

## Energies of substitution and solution in semiconductors

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The tight-binding theory of cohesion in pure semiconductors, based upon universal parameters, is presented and applied to systems with an impurity. Results are given in terms of an energy of substitution, defined as the energy required to remove a single atom from a semiconductor, leaving it as a free atom in the ground state, and replacing it by a free atom of another element; any excess or deficit of electrons is placed at the valence-band maximum. Calculated values are in reasonable accord with the recent measurements by Su and Brebrick [J. Phys. Chem. Solids **46**, 963 (1985)] for Zn, In, and Sn in Ge. Lattice distortions and relaxation energies are also calculated. Agreement with the limited amount of data is mixed but predictions are tabulated for a large array of systems. Relaxation is seen to reduce the misfit energy by a factor of order 4. Comparison of predicted force constants with experiment suggests that the theory underestimates the misfit energy by a similar factor so theoretical energies of unrelaxed substitution provide estimates of the experimental energies of relaxed substitution. Such predictions are in reasonable accord with experiment for homovalent substitutions, which are dominated by misfit energy. For heterovalent substitutions, the enthalpy is dominated by a redistribution of bond polarities in the substitution. Extensive tables of energies of substitution for elements and compounds from the third (silicon), fourth (germanium), and fifth (tin) rows of the Periodic Table are given, permitting direct estimates of the energy change for a wide variety of atomic rearrangements.

### I. INTRODUCTION

Enthalpies of solution of one semiconductor in another are only poorly known experimentally, partly because semiconductors are generally quite insoluble in each other so that the heat of solution is difficult to measure. In addition, their determination from experiment frequently involves paths through the liquid phase, and data are most frequently for the solid and the liquid at the melting temperature.<sup>1</sup> Heats of solution do exist for a number of isovalent solutions,<sup>2</sup> e.g., III-V compounds dissolved in each other, and a few recent direct measurements on heterovalent solutions have been made by Su and Brebrick.<sup>3</sup>

The theory is also difficult. An earlier phenomenological approach was made by Weiser<sup>4</sup> and a dielectric theory was given by Van Vechten,<sup>5</sup> both again directed principally at the segregation coefficients. More recently, there have been estimates of the heats of solution by Stringfellow<sup>2</sup> and Martins and Zunger<sup>6</sup> under the assumption that it was dominated by elastic misfit, which we shall see appears to be appropriate for isovalent solutions. There have also been microscopic quantum-mechanical theories of isolated cases of individual impurities,<sup>7-9</sup> based in most cases on using a Green's function to represent the crystalline environment. Baraff and Schlüter,<sup>10</sup> in particular, obtained reaction energies for transformation between various defects in gallium arsenide. Here, we seek a wider sampling of systems, again from microscopic theory, but in a simple enough way to allow very general application.

Recently, tight-binding theory, based on universal parameters,<sup>11</sup> and on individual bond energies with correc-

tions (called metallization) due to coupling with neighbors, proved successful in predicting equilibrium bond lengths and cohesive energies of elemental and compound semiconductors. This approach did not depend on lattice periodicity and is therefore directly applicable to the total energy of systems containing impurities. Preliminary accounts<sup>12,13</sup> of such calculations have been given; here we give a full account of the method and results.

We shall begin in Sec. II with a restatement of the total-energy change in forming a crystal from the free atoms—the cohesive energy—since that gives the basic approach for all of the calculations and since we shall need those numbers also. In Sec. III, we calculate the energy of substitution, defined to be the energy change if an atom is removed from the crystal, left as a free atom in the ground state, and a second atom of a different element replaces the first. This is done first without allowing the positions of the other atoms in the crystal to change. The results are compared with the few available experimental values. From such energies of substitution and the cohesive energies it is possible to predict heats of solution and a number of other interesting properties.

In Sec. IV, we allow for the relaxation of the neighbors to the impurity. We first discuss the determination of equilibrium spacings in pure semiconductors by minimization of the energy, writing down the terms in the energy which depend upon spacing. Then, when an impurity is substituted, we make the appropriate changes in the terms in the total energy and calculate the relaxed bond lengths.

In Sec. V, we obtain in the heats of solution which are compared with experiment for isovalent solutions, such as InSb in GaAs, which are the systems for which the

most data were available and at which most earlier theory is directed. These are seen to be dominated by the misfit energy, or elastic energy, as assumed in earlier theories. The heat of solution for heterovalent systems, such as germanium in gallium arsenide is seen to be dominated by electronic-structure effects with the misfit energies playing a smaller role. We also calculate interchange energies, such as a germanium atom from germanium with an arsenic atom from gallium arsenide. In the heterovalent case this dopes both semiconductors and the dependence of the interchange energy on the doping of the two systems is described.

## II. THE TIGHT-BINDING THEORY OF COHESION

We begin with free atoms, one metallic atom from column  $Z^+$  ( $\leq 4$ ) and one nonmetallic atom from column  $Z^- = 8 - Z^+$ . We will use these  $\pm$  superscripts to denote each of the parameters which enters, as we proceed step by step to construct the solid from the isolated free atoms. Values are given at each step for gallium arsenide using Hartree-Fock term values tabulated by Mann<sup>14</sup> and listed in Table I for the elements which will be needed here.

### A. Promotion energy

To form individual two-center bonds we must prepare each atom in an  $sp^3$  configuration. For all cases we consider ( $Z^+ \geq 2$ ), we must first raise one electron on each atom from an  $s$  state to a  $p$  state, with an energy change (or costing an energy)  $\epsilon_p^+ - \epsilon_s^+ + \epsilon_p^- - \epsilon_s^-$  per atom pair. Then, unless  $Z^+ = 4$ , we must transfer electrons from the nonmetallic  $p$  states to the metallic  $p$  states, costing  $(Z^- - 4)(\epsilon_p^+ - \epsilon_p^-)$ , for a total promotion energy of

$$E_{\text{pro}} = \epsilon_p^+ - \epsilon_s^+ + \epsilon_p^- - \epsilon_s^- + (Z^- - 4)(\epsilon_p^+ - \epsilon_p^-) \quad (1)$$

per atom pair. This is 19.12 eV for GaAs.

### B. Bond-formation energy

The eight electrons per atom pair may now be put, with no cost in energy, into hybrid states of energy

$$\epsilon_h^\pm = (\epsilon_s^\pm + 3\epsilon_p^\pm)/4 \quad (2)$$

corresponding in gallium arsenide to  $\epsilon_h^+ = -7.14$  eV and  $\epsilon_h^- = -11.46$  eV with an average hybrid energy of  $\bar{\epsilon}_h$  ( $-9.30$  eV). The energy difference is written as twice the polar energy  $V_3$  defined by

$$V_3 = (\epsilon_h^+ - \epsilon_h^-)/2 \quad (3)$$

and equal to 2.16 eV in GaAs. When they are placed in a solid, each of these hybrids is coupled to the other hybrid forming a two-center bond by the covalent energy<sup>15</sup>

$$V_2 = -3.22 \frac{\hbar^2}{md^2} \quad (4)$$

( $-4.09$  eV). The equilibrium bond length will be listed in Table III. In the solid, the hybrids form bonds of energy  $\bar{\epsilon}_h - (V_2^2 + V_3^2)^{1/2}$ , thus gaining a bond-formation (BF) energy of

$$E_{\text{BF}} = -8(V_2^2 + V_3^2)^{1/2} \quad (5)$$

( $-36.99$  eV) per atom pair. With  $V_3 \neq 0$  these are polar bonds and the polarity

$$\alpha_p = V_3 / (V_2^2 + V_3^2)^{1/2} \quad (6)$$

enters many of the formulae for their properties.

### C. Overlap energy

This attractive bond-formation energy, predominantly potential, is opposed by an overlap interaction  $V_0(d)$  arising principally from the excess kinetic energy of the electrons of the two overlapping hybrids. We derive a form for this interaction in Ref. 11,

$$V_0(d) = \eta_0 V_2^2(d) / |\langle \epsilon_h \rangle|, \quad (7)$$

TABLE I. Hartree-Fock term values in units of eV from Mann (Ref. 14). The upper number is  $-\epsilon_s$  and the lower number is  $-\epsilon_p$ . An asterisk denotes values extrapolated from surrounding values.

