

Entropy of ionization and temperature variation of ionization levels of defects in semiconductors

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We make simple estimates of the entropy of ionization of Coulombic, isoelectronic, and vacancy-type defects in semiconductors by considering the effect of localized and free-carrier charge distributions upon the lattice modes. The empirical values of these entropies are observed as the temperature variation of the corresponding ionization levels. We predict a crossing of vacancy donor and acceptor levels in Si and Ge, which is supported by quenching and diffusion experiments. We also conclude that some of the deep Coulombic defects, such as the Au acceptor in Si, are most likely a complex of the Coulombic center with some isoelectronic or vacancy defect, such as Au interstitial with Si vacancy, rather than a simple substitutional impurity as previously assumed.

I. INTRODUCTION

The forbidden band gap ΔE_{cv} of a semiconductor is properly defined as the standard chemical potential for electron-hole pairs created in the reaction



where e^+ and e^- denote a free hole and a free electron belonging to the thermal distribution at the valence-band edge and the conduction-band edge, respectively.^{1,2}

As a chemical potential, ΔE_{cv} is equal both to the increase in internal energy upon increasing the number of such pairs n_p by one at constant entropy and volume and to the increase in Gibbs free energy upon increasing n_p by one at constant temperature and pressure:

$$\Delta E_{cv} \equiv \left. \frac{\partial U}{\partial n_p} \right|_{S,V} \equiv \left. \frac{\partial G}{\partial n_p} \right|_{T,P}, \quad (2)$$

where U , G , S , V , T , and P denote the total internal energy, Gibbs free energy, entropy, volume, temperature, and pressure of the sample. It is $\partial U/\partial n_p|_{S,V}$ that is measured in optical experiments, when the "no-phonon" line is taken as ΔE_{cv} . It is $\partial G/\partial n_p|_{T,P}$ that is measured in transport experiments, such as temperature-dependent Hall effect. Both done correctly measure the same ΔE_{cv} .

For many purposes it is simpler and more transparent to use the second definition in (2) and treat ΔE_{cv} as a free energy.^{3,4} Then ΔE_{cv} may be decomposed into the standard enthalpy ΔH_{cv} and standard entropy ΔS_{cv} of reaction (1);

$$\Delta E_{cv}(T) = \Delta H_{cv}(T) - T\Delta S_{cv}(T). \quad (3)$$

The entropy of formation of these free e^+e^- pairs

ΔS_{cv} is identically (note Appendix A)

$$\Delta S_{cv}(T) \equiv - \frac{\partial \Delta E_{cv}}{\partial T}. \quad (4)$$

$\Delta S_{cv}(T)$ may be calculated very simply and rather accurately in terms of the effect of e^+ and e^- upon the phonon modes of the crystal^{3,4} using simple bond charge models.^{5,6} Because the presence of either e^+ or e^- usually softens the lattice in its vicinity, ΔS_{cv} is usually positive above $T=0$. It is generally found that ΔS_{cv} increases with increasing T up to the melting point.² This implies² that ΔE_{cv} decreases at an increasing rate while ΔH_{cv} increases with increasing T .

Just as ΔE_{cv} is defined as the standard chemical potential for reaction (1), the ionization ΔE_I of an arbitrary donor or acceptor D or A defect level is properly defined as the change in the standard chemical potential for the reaction to form an ionized defect and a free-carrier pair in the reactions



or



(The superscript x is used to denote the neutral state of the defect.) Just as ΔE_{cv} may be decomposed into ΔH_{cv} and ΔS_{cv} , ΔE_I may be decomposed into the enthalpy of ionization ΔH_I and the entropy of ionization ΔS_I

$$\Delta E_I(D) = \Delta H_I(D) - T\Delta S_I(D) \quad (7)$$

or

$$\Delta E_I(A) = \Delta H_I(A) - T\Delta S_I(A). \quad (8)$$

Of course, ΔE_I , ΔH_I , and ΔS_I are functions of T in general, and $\Delta S_I(T=0)=0$. Finally, just as

with Eq. (4)

$$\Delta S_I(T) \equiv - \frac{\partial \Delta E_I}{\partial T} \quad (9)$$

for either D or A .

The purpose of this paper is to use simple considerations of the effect of e^+ and e^- upon lattice modes^{3,4} and simple considerations of the localization of bound carriers around defect centers, such as have been used to calculate isotope shifts,⁷ in order to estimate ΔS_I for various types of defects. The consequences of these estimates upon the predicted temperature variation of the various ionization levels are noted. These consequences are particularly striking for the case of vacancies, where we find, e.g., that the donor and acceptor levels of the vacancy in⁸⁻¹⁰ Si should cross.

The crossing of the Si vacancy donor and acceptor levels is consistent with observations of the entropy of vacancies at high temperatures³ and of impurity diffusion.¹⁰ A detailed comparison with quenching experiments in Si and Ge is presented separately¹¹ because this comparison requires a somewhat involved discussion of quenching experiments that is rather outside the necessary scope of the present subject.

II. THREE TYPES OF DEFECTS

Three types of defects are to be distinguished: impurities with a Coulombic potential, with or without central-cell contribution^{12,13}; isoelectronic impurities; and vacancies. Examples of the first type include all interstitials and any substitutional impurities of valence different from that of the atom they replace, e.g., Cu, Zn, Ga, As, Se, or Br substitutional impurities in Ge. Examples of the second type include N and Bi substitutional impurities on the P site in GaP. (N_P is a deep acceptor and Bi_P is a deep donor. See Appendix B.) In addition to single atom defects, complexes of all three types do occur and may be treated with the present considerations.

The reason for the distinction between Coulombic, isoelectronic, and vacancy-type defects is that the neutral and ionized states of a Coulombic defect are quite different from those of an isoelectronic defect or a vacancy. (See Fig. 1.) This difference has fundamental consequence in considerations of ΔS_I .

Because a Coulombic defect provides one or more excess or deficit core charges in the central cell of the defect, the neutral state D^x or A^x must include one or more valence- or conduction-band carriers bound to the defect center. The number of valence-band states and of conduction-band

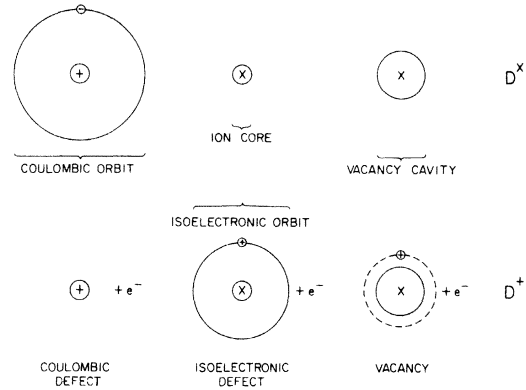


FIG. 1. Schematic diagram of the three types of defects, Coulombic, isoelectronic, and vacancy, distinguished here for the case of a donor ionization level. Both the neutral D^x and ionized states D^+ are shown. In the ionized state the e^- indicated is delocalized away from the center.

states is entirely fixed by the number of lattice sites in the sample, which is not altered by the presence of a substitutional or interstitial defect. Thus, there must be an excess of charge spread over antibonding (conduction-band) states around D^x or a deficit of charge in the bonding (valence-band) states around A^x . Either case will effect a softening of the lattice modes.^{3,4} The spatial distribution of the bound carrier(s) around the defect is determined by the shape and depth of the attractive potential, which may be gauged by ΔH_I .

