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Spectroscopic Analysis of Cohesive Energies and Heats of Formation of Tetrahedrally Coordinated Semiconductors

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The heats of formation and Gibbs free energies of atomization of the following crystals are discussed: BN, BeO, AlP, GaAs, ZnSe, InSb, CdTe, ZnO, AlAs, GaP, ZnS, InP, CdS, AlSb, GaSb, ZnTe, InAs, CdSe, CuI, CuBr, and CuCl. It is shown that these heats and energies can be predicted using certain spectroscopic parameters which describe covalent and ionic parts of tetrahedral bonds. The role played by *s-p* dehybridization in the tendency towards metallization among heavier elements is also treated quantitatively. With one free parameter, the observed heats of formation can be fitted to about 10% accuracy. This may be compared to accuracies of order 50% for these crystals achieved by thermochemical molecular resonating-bond theories. Separate treatment of HgTe, HgSe, and HgS, is given in an appendix, where the anomalously small lattice constants of the Hg salts are explained.

1. INTRODUCTION

The heats of formation of chemical bonds play a fundamental role in molecular and crystal physics. In this paper we discuss these quantities for a number of semiconductors. Most of the crystals treated are binary compounds of formula $A^N B^{8-N}$, i.e., with eight *s-p* valence electrons per atom pair. The structures are then of the zinc-blende or wurtzite type, with ideal, or nearly ideal, tetrahedral coordination of four anions about each cation, and vice versa. According to conventional chemical usage, this means that the bonds in the crystal can be idealized as hybridized sp^3 valence orbitals oriented towards nearest neighbors. Differences in cohesive energy arise because of differences in ionicity of the bonds and differences in completeness of hybridization.

These are at least two ways in which one might hope to approach the problem of understanding the cohesive energies and heats of formation of these crystals. The first way involves solving the crystalline wave equation as well as possible, using the best obtainable one-electron potential, which has been made self-consistent and which includes an accurate approximation to exchange and correlation energies. To our knowledge, the only study which has seriously attempted to carry out this program is one for diamond.[1] This program has the drawback of being extremely complex and dealing with small differences between large quantities. For example, the energy required to remove eight electrons from two Ge atoms is about 200 eV or 4600 kcal/mole. This makes it very difficult to achieve sufficient accuracy to explain, e.g., the differences in heats of formation ΔH between GaAs, GaSb, InAs, and InSb which are 17, 10, 14, and 7.3 kcal/mole, respectively.

The second approach does not utilize the wave equation at all, but attempts to identify the factors which are responsible for the variations in the observed energies in terms of other observables. For example, one may construct a theory based on the heats of formation of molecular bonds, and use these to estimate heats of formation of crystals. To the extent that such a theory succeeds, one learns that the crystalline bonds are similar to molecular bonds and to the extent that it fails, one learns that the two situations are dissimilar.

We have chosen here a middle way between these two approaches. The basic elements of our theory are spectroscopic.[2-4] It is now believed[5] that the optical spectra of these crystals can be described almost entirely in one-electron terms. Thus, from the observed spectra it has proved possible to derive[6] pseudopotential form factors for each atom. These can be transferred[7] from one crystal structure to another, e.g., zinc-blende ZnS to wurtzite ZnS, and the spectrum of the second structure is then explained from parameters determined from the spectrum of the first structure. Thus the determination of parameters from the optical spectrum gives our theory a basis in quantum mechanics. For completeness this basis is reviewed in Sec. 2.

The basic difference between total energies (cohesive energies, heats of formation) on the one hand and one-electron energies on the other is that the former are much smaller than the latter. This is a general rule; it applies, e.g., to molecules such as aromatic hydrocarbons as described by Hückel theories.[8] As a result of this disparity it is generally thought that there is no simple relation between the two kinds of observables.[8] For the family of crystals described here, however, where the valence hybridization configuration is confined to rather narrow limits, we find that such a relation does exist. We believe this is the first time such a relation has been established over so wide a range of ionicity and lattice constant, i.e., over so large a domain of the Periodic Table.

It seems likely to us that the smallness of total energies compared to one-electron energies arises from the restrictions imposed on the bond wave functions by boundary conditions and by the exclusion principle. The way in which these reduce total energies is discussed in Sec. 3.

A related effect which greatly reduces heats of formation is the tendency towards metallic structures found in compounds composed of heavier elements, e.g., Pb compared to diamond and Si. The fact that this tendency contributes to heats of formation and crystalline stability as much as ionicity does was first discussed systematically from an entirely phenomenological point of view.[9] A quantum-mechanical explanation can be given[10] in terms of lowering of *s* valence energies compared to *p* valence energies. The importance of this effect for heats of formation is discussed in Sec. 4.

These sections complete our discussion of the factors which influence heats of formation and cohesive energies. In Secs. 5 and 6 we present formulas which fit the observed energies rather well, and which employ a minimal number of scaling parameters. The formulas are compared in Sec. 7 with Pauling's thermochemical molecular model.[11] Our model explains how the resonating-bond picture applies to this family of crystals, and does so within a quantum-mechanical framework.

2. SPECTROSCOPIC THEORY OF COVALENCY AND IONICITY

The spectroscopic theory is based on two average energy gaps, denoted by E_h and C, which represent, respectively, the effects of symmetric $(V_A + V_B)$ and antisymmetric $(V_A - V_B)$ potentials in the AB unit cell. The average is defined in terms of an isotropic energy gap E_g which appears in Penn's model[12] of the energy bands of a tetrahedrally coordinated semiconductor. Denote the Fermi energy of a free-electron gas with density equal to that of the s-p valence electrons by E_F, where

$$E_F = E(k_F) - E(0) \qquad (2.1)$$

and k_F is the Fermi momentum of the valence gas. Denote the valence plasma energy by $\hbar\omega_p$. Further, denote the real part of the electronic dielectric constant at long wavelengths and low frequencies by $\epsilon_1(0)$. Then to lowest order in E_g/E_F, Penn's relation is

$$\epsilon_1(0) = 1 + (\hbar\omega_p/E_g)^2(1 - E_g/4E_F). \qquad (2.2)$$

Typical values of $E_g/4E_F$ are 0.1, from which it follows that (2.2) gives results for E_g which are close to those which would be obtained from a simple two-level bonding-antibonding model.

To calculate E_h and C one now notes that the structure factors for $V_A + V_B$ and $V_A - V_B$ are proportional to $\cos \vec{G} \cdot \vec{\tau}$ and $i \sin \vec{G} \cdot \vec{\tau}$, respectively, where $2\vec{\tau}$ is the vector connecting nearest-neighbor A and B atoms and $\vec{G}$ is a reciprocal-lattice vector. Thus the scattering associated with $V_A - V_B$ is $\frac{1}{2}\pi$ out of phase with that associated with $V_A + V_B$. We therefore write

$$E_g = E_h + iC , \qquad (2.3)$$

and interpret E_g^2 in (2.2) as $|E_g|^2$, i.e.,

$$E_g^2 = E_h^2 + C^2. \qquad (2.4)$$

To include crystals containing atoms from the Ge, Sn, and Pb rows of the Periodic Table, allowance must be made for the presence of *nd* core electrons in *n*th-row atoms. The binding energies of these *d* subshells are only a few rydbergs or less. As a result, there is appreciable mixing of valence and conduction bands with *d* levels, and even before the onset of real *d*-core → *p*-conduction-band transitions at energies of order 1 Ry or more, the oscillator strengths of bonding → antibonding transitions are modified.[13] These modifications can be treated empirically with parameters for the Ge and Sn row.[13] The parameters needed for the Pb row are given in Appendix A of this paper.

