impurities and to other host semiconductors. First, in Table XII I compare the result of my calculation with that using Weiser's method for all impurities in Si and Ge for which I have data. [The empirical values for T^F, ΔS^F, and H^v required for Weiser's method were taken from the compilations[146] of Wagman *et al.* (U.S. National Bureau of Standards). Weiser did not indicate where he obtained his values, but, where direct comparison can be made, the discrepancies are small.]

As can be seen, Weiser's method is not reliable for group I, II, or VI impurities. I believe this results from his neglect of the effect of adding or removing electrons from the semiconductor's eight electron bands. In some cases, such as O in Si, it is obvious why the calculation is in error by a factor of 10^{22}, but it is not clear how the various complexes should be treated in the Weiser model. The present method provides a simple prescription and accuracy comparable with that of the experiment.

TABLE XII. Comparison between the previous semiempirical theory of Weiser (Ref. 133) and the present work. As Weiser's calculation uses experimental values of b to improve its accuracy, I feel justified in using the empirical correction for liquid-phase nonideality for the purpose of comparison also.

Impurity	Host	K_{expt}	K_{calc} Weiser	K_{calc} ideal liq. present work	$(Ke^{-b/RT})_{\text{calc}}$ present work
C	Si	0.1–1.0	1.6×10^{-4}	1.81	...
Ge	Si	0.33	0.18	0.21	...
Si	Ge	5.5	1.7	2.42	...
Sn	Si	1.6×10^{-2}	9.7×10^{-3}	7.4×10^{-2}	1.6×10^{-2}
Sn	Ge	0.020	0.022	0.084	0.062
Pb	Ge	1.7×10^{-4}	1.9×10^{-4}	3.3×10^{-4}	6.4×10^{-5}
B	Si	0.8	0.027	1.38	...
B	Ge	17	1.9×10^{-5}	1.63	...
Al	Si	2×10^{-3}	3.5×10^{-2}	8.0×10^{-3}	...
Al	Ge	0.073	0.16	0.065	...
Ga	Si	8.0×10^{-3}	6.8×10^{-3}	1.4×10^{-2}	8.6×10^{-3}
Ga	Ge	0.087	0.030	0.0070	...
In	Si	4×10^{-4}	2.4×10^{-4}	4.9×10^{-3}	8.7×10^{-4}
In	Ge	1×10^{-3}	1.5×10^{-3}	1.4×10^{-3}	1.0×10^{-3}
Tl	Si	4.8×10^{-5}	2.6×10^{-7}	3.3×10^{-3}	...
Tl	Ge	4×10^{-5}	4.2×10^{-5}	3.0×10^{-5}	6.8×10^{-6}
Zn	Si	4×10^{-4}	3.2×10^{-7}	9.8×10^{-4}	...
Zn	Ge	4×10^{-4}	2.2×10^{-6}	1.9×10^{-4}	...
Cd	Ge	$>1\times10^{-5}$	5×10^{-9}	1.1×10^{-4}	...
Hg	Ge	2×10^{-7}	5.2×10^{-13}	1.4×10^{-7}	...
Cu	Si	4×10^{-4}	0.028	1.0×10^{-3}	...
Cu	Ge	1.5×10^{-5}	0.28	2.4×10^{-4}	...
Ag	Si	4×10^{-5}	1.4×10^{-5}	3.2×10^{-5}	...
Ag	Ge	4×10^{-7}	4.9×10^{-4}	1.6×10^{-5}	...
Au	Si	2.5×10^{-4}	7.3×10^{-4}	2.6×10^{-4}	...
Au	Ge	1.3×10^{-5}	9.4×10^{-3}	4.7×10^{-5}	...
P	Si	0.35	0.096	0.41	...
P	Ge	0.080	0.49	0.055	...
As	Si	0.3	0.013	0.22	...
As	Ge	0.02	0.16	0.016	...
Sb	Si	0.023	0.0027	0.082	0.020
Sb	Ge	3×10^{-3}	2.4×10^{-2}	6.3×10^{-3}	4.4×10^{-3}
Bi	Ge	4.5×10^{-5}	1.5×10^{-4}	4.9×10^{-4}	1.7×10^{-4}
O	Si	0.5	1.1×10^{-22}	1.84	...
S	Si	10^{-5}	6.7×10^{-3}	1.9×10^{-3}	...
Te	Ge	$>10^{-4}$	3.0×10^{-5}	8.0×10^{-4}	...

One could conjecture that the problem with Weiser's method lies with the use of the Pauling–Huggins tetrahedral covalent radii.[145] Use of the Van Vechten–Phillips tetrahedral covalent radii[15] would significantly change many values, but would not greatly improve the over-all accuracy of the method. If the radius of the impurity is treated as an adjustable parameter, it would be possible to fit many experimental values. However, for some cases, such as Hg in Ge, even setting $\Delta R = 0$ so $E^s = 0$ would not suffice to obtain the experimental value.[131]

Now consider the application of both methods to host materials other than Si and Ge. The adaptation of the two methods is trivial but, as noted earlier, good quantitative experimental values of K_{IH} are lacking. However, I can make a qualitative point. Weiser's calculation is independent of the forbidden gap of the host, whereas, in the present theory, the term ΔH_e in the heat of mixing is proportional to the forbidden gap. For charged impurities in Si and Ge the ΔH_e term is dominant. However, for small-band-gap semiconductors, ΔH_e will be proportionately smaller and the distribution coefficients will be much larger. It is well established[147,148] that the distribution coefficients in PbTe, SnTe, etc., are all greater than 0.01. (Charged impurities in semiconductors with a gap less than about 0.2 eV tend to not be electrically active.[12] This makes accurate measurement of K difficult.) The distribution coefficients in metals are also generally much larger than for, say, Zn in Ge. Therefore, one may conclude that the present theory is in at least qualitative agreement with experiment in the small-band-gap semiconductors and semimetals. However, this will clearly not be true if Weiser's method is applied. The value of K for Hg in SnTe, for example, will be in error by at least a factor of 10^8.

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