In contrast, the neutral state of an isoelectronic substitutional impurity must involve the same number of valence electrons as the normal host atom. These would exactly fill the valence-band states of the perfect host crystal. In general, there is distortion of the lattice around the defect^{12,13} so the impurity wave functions are described as a superposition of Bloch waves of the perfect crystal containing contributions from the conduction band as well. However, because the distortion minimizes the energy of the defect, it generally stabilizes the lattice as much as possible. Thus, the relaxed electronic configuration is as "bonding" as possible in the chemical and lattice dynamic senses. There is no bound carrier in the neutral states D^x or A^x of an isoelectronic impurity, and the central cell is neutral.

For the neutral state of a vacancy, the missing core charge is equal to the missing valence-band charge. Thus, the central cell is neutral, as in the case of the isoelectronic defect and in contrast to the Coulombic defect.

Now, when an isoelectronic or vacancy defect is ionized, two new carriers of opposite charge are created. One is bound in the vicinity of the defect

with a spatial distribution depending on ΔH_I . The other is a free carrier in either the conduction band or the valence band for donor or acceptor states, respectively. (See Fig. 1.) However, when a Coulombic defect is ionized, the erst-while bound carrier is freed and no carrier of opposite charge is created.

The effect of the free carrier produced by ionizing a defect of any kind upon the lattice modes of the host crystal must be exactly the same as that of the indistinguishable carrier created by excitation across ΔE_{cv} in reaction (1). All we need do is to estimate the effect of the bound carriers and core charges.

III. IONIZATION OF ISOELECTRONIC DEFECTS

A. General considerations

For the case of the isoelectronic impurity, the core charge is always neutral, i.e., the same as that of the perfect crystal, and a bound carrier only appears in the ionized state D^+ or A^- . The lattice modes in the vicinity of the defect will certainly be affected by the mass difference between the impurity and the host atom it replaces, but this mass difference will not change upon ionization. Therefore, we shall ignore the mass effect and assume that, apart from the usual degeneracy factors noted in Appendix A, the entropy of the neutral state D^x or A^x is the same as that of the host ground state.

The degree of localization of the bound carrier of the ionized state varies with ΔH_I .^{7,12-14} Thus, the degree to which this bound carrier approximates the free carrier of the same charge varies. Because it is the ionized state in which the carrier is bound, the deeper the ionization level, i.e., the greater ΔH_I , the more loosely is this carrier bound to the defect center. In this case, it is a common and convenient practice to subtract reaction (1) from reactions (5) and (6) to obtain

$$D^x + e^* \rightarrow D^+, \quad \Delta E_I(D) - \Delta E_{cv} \quad (10)$$

and

$$A^x + e^- \rightarrow A^-, \quad \Delta E_I(A) - \Delta E_{cv} \quad (11)$$

and then to define a "binding" free energy, enthalpy, and entropy for the carrier:

$$\begin{aligned} \Delta E_B &= \Delta E_{cv} - \Delta E_I, \\ \Delta H_B &= \Delta H_{cv} - \Delta H_I, \\ \Delta S_B &= \Delta S_{cv} - \Delta S_I. \end{aligned} \quad (12)$$

It is also a common practice to assume an envelope function for the bound carrier's wave function of the effective-mass form⁷

$$\psi = (2\pi a)^{-1/2} r^{-1} e^{-r/a_B}, \quad (13)$$

where

$$a_B = (\hbar^2/2m^*\Delta H_B)^{1/2}. \quad (14)$$

In (14) r is the distance from the defect center and m^* is the density-of-states effective mass of the valence band for D and of the conduction band for A . (In the case of multiple conduction-band minima, as in Si, Ge, and GaP, the appropriate value of m^* is that of a single valley.) Of course, the carrier's complete wave function is modulated within each unit cell, as are the Bloch waves of the band from which it was formed, and Eq. (13) is unrealistic within the central cell.¹⁵ Nevertheless, the magnitude of a_B provides a useful gauge of the degree of localization of the bound carrier.

For the case of the N acceptor in GaP, $m_c^* = 0.40m_0$,¹⁶ where m_0 is the free-electron mass, and $\Delta H_B = 11$ meV,¹⁷ so that $a_B = 29.4$ Å. Now, 60% of the density of the envelope function, Eq. (13), lies outside $r = \frac{1}{4}a_B = 1.35a$, where a is the lattice constant (5.45 Å). As an extent of one unit cell in real space corresponds to an extent of one Brillouin zone in reciprocal space and as the effective radius of a unit cell ($\frac{1}{4}a^3$) is $R_v = 0.39a$, 60% of the contributions to the wave packet of the bound carrier come from within 0.29 the radius of the Brillouin zone from the band edge. This region contains only 2.4% times the degeneracy of the band extrema (3 in the case of e^- in GaP) of the volume of the zone. Therefore, the distribution of the bound e^- over the antibonding regions in the vicinity of the defect is very much the same as that of the free e^- in whatever portion of the sample it happens to be. Consequently, the effect of this bound e^- upon the lattice modes will be essentially the same as that of a free e^- created in reaction (1).

As remarked above, the effect of the free e^* created when N_p in GaP is ionized is exactly the same as that of the e^* in reaction (1). Therefore,

$$\Delta S_I(N_p) = \Delta S_{cv}(\text{GaP}), \quad \Delta S_B = 0 \quad (15)$$

to a very good approximation. This means that the N_p acceptor ionization level will stay a constant (free) energy below the conduction band as ΔE_{cv} varies with T . (It will also stay a constant enthalpy below the conduction band as ΔH_{cv} varies with T .)

If an isoelectronic acceptor in GaP had $\Delta H_B = 106$ meV, then $\frac{1}{4}a = 2.36$ Å, which is the nearest-neighbor distance. Then the use of Eq. (13) would be a severe approximation, but it would be clear that the bound e^- in the ionized state is so localized that contributions to its wave packet would come almost uniformly from all over the Brillouin zone. Thus, we cannot equate the bound electron with e^- , the free electron in the band-edge thermal distribution. We must consider the

variation of the electron's mode-softening efficacy with position in the zone when we treat defects with a large ΔH_B .

B. Consequence of tight binding

The charge distribution of the Bloch waves at different points in the top valence bands differs only moderately while that of the conduction bands differs substantially.¹⁸⁻²⁰ While the valence-band charge distribution peaks in the bonds, the conduction-band states at X_1 , near where the conduction-band minimum occurs in Si, have their maximum in the antibonding region. The conduction-band states around L_1 have large density both in the antibonding sites and around the atom core. At the zone center in the conduction band, the Γ_{15} density is heavily localized in the antibonding region while that of $\Gamma_{2'}$ is strongly peaked at the atom. The conduction band L_1 state has about one-fifth the density in the bond region that a valence-band state has—the others have far less density there.¹⁸

Therefore, when electrons are excited across the various direct gaps of the semiconductor, approximately equal amounts of charge are removed from the bond charge Z_b and placed in various regions according to the nature of the final state. We can investigate the effect of the varia-

tion with the final state by observing the differences in the temperature dependence of the various band gaps.^{3,4} This is because we can define any particular band gap E_i as the standard chemical potential for the creation of electron-hole pairs in thermal distributions around particular points i and f in the valence and conduction bands in the reaction

$$0 \rightarrow e_i^+ + e_f^-, E_i, \quad (16)$$

exactly as with reactions (1), (5), and (6). Although transport measurements are not practical for gaps other than the fundamental ΔE_{cv} the optical measurements are easily done and the analog of Eq. (2) holds to guarantee that a well-defined free-energy difference is obtained. Thus,

$$S_i \equiv - \frac{\partial E_i}{\partial T} \quad (17)$$

is a well-defined (standard) entropy for the transition (reaction) (16).

