which restricts our results to the multiphoton limit for the transverse case. We know that the interband electric term $[\mathcal{H}_2{}^{(D)},S]$ is small since it leads either to tunneling or multiphoton absorption, both of which are relatively weak effects.

We estimate the Fourier components $\mathbf{k}$ of our solutions in Secs. II and III at the saddlepoints $u_\pm = \sin\omega t_\pm \approx i\gamma$. For a longitudinal magnetic field, k_z is increased by $(eE/\hbar\omega)\sin\omega t_\pm \approx i(2\mu\mathcal{E}_n)^{1/2}/\hbar$, so the restriction $|k_z|a \ll 1$ gives the condition

$$(p_{cv}/m_0)^2 \ll \mathcal{E}_g{}^2/2\mu\mathcal{E}_n. \tag{A2}$$

We obtain essentially the same condition in a transverse magnetic field, where we use $\Delta k_x \approx \alpha_j/\lambda \approx i(2\mu\mathcal{E}_{n'n})^{1/2}/\hbar$ at the saddlepoints $u_\pm$. But, from the two-band model $(p_{cv}/m_0)^2 \approx \mathcal{E}_g/4\mu$, which gives the condition

$$\mathcal{E}_{n'n}, \mathcal{E}_n \ll 2\mathcal{E}_g \tag{A3}$$

which again limits our results to the first few Landau levels in high magnetic fields. The accuracy of our approximation is not very good: At $H \to 0$, $\mathcal{E}_{n'n}$, $\mathcal{E}_n \to \mathcal{E}_g$ which gives $|k|a \approx \frac{1}{2}$ which is not very much smaller than 1. Thus our results must be used carefully, in that the conditions (A2) and (A3) must be checked for a given material, and estimates of transition strengths can be expected to be only approximate.

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Calculation of the Formation Energy of a Schottky Defect in Germanium*

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The formation energy of a Schottky defect in germanium has been calculated from first principles by using the valence-bond method of Heitler and London. The formation energy of a vacancy is given by the difference between the ground-state energy of the crystal containing the defect and that of the perfect crystal. The latter is derived by using a method based on the general directional theory of valence. The energy of the defect crystal is obtained by using the same general method but taking into account the possible pairing schemes for the vacancy electrons and applying the method of resonance. The tetrahedral valence state of germanium is used as the reference level for the various energies in the calculation. The numerical result obtained depends on the value chosen for the cohesive energy of germanium. Using an average of the three reported values for this quantity, we find for the formation energy at a Schottky defect $E_v = 2.21 \pm 0.18$ eV. This is in good agreement with the experimental values.

1. INTRODUCTION

A KNOWLEDGE of the energy required to form a Schottky defect in a semiconductor is necessary for the analysis of experiments on diffusion, quenching, and radiation damage. Calculations of this energy for germanium have been reported by Swalin,[1] Scholz,[2] Scholz and Seeger,[3] and Bennemann.[4] Swalin assumed a Morse potential to describe the covalent bond in the crystal while Scholz, and Scholz and Seeger used a combination of the harmonic approximation to Born's lattice potential with a Morse potential. Bennemann[4] developed a method using first principles. The purpose of this paper is to present a calculation, also from first principles, based on the method of atomic functions developed initially by Heitler and London. Experimental values for the energy of formation of a singly charged negative vacancy in germanium have been reported by a number of workers.[5–11] The values range from 1.7 to about 2 eV. The corresponding values for the neutral vacancy can be calculated by the method used by Kröger.[11]

The calculations by Swalin, by Scholz, and by Scholz and Seeger are open to criticism on a number of grounds. The use of a Morse function to represent the potential is questionable on theoretical grounds. Even assuming that the Morse function could be used as a reasonable approximation, the reference level for the dissociation energy of a covalent bond should be the sp^3 valence state of the constituent atom of the solid, not the free ^3P state used by these authors. This can be seen most

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easily from the work of O-Ohata.[12] Since the energy difference between the sp^3 and ^3P states is quite large, a correction based on using the sp^3 valence state would lead to an appreciable modification in their calculated values. Swalin further assumed that the possible pairings of the vacancy electrons would contribute to the entropy of formation of the vacancy whereas the general theory of resonance shows that the possible pairing schemes that form delocalized bonds will change only the energy of the crystal, not the entropy.

Bennemann's method is not subject to the above criticisms since it is based on first principles and makes no assumption as to the interaction potential. In his work, the formation energy of a vacancy is given by the change in electrostatic energy of the system of ions arising from the point defect plus the change in the energy of the system of valence electrons as a result of their redistribution about the vacancy. He assumed that there would be no relaxation of the lattice ions about the vacancy.

The energy levels of an isolated vacancy can be calculated by using the concept of a defect molecule, which was introduced by Coulson and Kearsley[13] and later extended and modified by Yamaguchi.[14] They applied the molecular orbital theory to determine the electronic structure of the defect by taking into consideration the effect of configuration interactions among various states. They found that the ground state for a neutral vacancy is the ^1E state, i.e., the state with the sum of the spins of the four vacancy electrons equal to zero. This is in accord with the principle of minimum multiplicity of Watkins.[15] Furthermore, Coulson and Kearsley showed that for the undistorted vacancy the valence-bond method gives a good approximation to the ground-state energy of the defect molecule.

The calculation presented in this paper is based on the Heitler-London (valence-bond) method and assumes that ^1E is also the ground state for the defect molecule in Ge. The formation energy of a vacancy is given by the difference between the ground-state energy of the crystal containing the defect and the ground-state energy of the perfect crystal. The latter is derived by using a method formulated by Schmid[16] from the general Slater-Pauling[17] directional theory of valence for the use of localized bonds and used by him to calculate the cohesive energy of diamond. The energy of the crystal containing the vacancy is calculated by using the same general method but taking into account the possible pairing schemes for the vacancy electrons and applying the method of resonance. In this method, the effect of the crystal field on the electrons is taken into account by orthogonalizing the valence orbitals of one particular atom to those of its nearest neighbors. It is also assumed in our calculation that there is no relaxation of the lattice ions in the neighborhood of the vacancy. This will be a valid approximation whenever the main contribution to the relaxation energy is due to the electrons rather than to the lattice ions. Since there will always be some ionic relaxation, the energy calculated using this assumption will be somewhat higher than the true value.

The tetrahedral valence state of Ge is used as the reference level for the various energies in the calculation. Since no ^5S state has ever been identified in the spectral analysis for the free Ge atom, the semiempirical value of this state with respect to the free-atom ground state, ^3P, was employed. The observed cohesive energy per atom for the Ge crystal was also used in our calculation. The calculations were done graphically using Hartree functions for the free Ge atom.

The derivation of the energy expression for the perfect Ge crystal and the cohesive energy per atom for Ge are presented in Sec. 2. Section 3 is devoted to deriving an expression for the energy of the defect crystal by using the method of resonance. The formation energy is then evaluated in Sec. 4. Finally, in Sec. 5, we compare our numerical result with the experimental values and the value obtained by Bennemann. The nature of the relaxation of the electrons on atoms surrounding the vacancy is also discussed.

2. ENERGY EXPRESSION FOR THE PERFECT Ge CRYSTAL

The wave function for the crystal is built up of bond wave functions each of which consists of two orbitals of a bonded partner. The space part of each of these orbitals is orthogonal to all of the other orbitals in the crystal, except in the case of ion-core orbitals. The valence orbitals are lobelike functions each of which points in the direction of a neighboring atom and is met head-on by its bonded partner pointing in the opposite direction. The configuration interaction between the covalent state and the ionized state involves just the two orbitals of a bonded pair rather than all the orbitals in the crystal. Thus, following Schmid,[16] the normalized bond function φ_{ij} may be assumed to have the form

$$\begin{aligned}\varphi_{ij}(k,l)=[2(1+A^2)]^{-1/2}\{&[u_i(k)v_j(l)-v_j(k)u_i(l)]\\&+A[u_i(k)u_i(l)+v_j(k)v_j(l)]\}\\&\times\{[\alpha(k)\beta(l)-\beta(k)\alpha(l)]/\sqrt{2}\}, \quad (2.1)\end{aligned}$$

where u_i and v_j are the space parts of the bonded pair, α

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and β are spin functions, and the arguments k and l designate the kth and lth sets of electron coordinates, respectively. The quantity in the first square brackets inside the curly brackets is the Heitler-London covalent function while that in the second square brackets may be called an "ionized-bond" function and corresponds to having two electrons on one bonded atom and none on the other. The adjustable parameter A, which measures the relative proportions of these two functions in φ_{ij}, will be so determined as to minimize the energy for the observed value of the lattice parameter. Two core orbitals ($1s$, $2s$, $2p$, $3p$, and $3d$) with identical space parts but opposite spins may be regarded as constituting a bonded pair. Let us designate the space parts of these core orbitals by u_i^0 and u_j^0; then $u_i^0=u_j^0$ and the corresponding φ_{ij} is

$$\varphi_{ij}(k,l)=u_i^0(k)u_j^0(l)[\alpha(k)\beta(l)-\beta(k)\alpha(l)]/\sqrt{2}. \qquad (2.2)$$