So far as E_h is concerned, we see that the effect of $V_A + V_B$ should depend only on the lattice constant a. From E_h (diamond) and E_h(Si) one finds that[13]

$$E_h \propto a^{-2.5}, \qquad (2.5)$$

and from (2.2), (2.3), (2.5), and a and $\epsilon_1(0)$ for each crystal, one can solve for E_h and C. Values for 70 $A^N B^{8-N}$ crystals are given elsewhere.[13] In Appendix A, values are given for HgS, HgSe, and HgTe. Some representative values of E_h and C are given for the reader's convenience in Table I.

3. BOUNDARY CONDITIONS AND DEHYBRIDIZATION

Values for the cohesive energy ΔG_s (which represents the Gibbs free energy per atom of atomization at STP) and the homopolar energy gap E_h are

TABLE I. Some typical values of E_h and C in eV for some tetrahedrally coordinated $A^N B^{8-N}$ crystals. A complete list can be found in Ref. 13.

Crystal	E_h(eV)	C(eV)	Crystal	E_h(eV)	C(eV)
BN	13.1	7.71	InP	3.93	3.34
BeO	11.5	13.9	CdS	3.97	5.90
AlP	4.72	3.14	AlSb	3.53	3.10
GaAs	4.32	2.90	GaSb	3.55	2.10
ZnSe	4.29	5.60	ZnTe	3.59	4.48
InSb	3.08	2.10	InAs	3.67	2.74
CdTe	3.08	4.90	CdSe	3.61	5.50
ZnO	7.33	9.30	CuI	3.66	5.50
AlAs	4.38	2.67	CuBr	4.14	6.90
GaP	4.73	3.30	CuCl	4.83	8.30
ZnS	4.82	6.20			

shown for diamond, Si, Ge, and grey Sn in Table II. One-electron energies and total energies differ by the sum of electron-electron interaction energies, which in effect are counted twice in the sum of the one-electron energies.[14] It seems likely that electron-electron interaction energies are not very different in polyvalent atoms or in crystals, so that the main source of ΔG_s is the change in one-electron energy levels.

For the isolated atoms, one may imagine that one still has bonding and antibonding energy levels, but these are degenerate. In the crystal, the bonding level is depressed by $\frac{1}{2}E_g$, and the antibonding one raised by the same amount (see Fig. 1). With four electrons per atom, the average energy gain is apparently $4\times\frac{1}{2}E_g = 2E_g$. The values shown in Table II do not satisfy this relation very well. Moreover, in partially ionic compounds, the energy gap is larger than in purely covalent crystals of equal valence electron density. The total cohesive energy, however, is less. For these reasons, as mentioned in the Introduction, it is usually assumed that one cannot relate one-electron energy levels to total energy in a simple way. We shall now argue that this may be possible, and later enhance the plausibility of our arguments by actually finding such a relation.

One of the reasons the two-level estimate illustrated in Fig. 1 fails is that the actual electronic energy levels are broadened into energy bands $E_n(\vec{k})$, where k is the crystal momentum and n labels a band. Banding was not a serious problem in (2.2) because we were able to fix the total oscillator strength in terms of ω_p^2, which is simply proportional to the electron density N. It *is* a serious problem so far as the bonding and antibonding states are concerned. For example, if one represents the wave functions through linear combinations of atomic orbitals[15] (LCAOs) then a valence wave function $\varphi_{\vec{k}}$ will include some antibonding contribution at almost every point $\vec{k}$ in the valence band. (The only exception is the point $\vec{k}=0$ for diamond-type crystals, where inversion is included in the group of $\vec{k}$.) For a given *average* energy gap E_g, this mixing will be of order E_F/E_g, which means that for most points $\vec{k}$ in the valence band there is actually very little bonding.[12] This explains the smallness of ΔG_s compared to E_g.

TABLE II. Gibbs free energies of atomization at STP for diamond-type crystals. All energies in kcal/mole.

Crystal	E_g	ΔG_s	$\Delta G_s/E_F$
C	313	320	1.02
Si	111	197	1.78
Ge	100	161	1.61
Sn	71	128	1.80

This discussion can be rephrased in a manner that includes molecular bonds as well. The point is that the valence wave functions must satisfy certain boundary conditions; the symmetry and nature of these boundary conditions, in the crystal or in the molecule, is, in general, quite complex. (For an attempt to present these conditions pictorially for monatomic crystals, see Wigner and Seitz.[16] For covalent or diatomic crystals a pictorial approach is not even of much qualitative help.) After the boundary conditions have been satisfied, little of the energy associated with the original lowering of bonding energy remains.

A rough estimate of the amount of dehybridization caused by boundary conditions can be made using Penn's model.[12] One can calculate[17] the reduc-

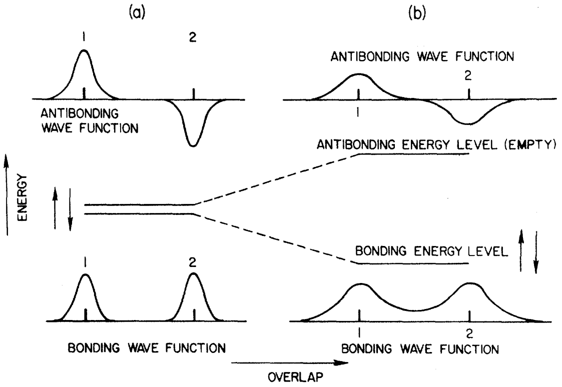

FIG. 1. Sketch showing how overlap effects lower total energy. (a) No overlap effects, bonding and antibonding levels degenerate in energy. (b) Overlap effects included, only bonding level is occupied by one electron of up spin and by one electron of down spin. The two atoms which are bonded are labeled 1 and 2, and the wave functions which are shown are only schematic.

tion in total one-electron energy in this model. For diamond and Si the results are of the right order of magnitude, but the trends in Table II are not reproduced, presumably because of the importance in Si of *p-d* hybridization,[18] which is not treated explicitly in the Penn model. Further comments on the role played by *p-d* hybridization can be found in Appendix B.

4. METALLIZATION AND DEHYBRIDIZATION

We now turn our attention to a specific dehybridization mechanism which is of great importance in determining heats of formation, especially for compounds composed of atoms from the Ge, Sn, or Pb rows of the Periodic Table. First consider a crystal with fixed E_g determined by (2. 2). Then we expect the largest bond energy when nearly all the optical oscillator strength is concentrated near $\hbar\omega = E_g$ with a small tail extending to higher energies. For example, if one conduction band should shift to much lower energy, then we would see appreciable absorption at an energy $E_1 \ll E_g$. Perturbation theory tells us that this lowered conduction band will hybridize with the valence bands by an amount proportional to $1/E_1 \gg 1/E_g$. This will reduce cohesive energies and heats of formation.

