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Theory of deep impurities in silicon-germanium alloys

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Calculations of the deep-energy levels of substitutional sp^3-bonded defects in Si_xGe_{1-x} alloys suggest that the standard shallow dopants As and P and the isoelectronic C defect may become deep traps for $x \simeq 0.2$.

I. INTRODUCTION

It has been recently accepted that the *deep* energy levels in the fundamental band gaps of semiconductors are bound primarily by the central-cell atomiclike defect potential.[1–3] Theories have been developed to predict quantitatively the chemical trends for the defect levels of a variety of sp^3-bonded impurities in several hosts.[2,4] Important applications have been made to technologically important alloy systems, such as $GaAs_{1-x}P_x$ (Refs. 2, 5 and 6), $Hg_{1-x}Cd_xTe$,[7] and $In_{1-y}Ga_yAs_{1-x}P_x$,[8] where the variations of the deep levels with alloy composition are especially interesting.

In this paper we examine one of the prototype semiconductor alloy systems, Si_xGe_{1-x}, and predict its deep levels. We study the crystalline form of these alloys that is of interest as a high-temperature thermoelectric material.[9] It has energy-band edges that vary almost linearly as functions of composition x.[10] The band gap, E_{gap}, is indirect, with the valence-band maximum at the center of the Brillouin zone (point Γ) and the conduction-band minimum changing from the point L $[=(2\pi/a_L)(\frac{1}{2},\frac{1}{2},\frac{1}{2})]$ to near the point X $[=(2\pi/a_L)(1,0,0)]$. The change occurs at the crossover point, approximately $x=0.15$.[10,11] It is this feature that makes the defect levels of this alloy interesting to study, since alloys with compositions near the crossover can possibly produce *deep* levels in the gap for impurities such as As and P, which have only *shallow* levels in the gap for both Si and Ge.

Near the band gap, every sp^3-bonded substitutional impurity with a valence greater than that of the tetrahedrally bonded host by unity is expected to have an A_1 (s-like) level, a triply degenerate T_2 (p-like) deep level, and an infinite number of shallow levels.[2] For impurities such as P in Si, the A_1 and T_2 deep levels are *resonances above* the conduction-band minimum—and are normally unobserved; only the shallow levels are observed in the gap. The deep resonant levels are distinct from the well-known shallow effective-mass levels. The present paper considers the conditions under which the lowest of these resonant levels can be driven in the band gap by changing the alloy composition of the host. When this happens, the lowest impurity level in the gap is the A_1 deep level, and the effective-mass shallow levels are above it; as a result, the P impurity switches from being a shallow donor to being a deep trap. We do not consider the shallow levels explicitly or the long-ranged Coulomb interaction responsible for them; we merely recognize that once a deep level descends into the gap, it provides the ground state for the extra electron of a donor impurity.

II. THEORY

We use a modified version of the theory of Hjalmarson *et al.*[2] to calculate the sp^3-bonded defect levels of A_1 (s-like) and T_2 (p-like) symmetry for the tetrahedral (T_d) point group. The Hjalmarson theory requires a determination of the local spectral density of states, which is calculated from the Vogl *et al.*[12] empirical tight-binding theory of the host energy band structure. This band structure was obtained using a simple nearest-neighbor tight-binding method,[13] with emphasis placed on accurate determination of the local spectral density of both valence and conduction bands. For that reason, the theory of Vogl *et al.* includes only five basis orbitals per atom: the usual sp^3 basis plus one excited s orbital, s^*. The parameters of the Vogl model are fitted to band structures determined by Chelikowsky and Cohen[14] at the symmetry points Γ and X in the Brillouin zone. Since we expect the interesting phenomena of the Si_xGe_{1-x} alloys to occur near the crossover composition, where the indirect gap at L in Ge switches to a gap at X in Si,[11] it is important that the Vogl model be generalized to fit the band structure at the L point as well as at the X point. Thus we include two second-neighbor parameters[15] to improve the fit to the band structure at L for both pure materials, and we modify the Hjalmarson theory to account for these second-neighbor interactions.

A. The model Hamiltonian

1. Band structures of Si and Ge

We provide first the theory for determination of the band structures of the unalloyed materials, Si and Ge. We use a zinc-blende-structure tight-binding Hamiltonian for a basis of quasiatomic functions localized in the unit cell at $\vec{R}_i$, $|n,b,\vec{R}_i\rangle$. The Bloch-type tight-binding states are

$$|n,b,\vec{k}\rangle = N^{-1/2}\sum_{i,b}\exp[i(\vec{k}\cdot\vec{R}_i+\vec{k}\cdot\vec{v}_b)]\,|n,b,\vec{R}_i\rangle \ . \quad (2.1)$$

