

Lattice relaxation around substitutional defects in semiconductors

Friedhelm Bechstedt* and Walter A. Harrison

Department of Applied Physics, Stanford University, Stanford, California 94305-4090

(Received 27 June 1988)

The tight-binding theory of total energies in semiconductors, based upon universal parameters, is modified following the findings on the overlap repulsion by van Schilfgaarde and Sher. The nonorthogonality S of neighboring orbitals is thus taken to vary as $1/d$ rather than $1/d^2$, giving a repulsion proportional to $1/d^3$. An additional repulsion due to nonorthogonality of valence orbitals with neighboring cores is taken to vary as $1/d^{12}$. The two coefficients are chosen to give the observed equilibrium spacing and bulk modulus of the homopolar materials. The fit gives nonorthogonalities S near the expected value of 0.5. A natural generalization of the repulsion to polar materials predicts spacings and bulk moduli in reasonable accord with experiment in the compounds. The method is then applied to the prediction of lattice distortion around substitutional impurities and energies of substitution. The results are in excellent agreement with the known experimental values.

I. INTRODUCTION

When an impurity atom is placed at an atomic site of an ideal bulk semiconductor, it exerts forces which displace the surrounding host atoms from their equilibrium positions in the unperturbed crystal. This lattice relaxation¹ influences both the solubilities and the electronic properties of the impurities in semiconductors. Furthermore, it seems that lattice relaxation also affects the transport properties, more strictly the capture cross sections, especially at low temperatures. It is therefore of scientific and technological interest.

Experimental studies are mainly restricted to extended x-ray-absorption fine structure (EXAFS) experiments.²⁻⁸ However, information about the lattice distortion may also be extracted from spectroscopic investigations.^{9,10} The spectroscopic methods are especially powerful for the measurement of the lattice distortion energies.¹¹ From solubility data¹² substitution energies can be extracted. A variety of theoretical studies exists. The more sophisticated calculations for both the lattice distortion and the energy use the local version of the density-functional theory.¹³⁻¹⁸ However, semiempirical models are also applied.¹⁹⁻²⁴

We continue this line of semiempirical calculations and apply the well-known tight-binding theory^{25,26} to the ground-state properties of the perturbed system. In Sec. II we restate the total-energy problem using a new form of the pair repulsion energy. The purpose is to obtain a form and associated parameters which may be expected to apply to the system with impurities. The theory is tested by calculating important ground-state properties of the ideal crystals: the equilibrium interatomic spacing, the cohesive energy, and the bulk modulus. In Sec. III the theory is extended to perturbed systems and used to estimate impurity-host interatomic distances and total-energy changes. In Sec. IV the results are compared with experimental and other theoretical values and are discussed.

The principal goal is to provide a simple theory for interatomic distances since an earlier tight-binding analysis²⁴ appeared unreliable in this regard. Certainly for this purpose the metallization of bonds through coupling to neighboring antibonds cannot be ignored since it is responsible for the lack of dependence of bond length on polarity in the series isoelectronic with germanium while there is a strong dependence on polarity in the series isoelectronic with carbon.²⁴ Therefore, a rather complete analysis is necessary.

II. IDEAL SEMICONDUCTOR CRYSTALS: A TEST OF THE THEORY

A. Total energy of the bulk

We consider a tetrahedrally coordinated compound with two atoms A and B , cation and anion, in the elementary cell. The numbers of valence electrons of each atom are Z_A and Z_B , with $Z_A + Z_B = 8$. The principal quantum numbers of the valence electrons (which corresponds to the row in the periodic table in which the atom is situated) are denoted by n_A or n_B . The valence electrons form two chemical bonds per atom by interaction between opposing sp^3 hybrids. A complete theory of the total energy of such a system is rather difficult. However, reasonable approaches are possible within the tight-binding method which moreover allows physical insights into the bonding process. We follow the procedure given in detail by Harrison and Kraut.²⁴ In the bond-orbital approximation^{25,26} the total energy of a zinc-blende (or diamond) structure with N atoms per unit volume can be approximated as²⁴

$$E_{\text{tot}}^{AB} = 4N(E_{\text{bond}} + E_{\text{met}} + E_{\text{rep}} + E_{\text{cor}}). \quad (1)$$

The four contributions are the following.

(a) The one-electron energy E_{bond} of an electron occupying a bond

$$E_{\text{bond}} = \frac{1}{2}(\epsilon_h^A + \epsilon_h^B) - (V_2^2 + V_3^2)^{1/2}, \quad (2)$$

where the sp^3 hybrid energies of cation and anion

$$\epsilon_h^A = \frac{1}{4}(\epsilon_s^A + 3\epsilon_p^A) \quad (3)$$

are given in terms of atomic s and p orbital energies, ϵ_s^A and ϵ_p^A , respectively. We use the atomic Hartree-Fock values of Mann.²⁷ A complete collection can be found in Ref. 28. The difference of these hybrid energies is written as twice the polar energy V_3 defined by

$$V_3 = \frac{1}{2}(\epsilon_h^A - \epsilon_h^B). \quad (4)$$

Each of these sp^3 hybrids is coupled to another forming a two-center bond with the covalent energy V_2 which is given as in Refs. 28 and 29. We define here V_2 to be the *magnitude* of the coupling, positive rather than the negative values defined earlier,

$$V_2 = 3.22\hbar^2/md^2 \quad (5)$$

in terms of the nearest-neighbor interatomic distance d . The energy E_{bond} neglects any coupling between bonds and neighboring antibonds.