We show in Fig. 2 the absorptive part of the dielectric constant $\epsilon_2(\omega)$ for diamond, Si, and Ge plotted against the reduced frequency variable $x = \hbar\omega/E_h$. The largest peak in ϵ_2, labeled E_2, occurs near $x = 1$, as expected. However, as we go down the Periodic Table, a low-energy peak develops which has shifted to $E_1/E_2 = 0.5$ by the time we reach Ge. (It shifts even further, to $E_1/E_2 = 0.4$, in grey Sn, which is not shown.) This structure labeled E_1 has been identified as the "Λ peak" in a number of energy-band studies.[5,6,19] It is associated with transitions from a valence band of bonding *p* character to a conduction band of antibonding *s* character. The reduction in the energy of the latter with increasing atomic number is explicable in terms of atomic energy levels.[10]

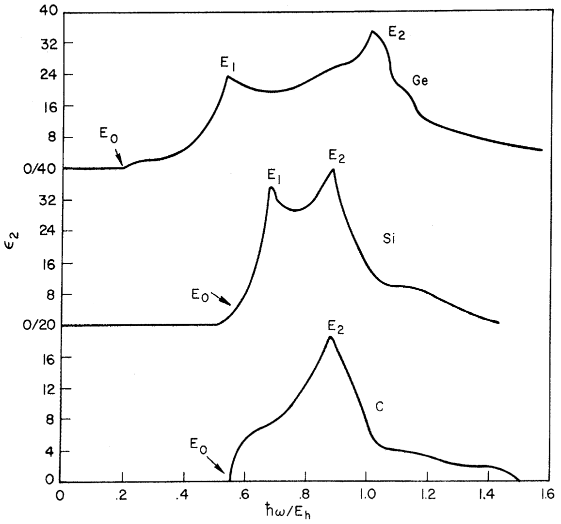

FIG. 2. Broad features of $\epsilon_2(\omega)$ for diamond-type crystals plotted in reduced units. The purpose of the figure is to show that the one-gap approximation is relatively good for diamond, but that a low-energy peak near $x = \hbar\omega/E_h = 0.5$ develops in Si and becomes stronger and shifts to smaller x in Ge and shifts further in grey Sn (not shown).

It has been known phenomenologically for some time[9] that with increasing atomic number of the constituent atoms (all other things, especially valence, being equal) that there is a tendency to replace covalent structures by metallic ones, a tendency which has been called "metallization." For example, in column IV C, Si, and Ge form the diamond structure, Pb is a fcc metal, and Sn may be either grey (diamond structure) or white (tetragonal metal).

Some authors have suggested that this tendency may be associated with the smallness of E_0, the smallest direct gap between valence and conduction bands. It is true that E_0 vanishes in grey Sn, but we regard this as an accident which plays no essential role in the metastability of Sn against grey or white forms. The reason for this is that the volume of k space near $\vec{k} = 0 = \Gamma$, for which the conduction-valence energy difference is E_0, is very small. A better measure of dehybridization and metallization is afforded by a suitably chosen average $\bar{E}$ of E_0 and of the energy E_1 of the lower peak in Fig. 2.

Using a drastically simplified band model, Heine and Jones have proposed[20] that the covalent metallic transition occurs when the first- and second-order pseudopotential contributions to E_h no longer interfere constructively, i. e., when the first-order contribution (which is V_{220} in pseudopotential language) goes through zero. We find this suggestion attractive, but the empirical pseudopotential form factors[6,7] are not sufficiently accurate for our present purposes. We therefore measure this effect spectroscopically, in terms of the factor

$$m = 1 - E_2/\bar{E}. \qquad (4.1)$$

Because $(1-m)$ measures the dehybridization of the wave function, the effect on the energy may depend on $(1-m)^2 = (E_2/\bar{E})^2$.

5. HEATS OF FORMATION

We now turn to the factors that influence specifically the heat of formation. We are concerned especially with crystals like InSb, GaSb, and InAs, which have small heats of formation, although our final formula fits all tetrahedrally coordinated binary crystals well.

First consider the energy which has received the greatest theoretical attention, the exchange and correlation energy. Doubtless the emphasis on this quantity stems from the pioneering work of Wigner and Seitz[14,16] (WS) on the alkali metals. There it was shown that exchange and correlation account for most of the cohesive energy. However, as emphasized by WS, the monovalent alkalies represent an exceptional case of quite low electron density. In covalent and ionic materials the role played by many-body effects is much less important. In particular, it was shown by WS (and it has since been confirmed by many others) that the exchange and correlation energy changes quite slowly with density. Contributions of many-body interactions to the heat of formation are therefore expected to be small.

Specifically, structure-dependent energies are likely to be associated with energy gaps. This appears explicitly in the Penn semiconductor model, as discussed elsewhere.[12,17] Metals like In do not have close-packed structures, and one expects some covalent contribution to their cohesive energy. However, these contributions are expected to be small, because (unlike tetrahedrally coordinated crystals) their Fermi surfaces are in general far from congruent to the Jones zone.[20]

In order to include the ionic-ordering energy which causes the atoms A and B to form interpenetrating sublattices in the A^NB^{8-N} crystal, we assume that the heat of formation ΔH is proportional to f_i, the spectroscopic ionicity which is defined by

$$f_i = C^2/(E_h^2 + C^2), \tag{5.1}$$

where E_h and C are the average covalent and ionic energy gaps defined in Sec. 2. Tables of f_i are available.[19] Dehybridization effects are included in two ways.

(a) The fraction of covalent energy which is not lost by dehybridization depends on the extent to which valence and conduction bands mix. This, in turn, depends on the lattice constant a through competition between kinetic and potential energies. Thus we assume $\Delta H \propto a^{-s}$ and determine s from experiment.

(b) The difference in energy between the tetrahedral binary structure and the elemental metals is proportional to $D = [1 - b(E_2/\bar{E})^2]$, where the value of b^{-1} is expected to be close to the ratio of $(E_2/\bar{E})^2$ in grey Sn, which is metastable relative to the metallic form white Sn.

We have mentioned previously that $\bar{E}$ is expected to lie between the optical energies E_0 and E_1. We find that any value of $\bar{E}$ in the range

$$E_0 \le \bar{E} \le E_1 \tag{5.2}$$

gives about the same fit to experiment. In the calculations reported below, we used

$$\bar{E} = \tfrac{1}{2}(E_0 + E_1) \tag{5.3}$$

because this appears plausible in view of the relative strengths of the E_0 and E_1 peaks. (The E_1 peak is several orders of magnitude larger than the E_0 peak, but as $E_0 \ll E_1$ in some cases, this increases its dehybridizing effects.)

In conclusion, our formula for ΔH is

$$\Delta H(AB) = \Delta H_0 \left(\frac{a_{Ge}}{a_{AB}}\right)^s \left[1 - b\left(\frac{E_2}{E}\right)^2\right] f_i(AB), \tag{5.4}$$

where $\bar{E}$ is given by (5.3) and ΔH_0 is an overall scaling factor.