We note that φ's defined by (2.1) and (2.2) are antisymmetric with respect to interchange of their electron coordinates, that is,

$$\varphi_{ij}(k,l)=-\varphi_{ij}(l,k). \qquad (2.3)$$

They also constitute an orthonormal system since

$$\begin{aligned}&[\varphi_{ij}(k,l)\,|\,\varphi_{ij}(k,l)]_{k,l}=1,\\&[\varphi_{ij}(k,l)\,|\,\varphi_{i'j'}(k,m)]_k=0,\end{aligned} \qquad (2.4)$$

where pair i, $j\neq i'$, j', $l\neq k$, and $m\neq k$. The double subscripts k, l mean that the integrations are carried out over the kth and lth electron coordinates, whereas the single subscript k means that the integration is over the kth coordinate only.

The total electronic wave function of the perfect crystal, Ψ, may be written in the form

$$\begin{aligned}\Psi=2^{-N'/2}\textstyle\sum_P(-1)^P P\varphi_{1,2}(1,2)\varphi_{3,4}(3,4)\cdots\\ \times\varphi_{N'-1,N'}(N'-1,\,N'),\end{aligned} \qquad (2.5)$$

where N' is the total number of electrons (including ion-core electrons) in the crystal and P is the permutation operator. The permutation should be made only for the electron coordinates and not for the subscripts of the φ's. Consequently, the summation over all the permutations in (2.5) will consist of $2^{-N'/2}N'!$ independent terms repeated $2^{N'/2}$ times because of the antisymmetric relation (2.3) and the $2^{N'/2}$ ways of pairing N' electrons. By multiplying the summation by $2^{N'/2}$ we have Ψ in the form of a sum of $2^{N'/2}N'!$ independent terms. Since the φ_{ij}'s are normalized, the norm of Ψ as defined by (2.5) is $2^{N'/2}N'!$.

Let N be the total number of valence electrons in the crystal; then the spin-independent Hamiltonian H can be written as

$$\begin{aligned}H=\sum_{k=1}^{N}O_1(k)+\sum_{k=1}^{N}\sum_{l<k}O_2(k,l)+\sum_{k=1}^{N}\sum_{n=1}^{N'-N}O_2(k,n)\\+\sum_{n=1}^{N'-N}\sum_{m<n}O_2(m,n)+\sum_{n=1}^{N'-N}O_1(n)\\+\sum_{L=1}^{N/4}\sum_{L'<L}\frac{Z_LZ_{L'}}{|\mathbf{R}_L-\mathbf{R}_{L'}|},\end{aligned} \qquad (2.6)$$

where, in atomic units,

$$\begin{aligned}&O_1(k)=-\tfrac{1}{2}\nabla_k^2-\sum_{L=1}^{N/4}\frac{Z_L}{|\mathbf{r}_k-\mathbf{R}_L|},\\&O_2(k,l)=|\mathbf{r}_k-\mathbf{r}_l|^{-1}.\end{aligned} \qquad (2.7)$$

Here $\mathbf{r}_k$ and $\mathbf{r}_l$ are the vectors specifying the kth and lth valence-electron coordinates, $\mathbf{R}_L$ and $\mathbf{R}_{L'}$ specify the Lth and L'th lattice points, and $\mathbf{r}_n$ and $\mathbf{r}_m$ specify the nth and mth core-electron coordinates. Z is the atomic number of the atom and $Z=32$ for Ge. The subscripts on the operators O_1 and O_2 mean that they involve coordinates of one or two electrons.

The energy for the perfect crystal,

$$E=(\psi|H|\psi)/(\psi|\psi),$$

can be found by using Eqs. (2.1)–(2.7). We can write

$$E=E_1+E_2+E_3+E_4.$$

Here E_1 is the energy expression resulting from the ordinary Heitler-London covalent function.[18] If $A=0$ this is the only term present. Using a notation which is explained below, we find

$$\begin{aligned}E_1=\sum_{i=1}^{N}(u_i|O_1|u_i)+\sum_{i=1}^{N}\sum_{n=1}^{N'-N}[C(ii;nn)-\tfrac{1}{2}C(in;ni)]\\+\sum_{\substack{i=1\\\{ij\}}}^{N/2}[C(ij;ji)+C(ii;jj)]\\+\sum_{i=1}^{N}\sum_{i<k}[C(ii;kk)-\tfrac{1}{2}C(ik;ki)].\end{aligned} \qquad (2.8)$$

The term E_2 represents the increase in Coulomb interaction between the two orbitals of a bonded pair when one of the electrons is moved from its own atom to its partner's atom. We have

$$E_2=\frac{A^2}{2(1+A^2)}\sum_{\substack{i=1\\\{ij\}}}^{N}[C(ii;ii)-C(ii;jj)]. \qquad (2.9)$$

E_3 is the energy associated with the new charge density $\sum_{i=1}^{N/2}u_iv_j$, which results from the mixing of ionic terms in the Heitler-London covalent wave function. The net charge of the charge density is zero because we

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[18] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 248.

have required $(u_i|v_j)$ to be zero. We find

$$E_3=\frac{4A}{1+A^2}\sum_{\substack{i=1\\\{ij\}}}^{N/2}(u_i|O_1|v_j)+\frac{4A}{1+A^2}\sum_{\substack{i=1\\\{ij\}}}^{N/2}\sum_{n=1}^{N'-N}[C(ij;nn)-\tfrac{1}{2}C(in;nj)]+\frac{2A}{1+A^2}\sum_{\substack{i=1\\\{ij\}}}^{N}C(ij;ii)$$
$$+\frac{4A}{1+A^2}\sum_{\substack{i=1\\\{ij\}}}^{N/2}\sum_{\substack{k=1\\k\neq l,j}}^{N}[C(ij;kk)-\tfrac{1}{2}C(ik;kj)]+\left(\frac{4A}{1+A^2}\right)^2\sum_{i=1}^{N/2}\sum_{i<k}[C(ij;kl)-\tfrac{1}{4}C(ik;lj)-\tfrac{1}{4}C(il;kj)]$$
$$-\frac{2A}{1+A^2}\sum_{\substack{i=1\\\{ij\}}}^{N/2}[C(ii;ji)+C(jj;ij)]. \quad (2.10)$$

The first term in (2.10) gives the kinetic energy and Coulomb interaction with nucleus of the charge density u_iv_j. The second term designates the Coulomb and exchange interactions between u_iv_j and core electrons. The third term denotes the charge density interacting with charge densities u_i^2 and v_j^2. The fourth term gives the Coulomb and exchange interactions between u_iv_j and valence electrons other than u_i and v_j. The fifth term represents Coulomb and exchange interaction between various charge densities u_iv_j. However, since the net charge in each of these is zero, this interaction will be neglected. The last term and the second part of the second and fourth terms are exchange integrals of similar order which may also be neglected.[16,19]

The remaining terms in E_3 can be rewritten in the form

$$E_3=\frac{4A}{1+A^2}\sum_{\substack{i=1\\\{ij\}}}^{N/2}\{(u_1|O_1|v_j)+[\sum_{n=1}^{N'-N}C(ij;nn)$$
$$+\sum_{k=1}^{N}C(ij;kk)-\tfrac{1}{2}(C(ij;ii)+C(ij;jj))]\}. \quad (2.11)$$

The terms in the square bracket represent the Coulomb interaction of the charge density u_iv_j with the entire real electronic charge density of the crystal diminished by half the charge density of the lobes u_i and v_j. Thus the hole is cut into the electronic charge clouds of the two atoms adjoining u_iv_j to see some of the nuclear charge of the neighboring two atoms which would otherwise be shielded. Since $(u_i|v_j)=0$ and the net real electronic and nuclear charge is zero, we may write

$$E_3\simeq\frac{4A}{1+A^2}\sum_{\substack{i=1\\\{ij\}}}^{N/2}\left[(u_i|-\tfrac{1}{2}\nabla^2|v_j)-\left(u_i\left|\frac{1}{\mathbf{r}}\right|v_j\right)\right]. \quad (2.12)$$

E_4 in the expression for E can be written as

$$E_4=\sum_{L=1}^{N/4}[S_L+\sum_{L'<L}\Gamma_{LL'}], \quad (2.13)$$

where S_L is the self-energy of the core electrons of the atom at the Lth lattice site and $\Gamma_{LL'}$ denotes the interaction between two ion cores at the L and L' lattice points. (The ion core here refers to the core electrons and the nucleus together.) The self-energy term can be written as

$$S_L=\sum\nolimits_n\{(u_n^0|O_1|u_n^0)+\sum\nolimits_{m<n}[C(nn;mm)$$
$$-\tfrac{1}{2}C(nm;mn)]\}, \quad (2.14)$$

where the summation is taken over all the core electrons. We shall assume that the distortion of the core orbitals due to the presence of the neighboring atoms can be neglected.