(b) The metallization energy E_{met} is a correction to E_{bond} due to the coupling of the bonds to nearest-neighbor antibonds, calculated in perturbation theory.²⁹ To second order in this coupling it has the form

$$E_{\text{met}} = -\frac{3}{8}(1 - \alpha_p^2)^{3/2}[(V_1^A)^2 + (V_1^B)^2]/V_2, \quad (6)$$

where

$$\alpha_p = \frac{V_3}{(V_2^2 + V_3^2)^{1/2}} \quad (7)$$

is the polarity of the bond. V_1^A or V_1^B arises from interaction of two different hybrids on the same atom A or B . It is called the metallic energy.^{25,28,29} Again it is taken here to be the magnitude of the coupling,

$$V_1^A = \frac{1}{4}(\epsilon_p^A - \epsilon_s^A). \quad (8)$$

(c) The interatomic repulsion energy E_{rep} (per electron) may be split into two terms,

$$E_{\text{rep}} = SV_2 + \Delta E_{\text{rep}}. \quad (9)$$

The first term originates from the nonorthogonality of the neighboring hybrids, with S the nonorthogonality or the overlap integral of the two sp^3 hybrids. If S is calculated numerically from Hartree-Fock wave functions, it is found to vary approximately as³⁰ $1/d$ rather than as the $1/d$ suggested by extended Hückel theory.²⁹ We recognize that its value will depend upon the principal quantum number but neglect any dependence upon the column in the periodic table. Since two different atoms are involved in the overlap we make the ansatz

$$S = [S_0(n_A) * S_0(n_B)]^{1/2} \frac{a_0}{d} \quad (10)$$

with the atomic unit $a_0 = 0.529 \text{ \AA}$. The correction ΔE_{rep} represents contributions from the valence-core and core-core nonorthogonality which van Schilfgaard and Sher³⁰ have found to be essential. We write these small corrections as a short-range potential

$$\Delta E_{\text{rep}} = \frac{\hbar^2}{2ma_0^2} [C(n_A) * C(n_B)]^{1/2} \left[\frac{a_0}{d} \right]^{12} \quad (11)$$

of the form of the Lennard-Jones potential.³¹ Whereas $S_0(n)$ is a weak function of the principal quantum number n of the valence electrons, the dependence of $C(n)$ on n is much stronger. We have chosen such functions so that the resulting total energy Eq. (1) gives the correct interatomic equilibrium spacing $d = d_0$ and bulk modulus B for the four covalent materials diamond, silicon, germanium and grey tin. The results for the pair repulsion energy are summarized in Table I. The nearly constant value of Sd_0 is consistent with the ansatz Eq. (10) and the findings of van Schilfgaard and Sher³⁰ that $S \sim 1/d$ for variations from material to material as well as for a single material. The overlap integrals are found to have the correct general magnitude, $S = 0.5$. The magnitude of the short-range contribution ΔE_{rep} is found to be approximately the same for all four homopolar semiconductors. Thus it varies as $\Delta E_{\text{rep}} = C(d_0/d)^{12}$ with a universal constant $C = 0.2 \text{ eV}$. Despite its small magnitude, its second derivative makes a large contribution to the bulk moduli B . The short-range part contributes to B as $156\Delta E_{\text{rep}}$ whereas the overlap interaction adds $12SV_2$. The inclusion separately of a $1/d^3$ and a $1/d^{12}$ term, rather

TABLE I. Overlap repulsion SV_2 and short-range repulsion ΔE_{rep} resulting from the requirement that the total energy Eq. (1) gives rise to the correct interatomic equilibrium spacings d_0 and the bulk moduli B in the case of group-IV materials C, Si, Ge, and α -Sn. Some derived parameters entering Eqs. (10) or (11) are also listed.

Parameter	C	Si	Ge	α -Sn
n	2	3	4	5
d_0 (Å)	1.54	2.35	2.44	2.80
B (10^{11} erg/cm ³)	44.20	9.78	7.72	5.31
SV_2 (eV)	6.032	1.717	1.428	0.761
ΔE_{rep} (eV)	0.150	0.233	0.213	0.231
S	0.584	0.387	0.347	0.244
S^*d_0 (Å)	0.899	0.909	0.846	0.683
$S_0(n)$	1.670	1.718	1.599	1.291
$C(n)$ (10^4)	0.408	96.199	145.15	819.75

than the single $1/d^4$ term used earlier,²⁴ is essential to obtaining both correct spacing and bulk modulus. Van Schilfgaarde *et al.* found that the short-range term is present and we explored possible forms, finding that a d^{-12} gave better results than a d^{-8} form.