The value of s is fixed chiefly by ΔH in three crystals: BN, BeO, and ZnO, which are the three crystals containing first-row atoms (and hence small a) about whose optical spectra the most is known. At STP, both N and O are found as gaseous diatomic molecules. Therefore, according to Pauling,[11] corrections should be made to ΔH of 55 and 26 kcal/mole, per N and O atom per formula unit, respectively (triple and double bonds, respectively, instead of single or metallic bonds). These corrections are somewhat arbitrary, but we have subtracted them from the observed (negative) heats of formation (corresponding to greater magnitude of ΔH). This gives

$$s = 4. \tag{5.5}$$

Some correction should also be made for the Cu salts, because part of the cohesive energy of metallic Cu stems from the d electrons, which play a less important role in salts. We have therefore subtracted 20 kcal/mole (about one-half of the difference in cohesive energy between K and Cu) from the observed values of ΔH for CuCl, CuBr, and CuI. The scaling factor

$$\Delta H_0 = 71.7 \text{ kcal/mole} \tag{5.6}$$

is chosen to make the average error in fitting to experiment zero for the crystals shown in Table III. The value of E_1 is not known experimentally for the crystals marked with an asterisk; in these cases the theoretical values[19] of E_1 were used. The value of b used is

$$b = 0.0467, \tag{5.7}$$

which is the same as the value of $(\bar{E}/E_2)^2$ in grey Sn. With these values of ΔH_0, s and b (5.4) is accurate to about 10%.

One of the interesting consequences of (5.4) is

TABLE III. Values of ΔH according to Pauling's thermochemical molecular theory and the present spectroscopic theory with $s = 4$ are compared to experimental values. The former and latter have been corrected for compounds containing N, O, or Cu as described in the text. All energies in kcal/mole.

Crystal	ΔH (Pauling)	ΔH (spectro)	ΔH (adj expt)
BN*	69.0	104.0	116.2
BeO*	184.0	199.3	169.1
AlP*	24.8	24.0	39.8
GaAs	11.0	17.0	17
ZnSe	29.4	41.4	39
InSb	2.8	8.2	7.3
CdTe	4.4	22.9	22.1
ZnO*	166.1	93.7	109.2
AlAs*	17.3	18.1	27.8
GaP	17.3	26.9	24.4
ZnS	37.3	45.9	49.2
InP	11.0	20.4	21.2
CdS	29.4	36.2	38.7
AlSb	11.0	19.5	
GaSb	6.2	9.2	10.0
ZnTe	11.5	25.1	28.1
InAs	6.2	11.3	14.0
CdSe	22.5	30.0	
CuI*	8.3	14.0	16.2
CuBr*	18.6	23.3	25.0
CuCl	27.8	39.9	32.8

that when $\bar{E}$ is small enough, $A^N B^{8-N}$ crystals need no longer be tetrahedrally coordinated even though $f_i \ll 0.78$, the critical value for all other cases to transform to the rock-salt structure.[3,19] Thus it appears that TlBi and TlSb are the only compounds with $N = 3$ that have the rock-salt structure.[21]

Some discussion of alternative values of the parameter s is in order. If Pauling's multiple-bond corrections for N and O are omitted, an equally good fit (accurate to about 10%) to the observed values is achieved with $s = 3$ and $\Delta H_0 = 68.6$ kcal/mole [see Table IV]. If we view the heat of formation as arising from the terms of order

$$(E_g^2/E_F)\ \ln(E_g/E_F), \tag{5.8}$$

calculated[17] for the model semiconductor, then at least for $N = 3$ crystals, where $C < E_h$, E_g scales like E_h, i.e., like $a^{-2.5}$ [see Eq. (2.5)]. Then because $E_F \propto a^{-2}$ to logarithmic order, (5.8) scales like a^{-3}. Thus there is some theoretical justification for using $s = 3$ and dropping the Pauling multiple-bond corrections. This appears to be largely a question of taste which we shall not pursue here.

There are two striking features in our results. The first is that ΔH is proportional to the spectroscopic ionicity f_i. This point will be discussed in more detail in Sec. 7. The second is our success in fitting the very small heats of formation of InSb, InAs, and GaSb at the same time that the much larger heats of formation of other crystals which have nearly the same lattice constant are explained. This success derives from the presence of the dehybridization factor D.

The importance of the E_0 gap in determining critical pressures for phase transitions from tetrahedral to metallic or rock-salt structures was first stressed by Jamieson.[22] It has, however, been pointed out by Adler[22] that the E_0 (and also E_1) gaps *increase* with pressure, which would appear to stabilize the tetrahedral structure. This effect can be explained by noting that

$$b = (\bar{E}/E_2)^2_{\text{grey Sn}} \tag{5.9}$$

will probably increase with pressure more rapidly than $(\bar{E}/E_2)^2_{AB}$. (Very little pressure is re-

TABLE IV. Comparison of values of ΔH obtained theoretically with $s = 3$ with experimental values. Only the values for compounds containing Cu have been adjusted, no correction has been made for N or O atoms. All energies in kcal/mole. The theoretical spectroscopic values in this table and in Table III for crystals marked with an asterisk have utilized theoretical values of E_1 and/or E_2 taken from Ref. 19, while the theoretical values for the remaining crystals are based entirely on observed values of E_0, E_1, E_2, and ϵ_0. The experimental values are taken from Wagman *et al.*,[a] the value for GaP is taken from Ref. 25.

Crystal	$-\Delta H$ (Pauling)	$-\Delta H$(spectro.)	$-\Delta H_{\text{expt}}$
BN*	13.6	63.6	60.8
BeO*	158.0	128.5	143.1
AlP*	24.8	22.2	39.8
GaAs	11.0	16.3	17
ZnSe	29.4	39.8	39
InSb	2.8	9.0	7.3
CdTe	4.4	25.1	22.1
ZnO*	140.1	72.5	83.2
AlAs*	17.3	17.3	27.8
GaP	17.3	24.8	24.4
ZnS	37.3	42.1	49.2
InP	11.0	20.3	21.2
CdS	29.4	35.8	38.7
AlSb	11.0	20.3	
GaSb	6.2	9.5	10.0
ZnTe	11.5	25.9	28.1
InAs	6.2	11.5	14.0
CdSe	22.5	30.9	32.6[b]
CuI*	8.3	14.8	16.2
CuBr*	18.6	22.7	25.0
CuCl*	27.8	34.9	32.8

[a] D. D. Wagman *et al.*, *National Bureau of Standards Technical Note No.* 270-3 (U. S. GPO, Washington, D. C., 1968).

[b] P. Goldfinger and M. Jeunehomme, Trans. Faraday Soc. 59, 2851 (1963).

quired to transform grey Sn into white Sn.) We hope to return to this question elsewhere.

6. COHESIVE ENERGIES

We define the cohesive energy ΔG_{AB} as the Gibbs free energy of atomization of the A^NB^{8-N} crystal at STP. This is given by

$$\Delta G_{AB} = \delta G_{AB} + \Delta G_A + \Delta G_B, \tag{6.1}$$

where ΔG_A and ΔG_B are the free energies required to atomize the elements and δG_{AB} is the free energy of formation.

To determine the dependence of ΔG_{AB} on E_h and C, consider the diamond-type crystals with $A = B$ and $N = 4$. Because E_h is a function of lattice constant a, one may investigate the equivalent question of the dependence of ΔG_{AA} on a. If one assumes that

$$\Delta G_{AA} \propto a^{-n}, \tag{6.2}$$

then one finds (broadly speaking) that $n = 2$ gives a good fit. Because kinetic energy also scales like (6.2) with $n = 2$, and because a convenient measure of kinetic energy is the Fermi energy E_F of a free-electron gas of density equal to that of the valence electrons, one may measure ΔG_{AA} in units of E_F. When this is done[18] the results shown in Table V are obtained. Clearly, $\Delta G_{AA}/E_F$ is not constant. This is because there is an important contribution to ΔG_{AA} from p-d hybridization. This contribution is virtually absent in diamond, because of the large energy required to promote $2p$ states to $3d$ states. It reaches a peak in Si, just before the $3d$ transition series begins. It is reduced in Ge and Sn, because the $4d$ and $5d$ valence wave functions, respectively, are orthogonal to $3d$ and $4d$ core states. This explanation of p-d hybridization has also been utilized to explain[11] trends in the molecular binding energies of diatomic halides and polyatomic hydrides.