An uncritical compilation of empirical values for the entropy (temperature dependence) of the various gaps in Si, Ge, GaP, and GaAs at room temperature is presented in Table I. The "Cardona notation"²¹ is used for the direct gaps and E_g denotes the dielectric average gap.²²⁻²⁴ Values are quoted in units of the Boltzmann constant, $k = 0.86167 \times 10^{-4}$ eV/K, the fundamental unit of entropy. Except for the ΔE_{cv} values, which are

TABLE I. Entropy of various direct and indirect band gaps as well as that of the dielectric average gap E_g for four common semiconductors.

Crystal	Transition	E_0	E_0'	E_1	E_1'	E_2	$E_{\Gamma X}$	$E_{\Gamma L}$	E_g
	Entropy ($\equiv -\partial E/\partial T$ at 300 K)	S_0	S_0'	S_1	S_1'	S_2	$S_{\Gamma X}$	$S_{\Gamma L}$	S_g
		(k)	(k)	(k)	(k)	(k)	(k)	(k)	(k)
Si		2.6 ^b	...	2.6 ^b 2.2 ^c	2.96 ^{a,d} 2.8 ^e	...	2.6 ^c
Ge		4.0 ^f	1.6 ^g	4.9 ^b	...	2.8 ^b 3.8 ^c	...	4.47 ^{a,d}	2.8 ^c
GaP		4.8 ^e 5.3 ^h	3.7 ⁱ	3.9 ⁱ	...	2.2 ^c 5.2 ^j	4.65 ^{a,d} 3.6 ^e	...	5.2 ^c
GaAs		5.25 ^{a,d} 4.5 ^e	...	6.2 ^b 4.9 ^k	...	4.2 ^b 4.1 ^c	4.2 ^c

^a $\leftrightarrow \Delta E_{cv}$ and ΔS_{cv} .

^b R. R. L. Zucca and Y. R. Shen, Phys. Rev. B **1**, 2668 (1970).

^c Reference 25.

^d Reference 2.

^e J. Camassel and D. Auvergne, Phys. Rev. B **12**, 3258 (1975).

^f D. E. Aspnes and A. Frova, Phys. Rev. B **2**, 1037 (1970).

^g D. E. Aspnes (unpublished); Phys. Rev. Lett. **28**, 913 (1972).

^h R. Zallen and W. Paul, Phys. Rev. **134**, A1628 (1964).

ⁱ A. G. Thompson, J. C. Woolley, and M. Rubenstein, Can. J. Phys. **44**, 2927 (1966).

^j J. D. Wiley and M. Di Domenico, Jr., Phys. Rev. B **1**, 1655 (1970).

^k E. W. Williams and V. Rehn, Phys. Rev. **172**, 798 (1968).

marked by a superscript, a, and are quite accurate,² the experimental uncertainty is rather large—as evidenced by the discrepancies shown between different measurements. Because $\partial S_i/\partial T > 0$, the practice of assuming $S_i = [E_i(T_2) - E_i(T_1)]/(T_2 - T_1)$ with T_2 room temperature and T_1 some lower temperature tends to underestimate S_i . This practice was not followed in Ref. 2, but was followed in most of the other references to Table I.

Noting that the discrepancies between measurements of a given S_i are about as great as the spread among different S_i 's for a given material, we conclude that all S_i are about the same for a given material at a fixed T

$$S_i(T) \approx \Delta S_{cv}(T) \quad (18)$$

to within a factor of 2. This implies that the mode-softening effect of the excitation is insensitive to the final-state distribution—as long as the charge is removed from the bond charge.^{3,4} This conclusion would also follow from the empirical conclusion of Heine and Henry based on isotope shifts,⁷ that the mode-softening effect of a bound hole is about four times that of a bound electron irrespective of ΔH_B .

In particular, we may conclude that the entropy (temperature dependence²⁵) of the dielectric average gap²²⁻²⁴ E_g is the same as that of the fundamental gap:

$$S_g(T) = \Delta S_{cv}(T) \quad (19)$$

to within about 25%. [In the case of Ge, the discrepancy is worse, but the empirical value reported²⁵ for S_g is less than that of all the other gaps, except $E_{\sigma'}$ ($\Gamma_{25'} \rightarrow \Gamma_{15}$), which has very little phase space. As the average cannot be less than the range, it seems the value of S_g must be underestimated.]

Equation (19) is significant to our problem because E_g , being the (dielectric) average gap over the entire Brillouin zone and over the several bands (light hole, heavy hole, spin-orbit split, etc.) within the valence and conduction bands, may be thought of as a transition between states having the same real-space distribution as that of the bound electron or hole in the ionized state of the isoelectronic impurity for the limit of large ΔH_B .

We now meet another problem. This is the question of the relative magnitudes of the contribution of e^+ and e^- to ΔS_{cv} and of the band-averaged hole and electron, which we denote e_g^+ and e_g^- , to S_g . A determination of ΔS_{cv} or S_g specifies only the sum of the two contributions, which we shall denote $\Delta S_{cv}(e^+)$, $S_g(e_g^+)$, $\Delta S_{cv}(e^-)$, and $S_g(e_g^-)$, so that

$$\Delta S_{cv} = \Delta S_{cv}(e^+) + \Delta S_{cv}(e^-) \quad (20)$$

and

$$S_g = S_g(e_g^+) + S_g(e_g^-). \quad (21)$$

There is no *a priori* reason that the contribution of the electron and of the hole should be equal; an initial consideration of the importance of Z_b to the stability of lattice modes^{3,4} seems to imply the hole contribution should be dominant, and this conclusion is supported by the insensitivity of the various S_i 's to the final-state charge distribution, as noted above. Although this problem could be treated by lattice-dynamical calculations,^{5,6} these have not yet been performed. The best information to date would seem to be the empirical conclusion by Heine and Henry,⁷ which is expressed in our terms as

$$\Delta S_{cv}(e^+) = (3.6 \pm 1.0) \Delta S_{cv}(e^-) \quad (22)$$

and

$$S_g(e_g^+) = (3.6 \pm 1.0) S_g(e_g^-). \quad (23)$$

[The fact that both equations follow from the Heine-Henry conclusions results from the fact that their observations seemed to be independent of ΔH_B . The equality of the proportionality factors, 3.6, between Eqs. (22) and (23) is also supported by the observation that the hole distribution is fairly uniform for the upper valence bands,^{19,20} so that $\Delta S_{cv}(e^+) \approx S_g(e_g^+)$.]

Finally, we may conclude that

$$\Delta S_I(A) = \Delta S_{cv}(e^+) + S_g(e_g^-) \cong \Delta S_{cv} \quad (24)$$

and

$$\Delta S_I(D) = S_g(e_g^+) + \Delta S_{cv}(e^-) \cong \Delta S_{cv} \quad (25)$$

for isoelectronic impurities with large ΔH_B (i.e., e.g., $\Delta H_B > 110$ meV for acceptors in GaP). Furthermore, in view of our consideration of the small ΔH_B limit [see text preceding Eq. (15)], we may conclude

$$\Delta S_I(T) \cong \Delta S_{cv}(T) \quad (26)$$

irrespective of ΔH_B for both isoelectronic donors and acceptors within an accuracy that is generally better than experimental accuracy, i.e., $\pm 20\%$. We shall compare this conclusion with experiment in Sec. VI (Table II).

The consequence of this conclusion on the temperature variation of the ionization level within the gap is illustrated in Fig. 2.

IV. IONIZATION OF VACANCIES

In view of the foregoing considerations, the case of the vacancy may be analyzed immediately. The vacancy is clearly analogous to the isoelectronic impurity because it too is neutral in the unit cell in the neutral state V^x .