I	II	III	IV	V	IV
	Mg	Al	Si	P	S
	6.88	10.70	14.79	19.22	24.01
	3.84*	5.71	7.58	9.54	11.60
	Zn	Ga	Ge	As	Se
	7.96	11.55	15.15	18.91	22.86
	4.02*	5.67	7.33	8.98	10.68
	Cd	In	Sn	Sb	Te
	7.21	10.14	13.04	16.02	19.12
	3.99*	5.37	6.76	8.14	9.54
	Hg	Tl	Pb	Bi	Po
	7.10	9.82	12.48	15.19	17.96
	3.95*	5.23	6.53	7.79	9.05

with  $\langle \epsilon_h \rangle$  the average of the hybrid energies of the two constituents, and we shall use that form here. The basis of the derivation was that the nonorthogonality  $S$  shifts both the bonding and antibonding levels upward by  $-SV_2$  and extended Hückel theory relates the coupling  $V_2$  to the nonorthogonality by  $V_2 = K |\langle \epsilon_h \rangle| S$ , with  $K$  an empirical constant. We adjusted the constant  $\eta_0$  such that the total energy was minimum at the observed spacing for diamond, silicon, germanium, and tin, and took these values ( $\eta_0 = 1.23, 1.95, 1.87,$  and  $2.16,$  respectively) to apply for compounds constructed from the same row (e.g., 1.87 for GaAs), using geometric means for "skew compounds." Here we use a fit that should be slightly more accurate. We fit  $\eta_0$  to give the correct spacing for each compound. For bonds which do not exist in the pure tetrahedral compounds (e.g., Zn-Sb) we take the geometric mean of the values for the two compounds which contain elements from the same rows and also contain one constituent (values for ZnTe and GaSb in the case of the Zn-Sb repulsion). This is a generalization of the use of a value fit to the observed spacing for the case of existing compounds.

This overlap interaction is perhaps the weakest part of the tight-binding theory of cohesion. It is necessary to adjust  $\eta_0$ , as suggested above, and use the same values to predict bond lengths. Using  $\eta_0$  values for elemental semiconductors did not give very accurate predictions of bond lengths for compounds isoelectronic with them and the limited tests we shall make of distortions here are not too encouraging. Cohesions predicted using this approach are quite good, but radial force constants,  $k = \partial^2 E_{\text{coh}} / \partial d^2$ , are not well given, typically being too small by a factor of as much as 3. Thus we can have much more confidence in our heats of solution than in our distortions and relaxation energies. The results will nevertheless be informative.

There are four bonds per atom pair so we may write the overlap energy per atom pair as

$$E_{\text{over}} = 4\eta_0 V_2^2 / |\langle \epsilon_h \rangle| \quad (8)$$

This is 13.72 eV for GaAs.

#### D. Metallization

The calculation to this point has neglected any coupling except between the two hybrids making up the two-center bond. Corrections to this approximation are called metallization, the leading term being from coupling between two different hybrids on the same atom. This coupling matrix element  $\langle h' | H | h \rangle$  is called the "metallic energy"

$$V_1^\pm = (\epsilon_s^\pm - \epsilon_p^\pm) / 4 \quad (9)$$

( $-1.47$  eV,  $-2.48$  eV). This couples bonds to neighboring bonds, but since both are fully occupied that does not affect the total energy. It also couples each bond to the neighboring antibonds and the corresponding lowering of the energy is called metallization. We compute it in second-order perturbation theory.

We note first (see, for example, Ref. 11) that the bond orbital is a linear combination of the two hybrids with a

coefficient on the nonmetallic atom of  $[(1 + \alpha_p)/2]^{1/2}$  and on the metallic atom of  $[(1 - \alpha_p)/2]^{1/2}$ , where  $\alpha_p$  is the polarity, given in Eq. (8). For the antibonding orbitals the magnitudes are interchanged and one is changed in sign. Thus, the coupling between the bond orbital and a neighboring antibonding orbital sharing a nonmetallic atom has the magnitude  $(1 - \alpha_p^2)^{1/2} V_1^- / 2$ . This is to be squared, divided by the energy difference,  $2(V_2^2 + V_3^2)^{1/2}$ , and multiplied by 3 for the three neighboring antibonds. The corresponding term for the coupling through the metallic atom is added, the result multiplied by 2 for spin and 4 for the number of bonds per atom pair to obtain the metallization energy of

$$E_{\text{met}} = -3(1 - \alpha_p^2)(V_1^{+2} + V_1^{-2}) / (V_2^2 + V_3^2)^{1/2} \quad (10)$$

per atom pair (for GaAs it is  $-4.22$  eV).

#### E. Cohesion

The total change in energy is the negative of the cohesive energy per atom pair,  $E_{\text{coh}}$ ,

$$-E_{\text{coh}} = E_{\text{pro}} + E_{\text{BF}} + E_{\text{over}} + E_{\text{met}} \quad (11)$$

This is 8.37 eV for GaAs. In Table II we give the corresponding values for a wide range of compounds, along with experimental values. These values differ from those given in Ref. 11 due to an error in the analysis of the  $V_0$  in Ref. 11, noted in Ref. 12.

We see that we predict a decrease in cohesion with polarity, as observed. Both that trend and the decrease with increasing average atomic number are rather well given.

#### F. The valence-band maximum

We need an additional parameter for the pure compound in our calculation of substitution energies; that is the energy of the valence-band maximum, on the same scale as the atomic term values we have used. This is needed since if we substitute an atom of column  $Z + 1$  for an atom of column  $Z$ , the extra electron is to be placed at the Fermi energy of the semiconductor, which we take by

TABLE II. Calculated and experimental cohesive energy (in units of eV per atom-pair). The observed bond length is  $d$  (in units of Å).

Compound	$d$ (Å)	Cohesion (eV/atom-pair)	
		Theory	Experiment <sup>a</sup>
Si	2.35	9.93	9.28
Ge	2.44	9.19	7.76
Sn	2.80	7.05	6.24
AlP	2.36	10.47	8.52
GaAs	2.45	8.37	6.52
InSb	2.81	6.20	5.60
ZnSe	2.45	8.87	5.16
CdTe	2.81	6.93	4.12

<sup>a</sup>Reference 16.

convention to be at the valence-band maximum. Thus, an additional promotion energy arises.

The energy of the valence-band maximum is obtained in tight-binding theory<sup>15,16</sup> as

$$E_v^{\text{TB}} = (\varepsilon_p^+ + \varepsilon_p^-) / 2 - \{ [(\varepsilon_p^+ - \varepsilon_p^-) / 2]^2 + (1.28\hbar^2 / md^2)^2 \}^{1/2}, \quad (12)$$

based upon the matrix elements we are using here. However, that energy is shifted by the same nonorthogonality which gives the overlap interaction, as noted by Enderlein.<sup>17</sup> Enderlein and Harrison<sup>17</sup> estimated this shift as the average shift for all electrons,  $V_0/2$ , but it may be preferable to estimate it specifically in terms of orbitals which enter the state, as in the calculations in the Appendix of Ref. 11. This reduces the shift by a factor of  $(1.28/3.22)^2$ . Then the valence-band maximum becomes

$$E_v = E_v^{\text{TB}} + (1.28/3.22)^2 V_0 / 2. \quad (13)$$

For GaAs it is  $-9.64 + 0.27 = -9.37$  eV. Corresponding values for the other semiconductors are listed in Table III. This correction to  $E_v^{\text{TB}}$  is considerably smaller than the average value used by Enderlein and Harrison. Values for the valence-band maximum, Eq. (12), have been widely used to estimate heterojunction band discontinuities; it would appear that this correction would have negligible effect on those predictions.