Here quantum numbers n run over the s, p_x, p_y, p_z, and s^* orbitals, the N wave vectors $\vec{k}$ lie in the first Brillouin zone, and the site index b is either a (for anion) or c (for

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cation). (We shall refer to the two sites in the unit cell of homopolar Si or Ge as anion and cation sites, treating the diamond-crystal structure as though it were zinc blende.) Anion positions are $\vec{R}_i$; cation positions are $\vec{R}_i+\vec{v}_i$ with $\vec{v}_b=\delta_{c,b}(a_L/4)(1,1,1)$, with a_L being the lattice constant. The quasiatomic functions are Löwdin orbitals, which are symmetrically orthogonalized atomic orbitals. The Schrödinger equation for the Bloch function $|\vec{k},\lambda\rangle$ is

$$[H-\epsilon(\vec{k},\lambda)]\,|\vec{k},\lambda\rangle=0\ , \tag{2.2}$$

or, for this basis

$$\sum_{m,b'}\{\langle n,b,\vec{k}\,|H\,|m,b',\vec{k}\rangle - \epsilon(\vec{k},\lambda)\delta_{n,m}\delta_{b,b'}\}\langle m,b',\vec{k}\,|\,\vec{k},\lambda\rangle=0\ . \tag{2.3}$$

The solutions are

$$|\vec{k},\lambda\rangle=\sum_{n,b}|n,b,\vec{k}\rangle\langle n,b,\vec{k}\,|\,\vec{k},\lambda\rangle\ , \tag{2.4}$$

where the band index λ has ten values and the bulk Hamiltonian matrix in the $|n,b,\vec{k}\rangle$ basis is given as in Eq. (2.5) shown at right.

	$\|sa\rangle$	$\|sc\rangle$	$\|p_xa\rangle$	$\|p_ya\rangle$	$\|p_za\rangle$	$\|p_xc\rangle$	$\|p_yc\rangle$	$\|p_zc\rangle$	$\|s^*a\rangle$	$\|s^*c\rangle$
$\|sa\rangle$	$E(s,a)$	$V(s,s)g_0$	$\epsilon(sa,p_xa')g_6$	$\epsilon(sa,p_xa')g_5$	$\epsilon(sa,p_xa')g_4$	$V(sa,pc)g_1$	$V(sa,pc)g_2$	$V(sa,pc)g_3$	0	0
$\|sc\rangle$	$V(s,s)g_0^*$	$E(s,c)$	$-V(pa,sc)g_1^*$	$-V(pa,sc)g_2^*$	$-V(pa,sc)g_3^*$	$-\epsilon(sc,p_xc')g_6$	$-\epsilon(sc,p_xc')g_5$	$-\epsilon(sc,p_xc')g_4$	0	0
$\|p_xa\rangle$	$\epsilon(sa,p_xa')g_6$	$-V(pa,sc)g_1$	$E(p,a)$	$\epsilon(p_xa,p_ya')g_4$	$\epsilon(p_xa,p_ya')g_5$	$V(x,x)g_0$	$V(x,y)g_3$	$V(x,y)g_2$	0	$-V(pa,s^*c)g_1$
$\|p_ya\rangle$	$\epsilon(sa,p_xa')g_5$	$-V(pa,sc)g_2$	$\epsilon(p_xa,p_ya')g_4$	$E(p,a)$	$\epsilon(p_xa,p_ya')g_6$	$V(x,y)g_3$	$V(x,x)g_0$	$V(x,y)g_1$	0	$-V(pa,s^*c)g_2$
$\|p_za\rangle$	$\epsilon(sa,p_xa')g_4$	$-V(pa,sc)g_3$	$\epsilon(p_xa,p_ya')g_5$	$\epsilon(p_xa,p_ya')g_6$	$E(p,a)$	$V(x,y)g_2$	$V(x,y)g_1$	$V(x,x)g_0$	0	$-V(pa,s^*c)g_3$
$\|p_xc\rangle$	$V(sa,pc)g_1^*$	$-\epsilon(sc,p_xc')g_6$	$V(x,x)g_0^*$	$V(x,y)g_3^*$	$V(x,y)g_2^*$	$E(p,c)$	$\epsilon(p_xc,p_yc')g_4$	$\epsilon(p_xc,p_yc')g_5$	$V(s^*a,pc)g_1^*$	0
$\|p_yc\rangle$	$V(sa,pc)g_2^*$	$-\epsilon(sc,p_xc')g_5$	$V(x,y)g_3^*$	$V(x,x)g_0^*$	$V(x,y)g_1^*$	$\epsilon(p_xc,p_yc')g_4$	$E(p,c)$	$\epsilon(p_xc,p_yc')g_6$	$V(s^*a,pc)g_2^*$	0
$\|p_zc\rangle$	$V(sa,pc)g_3^*$	$-\epsilon(sc,p_xc')g_4$	$V(x,y)g_2^*$	$V(x,y)g_1^*$	$V(x,x)g_0^*$	$\epsilon(p_xc,p_yc')g_5$	$\epsilon(p_xc,p_yc')g_6$	$E(p,c)$	$V(s^*a,pc)g_3^*$	0
$\|s^*a\rangle$	0	0	0	0	0	$V(s^*a,pc)g_1$	$V(s^*a,pc)g_2$	$V(s^*a,pc)g_3$	$E(s^*,a)$	0
$\|s^*c\rangle$	0	0	$-V(pa,s^*c)g_1^*$	$-V(pa,s^*c)g_2^*$	$-V(pa,s^*c)g_3^*$	0	0	0	0	$E(s^*,c)$