The cases where the cores of A and B are isoelectronic are of particular interest because in such cases a is virtually independent of N, i.e., only C varies appreciably as a function of N. This also holds true for any sequence A^NB^{8-N}, providing either A or B belongs to one row and B or A belongs to another. We therefore plot in Fig. 3 $\Delta G_s(AB)$ for all such sequences, with one exception. This is compounds with one, and only one, first-row atom. In this case, the size disparity between the cores of the two atoms is so great that there is no simple pattern.

TABLE V. Comparison of cohesive energies in kcal/mole in diamond-type crystals with Fermi energy of free-electron gas of density equal to that of the valence electrons.

Crystal	E_F	ΔG_S	$\Delta G_S/E_F$
C	667	320	0.478
Si	287	197	0.685
Ge	265	161	0.607
Sn	210	128	0.608

The results which are illustrated in Fig. 3 are the following.

(a) When the cores are strictly isoelectronic, i.e., both atoms belong to the row R, the following simple relation[18] holds to within the limits of experimental error:

$$\Delta G_s(R, f_i) = \Delta G_s(R, 0)[1 - k(R) f_i], \tag{6.3}$$

where f_i is the spectroscopically defined ionicity, accurate to 1%.

(b) When one atom comes from row R_1 and one atom from row R_2, a relation similar to (6.3) is approximately valid,[18] with $R \approx \frac{1}{2}(R_1 + R_2)$. However, there is a small tendency for $\Delta G_s(AB)$ to be displaced towards the value given by (6.3) with $R = R_B$, i.e., there is a small shift towards the linear relation valid for the row R to which the *anion* belongs. For GaSb and InAs ($R_1 = 3$, $R_2 = 4$), this shift amounts to ± 6 kcal/ mole, respectively, and it represents a core effect absent from any valence-bond model.

(c) The values of $k(R)$ are remarkably constant. The only appreciable variation is the difference between the value found for $R = 1$, $k(1) = 100$ kcal/mole and the values for other values of R, $k(R \geq 2) = 80$ kcal/mole. If one writes

$$k(R(a)) \propto a^{-n_2}, \tag{6.4}$$

then $n_2 \approx 0.5$.

The scaling results (6.3) and (6.4) suggest the following picture for the binding energy of tetrahedrally coordinated crystals. For the homopolar values $\Delta G_s(0)$ it appears that most of the binding energy has kinetic character and is therefore associated with delocalized (itinerant) valence electrons. This confirms the relevance of the single-particle approximation because even though the one-electron functions ψ_i have not been used to calculate ΔG, the translational periodicity of the crystal requires ψ_i to have the Bloch or delocalized form. If similar scaling arguments are applied to small molecules (such as MH_3, where M = N, P, As, or Sb), one finds $n_1 = 1$, i.e., the binding energy scales like a potential energy, as one would expect for localized bonds. Thus scaling provides a simple way of showing that localized bonds are appropriate for discussing cohesive energies in molecules, but that the valence electrons in covalent crystals are itinerant, in much the same way as in metals like Na or Al.

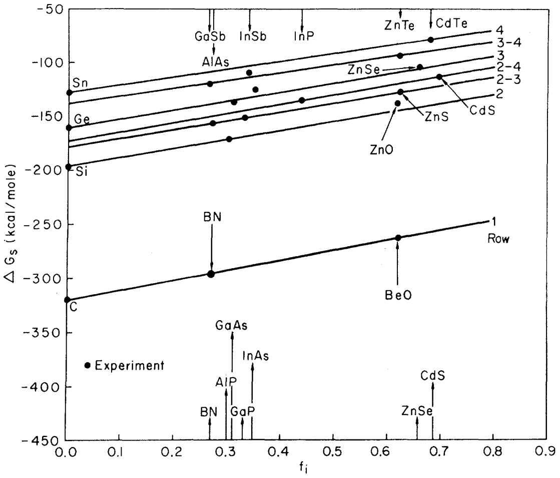

FIG. 3. Plot of the Gibbs free energy of atomization of $A^N B^{8-N}$ crystals for sequences in which one atom belongs to a row R_1 of the Periodic Table and the second atom belongs to a row R_2. The lattice constant is approximately the same for all crystals belonging to the same sequence. The energies of atomization are seen to be linear functions of ionicity. The significance of the slopes is discussed in the text.

The second scaling result concerns $k(R)$, the slope which describes the reduction in cohesive energy with increasing magnitude of C compared to E_h. The fact that $n_2 \approx 0.5$ suggests that $|\Delta G|$ is reduced because energy is required to screen $V_A - V_B = V_{\text{ionic}}$. Dielectric screening can be described at short wavelengths by the Thomas-Fermi screening wavelength $\lambda = k_s^{-1}$. This suggests

$$k(l) \propto V_{\text{ionic}}\,(a/\lambda), \tag{6.5}$$

since when λ is large, little screening of V_{ionic} has taken place. Of course, $V_{\text{ionic}} \propto a^{-1}$, and the Thomas-Fermi formula shows $\lambda \propto a^{-1/2}$. Thus (6.5) gives $n_2 = 0.5$, as observed experimentally.

7. RESONATING-BOND THEORY

It is instructive to compare Eq. (5.4) with Pauling's formula[11]

$$\Delta H_{AB} = N(X_A - X_B)^2 B_0. \tag{7.1}$$

Here ΔH_{AB} is the observed heat of formation augmented by multiple-bond corrections when $B = N$ or 0. The parameters X_A and X_B are adjustable and are fixed to fit molecular heats of reaction. One finds that (7.1) fits the observed heats of reaction with an rms accuracy of 50%, although in most cases the agreement is good to 30–50%. One should perhaps not expect better agreement between crystalline and molecular energies.

It has been noted[2] that C_{AB} is the crystalline analog of $\Delta X_{AB} = X_A - X_B$, so that to order ΔX_{AB}^2, (7.1) and (5.4) agree. However, when $C_{AB} > E_h$, one no longer can say that

$$f_i(AB) = C_{AB}^2/(E_h^2 + C_{AB}^2) \tag{7.2}$$

is proportional to C_{AB}^2. It turns out that $C_{AB} < E_h$ for $A^N B^{8-N}$ crystals with $N = 3$, but for $N = 2$ one has the reverse inequality $C_{AB} > E_h$. This saturation effect is simulated in Pauling's theory by the presence of the factor N, which measures the number of resonating bonds. In the spectroscopic theory C also doubles (if the bond length does not change, e.g., on going from GaAs to ZnSe), but saturation is achieved because of the demoninator $(E_h^2 + C^2)^{-1}$ in the definition