### G. The force constant

It will be useful in our discussion to obtain one more parameter, though it is not used in our numerical calculations. That is the force constant, equal to the second derivative of the energy per bond with respect to bond length (varying all bonds in the crystal together). We have adjusted  $\eta_0$  for each compound such that the minimum energy comes at the observed internuclear distance  $d$ . We may now evaluate the energy at a slightly larger and a slightly smaller  $d$  and extract the second derivative numerically. Such values are listed in Table III. They are considerably smaller than the correspond-

TABLE III. Calculated valence-band maximum, on the scale of Table I, obtained in tight-binding theory,  $E_v^{\text{TB}}$ , and corrected for nonorthogonality,  $E_v$ , as in Eq. (13). Also listed are the theoretical and experimental (Ref. 16) force constants  $k$  (in units of  $\text{eV}/\text{\AA}^2$ ).

Compound	$E_v^{\text{TB}}$ (eV)	$E_v$ (eV)	Force constant $k$ ( $\text{eV}/\text{\AA}^2$ )	
			Theory	Experiment
Si	-9.35	-9.04	4.06	9.96
Ge	-8.97	-8.70	2.74	8.01
Sn	-8.00	-7.80	1.39	
AIP	-10.22	-9.93	4.46	
GaAs	-9.64	-9.37	3.90	7.90
InSb	-8.61	-8.41	2.29	5.62
ZnSe	-11.06	-10.82	2.68	6.33
CdTe	-9.80	-9.63	1.43	5.12

ing values we obtained in Ref. 13. These values did not contain the effects of metallization and were considerably larger. An experimental value is directly obtainable from the bulk modulus; values are included in Table III for comparison.

We see that our procedure has considerably underestimated this constant, though the cohesive energies themselves are well given. This must ultimately be a failure of the form, Eq. (7), for the overlap interaction. If we were to adjust also the exponent of  $d$  in that expression to obtain the observed bulk modulus we would spoil the predictions of the cohesion. Changes in the form of the overlap interaction should not be made without a better understanding of their origin, so we shall simply note the discrepancy for later use, and proceed as we have described.

## III. THE SUBSTITUTION ENERGY

We turn now to the change in energy if an atom in the compound is replaced by an impurity atom. At first we neglect any distortion of the host lattice. We shall give numbers at each step for substituting a germanium atom for a gallium atom in gallium arsenide. This is directly evaluated as the change in the various contributions given above during this substitution, beginning with a gallium arsenide crystal and a free germanium atom and ending with a germanium impurity in GaAs and a free gallium atom.

### A. Promotion energy

The first step is to break four gallium-arsenide bonds (we return to that energy in Sec. III B) and carry out the gallium atom (actually a  $\text{Ga}^-$  ion) with one electron in each of the four hybrids. We then gain an energy  $\varepsilon_s^+ - \varepsilon_p^+$  by letting one of the  $p$  electrons drop into an  $s$  state. A second  $p$  electron should be inserted in the compound at the valence-band maximum, costing an energy  $(4 - Z^+)(E_v - \varepsilon_p^+)$ , leaving a free gallium atom in its ground state. We must then promote an electron in the germanium, costing  $(\varepsilon_p^s - \varepsilon_s^s)$ , where the super  $s$  refers to the substituting atom. If the column of the substituting atom were not 4, we would need to transfer  $4 - Z^s$  electrons from the valence-band maximum to the atom costing  $(4 - Z^s)(\varepsilon_p^s - E_v)$  in order to have one electron in each hybrid. This puts us in the promoted state with a change in the promotion energy given by

$$\begin{aligned} \delta E_{\text{pro}} = & \varepsilon_p^s - \varepsilon_s^s + (4 - Z^s)(\varepsilon_p^s - E_v) \\ & - (\varepsilon_p^+ - \varepsilon_s^+) - (4 - Z^+)(\varepsilon_p^+ - E_v). \end{aligned} \quad (14)$$

This is  $-1.76$  eV for  $\text{Ga}(\text{Ge})\text{As}$ .

### B. Bond-formation energy

Breaking the four bonds costs the entire bond-formation energy,  $8(V_2^2 + V_3^2)^{1/2}$ , for the four bonds surrounding the gallium atom, but reinserting the germanium atom between the four arsenic neighbors gains back a similar amount. Since the lattice is not allowed to dis-

tort, the bond length and, therefore  $V_2$ , remains the same. However, the polar energy is different. We define it to be

$$V_3^{s-} = (\epsilon_h^s - \epsilon_h^-) / 2. \quad (15)$$

In this case it is positive, 1.09 eV, but if we were to substitute the germanium for an arsenic,  $\epsilon_h^-$  would be replaced by  $\epsilon_h^+$  and  $V_3^s$  would be negative. The change in bond-formation energy becomes

$$\delta E_{BF} = 8(V_2^2 + V_3^2)^{1/2} - 8[V_2^2 + (V_3^s)^2]^{1/2}, \quad (16)$$

equal to 3.15 eV in this case.

### C. Overlap energy

The overlap energy for the four bonds surrounding the impurity is modified from the substitution. Before substitution it was given by Eq. (8) with  $\langle \epsilon_h \rangle$  the average of the gallium and arsenic hybrids and  $\eta_0$  determined as indicated in Sec. I C, in this case adjusted to give the correct spacing in gallium arsenide. After substitution  $\langle \epsilon_h \rangle$  becomes the average of the germanium and arsenic hybrids and  $\eta_0$  is replaced by  $\eta'_0$  determined as indicated in Sec. II C, in this case the geometric mean of values adjusted to give the correct spacings for germanium and gallium arsenide. [If silicon were substituted for gallium in gallium arsenide it would be the geometric mean of the values fit to give the correct spacing for SiGe (the average of the Si and Ge values, by Vegard's law) and for AlAs.] Thus the change is

$$\delta E_{\text{over}} = 8V_2^2(\eta'_0 / |\epsilon_h^s + \epsilon_h^-| - \eta_0 / |\epsilon_h^+ + \epsilon_h^-|). \quad (17)$$

This is  $-1.52$  eV for Ge substituted in GaAs.

### D. Metallization

Replacing a gallium atom by a germanium changes the metallization of the surrounding four bonds and also that of the three bonds which share each of the four neighboring arsenic atoms, illustrated in Fig. 1.

Enderlein and Harrison<sup>17</sup> also calculated this contribution. We see that it is small, but not negligible. We may specify the change by writing a formula for all metallization terms which are influenced by the substituted atom. We then should subtract the energy obtained from that formula with  $s$  replaced by  $+$ .

Each of the eight electrons in a germanium-arsenic bond has a metallization contribution with each of the other three germanium-arsenic antibonds with which it shares a germanium atom. We must be careful with the signs for these atoms. The coefficient of the bond orbital for the hybrid on the arsenic atom is  $[(1 + \alpha_p^s)/2]^{1/2}$ , where

$$\alpha_p^{s-} = V_3^{s-} / [V_2^2 + (V_3^{s-})^2]^{1/2}, \quad (18)$$

which in this case is positive. The coefficient for the anti-

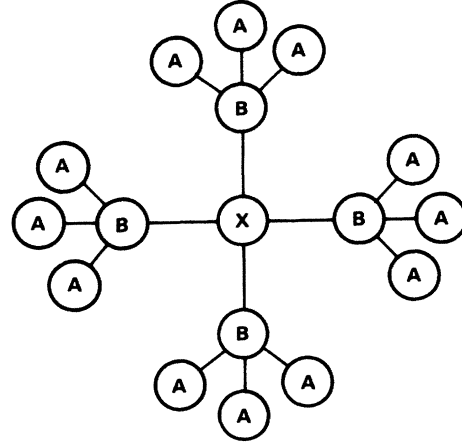


FIG. 1. An atom  $X$  is substituted for an atom  $A$  in the compound  $AB$ . Then, calculations of metallization and of distortion can be made on the cluster containing  $X$ , its four neighboring  $B$  atoms, and 12 second-neighbor  $A$  atoms. For  $X$ , a germanium atom,  $A$ , a gallium atom, and  $B$ , an arsenic atom, this cluster is sufficient for including all metallization terms which depend upon the Ge-As distance.

bond of the hybrid on the germanium is  $[(1 - \alpha_p^s)/2]^{1/2}$ . Thus, the coupling between a bond and an antibond is  $V_1^s [1 - (\alpha_p^s)^2]^{1/2} / 2$ , with  $V_1^s$  the coupling between the two hybrids on a germanium atom. The energy denominator is minus twice  $[V_2^2 + (V_3^s)^2]^{1/2}$  and the shift in energy of each bond electron due to coupling with one antibond sharing the germanium is thus

$$-(V_1^s)^2 [1 - (\alpha_p^s)^2] / 8[V_2^2 + (V_3^s)^2]^{1/2}.$$

Further, there is metallization of each electron in a germanium-arsenic bond with three antibonds which share the arsenic atom. The coefficient for the bond of the hybrid on the arsenic is  $[(1 + \alpha_p^s)/2]^{1/2}$  and that for the antibond hybrid on the arsenic is  $[(1 - \alpha_p^s)/2]^{1/2}$ .