(d) The energy E_{cor} represents the effects of the electron-electron interaction which are different in the solid than in the atom. The principal effect comes from promotion of electrons to an sp^3 electron configuration in the solid.³²⁻³⁴ Thus they affect the cohesive energy but, since they are largely intraatomic³²⁻³⁴ they have little effect on the interatomic forces. We adjust it to fit the cohesive energy for C, Si, Ge, and α -Sn and use the same value for any atom in the same row.

The resulting total energy per atom Eq. (1) as a function of nearest-neighbor distance d is shown in Fig. 1 for C, Si, and α -Sn. The curves are shifted on the energy scale in such a way that the negative value of E_{tot}^{AB}/N at the minimum position, i.e., the equilibrium position $d=d_0$, is equal to the cohesive energy of these elemental semiconductors. For large distances d , larger than the second-nearest-neighbor spacing $(\frac{8}{3})^{1/2}d$, the perturbation theory used in calculating E_{met} becomes inappropriate and E_{tot}^{AB}/N begins to grow in proportion to $-d^2$. However, E_{tot}^{AB} is well behaved up to third-nearest-neighbor distances. Furthermore, this artifact of the approximation is remarkably softened in the case of the polar compounds since the separation of antibonding and bonding level is increased by the polar energy V_3 .

B. Ground-state properties of the materials

1. Cohesive energy E_{coh}

Within the same approximations used in the derivation of E_{tot}^{AB} in Eq. (1) the total energy of a free atom A with two s electrons and $(Z_A - 2)$ electrons follows as^{33,34}

$$E_{\text{tot}}^A = 2\epsilon_s^A + (Z_A - 2)\epsilon_p^A + 4E_{\text{cor}}^A. \quad (12)$$

Now the cohesive energy E_{coh} per atom of the bulk compounds can be represented by a combination of expressions (1) and (12) as

$$E_{\text{coh}}^{AB} = \frac{1}{2}(E_{\text{tot}}^A + E_{\text{tot}}^B) - E_{\text{tot}}^{AB}(d=d_0)/N, \quad (13)$$

where the total energy of the bulk semiconductor has to be taken at the equilibrium nearest-neighbor spacing d_0 . With Eqs. (1) and (12) the well-known form²⁵

$$-E_{\text{coh}}^{AB} = 4[E_{\text{pro}} - (V_2^2 + V_3^2)^{1/2} + E_{\text{met}} + E_{\text{rep}} + E_{\text{cor}}] \quad (14)$$

results if the promotion energy (per solid-state electron)

$$E_{\text{pro}} = \frac{1}{2}[V_1^A + V_1^B + (1 - \frac{1}{4}Z_A)(\epsilon_p^A - \epsilon_p^B)] \quad (15)$$

is introduced. The small additional contribution due to the difference in the electron correlation in the bulk and the free atoms we have represented as

$$\Delta E_{\text{cor}} = \frac{1}{2} \sum_{i=A,B} U(n_i) [1 + 2(1 - \frac{1}{4}Z_i) + 1.41(1 - \frac{1}{4}Z_i)^2] \quad (16)$$

according to a more detailed analysis of the inclusion of the electron-electron interaction into the tight-binding theory.^{28,32-34} $U(n)$ in Eq. (16) is taken to be the value fit for C, Si, Ge, and α -Sn.

2. Equilibrium conditions

The equilibrium conditions and formula for the bulk modulus for zero temperature are

$$\frac{\partial}{\partial V} E_{\text{tot}}^{AB}(\text{equ}) = 0, \quad (17a)$$

$$V \frac{\partial^2}{\partial V^2} E_{\text{tot}}^{AB}(\text{equ}) = B. \quad (17b)$$

The dependence upon d of each term in the total energy has been written explicitly. Thus Eqs. (17) may be rewritten with respect to d instead of V in equations defining the equilibrium bond length d_0 and the bulk modulus B . The bond length d has to be replaced by the equilibrium value d_0 and the bulk modulus by the experimental one to obtain the functions $S_0(n)$ [Eq. (10)] and $C(n)$ [Eq. (11)] so determining the repulsive interaction for the homopolar semiconductors. The generalizations Eqs. (10) and (11) to compounds then allow prediction of their properties.