$$f_i = C^2/(E_h^2 + C^2). \tag{7.3}$$

One may compare this with Pauling's expression (7.1) by rewriting (7.3) as

$$f_i = (C^2/E_h^2)(E_h^2/E_h^2 + C^2) = (C^2/E_h^2) f_c, \tag{7.4}$$

where f_c is the fraction of covalent character defined by Eq. (5.26). One sees that the factor C^2/E_h^2 corresponds to $(X_A - X_B)^2$, while f_c corresponds to $\frac{1}{4}N$. The variation of N is integral, while f_c is a continuous spectroscopic variable which has no artificial atomistic character (i.e., counting s and p states in a partial-wave expansion as one does to define valence). In general, f_c is not proportional to N, i.e., f_c is *not* the same for all $N = 3$ crystals, and the average value of f_c for all $N = 2$ crystals is *not* $\frac{2}{3}$ the value of f_c for all $N = 3$ crystals. (The actual ratio is closer to $\frac{3}{7}$.) This explains, to some extent, the point[23] that Pauling's choice of molecular parameters gives good results for $N = 2$ crystals, but not for $N = 3$. Indeed it was shown[23] that when the scaling energy B_0 in (7.1) is chosen to fit the case $N = 2$, one may solve (7.1) for all $N = 3$ crystals for N itself, regarded as an unknown. The value obtained is 4.2 ± 1.5. [The large error presumably stems from the inability of (7.1) to absorb the factors $D(E_0, E_1, E_2)$ and a^{-s} in (5.4) entirely into the electronegativity parameters X_A and X_B.] Note that

$$\tfrac{2}{4.2} \approx \langle f_c \rangle_{N=2} / \langle f_c \rangle_{N=3} / \approx \tfrac{3}{7} \neq \tfrac{2}{3}. \tag{7.5}$$

Thus (7.5) gives fairly good statistical evidence that $4f_c$ is a better measure of the number of "effective" or "resonating" bonds than is the classical valence N. This is in accordance with the intuitive interpretation of $f_c = 1 - f_i$ as a measure of the fraction of covalent character of the sp^3 bonds.

Another way of interpreting the ratio

$$\langle f_c\rangle_{N=2}/\langle f_c\rangle_{N=3}$$

present in (7.5) is to note that it is approximately equal to $(\frac{2}{3})^2$, i.e., Pauling's formula (7.1) would give better agreement with experiment *for crystals* if NB_0 were replaced by $\frac{1}{2}N^2B_0$. The appearance of the factor N^2 is consistent with the itinerant nature (energy scales like a^{-2}) of semiconductor binding noted previously in Sec. 6. It has the simple physical interpretation that the heat of formation depends on the ability of an electron in one of N bonds in the crystal to "hop" to one of N neighboring bonds. In some molecules, on the other hand, different kinds of scaling are found. In the CH_4 family, bond energies scale like $a^{-3/2}$; in the NH_3 family, like a^{-1}. In the latter family the bonds are nearly perpendicular, there is little hybridization, and the binding is of a more localized nature; so that a factor N would be approprate. Although one cannot argue that the present picture is unique, we find the factor N^2 for itinerant crystalline bonds to be a natural reflection of the difference in binding between nonaromatic covalent molecules and covalent crystals. In conclusion, note that this argument applies only to the *average* of all $N = 2$ crystals compared to the *average* of all $N = 3$ crystals. In any individual case, f_c is a better variable to use than N^2, because of the continuous nature of the former and the discrete nature of the latter.

8. $A^{II}B^{IV}C^{V}{}_2$ COMPOUNDS

Compounds such as $ZnSiP_2$ and $CdSiP_2$ have been discussed in a number of papers by Russian workers.[24] The atoms in these crystals are either exactly tetrahedrally coordinated (sphalerite structure) or nearly so (chalcopyrite structure) and the compounds can be regarded as analogues of A^NB^{8-N} crystals with $N = 3$. At present the dielectric constants and optical spectra of these crystals are not known with sufficient precision to warrant an extension of the spectroscopic theory of A^NB^{8-N} crystals to them. However, the heats of formation of $ZnSiP_2$ and $CdSiP_2$ have recently been measured,[23] and it is of interest to compare these with the heat of formation of GaP.[25] The values are (in kcal/equivalent two-atom mole)

$ZnSiP_2$ and $CdSiP_2$ ~19,

GaP: 24.4.

Our formula (5.4) for ΔH depends on several factors. The lattice constants, or more properly bond lengths, are all very similar. The experimental values of E_2 and $\overline{E}$ seem to be quite similar in all three crystals as well.[24] We are thus left with the factor f_i.

We suggest that f_i be decomposed as in (7.4), and that the factor C^2/E_h^2 be treated as approximately the same in the three crystals. We saw in Sec. 7 that f_c is similar to $(\frac{1}{4}N)^2$, where N is the number of resonating bonds in Pauling's classical chemical model. In $ZnSiP_2$ we have two kinds of bonds to consider: Zn-P and Si-P. In the case of ZnP, the Zn atom can contribute only two electrons, so that f_c for this bond may be close to f_c in ZnS. Similarly, in the Si-P bond, f_c may be close to the AlP-bond value. This suggests that

$$\begin{aligned} f_c(ZnSiP_2) &= \tfrac{1}{2}[f_c(ZnS) + f_c(AlP)] \\ &= \tfrac{1}{2}(0.37 + 0.70), \qquad (8.1) \end{aligned}$$

where the numerical values are taken from Ref. 19. By comparison, f_c in GaP is 0.63. Thus one has

$$\begin{aligned} \Delta H(ZnSiP_2) &= \Delta H(GaP)(0.53/0.63) \\ &= 20.5\ \text{kcal/(equiv. mole)}. \qquad (8.2) \end{aligned}$$

Of course, (8.2) is in good agreement with experiment (by construction). The analogies made *are* arbitrary, but at the same time we believe them to be of some interest, as they suggest that bond counting may be a useful way of approaching heats of formation in cases where the number of valence electrons per atom pair is equal to eight only on the average.

9. CONCLUSIONS

The heats of formation of crystalline compounds have traditionally been considered by solid-state theorists to be beyond the limits of accuracy achievable in quantum-mechanical calculations. We have shown here that by focusing attention on the single family of compounds with tetrahedral coordination one can exploit the similarities in optical spectra to construct a quantitative theory. The theory elucidates the specific mechanisms which play an important role in determining heats of formation in this family. Thus it is not only more accurate than general thermochemical theories of the heats of formation of molecular bonds but it also provides insight into characteristically crystalline effects. One of these is dehybridization, another is the importance of the factor f_c or N^2 in measuring resonating-bond effects.

Another way of appreciating the content of this theory is to assess both the number of independent factors in the theory and the number of independent parameters. There are about three of each in the present theory. By contrast, Pauling's theory [11] has basically one idea (the concept of extra-ionic energy) and several score parameters (the elemental electronegativities). We feel that the present theory provides a more informative and less arbitrary picture of the heats of formation of tetrahedrally coordinated compounds.

ACKNOWLEDGMENTS

We are grateful to the authors of Ref. 23 for permission to quote their experimental values prior to publication.

APPENDIX A

The two parameters E_h and C which characterize the spectroscopic theory of covalent bonding were determined in previous papers [2,13,19] by studying the electronic spectra of diamond-type *AA* crystals (to determine E_h) and then by extending the analysis to zinc-blende *AB* crystals, especially in cases where the cores of *A* and *B* are isoelectronic. (The latter form horizontal sequences such as Ge, GaAs, and ZnSe.) The theory was worked out completely for elements belonging to the first four rows of the Periodic Table.