The energy denominator is the difference between the Ge—As antibond and the Ge—As bond,

$$(\epsilon_h^s)_{\text{av}} - [V_2^2 + (V_3^s)^2]^{1/2} - [(\epsilon_h^-)_{\text{av}} + (V_2^2 + V_3^2)^{1/2}]. \quad (19)$$

The parameters in the second two terms, apply to the gallium-arsenic antibond. There is also metallization of the two electrons in each of the twelve Ga—As bonds with a Ge—As antibond. It differs from contributions we have just estimated only in that the product of the squared coefficients is  $(1 - \alpha_p^s)(1 + \alpha_p)/4$  and the  $(\epsilon_h^-)_{\text{av}}$  and  $(\epsilon_h^s)_{\text{av}}$  in the denominator are changed in sign. It is convenient also to note that

$$(\epsilon_h^-)_{\text{av}} - (\epsilon_h^s)_{\text{av}} = V_3^{s+} = (\epsilon_h^+ - \epsilon_h^s) / 2.$$

We may combine the three sets of terms to obtain

$$E_{\text{met}} = -3(V_1^s)^2 [1 - (\alpha_p^s)^2] / [V_2^2 + (V_3^s)^2]^{1/2} - 6(V_1^-)^2 (1 + \alpha_p^s)(1 - \alpha_p) / \{ (V_2^2 + V_3^2)^{1/2} + [V_2^2 + (V_3^s)^2]^{1/2} - V_3^s + \} - 6(V_1^-)^2 (1 - \alpha_p^s)(1 + \alpha_p) / \{ (V_2^2 + V_3^2)^{1/2} + [V_2^2 + (V_3^s)^2]^{1/2} + V_3^s + \}. \quad (20)$$

We are to evaluate this, obtaining  $-10.19$  eV for germanium in a gallium site in gallium arsenide, and subtract the value obtained with  $V_1^s$  replaced by  $V_1^+$  and  $\alpha_p^-$  replaced by  $\alpha_p$ ,  $V_3^-$  replaced by  $V_3$ , and  $V_3^+$  replaced by zero. This value is  $-7.35$  eV, giving a change in metallization of  $-2.86$  eV.

If we were instead to substitute a germanium atom for an arsenic atom, metallic and nonmetallic atoms are interchanged everywhere. This has the effect of replacing  $V_3^-$  by  $V_3^+$ , which is negative, in the corresponding  $\alpha_p^+$  from Eq. (18).  $V_1^-$  is replaced by  $V_1^+$ ,  $V_3^+$  is replaced by  $V_3^-$ , and  $\alpha_p$  is replaced by  $-\alpha_p$ . From this we are to subtract the value obtained with  $V_1^s$  replaced by  $V_1^-$  and with  $\alpha_p^+$  replaced by  $-\alpha_p$ ,  $V_3^+$  replaced by  $-V_3$ , and  $V_3^-$  replaced by zero.

#### E. The total

We may add the four contributions to obtain a substitution energy of germanium in the gallium site of gallium arsenide of  $E_{\text{GaAs}}(\text{Ge}_{\text{Ga}}) = -3.01$  eV; the energy is lowered by the substitution. Such a value was used directly with the Born-Haber cycle to discuss core shifts in Refs. 12 and 17. Values obtained in exactly this way for a wide range of energies of substitution are given in Table IV.

Interestingly enough exactly these substitution energies have been measured carefully for a few systems by Su and Brebrick.<sup>3</sup> They give values of 3.47, 1.95, and 0.83 eV per atom for neutral Zn, In, and Sn in germanium. In our calculation for zinc we have removed two electrons from the valence band, by convention, whereas in a neutral zinc impurity the corresponding two holes would be bound in a deep acceptor level. Su and Brebrick give the energy to remove those two holes to the valence band as 0.12 eV, so one should really add this to obtain 3.59 eV to be compared with ours; the correction is small, and even smaller for indium. Our predicted values are 6.06, 3.91, and 1.12 eV for Zn, In, and Sn, respectively.

Our values have given the correct general magnitudes for the heterovalent as well as the isovalent substitutions. We would guess the accuracy of the measurements to be much better than that of the theory so the comparison should give some idea of our accuracy. They are the only values we found for the substitution energy, and the only experimental quantities related to heterovalent substitutions. Our other comparisons with experiment will be for homopolar systems only, and will be enthalpies of solution, obtainable in terms of the energies of substitution.

Energies of substitution may not be interesting in themselves, but they may be used directly to obtain other quantities of interest. Their lack of direct interest is reflected in the lack of apparent systematics from one system to another. When we substitute a germanium for a gallium in gallium arsenide, we are left with an isolated gallium atom rather than an isolated germanium, with quite different electronic energy. Further, the smaller germanium atom has an overlap repulsion lower than the gallium it replaces by a large amount, of first order in the size difference. On the other hand, when we interchange a gallium and a germanium across an interface, by com-

binning the two substitution energies, there is no change in external isolated atoms and the first-order change in overlap interaction cancels out, leaving only a second-order effect. There is always a considerable degree of cancellation of terms when we calculate quantities of physical significance and the systematics may be present in the final result.

#### IV. LATTICE DISTORTIONS

For systems such as an In atom substituted for Ga in GaAs, we may readily estimate lattice distortions with an elastic model, such as that used by Martins and Zunger<sup>6</sup> and Shih *et al.*,<sup>18</sup> assuming that the equilibrium bond lengths for the In—As and Ga—As bonds are the same as those of the pure InAs or GaAs compound. However, in other solutions, such as Zn in Ge, we do not know what equilibrium bond length to use, so we turn first to a discussion of these equilibrium lengths.

##### A. Natural bond lengths

We have given the total energy for pure materials in Sec. II, and a procedure for obtaining parameters for the overlap interaction. We could in fact have written it in terms of each individual bond length  $d_i$  in the system and the partial derivative of the energy with respect to each  $d_i$  would have been zero at the equilibrium spacing, just as was the total derivative with respect to all of the  $d_i = d$  in the crystal. In Sec. III we gave that total energy for a system containing an impurity without distortion of the lattice; that is, with each  $d_i$  equal to the host  $d$ . This also could be written in terms of the individual  $d_i$ . The bond-formation energy, the overlap interaction, and the metallization are all modified and the partial derivatives of the energy with respect to the  $d_i$  near the impurity are no longer zero. *This suggests that we define a natural impurity-host bond length by minimizing the energy with respect to the impurity-host  $d_i$ , holding all other  $d_i$  constant.* It yields the impurity-host bond length that the system would “like to have” if there were no elastic constraints from the host lattice. (We shall return to the calculation of the equilibrium bond length when the elastic constraints are included.) We could obtain, for example, a natural indium-arsenic bond length for indium substituted for gallium in gallium arsenide. This seems a very useful set of numbers to have, and we have a means of predicting them. Unfortunately, the results do not appear to be very reliable but they may nevertheless be informative.