In the above expressions we have used a condensed notation for convenience. Since the integral $(u_iu_j|O_2|u_ku_l)$ may be thought of as the Coulomb interaction between the charge densities u_iu_k and u_ju_l, it is denoted by $C(ik;jl)$. The indices m and n are used for core orbitals. The indices i and j, when they appear in the same summation, will designate a bond pair and similarly for the indices k and l. If an index j or l appears in the summand of a summation over i or k this means that j or l is not a fixed index but is always a bonded partner of the index i or k which is being summed. The symbol $\{ij\}$ under a summation means that the orbitals i and j are bonded and the summation is extended only over all sets of bonded pair orbitals. If i, j, and k appear in the same summand, we mean that i and j are bonded partners and k is neither a partner of i nor of j. The upper limit $N'-N$ for summation means that the summations are taken over all the ion-core orbitals in the crystal and the summations whose upper limit is $\frac{1}{2}N$ are to be extended over all bonded pairs of valence orbitals.

It will be convenient for later work to derive the expression for the energy per atom or cohesive energy. In doing so, the exchange integrals between lobe u_i and a lobe belonging to a neighboring atom other than one forming a bonded pair with u_i will be neglected.[19,20] Thus only the following four kinds of integrals are taken into account: $C(ij;ji)$, in which

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[19] S. Asano and Y. Tomishima J. Phys. Soc. Japan **11**, 644 (1956).

[20] L. A. Schmid, Ph.D. thesis, Princeton University, 1953 (unpublished).

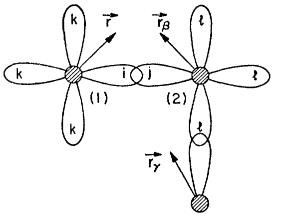

FIG. 1. Sketch of a bonded pair of atoms showing the relative position of the lobes.

the valence orbitals i and j make a bonded pair; $C(ik;ki)$, in which the valence orbitals i and k belong to the same atom; $C(in;ni)$, in which the valence orbital i and core orbital n belong to the same atom; and $C(im;mi)$, in which the core orbital m belongs to one of the atoms toward which the valence orbital i of the adjacent atom is directed. All of the Coulomb interactions are taken up to second nearest neighbors. The energy per atom E_a or the energy per bond ϵ can then be expressed in the form $E_a=4\epsilon_0+2\epsilon_i+S$ and $\epsilon=2\epsilon_0+\epsilon_i$, where

$$\epsilon_0=(u_i|-\tfrac{1}{2}\nabla^2|u_i)-Z\left(u_i\left|\frac{1}{\mathbf{r}}\right|u_i\right)+I[u_i^2,\sum_{n=1}^{28}(u_n^0(\mathbf{r}))^2]$$
$$+\tfrac{3}{2}C(ii;kk)-\tfrac{1}{2}\times\tfrac{3}{2}C(ik;ki)-\tfrac{1}{2}J_{i\alpha}, \quad (2.15)$$

and

$$\epsilon_1=2\left\{-Z\sum_{\beta=1}^{4}\left(u_i\left|\frac{1}{\mathbf{r}_\beta}\right|u_i\right)+\sum_{\beta=1}^{4}I[u_i^2,\sum_{m=1}^{28}(v_m^0(\mathbf{r}_\beta))^2]\right.$$
$$\left.+\tfrac{1}{2}\sum_{\beta=1}^{4}I[u_i^2,\sum_{j=1}^{4}(v_j(\mathbf{r}_\beta))^2]-\tfrac{1}{2}J_{i\beta}+\tfrac{1}{2}C(ij;ji)+\tfrac{1}{2}\Gamma_\beta\right\}$$
$$+2\left\{-Z\sum_{\gamma=1}^{12}\left(u_i\left|\frac{1}{\mathbf{r}_\gamma}\right|u_i\right)+\sum_{\gamma=1}^{12}I[u_i^2,\sum_{n=1}^{28}(u_n^0(\mathbf{r}_\gamma))^2]\right.$$
$$\left.+\tfrac{1}{2}\sum_{\gamma=1}^{21}I[u_i^2,\sum_{i=1}^{4}(u_i(\mathbf{r}_\gamma))^2]+\tfrac{3}{2}\Gamma_\gamma\right\}$$
$$+\left\{\frac{4\bar{A}}{1+\bar{A}^2}(u_i|-\tfrac{1}{2}\nabla^2|v_j)-\left(u_i\left|\frac{1}{\mathbf{r}}\right|v_j\right)\right.$$
$$\left.+\frac{\bar{A}^2}{1+\bar{A}^2}[C(ii;ii)-C(ii;jj)]\right\}. \quad (2.16)$$

Here $\bar{A}$ is the value of A which minimizes E_a. Referring to Fig. 1, $\mathbf{r}$, $\mathbf{r}_\beta$, and $\mathbf{r}_\gamma$ are vectors pointing toward the running point of the integration from atom 1, one of the four nearest neighbors of atom 1, and one of the 12 next-nearest neighbors of atom 1, respectively. The summations

$$\sum_{n=1}^{28}u_n^0(\mathbf{r}) \quad\text{and}\quad \sum_{m=1}^{28}v_m^0(\mathbf{r}_\beta)$$

are to be carried out over all orbitals of the 28 core electrons in atoms 1 and 2. The arguments of these expressions automatically indicate to which atom the core electrons belong. The notation

$$I[u_i^2,\sum_{m}^{28}(v_m^0(\mathbf{r}_\beta))^2]$$

stands for the Coulomb integral of the type

$$\int(u_i(\mathbf{r}))^2\{[\sum_{m}^{28}(v_m^0(\mathbf{r}_\beta))^2]/|\mathbf{r}-\mathbf{r}_\beta|\}d\mathbf{r}d\mathbf{r}_\beta.$$

The indices i and j or lobes u_i and v_j correspond to the bond pair ij. The indices k and l designate one of the other lobes belonging to atom 1 or 2, respectively. The summation with respect to β is to be taken over the four nearest neighbors surrounding atom 1. The summation over γ is to be taken over the 12 next-nearest neighbors surrounding atom 1. $J_{i\alpha}$ is the exchange integral between u_i and the core orbitals belonging to the same atom, whereas $J_{i\beta}$ is the exchange integral between u_i and the core orbitals belonging to the neighboring atom to which u_i points. Γ_β is the Coulomb interaction between the ion-core of atom 1 and that of one of its four nearest neighbors. Γ_γ is the Coulomb interaction between the ion core of atom 1 and that of one of its second nearest-neighboring atoms. S is the self-energy of the ion core.

The four lobelike u's for atom 1 of Fig. 1 may be written in the form

$$\begin{aligned}u_1&=\tfrac{1}{2}[g^s+g_x^p-g_y^p-g_z^p],\\u_2&=\tfrac{1}{2}[g^s+g_x^p+g_y^p+g_z^p],\\u_3&=\tfrac{1}{2}[g^s-g_x^p-g_y^p+g_z^p],\\u_4&=\tfrac{1}{2}[g^s-g_x^p+g_y^p-g_z^p],\end{aligned} \quad (2.17)$$

where g^s, g_x^p, g_y^p, and g_z^p are the 4s orbital and the three 4p orbitals on the Ge atom in the crystal. The v orbitals which point in the opposite directions from the u_i's would be defined in a similar way except that the sign in front of g_x^p, g_y^p, and g_z^p would be changed.