(2.5)

Here we have

$$\begin{aligned} g_0(\vec{k})&=\cos(\pi k_1/2)\cos(\pi k_2/2)\cos(\pi k_3/2) -i\sin(\pi k_1/2)\sin(\pi k_2/2)\sin(\pi k_3/2)\ ,\\ g_1(\vec{k})&=-\cos(\pi k_1/2)\sin(\pi k_2/2)\sin(\pi k_3/2) +i\sin(\pi k_1/2)\cos(\pi k_2/2)\cos(\pi k_3/2)\ ,\\ g_2(\vec{k})&=-\sin(\pi k_1/2)\cos(\pi k_2/2)\sin(\pi k_3/2) +i\cos(\pi k_1/2)\sin(\pi k_2/2)\cos(\pi k_3/2)\ ,\\ g_3(\vec{k})&=-\sin(\pi k_1/2)\sin(\pi k_2/2)\cos(\pi k_3/2) +i\cos(\pi k_1/2)\cos(\pi k_2/2)\sin(\pi k_3/2)\ ,\\ g_4(\vec{k})&=\sin(\pi k_1)\sin(\pi k_2)\ ,\\ g_5(\vec{k})&=\sin(\pi k_1)\sin(\pi k_3)\ , \end{aligned} \tag{2.6}$$

and

$$g_6(\vec{k})=\sin(\pi k_2)\sin(\pi k_3)\ .$$

In Eq. (2.5), on-site matrix elements are denoted by $E(n,b)$, nearest-neighbor matrix elements by $V(nb,mb')$, and second-neighbor matrix elements by $\epsilon(nb,mb')$, where the prime on b is used to denote different anion or cation atoms. For example, we define

$$\begin{aligned}\epsilon(sa,p_xa')&=-4\langle sa\,|H\,|p_xa'\rangle\ ,\\ \epsilon(p_xa,p_ya')&=4\langle p_xa\,|H\,|p_ya'\rangle\ .\end{aligned} \tag{2.7}$$

The first of these is a three-center integral[15] that is nonzero because of tetrahedral symmetry.

The determination of the values of matrix elements $E(n,b)$ and $V(nb,mb')$ for tetrahedral semiconductors emphasizes the band structure at Γ and X, and has been

TABLE I. Empirical matrix elements of the sp^3s^* Hamiltonian in eV and nearest-neighbor bond distance d in Å. Note anion (a) and cation (c) sites are equivalent for the diamond lattice. Except for $V(sa,pc)$ and $V(s^*a,pc)$ for Ge, these parameters are the same as in Ref. 12.

	Si	Ge
$E(s,a)$	−4.2000	−5.8800
$E(p,a)$	1.7150	1.6100
$E(s^*,a)$	6.6850	6.3900
$V(s,s)$	−8.3000	−6.7800
$V(x,x)$	1.7150	1.6100
$V(x,y)$	4.5750	4.9000
$V(sa,pc)$	5.7292	4.9617
$V(s^*a,pc)$	5.3749	4.5434
$\epsilon(sa,p_xa')$	0.24	0.0
$\epsilon(p_xa,p_ya')$	0.0	0.157
d	2.35	2.45

described elsewhere.[12] Two of the second-neighbor parameters, Eqs. (2.7), are used in the present work to improve the fit to the conduction band near the symmetry point L. Neither parameter in (2.7) has an effect on the band structure in the $\Delta[100]$ or $\Sigma[110]$ directions in the Brillouin zone. The first parameter, $\epsilon(sa,p_xa')$, is used for adjusting the higher relative minimum of the conduction band at L_2' in Si. It affects only the Λ_1 bands and only its absolute value is of importance. We use this parameter to remove the accidental approximate degeneracy of L_1 and L_2' found using the tight-binding parameters of the Vogl model.[12] Since the shift in energy at L_1 caused by this parameter is of the wrong sign for Ge, a second parameter, $\epsilon(p_xa,p_ya')$, is used to fit L_1 for the conduction band in Ge. Table I shows the values of $E(n,b)$, $V(nb,mb')$, and $\epsilon(nb,mb')$ used for the band structures of Si and Ge.