Note that the natural bond length for a particular pair will depend upon the compound in which the bond is embedded. Thus the In—As natural bond length will be different for In in GaAs than it will be for pure InAs. In tight-binding theory such dependencies arise from the metallization energy. We find the differences to be large in some cases; if true this argues against the use of *any* covalent radii since the bond lengths obtained from such radii do not distinguish different environments.

The calculation may be understood in terms of Fig. 1. We let the bond length between the central atom and the four  $B$  neighbors be  $d'$ , different from the host  $d$ ; the

TABLE IV. Calculated energies of substitution  $E_{AB}(X_A)$  and  $E_{AB}(X_B)$  (in units of eV, for atom  $X$  substituted, respectively, for atom  $A$  or for atom  $B$  in compound  $AB$ ).

$X$	Mg	Zn	Cd	Al	Ga	In	Si	Ge	Sn	P	As	Sb	S	Se	Te
$E_{AB}(X_A)$ or $E_{AB}(X_B)$															
$E_{Si}(X_{Si})$	6.22	7.20	8.09	3.03	3.74	4.94		0.42	1.85	-2.00	-1.50	0.32	-2.65	-2.08	-0.87
$E_{Ge}(X_{Ge})$	5.31	6.06	6.62	2.34	3.11	3.91	-0.33		1.12	-2.04	-1.51	0.0	-2.30	-1.91	-0.79
$E_{Sn}(X_{Sn})$	3.38	4.14	4.13	1.46	1.83	2.32	-1.30	-1.14		-3.08	-2.58	-1.01	-3.05	-2.43	-1.25
$E_{Al}(X_{Al})$	2.49	3.79	4.20		0.93	1.34	-2.32	-1.90	-1.30	-4.80	-4.30	-2.82	-7.43	-6.53	-4.61
$E_{Ga}(X_{Ga})$		2.83					-3.19	-2.77		-5.59	-5.10	-3.67		-17.81	
$E_{GaAs}(X_{Ga})$	1.49	2.62	2.83	-1.03		0.25	-3.46	-3.01	-2.35	-6.39	-5.62	-3.87	-9.33	-8.25	-5.77
$E_{GaSb}(X_{Ga})$		2.27					-3.38	-3.18		-6.46	-5.89	-3.70		-7.54	
$E_{InP}(X_{In})$		2.40			0.06		-2.96	-2.59		-6.46	-5.79	-3.88		-17.28	
$E_{InSb}(X_{In})$	0.96	1.93	1.74	-0.66	-0.13		-3.89	-3.71	-2.42	-8.44	-7.62	-4.66	-11.71	-10.42	-7.15
$E_{ZnS}(X_{Zn})$					-3.28		-6.59	-6.03		-9.02	-8.57	-8.44		-12.46	
$E_{ZnSe}(X_{Zn})$	-1.22		-0.18	-3.91	-2.85	-3.29	-6.11	-5.75	-6.06	-9.73	-8.98	-7.89	-16.72	-14.45	-10.75
$E_{CdTe}(X_{Cd})$	-0.69	0.53		-2.17	-1.39	-1.98	-4.88	-4.62	-4.22	-18.00	-10.47	-6.89	-27.13	-18.75	-11.82
$E_{AlP}(X_P)$	17.88	18.63	20.45	11.11	11.82	14.32	4.68	5.44	8.24		1.11	4.17	-2.85	-1.53	0.70
$E_{GaP}(X_P)$		18.06			11.55		4.34	5.16			1.24	3.71		-1.39	
$E_{InP}(X_P)$		18.67			12.01		4.73	5.36			1.13	3.57		-1.63	
$E_{GaAs}(X_{As})$	13.53	14.23	15.34	7.76	8.68	10.34	2.49	3.21	5.21	-1.12		2.17	-2.90	-1.86	-0.22
$E_{GaSb}(X_{Sb})$		8.65			4.59		-0.11	0.45		-2.72	-1.78			-2.55	
$E_{InSb}(X_{Sb})$	9.28	9.88	10.33	4.94	5.36	6.53	0.22	0.71	2.34	-2.91	-1.93	-4.12	-4.12	-3.00	-1.46
$E_{ZnS}(X_S)$	31.02	31.17	32.78	19.97	20.85	23.42	14.36	15.54	14.32	5.98	7.88	11.43	-1.74	1.88	2.57
$E_{ZnSe}(X_{Se})$	23.42	23.47	24.25	14.33	14.71	16.53	5.84	6.66	8.98	-0.23	1.25	-3.86	-3.79	-2.18	

$A-B$  bond lengths remain as  $d$ . One of the terms in the energy which depends upon  $d'$  is the  $X-B$  overlap repulsion. In its evaluation we indicated in Sec. IIC that for Si—As, for example, for  $\langle \epsilon_h \rangle$  we use the average of the hybrid energies for Si and As. For  $\eta_0$  we use the geometric mean of the values fit for SiGe and AlAs (since Ge is in the same row as As and Al is in the same row as Si). The other terms depending upon  $d'$  are the  $X-B$  bond-formation energy, the metallization energy of the  $X-B$  bonds with the  $X-B$  antibonds and with the  $A-B$  antibonds, and the metallization of the  $A-B$  bonds with the  $X-B$  antibonds. We have written all of these energies, though up to now we have not distinguished the  $V_2$  which are determined by  $d'$  from those determined from  $d$ .

Making that distinction we wrote a small program which evaluates the energies for the pure compound, adjusting the  $\eta_0$  for the overlap interaction such that the total energy is minimum at the observed bond length. It then evaluated the cohesive energy, the force constant, and the valence-band maxima which we have tabulated. Then for any specified impurity it obtained the substitution energy without distortion and minimized the energy by varying the impurity-host  $d'$  numerically. Finally, it evaluated the relaxation energy for that impurity-host combination.

We consider first the natural bond lengths obtained with the program. Listed in Table V are the natural bond lengths obtained for a wide range of impurities in the compounds in Tables II and III. In discussing the results we use these values, as well as other values obtained with the same program.

There is seen to be significant dependencies upon environment. Note from Table V that we obtain a natural bond length of 2.19 Å for the Si—P bond in AlP, while from Table V it is 2.24 Å for P embedded in silicon, which is nonpolar. Similarly the natural Zn—P bond length was found to be 2.63, 2.64, and 2.59 Å in AlP, GaP, and InP, respectively (with of course Zn substituted for the metallic atom). On the other hand, it was the single value 2.53 Å in ZnS, ZnSe, and ZnTe (with P substituted for the nonmetallic atom). The larger natural bond lengths occur when the polarity is lower and therefore the effects of metallization larger, the differences being largest when one of the environments is homopolar.

We see that for a given environment the natural bond length ordinarily decreases as the impurity is taken from further right in the Periodic Table due to the increasing energy in the denominator of the overlap interaction. For an extreme case, such as Zn substituted for As in GaAs, the energy decreases monotonically with spacing so there is no natural bond length in our model. This is also true in the other extreme with Se substituted for Ga in GaAs, due in this case to the very large metallization energy. The difficulty appears to be the very soft, long-range interatomic repulsion obtained with this formulation; it led also to force constants much smaller than experiment. We may surmise that we have overestimated the effects in other cases also, but expect that the qualitative trends are correct.

An interesting comparison is the In—As natural bond

length of 2.65 Å in GaAs, as opposed to 2.61 Å in InAs; the Ga—As natural bond length is 2.43 Å in InAs as opposed to 2.45 Å in GaAs. Note that the two deviations are of opposite sign so the average of the impurity-host bond lengths, 2.54 Å, is almost exactly equal to the average of the bulk bond lengths, 2.53 Å, so we predict Vegard's law to be accurately satisfied.