In attempting to extend the theory to the compounds of elements in the fifth or Pb row of the Periodic Table, one faces several difficulties not encountered with the first four rows. The group-IV element of the fifth row, Pb, does not form a diamond-type crystal. Indeed none of the horizontal sequence of compounds (Pb, TlBi, HgPo, and AuAt) forms a tetrahedrally coordinated structure. Values of the low-frequency limit of the electronic contribution to the dielectric constant, the primary empirical parameter of the theory, [2,13] are not available for the few skew compounds that do form tetrahedrally coordinated diatomic crystals containing one element from the fifth row.

Because of the above difficulties and because of the limited number of tetrahedrally coordinated compounds containing fifth-row elements that have been prepared and studied, the following discussion should be considered tentative. Furthermore, only HgS, HgSe, and HgTe in the zinc-blende structure will be explicitly discussed.

It is now generally agreed that HgSe and HgTe are semimetals[26-31] having the Γ_6 and Γ_8 levels inverted relative to the normal zinc-blende semiconductors (e.g., InSb) in the manner proposed by Groves and Paul[32] for gray tin. Reflectivity spectra in the visible and ultraviolet [33,34] and thermoreflectance in the visible[35] are also available for HgSe and HgTe. However, we are not aware of any spectra that have been obtained for HgS in the zinc-blende structure. (It is known that the color of this substance is black, as opposed to the cinnabar form which is red, so that its lowest band gap must be below the visible.) Preliminary orthogonalized-plane-wave (OPW) calculations for these three materials have been presented by Herman, Kortum, Kuglin, and Shay. [36]

When one attempts to fit the parameters of the spectroscopic theory, [19] C and D_{av}, to the spectra observed in HgSe and HgTe, three anomalies are apparent. Whereas one would expect the lattice constants of Hg salts to be larger than the lattice constants of the corresponding Cd salts, the observed lattice constant of HgTe is less than that of CdTe, InSb, and Sn and that of HgSe is about the same as that of CdSe, ZnTe, InAs, and GaSb. [21] Although a reasonable choice of parameters fits [19] the higher band gaps to experiment with no difficulty, there is no choice of C and D_{av} for either HgSe or HgTe which can fit E_0 and E_1 to experiment within the accuracy expected (±0.2 eV) from our experience with 19 other semiconductors. [19] The temperature dependence of the E_0 band gap is anomalously large and is opposite in sign to that in normal semiconductors (e.g., InSb). [26]

We propose that these three anomalies have the same origin. We suppose that the reduction of the observed lattice constant results from the compression of the crystal from the density expected on the basis of covalent radii. [37,38] This compression occurs because the bulk modulus of the crystal at the expected density is small[39] and the band contribution to the cohesive energy (and heat of formation) increases rapidly with compression. Therefore we shall estimate the uncompressed lattice constants of the Hg salts and calculate band structure fixing the parameters, so that after the crystal is compressed to the observed density, the calculated gaps agree with experiment. We then show that this assignment of parameters yields calculated values of the heats of formation in good agreement with experiment. [40]

To determine the uncompressed lattice constants, we shall assume that the covalent radius of the fifth-row elements is 4% greater than that of the fourth-row elements. (Indeed, Pauling[38] indicates that the covalent radius of Pb is 4% greater than that of Sn.) Thus the uncompressed lattice constants of HgTe, HgSe, and HgS are taken to be 6.621, 6.203, and 5.977 Å, respectively, as compared with the observed (compressed) values[21] 6.429, 6.084, and 5.852 Å. Thus we shall assume that the volume compression is 9.2, 6.0, and 6.6%, respectively. We estimate the energy shift per unit dilatation as 7 eV for E_0[41] so that the effect of the compression will be to raise the E_0 ($\Gamma_{15}-\Gamma_1$) gaps by 0.7, 0.4, and 0.5 eV, respectively. We also assume that the E_1 ($\Lambda_3-\Lambda_1$) gaps should be raised about 0.5 as much as the E_0 gap and the $E_2\,(X_4 - X_1)$ gaps about 0.2 as much while the effect on the other gaps should be negligible for our purpose.[41]

With these assumptions we may calculate[19] the band gaps shown in Table VI using the parameters shown in Table VII. All values shown are for the gaps with the effect of spin-orbit splitting removed. (We have assumed the E_0 splittings for HgTe and HgSe are 1.20 and 0.45 eV, respectively.) The values of C and D_{av} for HgTe and HgSe were selected to give a good fit of the compressed spectra to experiment. The C and f_i values so obtained are consistent with the values expected from the theory of Ref. 13. The value of f_i for HgS was fixed at 0.79 because that compound also occurs in the cinnabar structure, which may be viewed as a distortion of the NaCl structure.[21] It has previously been demonstrated[3,4,19] that the critical ionicity delineating the boundary between the compounds forming tetrahedral crystals and those forming NaCl-type crystals is 0.79. This value of f_i and thus C is also consistent with Eq. (4.5) and $b = 1.5$ in Ref. 13. The value of D_{av} for HgS was estimated from the value assumed for HgSe.[42]

In comparing the calculated and observed band gaps of HgTe and HgSe, we have identified the peaks observed at 6.55 and 7.6 eV, respectively, with $E_{1'}$ transition. This is the same assignment as was made by Cardona and Greenaway.[33] However, Scouler and Wright[34] and Phillips[5] have argued that this assignment could not be correct because the spin-orbit splitting did not correspond to that observed in the E_1 peaks. This argument has proved most useful in analyzing the spectra of most zincblende crystals.[5] However, here we believe that this objection is not valid because of the inversion of the Γ_6 and Γ_8 levels. Such an inversion distorts the spin-orbit splitting of the E_1 peaks because of the proximity[5] of the Λ critical point to Γ.

In Table VII we also indicate the values of ΔH calculated on the basis of the predicted band structure using Eq. (5.4) and $s = 3$. It is seen that the calculated and experimental values agree to within 4 kcal/mole, compared with the experimental uncertainty[43] of order 2 kcal/mole.

The results in Tables VI and VII yield some information as to the adequacy of the assumptions we have made. For both HgTe and HgSe, the calculated E_0 gap is 0.2 eV lower than observed while the calculated E_1 gap is 0.2 eV too high. This suggests that either we have underestimated the extent of the compression from the density indicated by the covalent radii, i.e., underestimated the radii of the fifth-row elements, or we have underestimated the derivative of the E_0 gap with compression and overestimated the derivative of the E_1 gap. It would be useful if experiments similar to those of Zallen and Paul[41] could be performed on HgTe and HgSe to determine these derivatives.

TABLE VI. Band-structure parameters for the Hg salts. The energies quoted for the E_0, E_1, and E_1' gaps represent weighted averages of the spin-orbit split energies.