2. *Band structure of the Si_xGe_{1-x} alloys*

To calculate the band structure of the alloy, the virtual-crystal approximation is assumed.[16] The nearest-neighbor distance d, the on-site matrix elements $E(nb,mb')$, and second-neighbor parameters $\epsilon(na,mb')$ are linearly interpolated as function of x, while the first-neighbor matrix elements $V(nb,mb')$ are interpolated assuming that Vd^2 is a constant,[17]

$$Vd^2=x(d_{\mathrm{Si}})^2V_{\mathrm{Si}}+(1-x)(d_{\mathrm{Ge}})^2V_{\mathrm{Ge}}\ . \tag{2.8}$$

The assumption is thus made that the symmetry of the alloy remains that of either perfect crystal, that is, tetrahedral. Since there is little bowing in the fundamental band edge of this alloy, this approximation is known to be quite reasonable.[18]

B. Deep-trap theory

The defect theory of Hjalmarson *et al.*[2] is a Green's-function method developed from formalism derived by Koster and Slater and others.[19] The Hamiltonian for the defect problem is given by

$$H=H_0+V\ , \tag{2.9}$$

where H_0 is the Hamiltonian (2.5) that produces the band structure of the perfect (virtual) crystal host. A Dyson equation relates the defect Green's function,

$$G(E)=(E-H)^{-1}=[1-G_0(E)V]^{-1}G_0(E)\ , \tag{2.10}$$

to the Green's function of the unperturbed "perfect crystal,"

$$G_0(E)=(E-H_0)^{-1}\ . \tag{2.11}$$

Defect levels of energy E are found by solving the equation

$$\det[1-\mathrm{Re}G_0(E)V]=0 \tag{2.12}$$

for states of symmetry l, where $l=A_1$ (s-like) or T_2 (p-like). We write the partial Green's function in terms of the Hilbert transform of the local spectral density,

$$G_{0,l}(E)=\mathrm{P}\int\frac{D_l(E')}{E-E'}dE'\ , \tag{2.13}$$

and determine the spectral density $D_l(E')$ using the Lehmann-Taut formalism.[20] For energies E within the band gap, the integral may be calculated using the special-points method.[21] The defect potential V is constructed along lines suggested by Hjalmarson *et al.*[2] Lattice relaxation around the defect and the long-ranged Coulombic tail of the potential (for a nonisoelectronic defect) are neglected because the energies of deep levels are controlled mainly by the central-cell part of the potential.[2] Since the off-diagonal matrix elements do not change unless the bond length is altered, Harrison's rule[17] implies that the defect potential is diagonal in the Löwdin-orbital basis. The diagonal elements V are, by definition, the differences between host- and impurity-atom matrix elements

$$\begin{aligned}V_{A_1}&=E^{\mathrm{host}}(s)-E^{\mathrm{impurity}}(s)\ ,\\ V_{T_2}&=E^{\mathrm{host}}(p)-E^{\mathrm{impurity}}(p)\ .\end{aligned} \tag{2.14}$$

Because of the chemical trends in the diagonal matrix elements E of the host Hamiltonians for a variety of hosts, the defect potentials V are found to be proportional to atomic-energy differences.[2,11] Finally, since this is a one-electron potential-scattering theory, the different charge states of an impurity are found to be degenerate in this model.[22]

III. RESULTS

The band structure for Si_xGe_{1-x} alloys was calculated using Eqs. (2.5) and (2.8). Figures 1(a)–1(d) display the calculated band structures for $x=0$, 0.2, 0.74, and 1 compared with those of Bassani and Brust.[11] In our calculation, we found that the crossover point from an indirect gap at L to one near X (for 4 K) occurs at $x=0.25$, in reasonable agreement with experimental results for room temperature, $x\simeq0.15$.[10] (Our results differ from those of Bassani and Brust,[11] who obtain $x=0.2$, since we fitted the band edges of Si and Ge to the more recent results used by Chelikowsky and Cohen.[14])