The case of the single vacancy in Si, V_{Si} , is

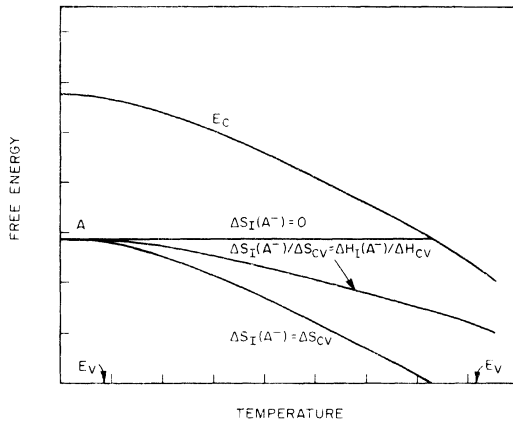
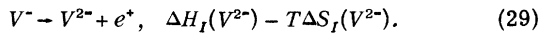
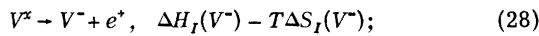
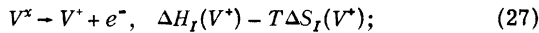


FIG. 2. Variation with temperature of the free energy of a deep acceptor for the cases that the entropy of ionization $\Delta S_I(A^-) = 0$, $= \Delta S_{cv}$, or $= \Delta S_{cv} \Delta H_I / \Delta H_{cv}$. The specific curves are appropriate for Si with $\Delta H_I = \frac{1}{2} \Delta H_{cv}$ in the temperature range from zero to the melting point.

particularly well studied^{3, 8-11, 26, 27} and will serve as an example. This vacancy is known to exist in four different charge states^{8, 26, 27} V^+ , V^x , V^- , and V^{2-} . Therefore, three ionization reactions are defined:



The values for the ΔH_I 's at $T=0$ deduced from experiment⁸⁻¹⁰ are shown in Fig. 3. The value of $\Delta H_I(V^+)$ is controversial; Watkins offers evidence that the level is less than 0.1 eV above the valence-band edge,⁸ i.e., $\Delta H_I(V^+) \geq \Delta H_{cv} - 0.1$ eV, while Naber *et al.*⁹ and Fair¹⁰ infer the level to be 0.35 eV or more above the valence-band edge, i.e., $\Delta H_I(V^+) \leq \Delta H_{cv} - 0.35$ eV. We do not know the resolution of this controversy and will assume

$$\Delta H_I(V^+) = \Delta H_{cv} - 0.35 \text{ eV} \quad (30)$$

for the purpose of clear illustration. The reader will please note that this assumption is tentative and subject to the criticism raised by Watkins.⁸ The particular value of $\Delta H_I(V^+)$ is not critical to our argument, and the qualitative result would be the same for either case.

The entropies of reactions (27)–(29) are, in our notation

$$\Delta S_I(V^+) = \Delta S(V^+) + \Delta S_{cv}(e^-); \quad (31)$$

$$\Delta S_I(V^-) = \Delta S(V^-) + \Delta S_{cv}(e^+); \quad (32)$$

$$\Delta S_I(V^{2-}) = \Delta S(V^{2-}) - \Delta S(V^-) + \Delta S_{cv}(e^+). \quad (33)$$

Now, about 60% of the charge of V^+ or V^- is spread over the four nearest-neighboring atoms, and the

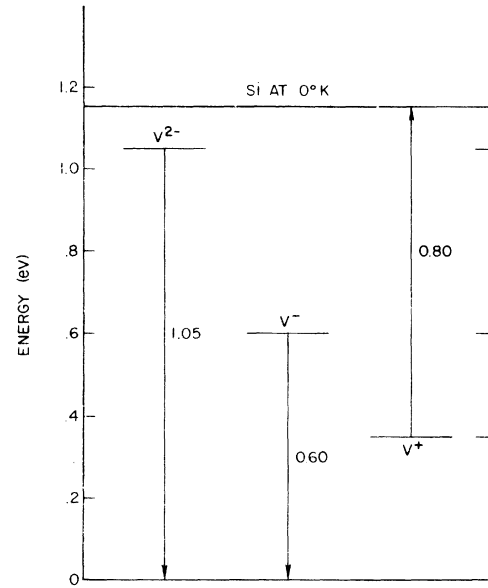


FIG. 3. Vacancy levels in Si at 0 K assumed by the authors for the purposes of this paper. The actual position of the donor level V^+ is controversial. Watkins, Ref. 8, gives evidence that it is about 0.3 eV lower than shown. The other levels are accurate to ± 0.1 eV.

remaining 40% is spread over more distant neighbors with very little in the vacancy cavity itself.^{8, 26-30} Therefore, the bound charges of the ionized states are relatively well delocalized. Consequently, their effect upon the lattice modes should be essentially that of the corresponding free carrier:

$$\Delta S(V^+) = \Delta S_{cv}(e^+), \quad (34)$$

$$\Delta S(V^-) = \Delta S_{cv}(e^-) = \frac{1}{2} \Delta S(V^{2-}), \quad (35)$$

just as with Eqs. (15), (24), and (25). The conclusion is then

$$\Delta S_I(V^+) = \Delta S_{cv} = \Delta S_I(V^-) = \Delta S_I(V^{2-}). \quad (36)$$

Due to the importance of this result, we will elaborate upon Eqs. (34) and (35) somewhat. Consider first the donor state V^+ . As the vacuum has no electrons to donate to anything, this state can only arise from the perturbation of the valence-band states of the surrounding atoms up into the forbidden gap. Then when the Fermi level E_F passes below these perturbed states, they will donate their electron to the Fermi distribution. This will leave the vacancy in the positively charged donor state V^+ . Due to the requirement of charge balance, the number of electrons in the thermal distribution at the conduction-band edge will then increase by one. What we are assuming at Eq. (34) is that these perturbed states about the vacancy just track the valence-band states

from which they are formed as the temperature varies.

The reader might wish to object to this assumption on the ground that the perturbation due to the vacancy may mix states from the conduction band of the perfect crystal with valence-band states to form the donor-vacancy-state wave function. We do not feel this is a valid objection; to the extent that the parentage of such states is mixed, we feel this only indicates that the Bloch waves of the perfect crystal are not an ideal basis set for the defect. One can be confident that in the ground state of the defect, the localized wave functions are as bonding as possible in the chemical and lattice-dynamic senses. Therefore, the introduction of a hole into this distribution of localized states should have a very similar effect to that of introducing a hole into the valence band of the perfect crystal.

The acceptor states of the vacancy may result from two sources. One is the perturbation of the antibonding conduction-band states of the surrounding atoms which shift a localized antibonding state down into the forbidden gap in analogy to the upward shift of the localized bonding state which produces the donor state. This localized antibonding state will be occupied if the Fermi level lies above it so that it is an acceptor state. An acceptor state may also be produced from the new Bloch state that is introduced into each band by the creation of the vacancy due to the concomitant increase by one of the number of lattice sites. As no new electrons are introduced by the formation of the vacancy, such states are acceptors. Of course, the acceptor states actually formed are apt to have strongly mixed parentage.

However, the bound electrons of an ionizing donor state are not to be found in the local bonding network around the defect because covalent bonding implies a saturation of the available atomic orbitals. Thus, the insensitivity of ΔS_i to the distribution of the electronic charge, as long as it is not in the bond, that was noted at Eq. (18) and in Table I, supports the approximation of Eq. (35).