An important case is the substitution of As for Ga in GaAs; that is, the arsenic antisite defect in GaAs. The natural bond length from Table V is 2.40 Å, which we shall see corresponds to a relaxed bond length in the crystal of 2.41 Å. Bachelet and Scheffler<sup>19</sup> have made a much more complete calculation of the relaxation of the neighbors to arsenic and find the displacements to be very small. In the doubly ionized state, appropriate to our calculation, they also find an inward relaxation, but smaller than the one we find.

The particular combinations Si—P and Zn—P are of interest since there are nontetrahedral compounds SiP<sub>2</sub> and Zn<sub>3</sub>P<sub>2</sub> containing these bonds. In the case of SiP<sub>2</sub>, the P is tetrahedrally coordinated and there is a P—P bond of 2.13 Å, in good agreement with the 2.15 Å from Table V. In Zn<sub>3</sub>P<sub>2</sub> the phosphorus is sixfold coordinated and the Zn fourfold coordinated with a separation of 2.48 Å, smaller than the 2.53 Å (P in ZnSe) and the 2.63 Å (Zn in AlP) obtained from Table V. There must be important effects aside from coordination. This and some further comparisons in Sec. IV B suggest that the predictions are not reliable.

Our natural bond lengths are very nearly equal to the pure-material bond lengths for tetrahedral, IV-IV, III-V, and II-VI bonds. These are the systems where the variations of natural bond length are important to the heats of solution; extrapolations to the other bonds, II-V, etc., are less important to the heats of solution since other terms dominate.

## B. Distortion and relaxation energy at impurity atoms

We now wish to use the natural bond lengths discussed in the preceding section to predict the properties of impurities. To do this we use a simple model which will give us the relaxed bond length in terms of the natural impurity-host bond length and the host bond length; it will also give us the relaxation energy in terms of that which we have already calculated for full relaxation without constraints from the lattice. We can then obtain the needed results directly from the numbers obtained above.

### 1. The relaxation

In the cluster model,<sup>6,18</sup> the outer 12 atoms in Fig. 1, labeled  $A$ , are held fixed. It is very easy to solve for a small radial displacement  $u$  of the nearest-neighbor atoms labeled  $B$  by setting the total force on one of them equal to zero, assuming that the radial forces dominate the problem and a single force constant  $k$  is appropriate. There is a force on the  $B$  atom given by  $k$  times the natu-



TABLE V. Calculated natural bond lengths  $d'_{X-B}(AB:X_A)$  and  $d'_{X-B}(AB:X_B)$  (in units of angstroms), between atom  $X$  and atom  $B$  for  $X$  substituted, respectively, for atom  $A$  or atom  $B$  in the compound  $AB$ . In all cases,  $A$  and  $B$  are from the same row of the Periodic Table.

$d'_{X-B}(AB:X)$ or $d'_{X-B}(AB:X_B)$	X														
	Zn	Ga	Ge	As	Se	Mg	Al	Si	P	S	Cd	In	Sn	Sb	Te
$d'_{X-Si}(SiSi:X_{Si})$	2.96	2.56	2.39	2.31	2.16	3.18	2.55		2.24	2.06	3.47	2.80	2.56	2.49	2.31
$d'_{X-Ge}(GeGe:X_{Ge})$	3.35	2.66		2.38	2.21		2.64	2.40	2.30	2.13		2.92	2.61	2.54	2.36
$d'_{X-Sn}(SnSn:X_{Sn})$	3.37	2.84	2.67	2.61	2.41	4.44	2.84	2.62	2.54	2.35	4.25	3.06		2.78	2.56
$d'_{X-Al}(AlP:X_{Al})$	2.63	2.36	2.21	2.10		2.73		2.19	2.15		2.93	2.56	2.36	2.31	2.23
$d'_{X-Ga}(GaAs:X_{Ga})$	2.78		2.30	2.44		2.93	2.44	2.26	2.36		3.09	2.65	2.43	2.41	
$d'_{X-In}(InSb:X_{In})$	2.92	2.63	2.58			3.12	2.65	2.55			3.19		2.64		
$d'_{X-Zn}(ZnSe:X_{Zn})$		2.22	2.06	2.05		2.57	2.22	2.05	2.02	2.64	2.67	2.39	2.19	2.13	2.05
$d'_{X-Cd}(CdTe:X_{Cd})$	2.62	2.38	2.26			2.76	2.41	2.25	3.20	2.54		2.54	2.35	2.37	
$d'_{Al-X}(AlP:X_P)$	3.06		2.71	2.43	2.27	3.19	2.67	2.48		2.17	3.64	2.95	2.73	2.64	2.46
$d'_{Ga-X}(GaAs:X_{As})$		2.81	2.56		2.28		2.74	2.49	2.36	2.19		3.09	2.74	2.63	2.44
$d'_{In-X}(InSb:X_{Sb})$		2.98	2.73	2.63	2.45		2.93	2.68	2.56	2.38		3.23	2.90	2.62	2.62
$d'_{Zn-X}(ZnSe:X_{Se})$	3.05	2.85	2.69	2.62		3.08	2.78	2.63	2.53	2.34	3.23	3.01	2.85	2.81	2.64
$d'_{Cd-X}(CdTe:X_{Te})$	3.19	3.01	2.85	2.80	2.63	3.22	2.96	2.80	2.73	2.53	3.34	3.17	3.01	2.99	

ral bond length  $d_n$  for the  $X-B$  bond minus the host bond length  $d_0$ , minus the displacement of the  $B$  atom;  $F = k(d_n - d_0 - u)$ . There are also forces from the  $A$  atoms due to the displacement. We must take components of the displacement ( $u/3$ ) along the second-neighbor ( $A-B$ ) bonds, take the radial component of the resulting force ( $-ku/9$ ), and add it for the three bonds to  $A$  atoms to obtain  $ku/3$ . Setting the total equal to zero gives the equilibrium displacement

$$u = \frac{3}{4}(d_n - d_0). \quad (21)$$

The impurity-host bond stretches three quarters of the way from the host bulk length  $d_0$  to its natural bond length  $d_n$  as follows:

$$d = (d_0 + 3d_n)/4. \quad (22)$$

Note that we have taken all the same force constants and then they cancel from the result. Our underestimate of the force constants seen in Table III does not directly lead to error in the relaxed bond length.

We may then use the natural bond lengths from Table V to directly predict the equilibrium distortions for various impurities. Unfortunately, only a few have been measured or calculated by more accurate methods.

Recently Erbil, Weber, Cargill, and Boehme<sup>20</sup> used extended x-ray-absorption fine structure (EXAFS) to determine that the As-Si distance for As dissolved in silicon is  $2.41 \pm 0.02$  Å, greater than the bulk-silicon bond length by  $0.06$  Å. From Table V we obtain a natural As-Si bond length of  $2.31$  Å and thus a relaxed bond length of  $2.32$  Å. We find a relaxation of the opposite sense to that given by the measurements. Self-consistent Green's-function calculations by Scheffler *et al.*<sup>21</sup> appear to have been in the same direction as the experiment, but smaller by a factor of 2. Note that this is a shallow impurity level so no appreciable effects of the charge state of the impurity are expected.

More recently Sette, Pearton, Poate, Rowe, and Stöhr<sup>22</sup> similarly found the Ga-S distance for S dissolved in GaAs to be  $2.43 \pm 0.04$  Å compared with our estimated  $2.19$  Å using Table V. In this case we seem to have considerably overestimated the distortion.

Preliminary self-consistent local-density calculations by Froyen and Zunger<sup>23</sup> have given  $2.47$  Å for the Si-Mg distance for Mg substituted in Si. We considerably overestimate the spacing at  $2.97$  Å, obtained using the  $3.18$  Å natural bond length from Table V.

Mikkelsen and Boyce<sup>24</sup> have measured the In-As distance for In dissolved in GaAs and the Ga-As distance for Ga dissolved in InAs but these are fitted well by the use of pure-compound bond lengths as natural bond lengths and that is close to what we predict.