3. Explicit values: predictions for compounds

The data resulting from Eqs. (14) and (17) for the ground-state properties of bulk semiconductors are summarized in Table II. Note that parameters have been adjusted to fit the homopolar materials so the table represents the generalization of the equations to compounds. For comparison experimental data for the interatomic spacing d_0 and the bulk modulus are also given. We restrict ourselves to materials in the diamond

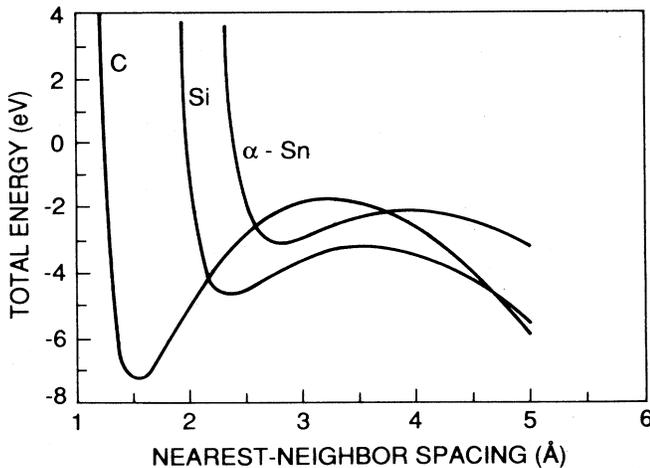


FIG. 1. Total energy per atom in diamond, silicon, and grey tin as a function of the bond length. The energy zero point is shifted so that the negative value of the energy in the minimum gives the cohesive energy of the material.

TABLE II. Equilibrium properties of a variety of diamond- and zinc-blende-structure semiconductors.

Semiconductor	d_0 (Å)	E_{coh} (eV)	Experiment		Theory	
			B (10^{11} erg/cm 3)	d_0 (Å)	E_{coh} (eV)	B (10^{11} erg/cm 3)
C	1.54	7.36	44.20	1.54	7.36	44.20
Si	2.35	4.64	9.78	2.35	4.64	9.78
Ge	2.44	3.87	7.78	2.44	3.87	7.78
α -Sn	2.80	3.12	5.31	2.80	3.12	5.31
SiC	1.88	6.34	9.70	2.22	5.12	12.57
BN	1.57	6.68		1.58	6.71	28.47
AlP	2.36	4.26	8.60	2.38	4.67	8.74
AlAs	2.43	3.78	7.73	2.41	4.39	8.94
AlSb	2.66		5.93	2.67	3.57	6.97
GaP	2.36	3.56	8.87	2.41	3.74	9.00
GaAs	2.45	3.26	7.48	2.43	3.49	9.48
GaSb	2.65	2.96	5.63	2.68	2.79	6.89
InP	2.54	3.48	7.25	2.58	3.86	7.72
InAs	2.61	3.10	5.80	2.61	3.45	7.48
InSb	2.81	2.80	4.66	2.79	2.72	6.38
MgTe	2.76	2.86		2.77	3.37	3.73
ZnS	2.34	3.18	7.80	2.57	2.94	3.01
ZnSe	2.45	2.58	5.95	2.54	2.60	4.48
ZnTe	2.64	2.28	5.09	2.66	2.20	5.29
CdS	2.53	2.84	6.44	2.91	2.89	1.58
CdSe	2.63		5.50	2.83	2.39	2.72
CdTe	2.81	2.06	4.24	2.88	1.87	3.66
HgTe	2.80		4.23	3.06	4.75	3.16

or zinc-blende structure. The experimental data are taken from different collections.^{25,30,31,33,35}

The comparison between theoretical and experimental values is considerably improved over the earlier analysis²⁴ which was based upon a d^{-4} repulsion. The chemical trends and approximate absolute values for the equilibrium bond length d_0 and the cohesive energy E_{coh}^{AB} are correctly predicted by the present theory in most cases. This holds also for the magnitude of the bulk moduli B . The smallest discrepancies are observed if the row and/or the column in the periodic table of the two atoms forming the compound are the same. The discrepancies increase with increasing differences between the two atoms. The general agreement suggests that the theory of the total energy may be applicable to the impurity problem, particularly for the study of the lattice relaxation and the energy of substitution. However, we should be aware of the limitations in accuracy suggested by discrepancies in predictions for the bulk.

One discrepancy worth noting is the cohesive energy of SiC, which we predict to be smaller than the average of that for Si and C values by 0.88 eV, whereas the experimental cohesion of SiC is seen to be *larger* than the average by 0.34 eV. This may be related to a tendency for tight-binding theory to overestimate cohesion in the carbon-row compounds by a factor of order two.²⁹ This does not appear in the diamond cohesion in Table II since we have adjusted a correlation correction to bring it into accord. With this large a correction we cannot have confidence in its extension to compounds and impurities.

Because of this we should be particularly skeptical of any estimates involving elements from the carbon row, and we shall restrict our consideration to elements below that in the periodic table, except for the solution of Be and C in Si. Predictions for these two cases should be considered as quite tentative.