In deriving Eqs. (2.8)–(2.11) it was assumed that the overlap integrals between u_i and all the other orbitals in the crystal are equal to zero, i.e., u_i and the other orbitals in the crystal are orthogonal. Since the overlap between valence orbitals on atoms which are nearest neighbors is much greater than the overlap between any other two orbitals in the crystal (valence-core and core-core on atoms which are nearest neighbors, and valence-valence, valence-core, and core-core on atoms other than first-nearest neighbors), the orthogonal correction will be made only on the valence orbitals and only those on the nearest-neighboring atoms will be taken into account. Thus we must have

$$(u_i|{}^kv_j)=0,\quad\text{with}\quad \begin{aligned}i&=1,2,3,4,\\j&=1,2,3,4,\\k&=1,2,3,4.\end{aligned} \quad (2.18)$$

The superscript k on v_j denotes one of the four nearest neighbors of u_i. Condition (2.18) implies that

$$\begin{aligned}&(g^s|{}^ig^s)=0, \quad (g^s|{}^ig_j^p)=0,\\ &(g_j^p|{}^ig^s)=0, \quad (g_j^p|{}^ig_j^p)=0,\\ &\text{for } i=1,2,3,4 \text{ and } j=x,y,z.\end{aligned} \tag{2.19}$$

Equation (2.19) may be constructed from a set of nonorthogonal orbitals, f's ($4s$ and $4p$ orbitals of a free Ge atom in the ${}^5S$ state), by applying the orthogonality correction formula given by Landshoff.[21] Thus we have

$$\begin{aligned}g^s=f^s\Big[1+\tfrac{3}{8}\sum_{i=1}^{4}(f^s|{}^if^s)^2+\tfrac{3}{8}\sum_{i=1}^{4}\sum_{j=x,y,z}(f^s|{}^if_j^p)^2\Big]\\ -\tfrac{1}{2}\sum_{i=1}^{4}(f^s|{}^if^s)\,{}^if^s-\tfrac{1}{2}\sum_{i=1}^{4}\sum_{j=x,y,z}\\ \times(f^s|{}^if_j^p)\,{}^if_j^p,\end{aligned} \tag{2.20}$$

$$\begin{aligned}g_x^p=f_x^p\Big[1+\tfrac{3}{8}\sum_{i=1}^{4}(f_x^p|{}^if^s)^2+\tfrac{3}{8}\sum_{i=1}^{4}(f_x^p|{}^if_x^p)^2\\ +\tfrac{3}{8}\sum_{i=1}^{4}\sum_{j=y,z}(f_x^p|{}^if_j^p)^2\Big]-\tfrac{1}{2}\sum_{i=1}^{4}(f_x^p|{}^if^s)\,{}^if^s\\ -\tfrac{1}{2}\sum_{i=1}^{4}(f_x^p|{}^if_x^p)\,{}^if_x^p-\tfrac{1}{2}\sum_{i=1}^{4}\sum_{j=y,z}\\ \times(f_x^p|{}^if_j^p)\,{}^if_j^p,\end{aligned} \tag{2.21}$$

and similar expressions for g_y^p and g_z^p. We see that when the lattice parameter d increases to infinity, all the overlaps integrals in (2.20) and (2.21) are equal to zero and we have

$$\begin{aligned}&g^s\longrightarrow f^s,\\ &g_j^p\longrightarrow f_j^p(j=x,y,z) \quad \text{when} \quad d\longrightarrow\infty,\\ &u_i\longrightarrow u_{if},\end{aligned} \tag{2.22}$$

where

$$\begin{aligned}u_{1f}&=\tfrac{1}{2}[f^s+f_x^p-f_y^p-f_z^p],\\ u_{2f}&=\tfrac{1}{2}[f^s+f_x^p+f_y^p+f_z^p],\\ u_{3f}&=\tfrac{1}{2}[f^s-f_x^p-f_y^p+f_z^p],\\ u_{4f}&=\tfrac{1}{2}[f^s-f_x^p+f_y^p-f_z^p],\end{aligned} \tag{2.23}$$

in which f^s is the $4s$ atomic orbital and the f^p's are $4p$ atomic orbitals of the Hartree functions for Ge.[22] We note that when $d\longrightarrow\infty$, the interactions among the atoms are zero. Therefore, $\epsilon_1=0$ and $\epsilon_0=\epsilon_0{}^0$, where

$$\begin{aligned}\epsilon_0{}^0=(u_{if}|-\tfrac{1}{2}\nabla^2|u_{if})-Z(u_{if}|\mathbf{r}^{-1}|u_{if})+I\Big[u_{if}{}^2,\sum_{n=1}^{28}\\ (u_n{}^0(\mathbf{r}))^2\Big]+\tfrac{3}{2}C_f(ii;kk)-\tfrac{1}{2}\times\tfrac{3}{2}C_f(ik;ki)-\tfrac{1}{2}J_{i\alpha f}.\end{aligned} \tag{2.24}$$

In (2.24), the subscript f denotes the energies obtained by using free atomic orbitals. Since $\epsilon_0{}^0$ is only a function of orbitals involving the same atom (all the interaction with other atoms are zero), it is of interatomic origin. If the interaction energy of a bond may be described by a Morse potential, it is clear the $\epsilon_0{}^0$ should be used as the reference state for the dissociation energy of a bond. $\epsilon_0{}^0$ is called the valence-state energy of a valence electron.

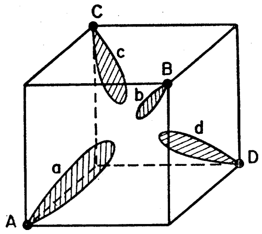

FIG. 2. Configuration around an isolated vacancy.

3. ENERGY EXPRESSION FOR THE DEFECT CRYSTAL

When an atom, which we shall call the central atom, is removed from its lattice position to the surface to create a vacancy, the four bonds to its neighbors are broken. By analogy with the bonds in conventional molecules we should not expect the adjacent bonds to be greatly affected. There will be some deformation of the lattice around the defect, but this is probably small, and we shall neglect it, using the undistorted lattice parameters to specify our model. The vacancy which is left behind will look as shown in Fig. 2. We denote the four atoms surrounding the vacancy by a, b, c, and d, respectively. Each of these four atoms will have three of its valence electrons still engaged in the formation of a localized bond to second nearest neighbors of the vacancy, leaving one electron dangling in the vacancy. Coulson and Kearsely[13] called these "vacancy electrons" and introduced the concept of a defect molecule to describe the vacancy. It has been shown from molecular orbital treatment that the ground state of these defect molecules for diamond is the ${}^1E$ state, that is, there are four vacancy electrons with the sum of their spins equal to zero. They also showed that the simple valence-bond method gives a good representation of the bonding in the defect molecule as far as the ground state is concerned. Since Ge has the same crystal structure as diamond (both lattices have the symmetry of group T_d) we would expect that the above statements are also true for Ge. We start out by recognizing that the most stable situations are those in which each atom a, b, c, and d has one and only one vacancy electron. We then notice that the lowest energy will be obtained if we pair electrons with opposite spins as in the conventional molecular calculation.

If the vacancy electrons are described by sp^3-type functions, then the wave functions of the other three electrons on each of the a, b, c, and d sites will also be sp^3-type functions and will give maximum overlap with those on the second nearest neighbors of the vacancy.

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[21] R. Landshoff, Z. Physik **102**, 201 (1936).

[22] W. Hartree, D. R. Hartree, and M. F. Manning, Phys. Rev. 59, 306 (1941).