Our results for defect levels of donor impurities are

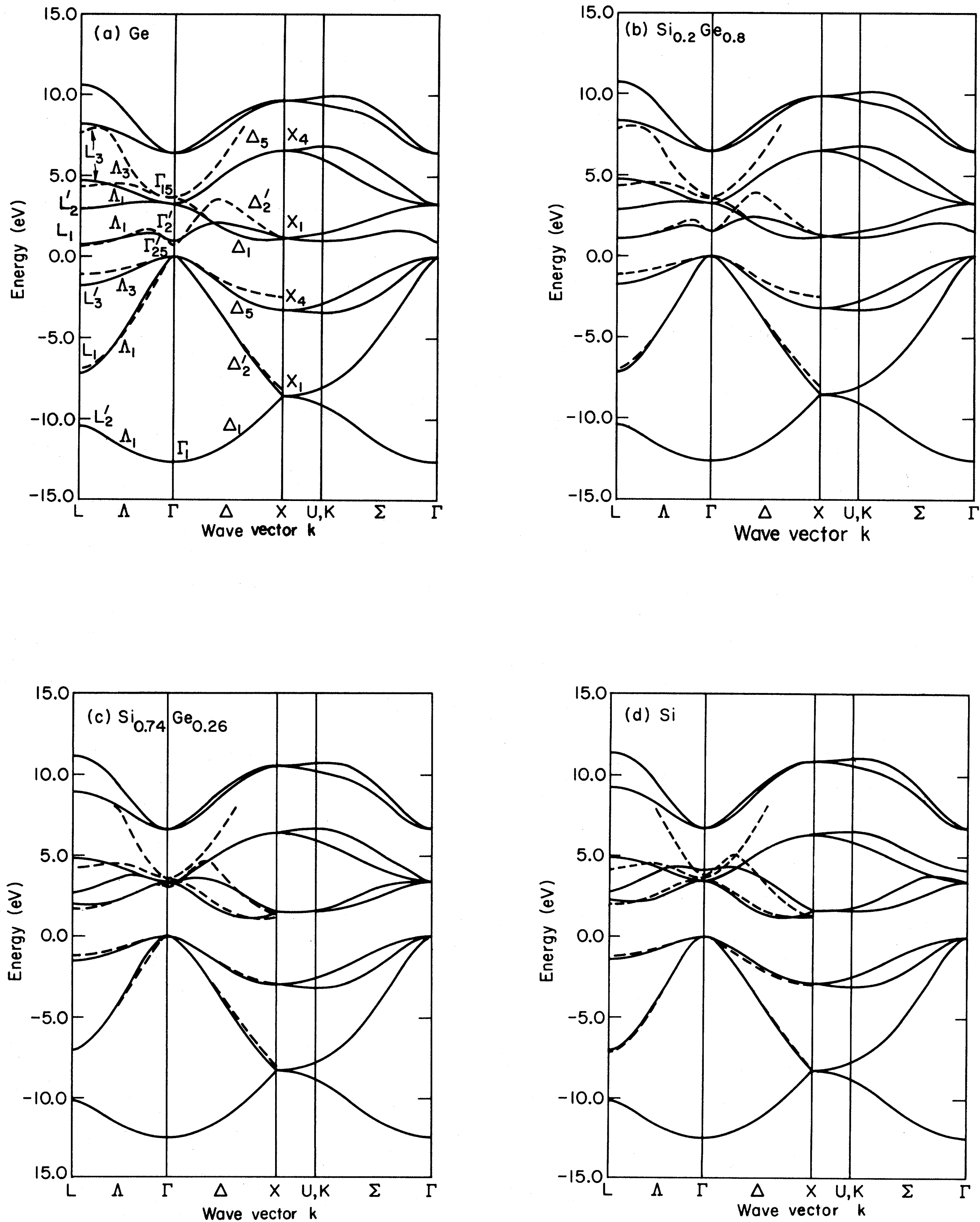

FIG. 1. Band structures $E(\vec{k})$ for the principal symmetry directions of the diamond lattice for (a) Ge, (b) $Si_{0.2}Ge_{0.8}$, (c) $Si_{0.74}Ge_{0.26}$, and (d) Si. The points $\vec{k}$ in the Brillouin zone are $k_\Gamma=(0,0,0)$, $k_L=(2\pi/a_L)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $k_X=(2\pi/a_L)(1,0,0)$, $k_U=(2\pi/a_L)(1,\frac{1}{4},\frac{1}{4})$, and $k_K=(2\pi/a_L)(\frac{3}{4},\frac{3}{4},0)$, where a_L is the lattice constant. We compare these with results of Bassani and Brust (Ref. 11) (dashed curve). Principal symmetry directions are labeled only for (a) Ge.

summarized in Figs. 2 and 3. Shown also in these figures are the conduction-band edges as functions of composition x, where the zero of energy is taken to be the top of the valence-band edge for all x. The fundamental band gap is wedge shaped due to the crossover of the indirect gap from L (L_1) to near X (Δ_1) at $x \simeq 0.2$.

Note first the trends in defect levels as a function of composition x. The deep defect levels do not follow the conduction-band edge, tending instead to follow a dominant feature in the density of states[5] (a characteristic of deep levels[2]). The impurity levels that are resonant[23] (shown as dashed lines) with the conduction-band edge for both Si and Ge cross the wedge of the band gap for x near 0.2. The existence of this wedge means that all defect levels will be deeper, relative to the conduction-band edge, at x near 0.2, than in either pure material, $x=0$ or 1.