III. SUBSTITUTIONAL IMPURITIES: AN APPLICATION OF THE THEORY

Harrison and Kraut²⁴ have given in detail a procedure for calculation of the *energy of substitution*

$$E_{AB}(X_A) = E_{\text{tot}}^{XB} + E_{\text{tot}}^A - E_{\text{tot}}^{AB} - E_{\text{tot}}^X + (Z_X - Z_A)E_v, \quad (18)$$

$E_{AB}(X_A)$ is the energy required to remove an atom A from the bulk compound AB , leaving it as a free atom, and substitute a free atom X in its place. Any excess or deficit of electrons due to substitution of an atom of different valence are placed at, or removed from, the valence-band maximum E_v . In circumstances for which this is not appropriate, as in n -type hosts, corrections are to be made for the difference. E_{tot}^{XB} means the total energy of the AB compound under consideration in which one atom A is replaced by an atom X . E_v denotes the energy of the valence-band maximum which can be well described by the tight-binding method.²⁵ As did Harrison and Kraut we include the change in metallization in the substitution. Our procedure differs from theirs principal-

ly in that we use the $1/d^3$ and $1/d^{12}$ repulsions described above for the overlap repulsion E_{rep} , while they used a $1/d^4$ repulsion fit to give the observed lattice distance. This change has allowed us to fit the bulk modulus, while their predicted value was generally too small by a factor of order two. It has also provided us with much better predictions of equilibrium bond lengths in the compounds.

A second change, for cases in which electrons are added to or subtracted from the valence band, is that we did not include the shift $S(\frac{4}{3}V_{pp\sigma} + \frac{8}{3}V_{pp\pi})$ in the valence-band maximum due to nonorthogonality of the orbitals on neighboring atoms. Harrison and Kraut took S to be 0.5 for hybrids and scaled it by the ratio of the coupling $\frac{4}{3}V_{pp\sigma} + \frac{8}{3}V_{pp\pi}$ to the hybrid coupling V_2 . We actually have obtained values of S , as listed in Table I, and could use the same scaling. The contribution is small and the significance of our estimate of S uncertain enough that we chose to drop the correction.

We also carefully considered the self-consistent shift in the term values due to charging of the atoms but concluded that they were sufficiently small to be neglected, consistent with the more detailed cluster calculations by Harrison and Klepeis.³⁶ We noted that, for example, replacing a single germanium atom by arsenic in bulk germanium adds a proton to the germanium nucleus producing a potential e/r , reduced to $e/r\epsilon$ by the dielectric relaxation of the bonds in the crystal. From Poisson's equation we see that this leaves the germanium atoms in the bulk of the material neutral, but leaves a local charge of e/ϵ on the arsenic atom at the center. This shifts the hybrid energy on the arsenic down by U/ϵ , where U is the Hubbard $U=8.31$ eV for arsenic (the difference between electron affinity and ionization energy of the atom), tabulated by Harrison.²⁸ There is no shift in the arsenic hybrid energy from the neighboring germanium atoms since they are all neutral. However, the charge of e/ϵ on the arsenic lowers the hybrid energies of the nearest-neighbor germanium atoms by $e^2/\epsilon d=5.90$ eV/ ϵ , almost as large as the arsenic shift. Thus the polarity of the bond is little affected, and we can proceed with free-atom-term values as did Harrison and Kraut.

In both analyses, two energies of substitution are calculated. The first retains all bond lengths at the bulk AB value. The second allows formally the impurity-host ($X-B$) bond length to vary, holding all others fixed, in order to obtain an $X-B$ natural bond length in AB , written d_n . (This is of course not geometrically possible in a real lattice, but is mathematically convenient as a first step.) A simple force-constant model (given, for example, by Harrison and Kraut²⁴) then shows that the relaxed impurity-host bond length in the system is three-quarters of this natural bond length d_n plus one-quarter of the host bond length d_0 .

We list in Table III our computed natural bond lengths d_n and relaxed impurity-host bond lengths $d=(3d_n+d_0)/4$ for a number of systems. These are compared with experiment and with the results of full self-consistent calculations where they exist. They are also compared with values obtained by Harrison and

Kraut using the $1/d^4$ repulsion and with the semiempirical estimates for isovalent substitutions given by Martins and Zunger.¹⁹

In Table IV we list the substitution energy we obtained $E_{AB}(X_A)$ while allowing the full relaxation of the impurity-host bond length to its natural value so that every bond in the system has its natural length. In the real system, according to the simple force-constant model,²⁴ the impurity-host bond is shifted to $d_0+3(d_n-d_0)/4$ and the three neighboring host bonds are approximately deformed to $d_0-(d_n-d_0)/4$. The total elastic energy from the distortion of these 16 bonds is found to be of the simple form $E_{\text{elast}}=\frac{1}{2}k(d_n-d_0)^2$, where k is the force constant (taken from the bulk modulus for the host material). It describes the elastic deformation of the surrounding bonds and the lowering of the deformation of the central bonds going from d_n to d and, therefore, has to be added to the full relaxed values to obtain the correct $E_{AB}(X_A)$ with inclusion of lattice relaxation. For comparison in Table IV the values of $E_{AB}(X_A)$ without consideration of lattice distortion, i.e., where all bond lengths are equal to d_0 , are also given. The difference of the two values for $E_{AB}(X_A)$ (with and without relaxation) defines the lattice relaxation energy.