According to the principle of maximum overlap,[23] we would then get a lower energy for the total system. Let u_i' be one of these sp^3 functions. We then have

$$\begin{aligned} u_1' &= \tfrac{1}{2}[g'^s + g_x'^p - g_y'^p - g_z'^p], \\ u_2' &= \tfrac{1}{2}[g'^s + g_x'^p + g_y'^p + g_z'^p], \\ u_3' &= \tfrac{1}{2}[g'^s - g_x'^p - g_y'^p + g_z'^p], \end{aligned} \tag{3.1}$$

and

$$u_4' = \tfrac{1}{2}[g'^s - g_x'^s + g_y'^p - g_z'^p].$$

Since each one of the a, b, c, and d atoms now has only three nearest neighbors, we must make the valence orbitals of each of these atoms orthogonal to the valence orbitals of its three neighbors. Thus from Landshoff's[21] formula we have

$$\begin{aligned} g'^s = f^s\Big[1 &+ \tfrac{3}{8}\sum_{i=1}^{3}(f^s|{}^if^s)^2 + \tfrac{3}{8}\sum_{i=1}^{3}\sum_{j=x,y,z}(f^s|{}^if_j^p)^2\Big] \\ &- \tfrac{1}{2}\sum_{i=1}^{3}(f^s|{}^if^s)\,{}^if^s - \tfrac{1}{2}\sum_{i=1}^{3}\sum_{j=x,y,z}(f^s|{}^if_j^p) \end{aligned} \tag{3.2}$$

and

$$\begin{aligned} g_x'^p = f_x^p\Big[1 &+ \tfrac{3}{8}\sum_{i=1}^{3}(f_x^p|{}^if^s)^2 + \tfrac{3}{8}\sum_{i=1}^{3}(f_x^p|{}^if_x^p)^2 \\ &+ \tfrac{3}{8}\sum_{i=1}^{3}\sum_{j=y,z}(f_x^p|{}^if_j^p)^2\Big] - \tfrac{1}{2}\sum_{i=1}^{3}(f_x^p|{}^if^s)\,{}^if^s \\ &- \tfrac{1}{2}\sum_{i=1}^{3}(f_x^p|{}^if_x^p)\,{}^if_x^p - \tfrac{1}{2}\sum_{i=1}^{3}\sum_{j=y,z}(f_x^p|{}^if_j^p)\,{}^if_j^p, \end{aligned} \tag{3.3}$$

and similar expressions for $g_y'^p$ and $g_z'^p$. The orbitals u_i' are thus different from the u_i's in Sec. 2. We consider the four vacancy electrons u_a', u_b', u_c', and u_d' (where the subscripts denote to which atom the vacancy electron belongs) as delocalized. They may be distinguished from the electrons in the rest of the crystal because the vacancy electrons may be paired in two independent ways while there is only one way of pairing for the others. The delocalized electron-bond wave functions are constructed from Heitler-London covalent wave functions. Since we have neglected the overlap between the valence orbitals on one atom and those on its second nearest neighbors, the parameter A may be set equal to zero in the expression (2.1). From (3.1)-(3.3), the valence orbitals (u_i''s) on a, b, c, and d are different from those u_i's on atoms in the rest of the crystal, and the 12 localized bond functions describing the bonds from a, b, c, and d to their immediate neighbors (the second nearest neighbors of the vacancy) will be characterized by the other parameter A'. The bond wave functions for the bonds in the rest of the crystal will be the same as (2.1). Since the terms involving A in (2.14) are a function of bond partners u_i and v_j only, we may consider that A and A' are independent. The energy of the defect crystal is determined by minimizing with respect to A and then A', respectively.

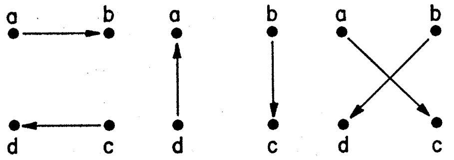

FIG. 3. Possible ways of pairing vacancy electrons.

The possible pairing schemes of the vacancy electrons are shown in Fig. 3. We denote the four atoms surrounding the vacancy by a, b, c, and d. The pairings of electrons are designated by arrows. We have three possible configurations A, B, and C. The wave functions of the crystal for these three configurations will be denoted by Ψ_A, Ψ_B, and Ψ_C, respectively. We have for core orbitals

$$\begin{aligned} \Psi_A = 2^{-N'/2}\sum_P(-1)^P P\eta_{ab}(1,2)\eta_{cd}(3,4) &\times\varphi'_{5,6}(5,6)\cdots\varphi'_{27,28}(27,28)\varphi_{29,30}(29,30)\cdots \\ &\times\varphi_{N'-1,N'}(N'-1,N'), \end{aligned} \tag{3.4}$$

$$\begin{aligned} \Psi_B = 2^{-N'/2}\sum_P(-1)^P P\eta_{ad}(1,2)\eta_{bc}(3,4) &\times\varphi'_{5,6}(5,6)\cdots\varphi'_{27,28}(27,28)\varphi_{29,30}(29,30)\cdots \\ &\times\varphi_{N'-1,N'}(N'-1,N'), \end{aligned} \tag{3.5}$$

and

$$\begin{aligned} \Psi_C = 2^{-N'/2}\sum_P(-1)^P P\eta_{ac}(1,2)\eta_{bd}(3,4) &\times\varphi'_{5,6}(5,6)\cdots\varphi'_{27,28}(27,28)\varphi_{29,30}(29,30)\cdots \\ &\times\varphi_{N'-1,N'}(N'-1,N'), \end{aligned} \tag{3.6}$$

where

$$\begin{aligned} \eta_{xy}(k,l) = \tfrac{1}{2}\sqrt{2}[u_x'(k)u_y'(l)+u_y'(k)u_x'(l)] \\ \times[\alpha(k)\beta(l)-\beta(k)\alpha(l)]/\sqrt{2}, \end{aligned} \tag{3.7}$$

$$\begin{aligned} \varphi_{ij}'(k,l) = [2(1+A'^2)]^{-1/2}\{[u_i'(k)v_j(l)+v_j(k)u_i'(l)] \\ +A'[u_i'(k)u_i'(l)+v_j(k)v_j(l)]\} \\ \times[\alpha(k)\beta(l)-\beta(k)\alpha(l)]/\sqrt{2}, \end{aligned} \tag{3.8}$$

$$\begin{aligned} \varphi_{ij}(k,l) = [2(1+A^2)]^{-1/2}\{u_i(k)v_j(l)+v_j(k)u_i(l)] \\ +A[u_i(k)u_i(l)+v_j(k)v_j(l)]\} \\ \times[\alpha(k)\beta(l)-\beta(k)\alpha(l)]/\sqrt{2}, \end{aligned} \tag{3.9}$$

and

$$\varphi_i(k,l) = u_i^0(k)u_j^0(l)[\alpha(k)\beta(l)-\beta(k)\alpha(l)]/\sqrt{2}. \tag{3.10}$$

Again the permutation operator P must act on the electron coordinates only. The orbitals u_i and v_j have the same meaning as specified in Sec. 2. The orbitals u_i are valence orbital on a (or b, c, d) which are obtained by orthogonalizing the free-atom valence orbitals to those on its three neighbors. x, y, may be any pair indicated by the arrows in Fig. 2, namely, (a,b), (c,d), (a,d), (b,c), (a,c), and (b,d). The subscript x on u' means

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[23] C. A. Coulson, *Valence* (Oxford at the Clarendon Press, Oxford, England, 1952).

the vacancy-electron wave function on atom x, and x denotes one of the four atoms (a, b, c, or d). The bond functions in (3.7)–(3.10) consist of an orthonormal system

$$\begin{aligned}
&(\eta_{xy}(k,l)\,|\,\eta_{xy}(k,l))_{k,l}=1 \quad (\eta_{xy}(k,l)\,|\,\eta_{x'y'}(k,m))_k=0 \\
&\qquad \text{for } \{xy\}=\{x'y'\}\,, \quad l\neq k \text{ and } m\neq k \\
&(\varphi_{ij}'(k,l)\,|\,\varphi_{ij}(k,l))_{k,l}=1 \quad (\varphi_{ij}'(k,l)\,|\,\varphi_{i'j'}'(k,m))_k=0 \\
&\qquad \text{for } \{ij\}\neq\{i'j'\}\,, \quad l\neq k \text{ and } m\neq k \\
&(\varphi_{ij}(k,l)\,|\,\varphi_{ij}(k,l))_{k,l}=1 \quad (\varphi_{ij}(k,l)\,|\,\varphi_{i'j'}(k,m))_k=0 \\
&\qquad \text{for } \{ij\}\neq\{i'j'\}\,, \quad l\neq k \text{ and } m\neq k \qquad (3.11) \\
&(\eta_{xy}(k,l)\,|\,\varphi_{ij}'(k,m))_k=0 \quad (\eta_{xy}(k,l)\,|\,\varphi_{ij}(k,m))_k=0 \\
&\qquad \text{for } \{ij\}\neq\{xy\}\,, \quad l\neq k \text{ and } m\neq k
\end{aligned}$$

and

$$(\varphi_{ij}'(k,l)\,|\,\varphi_{i'j'}(k,m))_k=0 \quad \text{for } \{ij\}\neq\{i'j'\}\,, \quad l\neq k \text{ and } m\neq k.$$

We note that all of the functions $\eta_{xy}(k,l)$, $\varphi_{ij}'(k,l)$ are antisymmetric with respect to the interchange of electron coordinates. Using (3.11) we see that the norms of Ψ_A, Ψ_B, and Ψ_C as defined by (3.7)–(3.9) are all equal to $2^{-N'/2}N'!$.