Impurities that are normally shallow in Si and Ge, such as P or As, may become deep near $x=0.2$. This is because the shallow-donor impurity levels *do* follow the conduction-band edge,[24] and one normally observes the lower lying of the shallow- and deep-energy levels [where the label shallow or deep refers to the origin of the level—from the Coulombic tail (omitted in the present model) or from an atomiclike central-cell potential[2]]. Thus a shallow to deep to shallow transition in defect levels, as shown schematically in Fig. 4, is possible as a function of x for some impurities in this alloy.

The chemical ordering of the donor-defect levels is easily explained in terms of the Periodic Table. For a given column of the Periodic Table, the highest-lying energy levels have the highest atomic numbers Z. For example, for column VI B, for A_1 symmetry (Fig. 3), the ordering is Po, Te, Se, S, and O. Similarly, for a given row of the Periodic Table, the highest-lying energy levels correspond to the lowest atomic numbers Z. For example, again for A_1 symmetry, the ordering is C, N, O, and F. These rules follow from chemical trends in the orbital energies of the defect atoms, which determine the quantity V of Eqs. (2.12) and (2.14). Solution of Eq. (2.12) yields the ordering of defect levels for impurities *not* in the same row or column of the Periodic Table. (In interpreting Figs. 2 and 3, some allowances must be made for the different charge

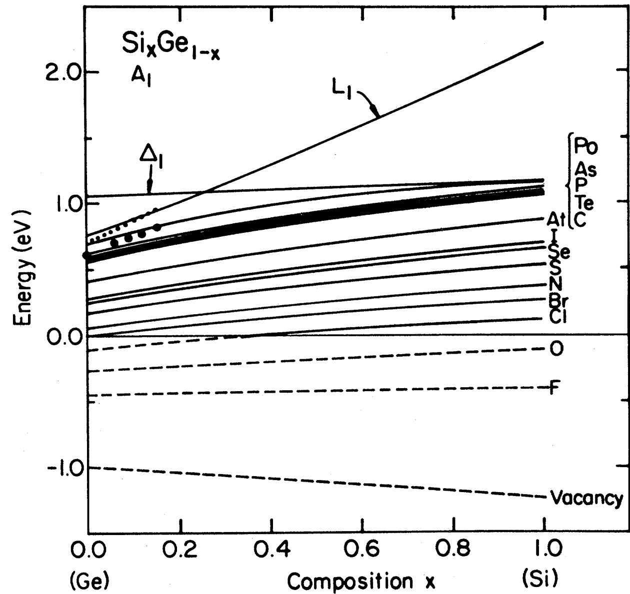

FIG. 3. Predicted single-impurity defect levels of A_1 symmetry as a function of composition x. Shown also are the theoretical conduction- and valence-band edges and experimental data for the conduction-band edge (dotted line) and Te deep-energy levels (data points) (Ref. 44). The dashed curves represent resonant levels.

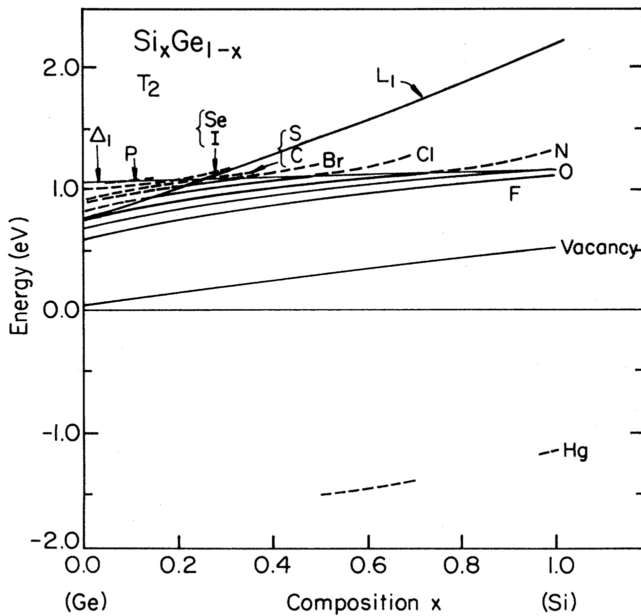

FIG. 2. Predicted single-impurity defect levels of T_2 symmetry as a function of composition x. Shown also are the conduction- and valence-band edges. The dashed curves represent resonant levels.