## 2. The relaxation energy

The total elastic energy initially arose from the distortion of the four impurity-host bonds and was  $4 \times \frac{1}{2}k(d_n - d_0)^2$ . After relaxation it included the reduced elastic energy of the four impurity-host bonds plus the elastic energy of the twelve  $B-A$  springs; that equals

$\frac{1}{2}k(d_n - d_0)^2$ . The reduction in energy therefore is three-quarters of the initial elastic energy. In our calculation of the natural bond length in Sec. IV A, we allowed the full unrestricted relaxation, corresponding to a relaxation of all of the elastic energy. Thus, the relaxation energy of the impurity is approximately three-quarters of the full unrestricted relaxation energy.

Because of this large cancellation it is essential to treat the relaxation in the same approximation that gave the initial misfit energy. This would be accomplished if we simply took three-quarters of the relaxation energy obtained in the tight-binding program described in the preceding section, though our underestimate of the spring constant by a factor of order 3 would suggest that we underestimate both misfit and relaxation by a factor of order 3, assuming that our natural bond lengths are well given. A simple way of approximately correcting the total-energy estimate is simply to use the unrelaxed energy of substitution. This underestimates the misfit by a factor of order 3, but neglects the fact that relaxation would reduce that misfit by a factor of order 4. It may not be the most appealing way to correct an intrinsic inaccuracy of the theory, but in the context of the cluster approximation and the inaccuracy of the force-constant prediction it may be as accurate as we can be.

As we have indicated, the substitution energies are not as easy to interpret as the properties we calculate in terms of them. We therefore turn to enthalpies of solution and heats of mixing.

## V. ENTHALPY OF SOLUTION AND THE HEAT OF MIXING

In order to use our tables for determining a property we must specify exactly what experimental quantity is being evaluated. We define an energy of substitution of a free atom  $X$  for an atom  $A$  in the compound  $AB$  leaving the atom  $A$  as a free atom. This was well defined but ordinarily not the quantity directly measured. The enthalpy of solution of the compound  $AB$  in the compound  $CD$  may be defined as the energy required to remove an  $A$  and a  $B$  atom from the compound, to substitute the  $A$  atom for a  $C$  atom and the  $B$  atom for a  $D$  atom in  $CD$ , and to return the  $C$  atom and the  $D$  atom to the bulk  $CD$ . This energy is

$$H_{CD}(AB) = E_{\text{coh}}(AB) + E_{CD}(A_C) + E_{CD}(B_D) - E_{\text{coh}}(CD) \quad (23)$$

per atom pair. This would be the energy for an  $AB$  pair to leave a step in a heterojunction between  $AB$  and  $CD$  and dissolve into the  $CD$ . The pair was removed from a step so the interface energy does not change; the step simply moves.

For example, the enthalpy of solution for Ge in GaAs from this formula is the cohesive energy of germanium, given in Table II as  $9.19$  eV per atom pair. Energies of substitution are obtained from Table IV. In particular,  $E_{\text{GaAs}}(\text{Ge}_{\text{Ga}})$  is  $-3.01$  eV,  $E_{\text{GaAs}}(\text{Ge}_{\text{As}})$  is  $+3.21$  eV, and  $E_{\text{coh}}(\text{GaAs})$  is  $8.37$  eV for a total of  $1.02$  eV per pair. This is a large positive enthalpy of solution. Germanium

is quite insoluble in gallium arsenide.

We may note here that the misfit and relaxation are rather small on the scale of  $H_{CD}(AB)$ . We calculate an unrestricted relaxation for the two cases of  $-0.193$  eV and  $-0.083$  eV, for germanium on the gallium and the arsenic sites, respectively. This corresponds to a misfit energy of  $0.27$  eV included in our calculated value, only a quarter of the total. We also argue that this is an underestimate, but that relaxation of the full value brings the total near to the  $1.02$  eV we obtain from the program.

These are heterovalent solutions, since Ge is from column IV and GaAs is a III-V compound. However, note that though in substituting Ge for Ga we place an electron at the valence-band maximum, we remove it in the substitution of Ge for As. This will generally be true for molecular solutions of this kind. If we dissolve GaAs in Ge, the  $p$ -type doping of the Ga cancels the  $n$ -type doping of the As. In contrast, if we were to dissolve Ga from metallic gallium into germanium, electrons would be removed from the germanium at the Fermi energy. If the germanium is  $p$  type the Fermi energy lies at the valence-band maximum as we have assumed. If the germanium is  $n$  type, the electrons would again be added at the Fermi energy, which now is at the conduction-band minimum. The enthalpy of solution would be reduced by an energy equal to the band gap in germanium. We shall consider such a case in Sec. V C.

It will generally be true for heterovalent solutions that  $H_{CD}(AB)$  is large and positive and that the relaxation is quite small in comparison. In contrast, for homovalent solutions, such as InAs in GaP,  $H_{CD}(AB)$  is dominated by the misfit energy, some three-quarters of which is cancelled by relaxation. Again we expect an underestimate of a factor of order 3 so our unrelaxed estimate should be approximately correct. Indeed, it was noted earlier<sup>13</sup> in a similar calculation that the unrelaxed estimate was in reasonable accord with experiment, while relaxation re-

duced it far below the experimental values. We now understand why.

The comparison with the experiment is frequently made for the heat of mixing, which for ideal solutions is given by  $\Delta H^m = \Omega X(1-X)$ , where  $X$  is the concentration of one constituent.<sup>2</sup> This assumes that  $H_{AB}(CD) = H_{CD}(AB)$ , which is only approximately true experimentally and in our calculation. However, we may compare experimentally determined values of  $\Omega$  with the average enthalpy of solution

$$\begin{aligned} \Omega_{\text{theor}} &= [H_{AB}(CD) + H_{CD}(AB)]/2 \\ &= [E_{CD}(A_C) + E_{CD}(B_D) + E_{AB}(C_A) + E_{AB}(D_B)]/2, \end{aligned} \quad (24)$$

where we have noted that when Eq. (23) is inserted, the cohesive energies cancel out.

Experimental values for  $\Omega$  are available for a number of isovalent solutions<sup>2</sup> so we consider those first. We then treat heterovalent solutions and ones which result in doping.

#### A. Isovalent solutions

Predicted values for  $\Omega$  are directly obtained from Eq. (24) using the energies of substitution from Table IV. These are listed in Table VI for a number of isovalent mixtures along with experimental values where available,<sup>2</sup> and predictions of the Martins and Zunger<sup>6</sup> model B discussed above. All are positive (or essentially zero), indicating energy must be supplied to transfer atoms across the interface. Our estimates are in reasonable accord with experiment, as are the Martins and Zunger values.

We may see from our calculations that our estimate is principally misfit energy by calculating that misfit energy using the cluster model and the force constant which

TABLE VI. Heat of mixing  $\Omega$  (in units of eV per molecule of mixture) for isovalent mixtures.

Compound	Total [Eq. (24)]	Misfit [Eq. (25)]	Martins <sup>a</sup> and Zunger	Experiment <sup>b</sup>
AlAs/GaAs	0.00	0.00	0.00	0.00
AlAs/InAs	0.22	0.11	0.31	0.22
AlSb/GaSb	0.00	0.00	0.00	0.00
AlSb/InSb	0.10	0.06	0.18	0.05
GaP/GaAs	0.06	0.03	0.10	0.03, 0.09
GaP/GaSb	0.50	0.31		
GaP/InP	0.24	0.12	0.39	0.30, 0.28
GaAs/GaSb	0.20	0.13	0.40	0.35, 0.39
GaAs/InAs	0.16	0.09	0.22	0.14, 0.26, 0.17
GaSb/InSb	0.10	0.06	0.22	0.13, 0.16
InP/InAs	0.03	0.02	0.06	0.03
InP/InSb	0.33	0.20		
InAs/InSb	0.16	0.11	0.25	0.20, 0.25
Ge/Si	0.09	0.03	0.14	0.10
Si/Sn	0.55	0.55	2.38	1.69
Ge/Sn	-0.02	0.27	1.33	0.65

<sup>a</sup>Reference 6.