The consequence of Eq. (36) upon the temperature variation of V_{Si} ionization levels is illustrated in Fig. 4. The corresponding variation of the enthalpies of vacancy ionization, the $\Delta H_i(V)$'s, is illustrated in Fig. 5. Note that while the (free energies of) vacancy donor and acceptor levels cross around 800 K in Fig. 4, the enthalpies (and internal energies) of these levels move further apart. The crossing of the levels results only from the increase in lattice entropy upon ionization, which is a consequence of the mode-softening effects of both the free carrier and the localized charge^{1-4,7,31} produced by each ionization event.

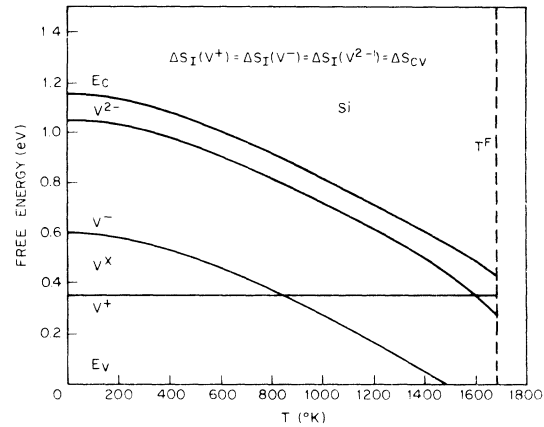


FIG. 4. Variation with temperature of the free energies of the four charge states of a vacancy in Si as argued here. Low-temperature values of the ionization energies are as in Fig. 3.

The consequent effect of the level crossing on the variation of the concentrations of the various charge species of V_{Si} as a function of the Fermi level is illustrated in Fig. 6. We see that at temperatures below the donor-acceptor crossover point, there is a range of E_F over which V^x is the dominant species separating the ranges over which V^+ and V^- are dominant. Above this crossover temperature, V^x is never the dominant species and, as E_F rises, one passes directly from a range in which V^+ is dominant to one in which V^- is dominant.

The situation in Ge is very similar to that in Si.^{3,8} The validity of the present conclusions is supported in both cases by the quenching experiment data we present separately.

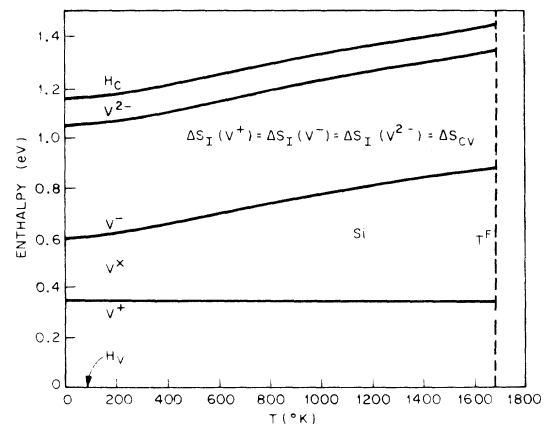


FIG. 5. Variation with temperature of the enthalpies of the four charge states of a vacancy in Si corresponding to the variation in free energy shown in Fig. 4.

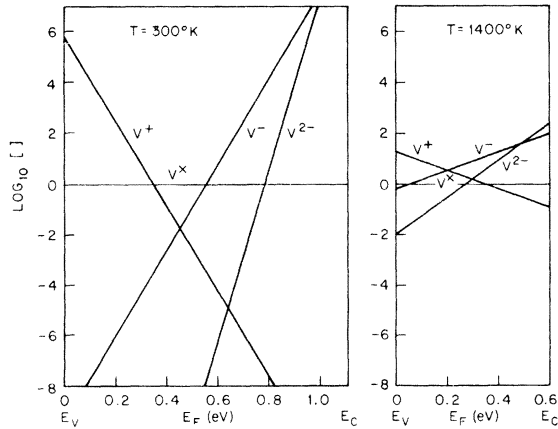


FIG. 6. Relative concentrations of the charge states V^+ , V^x , V^- , and V^{2-} for the single vacancy in Si as a function of the Fermi level E_F at $T = 300$ K and $T = 1400$ K for the variation of energy levels with T as argued here. E_v and E_c denote the valence- and conduction-band-edge free energies, respectively.

V. IONIZATION OF HYDROGENIC DEFECTS

In the case of Coulombic defects, it is evident in Fig. 1 that no new carriers are created in the ionization reaction, Eqs. (5) and (6), but that the bound carrier of the neutral state is freed from the vicinity of the ion core, which bears a net charge with respect to the perfect crystal.

In the effective-mass approximation the envelope function for the bound carrier of the neutral state has the form⁷

$$\psi = (\pi a_h^3)^{-1/2} e^{-r/a_h}, \quad (37)$$

where

$$a_h = (\hbar^2/2m^* \Delta H_I)^{1/2} = \epsilon a_0 m_0 / m^*. \quad (38)$$

In (38) ϵ is the dielectric constant, a_0 is the Bohr radius, and now m^* is the conduction-band density-of-state (single-valley) effective mass for donors and the valence-band density-of-states mass for acceptors. This envelope function is more delocalized than Eq. (13) due to the absence of the r^{-1} factor; more than 98% of its density lies outside of $\frac{1}{4}a_h$, and 57% lies outside a_h . Therefore, when ΔH_I is of the order of the hydrogenic value

$$\Delta H_0 = 13.6m^*/\epsilon^2 \text{ eV}, \quad (39)$$

the bound carrier's wave function is so delocalized that its effect on the bond charge and the lattice modes is essentially identical to that of the corresponding free carrier. Moreover, whatever effect the net charge on the ion core may have on the lattice modes is almost exactly the same in the neutral and ionized states. Therefore, there is essentially no change in the phonon frequencies

and lattice entropy upon ionization and so

$$\Delta S_I = 0 \quad (40)$$

for hydrogenic impurities.

Equation (40) implies that such donor levels are pinned to the conduction band, and such acceptor levels are pinned to the valence band. This result is in agreement with the empirical conclusions of Pearson and Bardeen³² in 1949, and the argument of the last paragraph is essentially the same as that Brooks presented¹ in 1955.

VI. IONIZATION OF COULOMBIC DEFECTS WITH CENTRAL-CELL CORRECTIONS

As we consider Coulombic-defect ionization levels progressively deeper than the hydrogenic value ΔH_0 , i.e., with progressively larger central-cell corrections, we know that the bound carrier of the neutral state becomes more localized around the (charged) defect ion core. Unfortunately, there is no known general prescription to describe the bound carrier's density in the presence of large central-cell corrections or within the central cell.^{15,33} However, Heine and Henry suggest an envelope function of the form which has shown some success in treating isotope shifts,^{7,31}

$$\psi = [2^{2n}/2\pi a_c^{2n+1} \Gamma(2n+1)]^{1/2} r^{n-1} e^{-r/a_c} \quad (41)$$

[note the error in the normalization constant of Eq. (51) of Ref. 7], where

$$a_c = (\hbar^2/2m^* \Delta H_I)^{1/2} \quad (42)$$

and

$$n = (\Delta H_0/\Delta H_I)^{1/2}. \quad (43)$$

In this approximation the envelope function for the carrier bound at the Coulombic center approaches that at an isoelectronic trap, Eq. (13), as ΔH_I increases or, equivalently, as n approaches zero.