It can be shown[24] that

$$\Psi_A+\Psi_C=\Psi_B. \tag{3.12}$$

Thus the configurations A, B, and C are mutually dependent. If we choose two configurations A and B as independent ones, the total wave function for the crystal with a point defect can be written as

$$\Psi'=C_1\Psi_A+C_2\Psi_B\,, \tag{3.13}$$

where Ψ_A and Ψ_B are given in (3.4) and (3.5).

Let the Hamiltonian for the crystal with a Schottky defect be H'. Then the energy of the defect crystal E' can be expressed as

$$E'=(\Psi'|H'|\Psi')/(\Psi'|\Psi'). \tag{3.14}$$

There are two eigenvalues E_1' and E_2' for the energy and these are given by

$$E_1'=\frac{H_{AA}+H_{AB}}{1+S_{AB}} \quad \text{and} \quad E_2'=\frac{H_{AA}-H_{AB}}{1-S_{AB}}\,, \tag{3.15}$$

where

$$H_{AA}=(\Psi_A|H'|\Psi_A)\,,$$
$$H_{AB}=(\Psi_A|H'|\Psi_B)\,,$$

and

$$S_{AB}=(\Psi_A|\Psi_B).$$

The energy to form a Schottky defect will then be the smaller of the two energies $E_1'-E$ or $E_2'-E$, where E is the energy of the perfect crystal. We note from the above derivation that the possible different pairing schemes will lead to different energies of formation of the vacancy but will not affect the configuration entropy.

Let

$$H_v=\sum_{k=1}^{4}\nabla_k^2+\sum_{k=1}^{4}\sum_{l<k}O_2(k,l)\,,$$

$$\begin{aligned}
H_l=\sum_{k=1}^{N-4}O_1(k)+\sum_{k=1}^{N-4}\sum_{l<k}O_2(k,l)+\sum_{k=1}^{N-4}\sum_{n=1}^{N'-N}O_2(k,n) \\
+\sum_{n=1}^{N'-N}\sum_{m<n}O_2(m,n)+\sum_{n=1}^{N'-N}O_1(n) \\
+\sum_{L=1}^{N/4}\sum_{L'<L}{}'\frac{Z_LZ_{L'}}{|\mathbf{R}_L-\mathbf{R}_{L'}|}\,,
\end{aligned}$$

and

$$\begin{aligned}
H_i=\tfrac{1}{2}\sum_{k=1}^{4}\sum_{l=1}^{N-4}O_2(k,l)-\sum_{k=1}^{4}\sum_{L=1}^{N/4}\frac{Z_L}{|\mathbf{r}_k-\mathbf{R}_L|} \\
+\sum_{k=1}^{4}\sum_{n=1}^{N'-N}O_2(k,n)\,,
\end{aligned} \tag{3.16}$$

where $\sum_L'$ is to be carried out over the lattice points in the crystal when one atom has been removed from its place to the surface. We see that H_v is the Hamiltonian for the four vacancy electrons if they do not interact with the lattice, H_l is the Hamiltonian for the crystal excluding the four vacancy electrons, and H_i is the interaction of the four vacancy electrons with the rest of the crystal. The total Hamiltonian H' for the defect crystal may be expressed as

$$H'=H_v+H_l+H_i. \tag{3.17}$$

From (3.16) and (3.17), it can be shown that[24]

$$E_1'=E_2'=H_{AA}\,, \tag{3.18}$$

so that the ground state is degenerate. According to the Jahn-Teller theorem, it will therefore not be stable and there will be geometrical distortions until a stable state is obtained. Thus, the vacancy model will no longer have the symmetry of Td. We would expect the Jahn-Teller distortion to remove the degeneracy in energy between states A and B. This means that the fundamental cube in Fig. 1 will cease to be a cube, but will become a rectangular parallelepiped. One such distortion, corresponding to the predominance of A over B or C in Fig. 3, would reduce the lengths of AB and CD while increasing those of AD and BC. A self-consistent treatment would be required in order to know exactly how large the distortion is, but in view of the rather strong valence bonds in the rest of the crystal, it would probably be small. Hence we shall take $E'=E_1'=E_2'=H_{AA}$. The energy expression E' for the defect crystal can then be written in the following form:

$$E'=\bar{E}_v+E_l+E_i. \tag{3.19}$$

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[24] C. J. Hwang, Ph.D. thesis, University of Washington, 1966 (unpublished).

The first term is given by

$$\bar{E}_v=\sum_{x=a}^{d}(u_x'|-\tfrac{1}{2}\nabla^2|u_x')+C(aa;bb)+C(cc;dd)+C(aa;cc)+C(aa;dd)+C(bb;cc)+C(bb;dd). \tag{3.20}$$

E_l can be written as the sum of seven terms;

$$E_l=E_{l1}+E_{l2}+E_{l3}+E_{l4}+E_{l5}+E_{l6}+E_{l7}, \tag{3.21}$$

where

$$E_{l1}=\sum_{i=1}^{12}(u_i'|O_1|u_i')+\sum_{i=1}^{N-16}(u_i|O_1|u_i)+\sum_{i'=1}^{12}\sum_{n=1}^{N'-N}[C(i'i';nn)-\tfrac{1}{2}C(i'n;ni')]$$
$$+\sum_{i=1}^{N-16}\sum_{n=1}^{N'-N}[C(ii;nn)-\tfrac{1}{2}C(in;ni)], \tag{3.22}$$

$$E_{l2}=\sum_{\substack{i'=1\\\{i'j\}}}^{12}[C(i'j;ji')+C(i'i';jj)]+\sum_{i=1}^{(N-28)/2}[C(ij;ji)+C(ii;jj)]+\sum_{i'=1}^{12}\{\sum_{k'<i'}[C(i'i';k'k')-\tfrac{1}{2}C(i'k';k'i')]$$
$$+\sum_{k=1}^{N-16}[C(i'i';kk)-\tfrac{1}{2}C(i'k;ki')]\}+\sum_{i=1}^{N-16}\sum_{k<1}[C(ii;kk)-\tfrac{1}{2}C(ik;ki)], \tag{3.23}$$

$$E_{l3}=\frac{2A'}{1+A'^2}\sum_{\substack{i'=1\\\{i'j\}}}^{12}[C(i'j;i'i')+C(i'j;jj)]+\frac{2A}{1+A^2}\sum_{\substack{i=1\\\{ij\}}}^{N-28}C(ij;ii)+\frac{A'^2}{2(1+A'^2)}\sum_{\substack{i'=1\\\{i'j\}}}^{12}[C(i'i';i'i')-C(i'i';jj)$$
$$+C(jj;ii)-C(jj;i'i')]+\frac{A^2}{2(1+A^2)}\sum_{\substack{i=1\\\{ij\}}}^{N-28}[C(ii;ii)-C(ii;jj)], \tag{3.24}$$

$$E_{l4}=\frac{4A'}{1+A'^2}\sum_{i'=1}\{\sum_{\substack{k'=1\\k'\neq 1',j}}^{12}[C(i'j;k'k')-\tfrac{1}{2}C(i'k;k'j)]+\sum_{k=1}^{N-16}[C(i'j;kk)-\tfrac{1}{2}C(i'k;ki)]\}$$
$$+\frac{4A}{1+A^2}\sum_{\substack{i=1\\\{ij\}}}^{(N-28)/2}\{\sum_{\substack{k=1\\k\neq i,j}}^{N-16}[C(ij;kk)-\tfrac{1}{2}C(ik;kj)]+\sum_{k'=1}^{12}[C(ij;k'k')-\tfrac{1}{2}C(ik';k'j)]\}, \tag{3.25}$$

$$E_{l5}=\frac{4A'}{1+A'^2}\{\sum_{\substack{i'=1\\\{i'j\}}}^{12}(u_i'|O_1|v_j)+\sum_{n=1}^{N'-N}[C(i'i;nn)-\tfrac{1}{2}C(i'n;nj)]\}+\frac{4A}{1+A^2}$$
$$\times\{\sum_{\substack{i=1\\\{ij\}}}^{(N-28)/2}(u_i|O_1|v_j)+\sum_{n=1}^{N'-N}[C(ij;nn)-\tfrac{1}{2}C(in;nj)]\}, \tag{3.26}$$