IV. DISCUSSION

The most reliable experimental determination of the lattice distortion around a substitutional defect comes from EXAFS measurements. From the comparison of the impurity-host bond length d in Table III we see that the present theory predicts changes of d with respect to the host-bulk bond length d_0 , $\Delta d=d-d_0$, which are in excellent agreement with all EXAFS results for isovalent but also nonisovalent impurities in covalent and polar semiconductors. Our predictions, compared with experimental values in parentheses, are for Si:As, 0.06 \AA ($0.06\pm 0.02 \text{ \AA}$);⁶ GaAs:In, 0.14 \AA (0.14 \AA);² AsGa:P, -0.02 \AA (-0.04 \AA);⁷ AsGa:S, 0.03 \AA ($-0.02\pm 0.04 \text{ \AA}$);⁵ PGa:As, 0.02 \AA (0.05 \AA);⁷ InAs:Ga, -0.15 \AA (-0.12 \AA);² SeZn:Te, 0.09 \AA (0.15 \AA);³ TeZn:Se, -0.09 \AA (-0.14 \AA);³ ZnTe:Cd, 0.18 \AA (0.11 \AA);⁴ and CdTe:Zn, -0.17 \AA (-0.12 to -0.13 \AA).⁴

The predicted Δd agrees less well with lattice distortions extracted from spectroscopic data via the relative volume changes.¹⁰ For group-V and group-VI donors in Si the trend of enlargement of the lattice distortion by heavier impurity atoms is correctly reflected. However the theory gives somewhat larger Δd . For the impurities P and S from the same row as the silicon host we predict a small outward relaxation while the experiment indicates a small inward displacement. At the same time we should note that the spectroscopic values do not agree so well with the presumably more accurate EXAFS determination⁶ where both have been made. The same conclusion holds for the agreement with the self-consistent pseudopotential calculations of Scheffler.¹⁶ On the other hand, we should mention that the IR measurements for Si:S, Se, Te (Ref. 10) are done for neutral donors.

The comparison with other self-consistent pseudopo-

TABLE III. (Continued).

Semiconductor	Impurity	$Z_X - Z_A$	d_n (Å)	d (Å) Theory	d (Å) EXAFS	d (Å) Spectrosc.	d (Å) SCPM	d (Å) Semtemp.	d (Å) TB
GaP	Ge	1	2.41	2.40			2.26		
			2.40						
PGa	As	0	2.41	2.43	2.41			2.41	
			2.43						
AlAs	Ga	0	2.40	2.42					
			2.43						
			2.40						
InAs	Ga	0	2.61	2.47	2.49				
			2.42						
PIn	In	2	2.58	2.72					
			2.76						
ZnSe	Ga	1	2.54	2.46					2.28
			2.44						
			2.41						
SeZn	Ge	-2	2.54	2.45					2.61
			2.41						
			2.46						
			2.66						
ZnTe	Cd	0	2.66	2.83	2.75			2.76	
			2.89						
			2.54						
TeZn	Se	0	2.66	2.57	2.50			2.50	
			2.54						
CdTe	Zn	0	2.88	2.71	2.68-2.69			2.67	2.67
			2.65						

TABLE IV. Energies of substitution with and without lattice relaxation. Results of an earlier tight-binding calculation (Ref. 24) are given for comparison.

Semiconductor	Impurity	$E_{AB}(X_A)$ (eV)		Ref. 24
		Without	With	
Si	Be	5.48	2.75	
	Mg	3.92	3.87	6.22
	Al	1.41	1.41	3.03
	Ga	3.13	3.11	3.74
	In	4.55	3.48	4.94
	C	-2.22	-4.04	-2.00
	P	-0.41	-0.46	-2.00
	As	-0.19	-0.30	-1.50
	Sb	1.04	-0.07	0.32
	S	1.08	0.94	-2.65
	Se	0.77	0.55	-2.08
	Te	1.65	0.31	-0.87
Ge	Zn	4.86	4.85	6.06
	In	2.99	2.34	3.91
	Ga	2.01	2.01	3.11
	Sn	0.93	0.36	1.12
	As	-0.87	-0.91	-1.51
	Se	0.19	0.05	-1.91
GaAs	Zn	2.96	2.91	2.62
	Al	-1.83	-1.84	-1.03
	In	0.84	-1.02	0.25
	Si	-3.13	-3.16	-3.46
	Ge	-2.31	-2.32	-3.01
	As	-4.46	-4.66	-5.62
AsGa	Ga	5.98	6.08	8.68
	P	-0.52	-0.52	-1.12
	Sb	1.33	0.80	2.17
	S	-0.18	-0.23	-2.90
	Se	-0.04	-0.10	-1.86
GaP	Ge	-2.25	-2.27	-2.77
PGa	As	0.53	0.51	1.24
AlAs	Ga	1.86	1.84	
	Si	-1.37	-1.37	
InAs	Ga	0.29	-0.09	
PIn	In	11.41	10.57	
ZnSe	Ga	-3.19	-3.33	-2.85
	Ge	-5.67	-5.99	-5.75

TABLE IV. (Continued.)