Qualitatively, one should expect ΔS_I to increase from zero, its value in the hydrogenic case (no central-cell correction) to a value comparable with ΔS_{cv} as ΔH_I approaches ΔH_{cv} . The form of this increase is problematic, but we shall make a simple plausible estimate and compare with available data. Let us assume first that

$$\Delta S_I(\Delta H_I(A)) = P(\Delta H_I) [\Delta S_{cv}(e^+) + \Delta S(A^-)], \quad (44)$$

$$\Delta S_I(\Delta H_I(D)) = P(\Delta H_I) [\Delta S_{cv}(e^-) + \Delta S(D^*)], \quad (45)$$

where $\Delta S(A^-)$ and $\Delta S(D^*)$ denote the contributions of the charged acceptor and donor ion cores to the entropy of the lattice resulting from the destabilizing effect of their deficit or excess charge with respect to the host ions. (Recall that the effects

of mass differences are neglected here because they should affect both initial and final states to the same degree.) $P(\Delta H_I)$ is the probability that the bound carrier of the neutral state be found inside a sphere of radius R_1 around the impurity nucleus,

$$P(\Delta H_I) = 4\pi \int_0^{R_1} \psi^2(\Delta H_I) r^2 dr. \quad (46)$$

Here $\psi(\Delta H_I)$ is taken from Eq. (31), and the core radius will here simply be assumed to be the largest radius among the following: that of the outermost completed shell of the host atom replaced by a substitutional impurity; that of the outermost completed shell of the defect atom; that of the uncompleted d or f shell of a transition or rare-earth defect atom. All these radii are to be calculated using the Slater effective charge method used to obtain the rationalized covalent radii of atoms in tetrahedrally coordinated semiconductors.³⁴

Of course, the motivation for Eq. (46) is that when the bound carrier lies within the core of the impurity, the two charges compensate each other. Then there should be no mode softening because neither charge produces a perturbation of the normal bonding charge density nor adds charge

to the perturbation of the normal bonding charge density nor adds charge to the antibonding region nor produces any perturbing electric field. However, when such a defect is ionized and the formerly bound carrier is removed to a Bloch state, the $P \cong 0$ and the lattice modes are softened by the full effect of both.

What is the magnitude of $\Delta S(A^-)$ or $\Delta S(D^+)$ relative to $\Delta S_{cv}(e^-)$ or $\Delta S_{cv}(e^+)$? In previous work,³⁵ one of us (J. A. V. V.) has implicitly assumed

$$\Delta S(A^-) = \Delta S_{cv}(e^-) \quad (47)$$

and

$$\Delta S(D^+) = \Delta S_{cv}(e^+), \quad (48)$$

when calculating the distribution coefficients of impurities in liquid-solid equilibrium. This assumption is supported by the observation noted at Eq. (18) that the E_0 transition ($\Gamma_{25'}^v \rightarrow \Gamma_{2'}^c$, or in zinc-blende $\Gamma_{15}^v \rightarrow \Gamma_1^c$) has about the same temperature dependence as ΔE_{cv} . This is because the $\Gamma_{2'}^c$ state is strongly localized at the atom site¹⁸ and thus approximates a negative charge on the ion core. Of course, the assumption is also supported by the general success of the calculation of distribution coefficients³⁵ and in the success of a calculation³¹ of the isotope shift of the charac-

TABLE II. Calculated and empirical values for the entropy of ionization ΔS_I of several defects in Si and in GaP. These entropies are referred to the entropy of the fundamental band gap ΔS_{cv} at the same temperature. Also shown are the values of the enthalpy of ionization ΔH_I at zero degrees, and the core radius R_1 assumed in the calculation of ΔS_I for the Coulombic defects. The entry N.A. in the R_1 column indicates that this parameter is not applicable to the calculation for the isoelectronic defects. The defects having a superscript “-” are acceptors, those with a “+” are donors.

Defect	R_1 (Å)	$\Delta H_I(0)$ (eV)	$\Delta S_I/\Delta S_{cv}$ (calc.)	$\Delta S_I/\Delta S_{cv}$ (expt.)	Ref.
$N_{\bar{p}}$ in GaP	N.A.	2.33	1.0	1.0 ± 0.2	37, 38
$Bi_{\bar{p}}$ in GaP	N.A.	2.30	1.0	1.0 ± 0.2	39
$Si_{\bar{p}}$ in GaP	0.497	0.20	0.0028	0 ± 0.2	40
$Ge_{\bar{p}}$ in GaP	0.482	0.30	0.010	0 ± 0.2	40
$Co_{\bar{c}a}$ in GaP	0.758	0.41	0.057	0 ± 0.2	41
$O_{\bar{p}}$ in GaP ^a	0.452	0.896	0.085	0.15 ± 0.15	42, 43
Au^- in Si ^b	1.511	0.67	0.42	1.0 ± 0.1	44, 45
Au^+ in Si	1.511	0.84	0.39	0 ± 0.2	46
Co^- in Si	0.758	0.635	0.17	1.0 ± 0.5	47
Co^+ in Si	0.758	0.787	0.18	1.0 ± 0.3	48
ZnO^- in GaP	N.A.	2.04	1.0	1.0 ± 0.2	49, 50
CdO^- in GaP	N.A.	1.94	1.0	1.0 ± 0.2	49

^a We have estimated the entropy of ionization of oxygen from the work of Kopylov and Pikhtin (Ref. 43) who conclude that at 300 K the ionization energy has not changed by more than 0.02 eV from its 0-K value. If we assume that the ratio $\Delta S_I/\Delta S_{cv}$ is independent of temperature, the value giving a change of 0.02 eV between 0 and 300 K in ΔE_I is 0.3.

^b The energy level is from Parrillo and Johnson (PJ) (Ref. 44) and the entropy from Engström and Grimmeiss (EG) (Ref. 45). The energy-level temperature dependence of PJ can be brought into agreement with EG by using $\frac{1}{4}$ (Ref. 53) for the degeneracy factor rather than $\frac{3}{2}$ ($=g_A$ as used by PJ).

teristic green luminescence line at the Cu substitutional impurity in ZnO.³⁶

Substituting Eqs. (47) and (48) into Eq. (46), we finally have

$$\Delta S_I(\Delta H_I, T) = P(\Delta H_I) \Delta S_{cv}(T) \quad (49)$$

for both donors and acceptors. The resultant predictions of ΔS_I for various defects in Si and GaP are shown in Table II. All the empirical values³⁷⁻⁵⁰ we have found are shown for comparison.

In Table II one can see that for the two isoelectronic impurities, N_P^- and Bi_P^+ in GaP and two isoelectronic complexes, $Zn_{Ga}O_P^-$ and $Cd_{Ga}O_P^-$, for which we found sufficient data,^{37-39, 49, 50} the conclusion reached in Sec. III is supported by experiment. Furthermore, the three Coulombic impurities that are shallower than one-quarter the band gap, Si_P^+ , Ge_P^+ , and Co_{Ga}^- in GaP, are found^{40, 41} to have small values of ΔS_I , equal within experimental error to the values calculated. The O_P^+ defect in GaP is more than a third the gap deep and has a ΔS_I that is detectably large. Although it has previously been asserted that $\Delta S_I \sim \Delta S_{cv}$ for this defect, a careful analysis⁴³ shows that it is much smaller and in satisfactory agreement with the value calculated here.

Two defects in Si, which are related to Au and to Co impurities, display two ionization levels each near midgap. The acceptor levels Au^- and Co^- are found^{44, 45, 47} to have values of ΔS_I that are much larger than those calculated on the assumption that the defect is a simple substitutional impurity. Indeed, the values are equal within experimental uncertainty to ΔS_{cv} —as if they were, in fact, isoelectronic or vacancy-type defects.

VII. NATURE OF Au AND Co DEFECTS IN Si

Consider now the possible sources, signs, and magnitudes of error in the calculation. The calculated ΔS_I increases with increasing R_1 . It seems that the procedure used to fix R_1 in Eq. (46) yields the maximum plausible values. Therefore, any error in this parameter is opposite in sign to that required to reconcile theory and experiment for the cases of Au^- and Co^- in Si.