<sup>b</sup>Reference 2.

come from our calculation. We see from Eq. (24) that our estimate of  $\Omega$  is one-half the energy to interchange an atom pair between the two compounds. Let the bond lengths and force constants for the two materials be  $d_1$ ,  $d_2$ ,  $k_1$ , and  $k_2$ . Let the natural bond length at an interchanged atom be  $\frac{1}{2}(d_1 + d_2)$  and the spring constant be  $\frac{1}{2}(k_1 + k_2)$ ; then without relaxation, as we calculate it, each of the 16 new bonds from the interchanged atom pairs has a bond differing by  $\frac{1}{2}(d_2 - d_1)$  from its natural bond length, for a misfit energy per bond of  $\frac{1}{2}[\frac{1}{2}(k_1 + k_2)][\frac{1}{2}(d_2 - d_1)]^2$ . There are 16 such bonds and we are to divide by 2 to obtain  $\Omega_{\text{misfit}}$ .

$$\Omega_{\text{misfit}} = \frac{1}{2}(k_1 + k_2)(d_2 - d_1)^2. \quad (25)$$

These values are also listed in Table VI. The two theoretical calculations are totally different, but the values are rather similar. This confirms the fact that for homopolar mixing the heat of mixing is dominated by misfit energy. To the extent that the solutions are ideal, it also follows that the individual enthalpies of solution are dominated by misfit.

Under these circumstances it is probably preferable to use the cluster model and experimental lattice constants and force constants as Martins and Zunger<sup>6</sup> did for homopolar substitutions where all of these parameters are known. Their values are essentially  $\Omega_{\text{misfit}}/4$ , based on empirical  $k_i$  and  $d_i$ . For heterovalent substitutions we must proceed with a more complete description, as we have done here. Then the fact that we have obtained reasonable results for the simpler homopolar case lends support to the method.

### B. Heterovalent solutions

We may immediately evaluate the enthalpies of solution using Eq. (23) and Table IV. Results for a number of heterovalent and isovalent systems are given in Table VII. The values are much larger than for the isovalent case. They are also much larger than the misfit contribution, obtained from Eq. (25). Unfortunately, there appear not to be experimental values with which to compare, although the comparison of experimental and theoretical energies of substitution in Sec. III E would suggest that they are approximately correct.

We may see what the principal contribution is by con-

sidering the individual terms. There is again no change in promotion energy in the solution process, but the sum of bond energies,  $-2(V_2^2 + V_3^2)^{1/2}$ , does change and this is the dominant term. This contribution is in fact the same as that treated empirically by Van Vechten<sup>25</sup> in the Phillips-Van Vechten dielectric model. For this reason, our treatment of antistructure defects in polar semiconductors,<sup>12</sup> gave values very close to those obtained earlier by Van Vechten. Indeed, antistructure defects consist of heterovalent substitutions. This is also the reason why the dielectric model did rather poorly in describing the heats of solution of isovalent impurities<sup>2,5</sup> which are dominated by misfit.

We may evaluate this contribution to the enthalpy of solution, by summing  $-2(V_2^2 + V_3^2)^{1/2}$  over the bonds before and after substitution. Since this is done bond by bond, it also makes it possible to make the evaluation for complex geometries such as transferring interface atoms across a heterojunction; this is the procedure used by Grant *et al.*<sup>26</sup> Applying it to an enthalpy of solution, for example, dissolving two germanium atoms into gallium arsenide, without relaxation, replaces four germanium-germanium bonds ( $8V_2$  with  $V_2 = -4.09$  eV) and four gallium-arsenide bonds [ $-8(V_2^2 + V_3^2)^{1/2}$  with  $V_3 = 2.16$  eV] by four gallium-germanium bonds and four germanium-arsenic bonds ( $-16[V_2^2 + (V_3/2)^2]^{1/2}$ ), for an increase in energy of 2.04 eV. This is to be compared with the value of 1.02 eV from Eq. (23) or Table VII. Adding the change in overlap interaction would raise our estimate even higher, but the change in metallization has brought it down to 1.02 eV. These estimates are qualitatively correct, indicating that the insolubility of the heterovalent systems arises because it is unfavorable energetically to replace strongly and weakly polar bonds by bonds of intermediate polarity. To be at all quantitative in the predictions requires the inclusion of the metallization.

### C. Solutions of dopants

The solutions described above were specifically chosen such that the atomic interchange involved no net transfer of charge. Of more importance are solutions, such as arsenic in germanium, in which there is a charge transfer and, as a consequence, carriers are added or subtracted—the system is doped.

TABLE VII. Enthalpy of solution  $H_{CD}(AB)$  of  $AB$  in  $CD$  (in units of eV per atom pair).

$AB \backslash CD$	SiSi	GeGe	SnSn	AlP	GaAs	InSb	ZnSe	CdTe
SiSi		0.08	0.28	1.82	0.59	0.06	5.19	3.96
GeGe	0.10		-0.14	2.26	1.02	-0.01	5.88	4.30
SnSn	0.82	0.106		3.52	1.54	0.77	6.44	4.88
AlP	1.57	1.58	1.80		-0.05	0.70	0.73	1.14
GaAs	0.68	0.78	0.57	-0.06		0.11	1.42	1.30
InSb	1.53	0.92	0.46	1.24	0.25		1.97	1.15
ZnSe	4.06	3.83	3.53	0.66	1.26	1.60		0.29
CdTe	4.22	3.57	-0.03	1.36	1.17	1.01	0.45	

In the case of arsenic, perhaps from gallium arsenide, being dissolved into germanium the germanium atom which is replaced can be returned to the germanium, but one must also specify what is to be done with the vacant arsenic site; we have been left with a nonstoichiometric gallium arsenide crystal unless, as in the preceding subsection, we also dissolve a gallium, but then there is no doping. One alternative is to fill the arsenic site with a germanium atom. In this case, we simultaneously dope the gallium arsenide  $p$  type and the germanium  $n$  type and the energy we calculate is the sum of the energies required to dope the two systems. This is the case which is treated here.

For the particular interchange we are discussing, we may directly add the energies of substitution  $E_{\text{GeGe}}(\text{As}_{\text{Ge}}) + E_{\text{GaAs}}(\text{Ge}_{\text{As}}) = 1.53$  eV. This process leaves a free arsenic and a free germanium atom before and after the interchange so they can be ignored. We should note, however, that in our substitution of the arsenic for germanium, we placed, by construction, the extra electron in the valence band. This would be appropriate if the germanium were  $p$  type, but if we are interested in the doping of otherwise intrinsic material (or further doping  $n$ -type germanium), we should move the electron to the conduction band, costing the gap energy for germanium, 0.76 eV. Thus the total energy for the interchange, which dopes the Ge  $n$  type and the GaAs  $p$  type, is the sum  $1.53 + 0.76 = 2.29$  eV.

We might instead wish to ask for the energy required to insert an arsenic atom into germanium, doping it  $n$

type, from a clump of arsenic on the germanium surface. We might do this by removing an arsenic atom from the arsenic metal, taking a cohesive energy of 2.96 eV, which we may obtain from a list for all elements given by Kittel.<sup>27</sup> We substitute this for a germanium atom, costing  $E_{\text{Ge}}(\text{As}_{\text{Ge}}) = -1.62$  eV, but we then require 0.76 eV to raise the extra electron to the conduction band of the germanium. Finally, we return the substituted germanium atom to the germanium, gaining the cohesive energy per atom of germanium of 4.60 eV, for a total cost in energy of 3.74 eV per dopant atom. Similarly, we could substitute a germanium atom from pure germanium for an arsenic atom in gallium arsenide, placing the resulting free arsenic atom in a pure arsenic crystal costing an energy of 0.19 eV. These two doping energies depend upon a use of empirical tables of the cohesive energy of the elements, but our theoretical values for cohesion are close enough to experiment that the combination of theoretical and experimental values should not cause problems.

The calculation of desired doping energies is so straightforward from our tables, and it is so important in any application to decide what the process is which is being considered, that we have not produced a table of these doping energies.

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