$$E_{l6}=\left(\frac{4A'}{1+A'^2}\right)^2\sum_{\substack{i'=1\\\{i'j\}}}^{12}\sum_{k'<i'}[C(i'j;k'l)-\tfrac{1}{4}C(i'k';lj)-\tfrac{1}{4}C(i'l;k'j)]$$
$$+\left(\frac{4A}{1+A^2}\right)^2\sum_{\substack{i=1\\\{ij\}}}^{(N-28)/2}\sum_{k<i}[C(ij;kl)-\tfrac{1}{4}C(ik;lj)-\tfrac{1}{4}C(il;kj)]$$
$$+\left(\frac{4A'}{1+A'^2}\right)\left(\frac{4A}{1+A^2}\right)\sum_{\substack{i'=1\\\{i'j\}}}^{12}\sum_{\substack{k=1\\\{kl\}}}^{(N-28)/2}[C(i'j;kl)-\tfrac{1}{4}C(i'k;lj)-\tfrac{1}{4}C(i'l;kj)], \tag{3.27}$$

and

$$E_{l7}=-\frac{2A'}{1+A'^2}\sum_{\substack{i'=1\\\{i'j\}}}^{12}[C(i'i;ji')+C(jj;ji')]-\frac{2A}{1+A^2}\sum_{\substack{i=1\\\{ij\}}}^{(N-28)/2}[C(ii;ji)+C(jj;ji)]+\sum_{L=1}^{N/4}S_L+\sum_{L}{}'\sum_{L'<L}\Gamma_{LL'}. \tag{3.28}$$

The third term in (3.19) is given by

$$E_i=\sum_{x=a}^{d}\Big\{\sum_{L'}{}'\left(u_x\left|\frac{Z}{\mathbf{r}_x-\mathbf{R}_L}\right|u_x\right)+\sum_{n=1}^{N'-N}[C(xx;nn)-\tfrac{1}{2}C(xn;nx)]+\sum_{k'=1}^{12}[C(xx;k'k')-\tfrac{1}{2}C(xk';k'x)]$$

$$+\sum_{k=1}^{N-16}[C(xx;kk)-\tfrac{1}{2}C(xk;kx)]\Big\}+\frac{4A'}{1+A'^2}\sum_{\substack{i'=1\\ \{i'j\}}}^{12}\sum_{x=a}^{d}[C(i'j;xx)-\tfrac{1}{2}C(i'x;xj)]$$

$$+\frac{4A}{1+A^2}\sum_{\substack{i=1\\ \{ij\}}}^{(N-28)/2}\sum_{x=a}^{d}[C(ij;xx)-\tfrac{1}{2}C(ix;xj)]. \tag{3.29}$$

The notation is the same as described in Sec. 2, except that we denote the valence orbitals orthogonal to the valence orbitals on three nearest neighbors by a prime on the upper right-hand side of the u's and of the index i.

4. FORMATION ENERGY OF A SCHOTTKY DEFECT

If we group terms like those shown in (2.11) and make the same approximations as in Sec. 2, we find that the value of A which minimizes E will be equal to $\bar{A}$ defined in (2.16). Let the formation energy of a Schottky defect be E_v and the value of A' which minimizes E' be $\bar{A}'$. Then

$$E_v=E'-E=2\epsilon_1+E_\gamma+E_S, \tag{4.1}$$

where ϵ_1 is defined in (2.16), and E_γ and E_S are given below. The first term in (3.23) denotes twice the energy per bond with respect to $2\epsilon_0$ or the energy per atom with respect to $4\epsilon_0+S$ as defined in Sec. 2. The second term represents the change in electronic energies resulting from the rearrangement of electrons on the four first-nearest neighbors of the vacancy. In the actual calculation, this term contributes most of the relaxation energy after the vacancy is formed. The third term consists of the change in the interaction energies in the rest of the lattice. We have

$$E_\gamma=4\Big\{\sum_{i=1}^{4}[(u_i'|-\tfrac{1}{2}\nabla^2|u_i')-(u_i|-\tfrac{1}{2}\nabla^2|u_i)]-\sum_{i=1}^{4}Z\left[\left(u_i'\left|\frac{1}{\mathbf{r}}\right|u_i'\right)-\left(u_i\left|\frac{1}{\mathbf{r}}\right|u_i\right)\right]+[I[\sum_{i=1}^{4}(u_i')^2,\sum_{n=1}^{28}(u_n{}^0(\mathbf{r}))^2]$$

$$-I[\sum_{i=1}^{4}(u_i)^2,\sum_{n=1}^{28}(u_n{}^0(\mathbf{r}))^2]]+6[C(i'i';k'k')-C(ii;kk)]-3[C(i'k';k'i')-C(ik;ki)]-2[J_{i\alpha}'-J_{i\alpha}]\Big\}. \tag{4.2}$$

For convenience E_S can be written as the sum of five terms;

$$E_S=E_{S1}+E_{S2}+E_{S3}+E_{S4}+E_{S5}, \tag{4.3}$$

where

$$E_{S1}=4\Big\{\sum_{\beta=1}^{3}[I[\sum_{i=1}^{4}(u_i')^2,\sum_{j=1}^{4}(v_j(\mathbf{r}_\beta))^2]-I[\sum_{i=1}^{4}(u_i)^2,\sum_{j=1}^{4}(v_j(\mathbf{r}_\beta))^2]]+\sum_{\beta=1}^{3}[I[\sum_{i=1}^{4}(u_i')^2,\sum_{m=1}^{28}(v_m{}^0(\mathbf{r}_\beta))^2]$$

$$-I[\sum_{i=1}^{4}(u_i)^2,\sum_{m=1}^{28}(v_m{}^0(\mathbf{r}_\beta))^2]]-Z\sum_{\beta=1}^{3}\sum_{i=1}^{4}\left[\left(u_i'\left|\frac{1}{\mathbf{r}_\beta}\right|u_i'\right)-\left(u_i\left|\frac{1}{\mathbf{r}_\beta}\right|u_i\right)\right]$$

$$-\tfrac{1}{2}\sum_{\beta=1}^{3}\sum_{i=1}^{4}(J_{i\beta}'-J_{i\beta})+3[C(i'j;ji')-C(ij;ji)]\Big\}, \tag{4.4}$$

$$E_{S2}=4\Big\{\sum_{\gamma=1}^{9}[I[\sum_{i=1}^{4}(u_i')^2,\sum_{i=1}^{4}(u_i(\mathbf{r}_\gamma))^2]-I[\sum_{i=1}^{4}(u_i)^2,\sum_{i=1}^{4}(u_i(\mathbf{r}_\gamma))^2]]+\sum_{\gamma=1}^{3}[I[\sum_{i=1}^{4}(u_i')^2,\sum_{i=1}^{4}(u_i'(\mathbf{r}_\gamma))^2]$$

$$-I[\sum_{i=1}^{4}(u_i)^2,\sum_{i=1}^{4}(u_i(\mathbf{r}_\gamma))^2]]-Z\sum_{\gamma=1}^{12}\sum_{i=1}^{4}\left[\left(u_i'\left|\frac{1}{\mathbf{r}_\gamma}\right|u_i'\right)-\left(u_i\left|\frac{1}{\mathbf{r}_\gamma}\right|u_i\right)\right]\Big\}, \tag{4.5}$$

$$E_{S3}=4\sum_{\gamma=1}^{12}[I[\sum_{i=1}^{4}(u_i')^2,\sum_{n=1}^{28}(u_n{}^0(\mathbf{r}_\gamma))^2]-I[\sum_{i=1}^{4}(u_i)^2,\sum_{n=1}^{28}(u_n{}^0(\mathbf{r}_\gamma))^2]], \tag{4.6}$$

$$E_{S4}=12\left\{\frac{4\bar{A}'}{1+\bar{A}'^2}\left[(u_i'|-\tfrac{1}{2}\nabla^2|v_j)-\frac{1}{2}\left(u_i'\left|\frac{1}{\mathbf{r}}\right|v_j\right)-\frac{1}{2}\left(v_j\left|\frac{1}{\mathbf{r}_\beta}\right|u_i'\right)\right]\right.$$
$$\left.-\frac{4\bar{A}}{1+\bar{A}^2}\left[(u_i|-\tfrac{1}{2}\nabla^2|v_j)-\frac{1}{2}\left(u_i\left|\frac{1}{\mathbf{r}}\right|v_j\right)-\frac{1}{2}\left(v_j\left|\frac{1}{\mathbf{r}_\beta}\right|u_i\right)\right]\right\}, \quad (4.7)$$

and

$$E_{S5}=12\left\{\frac{\bar{A}'^2}{2(1+\bar{A}'^2)}[C(i'i';i'i')+C(jj;jj)-C(i'i';jj)-C(jj;i'i')]\right.$$
$$\left.-\frac{A^2}{2(1+A^2)}[C(ii;ii)+C(jj;jj)-C(ii;jj)-C(jj;ii)]\right\}. \quad (4.8)$$

In Eqs. (4.2)–(4.8), $u_i'=u_\alpha'$ and $J_{i\alpha}'$ and $J_{i\beta}'$ represent the exchange interactions between u_i' and the core orbitals belonging to the same atom and those belonging to the bonded partner atom, respectively.