Semiconductor	Impurity	$E_{AB}(X_A)$ (eV)		Ref. 24
		Without	With	
SeZn	Ge	8.02	7.80	11.31
	As	2.78	2.72	4.77
	Te	1.01	0.81	2.57
ZnTe	Cd	1.42	0.75	
TeZn	Se	-0.69	-0.77	
CdTe	Zn	-0.29	-0.64	0.53

tential calculations^{14-18,37} gives similar results. The agreement with respect to the trends—inward or outward relaxation—is good but with respect to magnitude is scattered. In this context we mention two facts. (i) The self-consistent pseudopotential calculations give quite different results for the lattice relaxation depending upon the details. For example, in the case of the arsenic antisite in GaAs one calculation gives a strong outward relaxation $\Delta d = 0.2$ Å (Ref. 18) (as in our calculation) and another gives zero atomic displacements.¹⁷ (ii) If in our calculation an atom with a low metallic energy V_1^A is replaced by an atom with a much higher V_1^X , as for the As_{Ga} antisite formation in GaAs, the minimum of the total-energy change Eq. (18) with respect to the bond length d is rather flat so that small changes in the parameters produce strong changes in the lattice distortion Δd .

The semiempirical force-constant model¹⁹ is expected to be reliable for isovalent substitutions, such as In for Ga in GaAs, since all bonds present exist in pure compounds with known bond lengths. Our calculations, as expected, agree quite well with those semiempirical estimates, particularly for III-V and column IV systems.

Comparison with the recent tight-binding calculations of Harrison and Kraut²⁴ shows the effects of using the new pair repulsion. The new approach has predicted bulk lattice spacings too large in the strongly polar pure compounds. Harrison and Kraut²⁴ avoided this by adjusting the coefficient of the repulsion to obtain the correct spacing for every compound but this leads to less certainty in the extrapolation to impurities. Our discrepancies for the II-VI pure-compound bond lengths seem not to have caused serious problems for the impurities.

Considering the general trends among lattice relaxations in Table III, the most significant correlations, as expected, are that impurity atoms below the atom replaced in the periodic table cause outward relaxations and those above in the periodic table cause inward relaxations. The principal uncertainty in sign comes from substitutions from the same row. In that case the tendency is for atoms to the left to cause inward relaxation and those to the right to cause outward relaxations. These are in con-

trast to the predictions of tetrahedral radii.³⁸ The trend arises because of the increased metallization for elements to the right in the periodic table due to the larger V_1 . Exceptions arise when elements from column II in the periodic table are involved.

In the case of the substitution energies $E_{AB}(X_A)$ a comparison of theory and experiment is difficult. These energies are carefully measured only for a few systems. For neutral Zn, In, and Sn in germanium, Su and Brebrick¹² found values of 3.47, 1.95, and 0.83 eV, respectively, per impurity atom. Our values from Table IV of 4.85, 2.34, and 0.36 eV exhibit the same chemical trend as well as the same general magnitude as the experimental data. For comparison the predictions of Harrison and Kraut²⁴ were 6.06, 3.91, and 1.12 eV, respectively. This indicates that the new pair repulsion $1/d^3$ and $1/d^{12}$ is not only of importance for a correct prediction of the lattice distortion but also for the substitution energies. The general comparison of the substitution energies from Ref. 24 with our values (cf. Table IV) indicates the same chemical trends but considerable differences with respect to the magnitude of $E_{AB}(X_A)$.

The differences of $E_{AB}(X_A)$ (without lattice relaxation) and $E_{AB}(X_A)$ (with lattice relaxation) can be extracted from the corresponding values in the neighboring columns of Table IV. They vary between 0.0 and 2.7 eV. Usually these so-called lattice-distortion energies are rather small. Large values are only obtained if very small atoms (like Be and C in Si) or rather large atoms (like Te in Si and In in GaAs) are substituted in the host system. A comparison with experiment is only possible in the case of Si in GaAs and AlAs. The corresponding values from Table IV are 0.03 and 0.00 eV, respectively. These energies are in good qualitative agreement with the value obtained from photoionization of the DX center in lightly doped Si impurities in $\text{Al}_{0.33}\text{Ga}_{0.67}\text{As}$ (Ref. 11) as well as the Franck-Condon shifts estimated by Talwar *et al.*²⁰ to be 0.02 eV (GaAs) and 0.03 eV (AlAs).

ACKNOWLEDGMENT

This work was supported by the U.S. Office of Naval Research under Contract No. N00014-85-0167.