The Heine and Henry prescription,⁷ Eq. (14), for the wave function of the trapped carrier is certainly a crude approximation within the central cell, but it is properly normalized and generally thought to be a good approximation outside the central cell. Therefore, the principal inaccuracy resulting from this approximation is in the distribution of the carrier charge density within the central cell; the error in the total charge density

within the unit cell would seem to be small. Consider the sign of this error. The most evident inaccuracy of the assumed wave function ψ in Eq. (41) is that

$$\psi(r=0) \rightarrow \infty \quad (50)$$

if $n < 1$, which is definitely the case for the three defects under consideration. Of course, the radial factor of the carrier's true wave function ψ_r is finite at $r=0$. Therefore, one may conclude that the assumed ψ , Eq. (41), puts too much of the carrier's charge density within the core of the impurity atom and not enough on the bonds to the surrounding atoms. Consequently, this error is also opposite in sign to that required to reconcile theory with experiment.

There is also the assumption of Eqs. (47) and (48). However, for an acceptor defect, the term in question, $\Delta S(A^-) \approx \Delta S_{cv}(e^-)$, is small, and observations of the E_0 transition discussed after Eq. (47) make it difficult to see how the negative charge on the A^- nucleus could have an effect much greater than that of an electron. Therefore, this error does not seem to be the source of the discrepancy either.

It is our conclusion that this discrepancy between the calculated and observed values for ΔS_I for the Au^- and Co^- defects in Si results from the assumption that they are simple substitutional defects. We propose that these defects are instead complexes of the impurity atom with vacancies. Using the quotation marks to indicate the common appellation of these defects, as contrasted with their actual nature, we propose the following correspondence:

$$"Au_{Si}^- = Au_i V_{Si}, \quad (51)$$

$$"Co_{Si}^- = Co_i V_{Si}. \quad (52)$$

Here, the subscript i indicates the impurity atom is not at a normal lattice site but is in some interstitial position. The corresponding proposal for the actual scheme of ionization reactions is

$$"Au_{Si}^{-2x} - "Au_{Si}^{-x} + e^+ = Au_i^+ V_{Si}^- - Au_i^+ V_{Si}^{2-} + e^+, \quad (53)$$

$$"Au_{Si}^{-x} - "Au_{Si}^{-x} + e^- = Au_i^+ V_{Si}^- - Au_i^+ V_{Si}^x + e^-, \quad (54)$$

$$"Co_{Si}^{-2x} - "Co_{Si}^{-x} = Co_i^+ V_{Si}^- - Co_i^+ V_{Si}^{2-} + e^+. \quad (55)$$

Due to the uncertainty as to the nature of the Co^- defect, which may or may not be another ionization state of " Co_{Si}^- ", we will not commit ourselves on that reaction.

Let us first note that Eq. (36) implies that ΔS_I for reactions (53) and (55) should be essentially $\Delta S_I(V^{2-}) \approx \Delta S_{cv}(Si)$, as is observed^{44, 45} to within experimental error. As reaction (54) amounts to removing an e^- from a localized state at the V_{Si} ,

we conclude from our previous discussion (Table I) that the ΔS_I for this reaction should be nearly zero, which is consistent with the available data.⁴⁶

We further note that the correspondence scheme (51) to (55) is entirely plausible in view of the known ionization of V_{Si} , Fig. 3, the reasonable supposition that Au_i and Co_i are shallow donors,⁵¹ and the usual interaction between donors and acceptors that causes the ionization levels of both to become shallower when they form complexes.⁵² On the other hand, it seems quite implausible that Au, a univalent atom, could ever act as a donor when a substitutional impurity on a four-valent Si site. Moreover, the empirical degeneracy factor $g_A^{-1} = 0.25$ for the " Au_{Si} " level⁵³ is inconsistent with the assumption that the defect is a simple substitutional impurity, but is consistent⁵⁴ with Eq. (51).

It also seems worthwhile to make an additional comment about the complexes $Zn_{Ga}O_P$ and $Cd_{Ga}O_P$ in GaP, for which data are available^{49, 50} as shown in Table II. We regard the neutral state of these complexes to be $Zn_{Ga}^{\cdot-}O_P^+$ and $Cd_{Ga}^{\cdot-}O_P^+$ with no free or bound carriers; i.e., it is as if we had one unit cell of ZnO or tetrahedral CdO in its normal ground state imbedded in GaP. Then the acceptor reactions,



correspond to excitation across the gap of the imbedded species plus delocalization of the hole into the valence band of the GaP. In view of the present discussion, it is expected that the entropy of these reactions, (56) and (57), should be approximately ΔS_{cv} , as is observed (Table II).

APPENDIX A: DEGENERACY FACTORS

Throughout this paper we have discussed only the lattice mode contributions to ΔS_I . However, the relative concentrations of the various ionization states are calculated with the usual Fermi-Dirac expressions:

$$[A^-] = \frac{[A^{\cdot-}] + [A^-] + [A^{2-}] + \dots}{1 + g_A \exp[(E_A - E_F)/kT]}, \quad (A1)$$

$$[D^+] = \frac{[D^{\cdot+}] + [D^+] + [D^{2+}] + \dots}{1 + g_D \exp[(E_F - E_D)/kT]}, \quad (A2)$$

where g_A and g_D denote the spin-degeneracy factors. For impurities these factors are $g_D = 2$ because the neutral donor state is twofold spin degenerate and $g_A = 4$ because the valence-band maximum is twofold orbitally degenerate and twofold spin degenerate so that the neutral acceptor state has a total degeneracy of four whereas the

ionized state has no degeneracy in either case. However, for vacancies, the neutral state has no spin degeneracy while both V^+ and V^- are twofold degenerate so that $g_A = g_D = \frac{1}{2}$ for vacancies. It would seem that a consistent definition of the standard or site entropy of impurities or vacancies would require that these factors be included in ΔS_I . This would imply that values of $\Delta S_I(V^+)$ and $\Delta S_I(V^-)$ should be increased by $k \ln 2 = 0.69k$ while, for impurities $\Delta S_I(D^+)$ should be reduced by $k \ln 2$ and $\Delta S_I(A^-)$ should be reduced by $k \ln 4$. But then the g factors would have to be removed and E_A and E_D redefined. Due to the general use and acceptance of Eqs. (A1) and (A2), we have not followed this logical conclusion.

APPENDIX B: CLASSIFICATION OF ISOELECTRONIC TRAPS

Hopfield *et al.*⁵⁵ classified isoelectronic traps as either isoelectronic donors or acceptors. The classification was based upon the viewpoint that an electron trap such as N_P in GaP "... will bind a hole to the long-range Coulomb potential in an acceptorlike wave function. This bound exciton state might be called an isoelectronic acceptor."⁵⁵ Similarly, an isoelectronic hole trap will produce a bound exciton state with a donorlike wave function that might be called an isoelectronic donor. This classification leads to donors and acceptors that do not directly provide electrons or holes to the semiconductor⁵⁶ and therefore were not normal donors or acceptors.⁵⁷

We have taken the view that isoelectronic nitrogen in GaP is, in fact, a normal acceptor in that it does provide holes to the valence band. Bismuth is, in fact, a normal donor in that it does provide electrons to be the conduction band. The unusual feature is the very low concentrations of holes or electrons provided. They are unmeasurable but calculable.