Since we have assumed in the beginning of this section that the lattice is not distorted due to the formation of the vacancy (which implies that the bond energies in the rest of the crystal are unchanged), E_S may be neglected. This is roughly proved from the actual construction of the function u_i' and u_i.[24] If we regard the u_i's defined in (2.17) as a state specifying a valence electron in the crystal, then ϵ_0 may be thought of as the energy of a valence electron in the crystal since it is a function involving only u_i's of the same atom. Thus a physical interpretation may be assigned to the terms in (4.1). The first term arises from the fact that if there is no relaxation in the energy of electrons on atoms surrounding the vacancy, the energy to form a Schottky defect will be just equal to twice the bond energy with respect to a state characterizing a valence electron in the crystal. This is analogous to the statement that in order to remove an atom from inside the crystal to infinity, four bonds must be broken, but the energy corresponding to two bonds is gained when this atom is taken from infinity back to the surface. The second term E_γ is present because, after the vacancy is formed, the electrons surrounding the vacancy must redistribute themselves in accordance with the requirement that the wave functions of these electrons be orthogonal to those on their neighboring atoms. This may be considered as analogous to the usual statement concerning the rearrangement of the electronic charge surrounding the vacancy. The third term E_S can be interpreted as the change of the interaction energies in the rest of the crystal. This will cause the lattice to achieve a certain symmetry around the vacancy so that E_v is a minimum. It would be extremely difficult to obtain the precise value of E_v by taking this relaxation of the lattice into consideration. If the distances AB, CD, AD, and BC in Fig. 2 were changed, the wave functions (u_i's) would necessarily be changed and the variational parameter A' would be different for each set of separations of AB, CD, AD, and BC. The final equilibrium set of AB, CD, AD, and BC would be so determined that the corresponding A' made E_v a minimum. The expressions for E_γ and E_S would thus be related to each other. The calculation would then be prohibitively complicated in that a self-consistent method would have to be used.

If we neglect E_S and use $\epsilon_0{}^0$ as the reference level, the formation energy of a vacancy can be written in the form

$$E_v=E_{v1}+E_{v2}+E_{v3}+E_{v4}+E_{v5}+E_{v6}. \quad (4.9)$$

The first term E_{v1} is the absolute value of the cohesive energy per atom with respect to the free tetrahedral valence state of the Ge atom and can be written

$$E_{v1}=-2\epsilon_1-(4\epsilon_0-4\epsilon_0{}^0). \quad (4.10)$$

The remaining five terms represent the energy gained due to changes in various energies for the electrons on atoms surrounding the vacancy. Using the same notation and conventions as before, these terms are given by

$$E_{v2}=4\left\{\sum_{i=1}^{4}[(u_i'|-\tfrac{1}{2}\nabla^2|u_i')-(u_{if}|-\tfrac{1}{2}\nabla^2|u_{if})]-\tfrac{3}{4}\sum_{i=1}^{4}[(u_i|-\tfrac{1}{2}\nabla^2|u_i)-(u_{if}|-\tfrac{1}{2}\nabla^2|u_{if})]\right\}, \quad (4.11)$$

$$E_{v3}=-4\left\{\sum_{i=1}^{4}Z\left[\left(u_i'\left|\frac{1}{\mathbf{r}}\right|u_i'\right)-\left(u_{if}\left|\frac{1}{\mathbf{r}}\right|u_{if}\right)\right]-\tfrac{3}{4}\sum_{i=1}^{4}Z\left[\left(u_i\left|\frac{1}{\mathbf{r}}\right|u_i'\right)-\left(u_{if}\left|\frac{1}{\mathbf{r}}\right|u_{if}\right)\right]\right\}, \quad (4.12)$$

$$E_{v4}=4\left\{I\left[\sum_{i=1}^{4}(u_i')^2,\sum_{n=1}^{28}(u_n{}^0(\mathbf{r}))^2\right]-I\left[\sum_{i=1}^{4}(u_{if})^2,\sum_{n=1}^{28}(u_n{}^0(\mathbf{r}))^2\right]\right.$$
$$\left.-\tfrac{3}{4}\left[I\left[\sum_{i=1}^{4}(u_i)^2,\sum_{n=1}^{28}(u_n{}^0(\mathbf{r}))^2\right]-I\left[\sum_{i=1}^{4}(u_{if})^2,\sum_{n=1}^{28}(u_n{}^0(\mathbf{r}))^2\right]\right]\right\}, \quad (4.13)$$

$$E_{v5}=24\{[C(i'i';k'k')-C_f(ii;kk)]-\tfrac{3}{4}[C(ii;kk)-C_f(ii;kk)]\}$$
$$-12\{[C(i'k';k'i')-C_f(ik;ki)]-\tfrac{3}{4}[C(ik;ki)-C_f(ik;ki)]\}\,,\quad(4.14)$$

and

$$E_{v6}=-8\{[J_{i\alpha}'-J_{i\alpha f}]-\tfrac{3}{4}[J_{i\alpha}-J_{i\alpha f}]\}\,.\quad(4.15)$$

Values for the cohesive energy of Ge with respect to the ground state (^3P) of the free Ge atom have been reported by Pauling,[25] Seitz,[26] and Goldfinger.[27] They give 0.120, 0.135, and 0.137. a.u., respectively. The energy difference between the ^3P state and the tetrahedral valence state has been reported by Pritchard and Skinner[28] to be 0.25 a.u.

The evaluation of the change of various energies involved in the last five terms in (4.9) may be found in Ref. 24. The total value of these terms in (4.9) is calculated as $-0.300+0.0068$ a.u. The results are summarized in Table I. The uncertainty in E_v arises from possible errors introduced in the graphical calculation of the various energies of $\epsilon_0{}^0$ defined in (2.24). Using an average value for the cohesive energy, we find $E_v=2.21\pm0.18$ eV. From this the formation energy for a singly charged negative vacancy can be calculated. We get

$$\bar{E}_v=1.83\pm0.18\text{ eV}.$$

This agrees quite well with the experimental values which range from 1.7 to 2 eV. Our value for E_v is also in good agreement with Benneman's value of 1.91 eV.

5. CONCLUSIONS

In a perfect crystal of Ge, the valence electrons are in the state u_i defined in (2.17). This state is a mixing of the atomic states g^s, $g_x{}^p$, $g_y{}^p$, and $g_z{}^p$, which are distorted versions of the free atomic states f^s, $f_x{}^p$, $f_y{}^p$, and $f_z{}^p$. The distortion of the orbitals is accomplished by making the f^s and f^p's of one particular central atom orthogonal to the f^s and f^p's of the four first-nearest neighbors which are arranged tetrahedrally around this central atom. The energy per atom E_a is given by $4\epsilon_0+2\epsilon_1+S$, where $4\epsilon_0+S$ is interatomic in origin for atoms in the crystal, and $2\epsilon_1$ designates the interaction between neighboring atoms. When the central atom is removed to the surface of the crystal, an amount of energy equal to $2\epsilon_1$ must be spent. At the same time the electrons on the four neighbors rearrange themselves until the final state u_i''s defined in (3.1), which describe these electrons are achieved. u_i' is a combination of the functions g'^s, $g_x'^p$, $g_y'^p$, and $g_z'^p$, which are obtained by making the corresponding f^s and f^p's orthogonal to the f^s and f^p's on the remaining three neighboring atoms. The process of switching from u_i to u_i' releases some energy which we have called the relaxation energy of the electrons surrounding the vacancy. As is seen from our calculation,[24] the change in the Coulomb interaction of valence electrons with the nucleus and core electrons favors the relaxation while other changes in the various energies oppose it.

TABLE I. Summary of results.

Cohesive energy (a.u.)	$-(2\epsilon_0-4\epsilon_0{}^0)$ (a.u.)	E_v (eV)
0.120	0.370	1.91±0.18
0.135	0.385	2.33±0.18
0.137	0.387	2.38±0.18

The result obtained in this calculation of the formation energy of a Schottky defect in Ge is in good agreement with the experimental value and the value calculated by Benneman using the collective model.

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