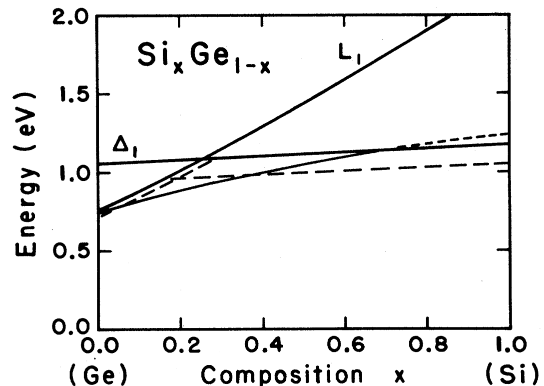

FIG. 4. Schematic illustration of the dependence of shallow and deep levels on alloy composition x in $Si_{1-x}Ge_x$ alloys. The band edges are denoted by thick lines. The deep level is "bound" (solid) for $0.0 \lesssim x \lesssim 0.7$, and "resonant" (short-dashed) when above the conduction-band edge. The shallow level follows the band edge (long-dashed). At the shallow-deep crossover, there is a level-crossing phenomenon and hybridization, which we ignore because it occurs rapidly as a function of x (Ref. 3).

TABLE II. Comparison of calculated unrelaxed-vacancy energy levels (in eV), relative to the valence-band maximum, determined by different authors for Si and Ge. Few of these authors list a theoretical uncertainty. The present simple theory is expected to predict levels typically uncertain by ∼0.3 eV. This table suggests that the present theory, although very simple, is comparably accurate with other theories, some of which are more complicated.

	A_1		T_2	
	Ge	Si	Ge	Si
This work	−1.0	−1.2	0.04	0.51
Hjalmarson *et al.*[a]	−1.4	−1.2	0.06	0.51
Kauffer *et al.*[b]		−0.88		0.12
Joannopoulos *et al.*[c]			0.47	
Bernholc *et al.*[d]			0.11	0.27
Papaconstantopoulos *et al.*[e]				0.75
Lindefelt			0.66[f]	0.18[g]
Baraff *et al.*[h]		−1.1		0.7
Bernholc *et al.*[i]		−0.6		0.8
Bernholc *et al.*[j]		−0.7		0.67

[a]Reference 2.
[b]Reference 25.
[c]Reference 26.
[d]Reference 27.
[e]Reference 28.
[f]Reference 29.
[g]Reference 30.
[h]Reference 31.
[i]Reference 32.
[j]Reference 33, Fig. 1.

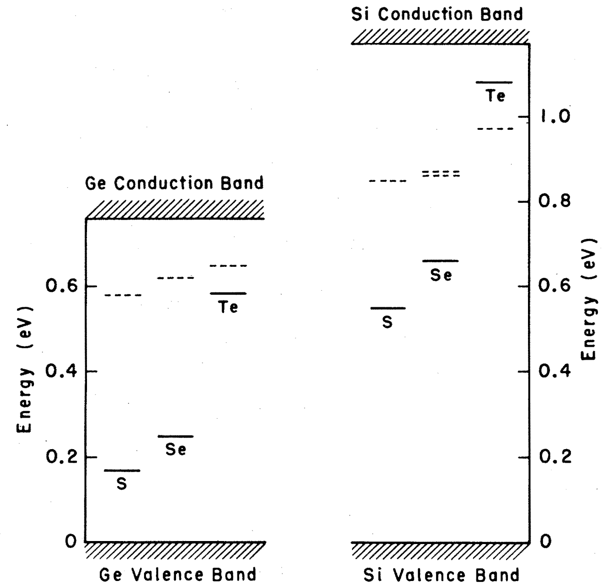

FIG. 5. The theoretical (solid levels) and experimental (dashed levels) energy levels of S, Se, and Te in Ge (Ref. 37), and Si (Refs. 35, 38—40).

states of the defects.) Since V has the opposite sign for acceptor impurities, these rules are then inverted. Unrelaxed-vacancy levels are the zeros of $G(E)$; thus acceptor impurity levels have energies lower than the unrelaxed-vacancy energy level.