	E_0 eV	E_1 eV	E_{2A} eV	E_{2B} eV	E_0' eV	E_1' eV
HgTe Expanded ($a = 6.621$ Å)	−0.8	2.40	4.60	5.17	4.63	6.40
HgTe Compressed ($a = 6.429$ Å)	−0.1	2.7	4.7	5.3	4.6	6.4
HgTe Experiment ($a = 6.429$ Å)	+0.1[a]	2.5[b]	4.9[c]	5.4[c]	4.3[c]	6.55[c]
HgSe Expanded ($a = 6.203$ Å)	−0.7	3.0	5.6	6.3	5.65	7.64
HgSe Compressed ($a = 6.084$ Å)	−0.3	3.2	5.7	6.4	5.7	7.6
HgSe Experiment ($a = 6.084$ Å)	−0.1[a]	3.0[b]	5.7[c]	6.45[c]	5.7[c]	7.6[c]
HgS Expanded ($a = 5.977$ Å)	−0.6	4.3	7.61	8.65	7.83	10.10
HgS Compressed ($a = 5.852$ Å)	−0.1	4.5	7.8	8.8	7.8	10.1

[a] References 27 and 29.
[b] Reference 35.
[c] References 33 and 34.

TABLE VII. Bond parameters for the Hg salts and values of heats of formation. For the reader's convenience the corresponding values for the Cd salts are listed to facilitate comparison.

	D_{av}	E_h eV	C eV	f_i	$-\Delta H$ calc kcal/mole	$-\Delta H$ expt kcal/mole
HgTe	1.60	2.92	4.0	0.65	10.2	10
HgSe	1.49	3.43	5.0	0.68	7.0	11
HgS	1.43	3.76	7.3	0.79	16.4	12.8
CdTe	1.43	3.1	4.4	0.68	25.1	22.1
CdSe	1.34	3.6	5.5	0.70	30.9	32.6
CdS	1.20	4.0	5.9	0.69	35.8	38.7

When considering the calculated heats of formation in Table VII, one should bear in mind that in these cases the dehybridization term is quite large. Thus the calculated values are quite sensitive to the values of $\overline{E}$ and E_2 used in Eq. (5.4). If, for example, for HgSe we were to assume E_2 were 5.7 eV instead of 6.0 eV (the average of the calculated E_{2A} and E_{2B} values), then the value calculated for $-\Delta H$ would be 10.4 instead of 7.0 kcal/mole. However, in view of the uncertainty of the experimental data,[43] we do not make such corrections here.

We conclude this appendix by comparing our band-gap calculation with the preliminary OPW calculation of Herman *et al.*[36] Herman *et al.* adjusted their calculation of HgTe and HgSe to fit the observed E_0 and E_1 gaps at the observed lattice constant. They did not present a theoretical ϵ_2 or reflectivity spectra so that the comparison with experiment is restricted. However, Herman *et al.*[36] concluded that the experimental identification of the large E_2 peak was incompatible with their calculation. Their E_1 peak is reasonably compatible with experiment if the Cardona-Greenaway[33] assignment is made instead of the Scouler-Wright[34] assignment. We feel that these two observations support our contention that the Cardona-Greenaway assignment is correct and that the spectra of HgTe and HgSe can only be understood as resulting from the compression of the crystal from the density predicted on the basis of covalent radii.

For HgS, Herman *et al.* made no adjustment to experiment as no values for E_0 and E_1 were available. They obtained estimates for E_0 and E_1 of 1.5 and 5.1 eV as compared with our estimates of -0.1 and 4.5 eV, respectively. The other gaps are in fair agreement. We note that before adjusting to experiment Herman *et al.* were overestimating the E_0 gap in HgTe and HgSe by about 1 eV.[36] Furthermore, with our estimate we obtain fair agreement with experiment in the calculated value of ΔH, whereas if we use Herman's estimate we would calculate $-\Delta H = 38$ kcal/mole which is three times the reported value.

The contraction of HgSe and HgTe discussed here casts some light on the question of excitonic instabilities which has received much theoretical attention.[44] In semiconductors it has been suggested that such instabilities may give rise to lattice distortions if valence- and conduction-band edges should occur at different points in $\vec{k}$ space and be quasidegenerate in energy (to 0.01 eV or better). It has been pointed out by one of us[10] that in two-dimensional crystals of the layer or sandwich type (such as GaSe), excitonic binding energies are much larger (of order 0.2 eV), but that even in those crystals such instabilities appear rather improbable. The Hg salts provide further experimental evidence to indicate why such instabilities have yet to be observed experimentally.

As we see from the definition (5.3) of $\overline{E}$, it is the *average* band gap between the highest valence band and lowest conduction band which controls dehybridization energies and produces lattice contractions. Such short-range bond energies are of order 1 eV and are thus 100 times larger than long-range band-edge exciton energies. According to Halperin and Rice[44] "in order for some kind of distorted phase to exist, it is necessary and sufficient that there should not be a "large" first-order transition, involving a discrete change in lattice constant but no change of symmetry, which takes one directly, at low temperatures, from" no band overlap to nonzero band overlap. In fact, however, the excitonic lattice distortion will also alter dehybridization energies. Because these bond energies are much larger than exciton energies, they should always tend to suppress the excitonic effect, and it would be a great accident if they were not successful in doing so. In particular, if one looks for the effect in mixed crystals, such as $\mathrm{Cd}_x\mathrm{Hg}_{1-x}$ ×Te as a function of x, the local strain fields associated with fluctuations in composition would be sufficient to suppress the effect. In this connection it is interesting that the materials proposed[44] as candidates for excitonic phase transitions differ from zinc-blende semiconductors primarily by the fact that very little is known about their band structures. This precludes giving a semiquantitative discussion of the type given here for these cases, but we see no reason why short-range bond energies should not dominate long-range excitonic energies in those cases as well.

APPENDIX B

It is remarked at the end of Sec. 3 and in Ref. 18 that the cohesive energy ΔG of diamond-type semiconductors can be explained semiquantitatively in terms either of Penn's model[12,17] or in terms of trends[18] as a function of lattice constant a. In Penn's model an amount of energy $\frac{1}{2}E_g$ is gained by a fraction $E_g/4E_F$ of the valence electrons. Because $E_g/4E_F$ is of order 0.1–0.2, one can explain in this way why cohesive energies are so much smaller than optical energy gaps. On the other hand, purely empirically ΔG scales like a^{-2}.

Both these pictures predict a cohesive energy for Si about 25% smaller than what is observed. The reason for this is that the $3p$-$3d$ promotion energy in Si is very much smaller than the $2p$-$3d$ promotion energy in diamond. As a result, p-d hybridization enhances the cohesive energy substantially in Si. It also makes a significant contribution to the binding energies[45] of donor electrons associated with group-V impurities in Si and Ge.

A striking feature of our formulas for the heat of formation ΔH is the absence of a p-d term. We believe that this comes about as follows. The high angular momentum of d electrons means that they have very high kinetic and potential energies. Thus the oscillator strength associated with $p \to d$ transitions is spread over a wide energy range of order several rydbergs. Now the *difference* in cohesive energies between the AB covalent crystal and the elemental A and B crystals (which are usually metals) arises mainly from the covalent energy gap E_g. This gap is of order a fraction of 1 Ry. Its magnitude may be changed somewhat by p-d hybridization, but this is already contained in the theory, as is the effect of s-p dehybridization. The large contribution to cohesive energies associated with p-d hybridization comes from high-energy transitions, and these are virtually the same in the metals as in the semiconductors. Thus little or no contribution to ΔH is expected from this source.

Note added in proof. After this paper was submitted for publication, Riccius and Siemsen[46, 47] and Zallen and Slade[48] presented experimental evidence which confirms the prediction of the dielectric two-band model calculation in Appendix A that cubic HgS is a semimetal.

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New Set of Tetrahedral Covalent Radii

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

1. INTRODUCTION

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

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

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

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

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

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

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