The ionization energy of nitrogen as an acceptor ($N_P^{\cdot-} = N_P^- + e^+$) is 2.330 eV at low temperatures (Table II). $N_P^{\cdot-}$ is a shallow electron trap of binding energy 8 meV; the sum of the electron binding energy and the ionization energy is the gap energy. Similarly for bismuth. A hole is bound by 38 meV. The sum of the trap binding energy and the ionization energy of $Bi_P^{\cdot+}$ equals the energy gap, thereby giving 2.300 eV for the ionization energy.

The complexes ZnO and CdO in GaP are also isoelectronic traps for electrons and consequently are acceptors. The electron binding energy for CdO is 0.4 eV. This is the shallowest of the isoelectronic acceptors. With 10^{17} cm^{-3} present in otherwise pure GaP, the crystal will be p type at all temperatures below 685 K with a maximum

hole concentration of about 10^{12} cm⁻³. This may be compared to N_p with a concentration of 10^{18} cm⁻³ in otherwise pure GaP. The crystal will be *p* type at temperatures below 78 K and with a maximum hole concentration of 10^{17} cm⁻³.

It should be noted⁵⁶ that random pairs of nitrogen

atoms are even deeper electron traps than N_p^- and consequently are somewhat more easily ionized as acceptors. However, the concentration of such pairs is always smaller than the concentration of N_p^- thereby causing the pairs to be even less effective than N_p^- in producing holes.

*Portions of this work were completed while at Bell Laboratories.

¹H. Brooks, *Adv. Electron.* **7**, 85 (1955).

²C. D. Thurmond, *J. Electrochem. Soc.* **122**, 1133 (1975).

³J. A. Van Vechten, in *Lattice Defects in Semiconductors 1974* (Institute of Physics, London, 1975), p. 212.

⁴V. Heine and J. A. Van Vechten, *Phys. Rev. B* **13**, 1622 (1976).

⁵R. M. Martin, *Phys. Rev.* **186**, 871 (1969).

⁶W. Weber, *Phys. Rev. Lett.* **33**, 371 (1974).

⁷V. Heine and C. H. Henry, *Phys. Rev. B* **11**, 3795 (1975).

⁸G. D. Watkins, in Ref. 3, p. 1.

⁹J. A. Naber, C. E. Mall, and R. E. Leadon, in *Radiation Damage and Defects in Semiconductors* (Institute of Physics, London, 1973), p. 26.

¹⁰R. B. Fair, *J. Electrochem. Soc.* **122**, 800 (1975).

¹¹J. A. Van Vechten and C. D. Thurmond, following paper, *Phys. Rev. B* **14**, 3551 (1976).

¹²A. Baldereschi and J. J. Hopfield, *Phys. Rev. Lett.* **28**, 171 (1972).

¹³A. Baldereschi, *J. Lumin.* **7**, 79 (1973).

¹⁴R. A. Faulkner, *Phys. Rev.* **175**, 991 (1968).

¹⁵S. T. Pantelides, in *Physics of Semiconductors*, edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 396.

¹⁶A. Onton, *Phys. Rev.* **186**, 786 (1969).

¹⁷D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **150**, 680 (1966).

¹⁸C. V. de Alvarez and M. L. Cohen, *Solid State Commun.* **14**, 317 (1973).

¹⁹J. P. Walter (unpublished).

²⁰M. L. Cohen (private communication).

²¹See, M. Cardona, K. L. Shaklee, and F. H. Pollak, *Phys. Rev.* **154**, 696 (1967).

²²J. C. Phillips, *Phys. Rev. Lett.* **20**, 550 (1968); *Rev. Mod. Phys.* **42**, 317 (1970).

²³J. A. Van Vechten, *Phys. Rev.* **182**, 891 (1969).

²⁴J. A. Van Vechten, *Phys. Rev.* **187**, 1007 (1969).

²⁵P. Y. Yu and M. Cardona, *Phys. Rev. B* **2**, 3193 (1970).

²⁶G. D. Watkins, *J. Phys. Soc. Jpn. Suppl.* **18**, 22 (1963).

²⁷G. D. Watkins, in *Radiation Damage in Semiconductors* (Dunod, Paris, 1964), p. 97.

²⁸J. C. Phillips and J. A. Van Vechten, *Phys. Rev. Lett.* **30**, 220 (1973).

²⁹J. A. Van Vechten, *Phys. Rev. B* **10**, 1482 (1974).

³⁰J. A. Van Vechten, *J. Electrochem. Soc.* **122**, 420 (1975).

³¹J. A. Van Vechten, *Phys. Rev. B* (to be published).

³²G. L. Pearson and J. Bardeen, *Phys. Rev.* **75**, 865 (1949).

³³S. T. Pantelides, *Phys. Rev. B* **12**, 2543 (1975).

³⁴J. A. Van Vechten and J. C. Phillips, *Phys. Rev. B* **2**, 2160 (1970).

³⁵J. A. Van Vechten, *Phys. Rev. B* **7**, 1479 (1973).

³⁶R. Dingle, *Phys. Rev. Lett.* **23**, 579 (1969).

³⁷J. D. Cuthbert and D. G. Thomas, *Phys. Rev.* **154**, 767 (1967).

³⁸R. Z. Bachrach and O. G. Lorimor, *Phys. Rev. B* **7**, 700 (1973).

³⁹P. J. Dean, J. D. Cuthbert, and R. T. Lynch, *Phys. Rev.* **179**, 754 (1969).

⁴⁰P. J. Dean, E. G. Schonherr, and R. B. Zetterstrom, *J. Appl. Phys.* **41**, 3475 (1970).

⁴¹D. H. Loescher, J. W. Allen, and G. L. Pearson, *J. Phys. Soc. Jpn. Suppl.* **21**, 239 (1966).

⁴²P. I. Dean and C. H. Henry, *Phys. Rev.* **176**, 928 (1968).

⁴³A. A. Kopylov and A. N. Pikhtin, *Fiz. Tekh. Poluprovodn.* **8**, 2398 (1974) [*Sov. Phys.-Semicond.* **8**, 1563 (1975)].

⁴⁴L. C. Parrillo and W. C. Johnson, *Appl. Phys. Lett.* **20**, 104 (1972).

⁴⁵O. Engström and H. G. Grimmeiss, *Appl. Phys. Lett.* **25**, 413 (1974).

⁴⁶D. C. Wong and C. M. Penchina, *Phys. Rev. B* (to be published).

⁴⁷C. M. Penchina and J. S. Moore, *Phys. Rev. B* **9**, 5217 (1974).

⁴⁸D. C. Wong and C. M. Penchina (to be published).

⁴⁹R. Z. Bachrach and J. S. Jayson, *Phys. Rev. B* **7**, 2540 (1973).

⁵⁰J. D. Cuthbert, C. H. Henry, and P. J. Dean, *Phys. Rev.* **170**, 739 (1968).

⁵¹J. A. Van Vechten, *Phys. Rev. B* (to be published).

⁵²T. N. Morgan, B. Welber, and R. N. Bhargava, *Phys. Rev.* **166**, 751 (1968).

⁵³M. Brown, C. L. Jones, and A. F. W. Willoughby, *Solid State Electron.* **18**, 763 (1975).

⁵⁴C. D. Thurmond and J. A. Van Vechten (unpublished).

⁵⁵J. J. Hopfield, D. G. Thomas, and R. T. Lynch, *Phys. Rev. Lett.* **17**, 312 (1966).

⁵⁶D. G. Thomas, *J. Phys. Soc. Jpn. Suppl.* **21**, 265 (1966), see discussion.

⁵⁷F. A. Trumbore, M. Gershenzon, and D. G. Thomas, *Appl. Phys. Lett.* **9**, 4 (1966).