Deep-energy levels are typically determined by our methods with accuracies of a few tenths of an eV. This is seen in the results of Table II for the unrelaxed-vacancy level determined by various authors using Green's-function methods. Results are quoted from tight-binding methods[2,25–28] (Refs. 25 and 26 calculate the Green's function for the *imperfect* crystal), from pseudopotentials,[29,30] and from self-consistent calculations.[31–33] We may *calibrate* our results to experimental results known for S, Se, and Te impurities in Ge and S and Se in Si.[34] S, Se, and Te are all double-donor impurities having two charge states [as well as a number of states for complexes of impurities; see, for example, the experimental results for S (Ref. 35)]. We compare our results with the results for the neutral impurity level of A_1 symmetry.[36] In Ge, the substitutional impurities S, Se, and Te have observed levels of 0.58, 0.62, and 0.65 eV,[37] respectively (i.e., 0.18, 0.14, and 0.11 eV below the conduction band). We find the same ordering in our theory: 0.17, 0.25, and 0.59 eV. In Si, Grimmeiss and co-workers.[38,39] find S, Se, and Te to have levels at 0.85, 0.87, and 0.97 eV, respectively (i.e., 0.32, 0.30, and 0.20 eV below the conduction band); others find for S, 0.85 eV,[35] and for Se, 0.86 eV.[40] We find 0.55, 0.66, and 1.08 eV for S, Se, and Te, respectively. We thus conclude that we have successfully reproduced the qualitative chemical trends, as shown in Fig. 5, but have a quantitative error that places our impurity levels too deep within the band gap by approximately 0.05 to 0.4 eV. Note that the theory predicts that As and P in Si and Ge are near the borderline of the shallow-deep transition; a 0.05 eV shift upwards of all theoretical curves causes As and P to become unambiguously shallow impurities in Si and Ge.[41] A significantly more accurate determination of defect energy levels will probably require a vast improvement over the tight-binding theory used here.[2] We note, however, that even the highly sophisticated contemporary self-consistent pseudopotential calculations of deep levels have quoted uncertainties of ±0.2 eV,[42] and so vast improvements over the ∼0.3 eV uncertainty of the present work will be difficult to achieve.[43]

A further difficulty with the current theory is the absence of deep levels for acceptor impurities of T_2 symmetry.[33] We suspect this is because our T_2-symmetric vacancy states lie somewhat too close to the valence band. We also note that an improved tight-binding theory, such as the one for Si by Papaconstantopoulos and Economou,[28] obtains higher-energy T_2-symmetric vacancy states (see Table II). If the host band structure in the present model were altered to produce a higher T_2 vacancy level, then the defects Hg, Cd, Zn, Tl, and In might become deep levels above the valence-band maximum as well. However, use of such a multineighbor theory introduces complications to the calculation of defect levels, since the proportionality of V to atomic-energy differences Eq. (2.14) is valid only if the on-site diagonal matrix elements of the theory exhibit manifest chemical trends.

Predictions of our deep-trap theory for Si_xGe_{1-x} alloys are as follows. First, we expect a deepening of impurity

levels for all deep-donor impurities of Si and/or Ge in the alloy for x near 0.2. This first result has been confirmed by experiment for Te in Si_xGe_{1-x}. Azhdarov *et al.*[44] (Fig. 3) found neutral-defect energy levels that follow the conduction-band edge, being deeper by 0.03 eV for $x=0.15$ compared with $x=0$.[34] Second, we predict that impurities that are shallow donors or isoelectronic resonances in Si and Ge may become deep for x near 0.2. Important examples may include the A_1-symmetric impurity levels for As and P and, for T_2 symmetry, perhaps also N and O. Furthermore, if As and P are deep impurities for x near 0.2, we also expect that the isoelectronic substitutional impurity C to be deep for a similar range of x. These predictions should be tested experimentally.

IV. DISCUSSION

We have determined the single-impurity sp^3-bonded deep-energy levels of Si_xGe_{1-x} alloys. Due to a crossover from an indirect gap at L to one near X that occurs at $x \simeq 0.2$, we have found that many of the shallow dopants of Si and Ge may have deep levels near the indirect-gap crossover point. Important examples of impurities that may have deep levels include As, P, C, N, S, Se, Te, and O.

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$$G_0(E)=(E-H_0)^{-1}=P(E-H_0)^{-1}-i\pi\delta(E-H_0)$$

to relate the density of states, $D(E)$, to the imaginary part of $G_0(E)$,

$$D(E)=-(\pi)^{-1}\mathrm{Tr}\,\mathrm{Im}\,G_0(E)=\sum_{\vec{k},\lambda}\delta(E-\epsilon(\vec{k},\lambda)) ,$$

where $\epsilon(\vec{k},\lambda)$ are the calculated band energies. The Lehmann-Taut method divides the irreducible wedge of the Brillouin zone into tetrahedra and evaluates, using a linear interpolation scheme, the surface-integral form of $D(E)$,

$$D(E)\propto\sum_{\lambda}\int_{\epsilon(\vec{k},\lambda)=E}\frac{dS}{|\vec{\nabla}\epsilon(\vec{k},\lambda)|} .$$

The spectral density $D_l(E)$ is determined from the A_1- and T_2-symmetric combinations of the eigenvectors (2.4) of $\epsilon(\vec{k},\lambda)$, e.g., for A_1 symmetry on the anion site, a factor $|\langle sa\vec{k}\,|\,\vec{k},\lambda\rangle|^2$ is included in the surface integral. An energy grid of 0.05 eV is taken in determining both $\mathrm{Re}\,G(E)$ and $\mathrm{Im}\,G(E)$; thus an intrinsic numerical error of about 0.05 eV is present in our calculations of impurity levels.

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