- *Permanent address: Sektion Physik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, DDR-6900 Jena, German Democratic Republic.
- ¹Compare to *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1966).
 - ²J. C. Mikkelsen and J. B. Boyce, Phys. Rev. Lett. **49**, 1412 (1982); Phys. Rev. B **28**, 7130 (1983).
 - ³J. C. Mikkelsen and J. B. Boyce (unpublished) (as cited in Ref. 19).
 - ⁴A. Balzarotti, A. Kisiel, N. Motta, M. Zimnal-Starnawska, M. T. Czyzyk, and M. Podgorny, Phys. Rev. B **30**, 2295 (1984); and unpublished (as cited in Ref. 19).
 - ⁵F. Sette, S. J. Pearton, J. M. Poate, J. E. Rowe, and J. Stöhr, Phys. Rev. Lett. **56**, 2637 (1986).
 - ⁶A. Erbil, W. Weber, G. S. Cargill III, and R. F. Boehme, Phys. Rev. B **34**, 1392 (1986).
 - ⁷T. Sasaki, T. Onda, R. Ito, and N. Ogasawara, Jpn. J. Appl. Phys. **25**, 231 (1986).
 - ⁸A. Balzarotti and N. Motta, Physica **146B&C**, 150 (1987).
 - ⁹G. W. Ludwig, Phys. Rev. **137**, A1520 (1965) (estimate of the lattice distortion for S^+ in Si has been deduced by Scheffler, Ref. 16, from the experimental data).
 - ¹⁰B. Pajot and A. M. Stoneham, J. Phys. C **20**, 5241 (1987).
 - ¹¹J. C. M. Henning and J. P. M. Ansems, Semicond. Sci. Technol. **2**, 1 (1987).
 - ¹²C.-H. Su and R. F. Brebrick, J. Phys. Chem. Sol. **46**, 963 (1985).
 - ¹³G. A. Baraff and M. Schlüter, Phys. Rev. B **30**, 1853 (1984); Phys. Rev. Lett. **55**, 1327 (1985).
 - ¹⁴M. Scheffler, J. P. Vigneron, and G. B. Bachelet, Phys. Rev. B **31**, 6541 (1985).
 - ¹⁵G. B. Bachelet and M. Scheffler, *Proceedings of the 17th International Conference on the Physics of Semiconductors*, edited by J. D. Chadi and W. A. Harrison (Springer-Verlag, New York, 1985), p. 755.
 - ¹⁶M. Scheffler, Physica **146B&C**, 176 (1987).
 - ¹⁷J. Dabrowski and M. Scheffler, Phys. Rev. Lett. **60**, 2183 (1988).
 - ¹⁸D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **60**, 2187 (1988).
 - ¹⁹J. L. Martins and A. Zunger, Phys. Rev. B **30**, 6217 (1984).
 - ²⁰A.-B. Chen and A. Sher, Phys. Rev. B **32**, 3695 (1985).
 - ²¹D. N. Talwar, M. O. Mansareh, K. S. Suh, and B. C. Covington, Appl. Phys. Lett. **51**, 1358 (1987).
 - ²²R. Jones, J. Phys. C **20**, L713 (1987).
 - ²³D. N. Talwar, K. S. Suh, and C. S. Ting, Philos. Mag. B **56**, 593 (1987).
 - ²⁴W. A. Harrison and E. A. Kraut, Phys. Rev. B **37**, 8244 (1988).
 - ²⁵W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).
 - ²⁶W. A. Harrison, Phys. Rev. B **23**, 5230 (1981).
 - ²⁷J. B. Mann, *Atomic Structure Calculations, I: Hartree-Fock Energy Results for Elements Hydrogen to Lawrencium* (1967), distributed by Clearinghouse for Technical Information, Springfield, VA 22125.
 - ²⁸W. A. Harrison, Phys. Rev. B **31**, 2121 (1985).
 - ²⁹W. A. Harrison, Phys. Rev. B **27**, 3592 (1983).
 - ³⁰M. van Schilfgaarde and A. Sher, Phys. Rev. B **36**, 4375 (1987).
 - ³¹C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976).
 - ³²O. F. Sankey and J. D. Dow, Phys. Rev. B **27**, 7641 (1983).
 - ³³F. Bechstedt, D. Reichardt, and R. Enderlein, Phys. Status Solidi B **131**, 643 (1985).
 - ³⁴F. Bechstedt and R. Enderlein, *Semiconductor Surfaces and Interfaces* (Akademie-Verlag, Berlin, 1988).
 - ³⁵*Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege (Springer-Verlag, Berlin, 1982), New Series, Group III, Vol. 17.
 - ³⁶W. A. Harrison and J. E. Klepeis, Phys. Rev. B **37**, 864 (1988).
 - ³⁷S. Froyen and A. Zunger (private communication).
 - ³⁸C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1967), p. 105.