PHYSICAL REVIEW B VOLUME 29, NUMBER 12 15 JUNE 1984

Mechanisms of charge-state determination in hydrogen-based impurity complexes in crystalline germanium

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(Received 31 October 1983)

Recent experiments suggest that hydrogen may become bound to, and then tunnel around, substitutional carbon, silicon, or oxygen impurities in crystalline germanium. All these complexes are electrically active; [H,C] and [H,Si] are shallow acceptors, while [H,O] is a shallow donor. This paper attempts to elucidate the basic physical mechanisms controlling the charge state of such complexes as a function of the choice of the substitutional atom. A minimal-basis Bethe-cluster approach is used with the cluster comprising the ten-atom tetrahedral cage (including the substitutional atom) and enclosed H site, the latter coupled to all ten atoms of the cage. The important local correlation effect which tends to favor single occupation of the H site is modeled with a Hubbard-type term at that site. The charge state of the [H,C], [H,Si], and [H,O] complexes is associated with double occupation of the H site. Four aspects of the model are involved in favoring double occupation: (1) a low value of the H-site energy, (2) a reduced local correlation effect at the H site, (3) small hybridization between the H site and cage, and (4) a low value of the substitutional-site energy relative to that of the host. Results for the charge state for H at the cage center and for H near the substitutional atom are discussed in detail. Several useful formal results for local self-energies and local Green's functions are presented.

I. INTRODUCTION

A very interesting class of impurity complexes in ultrapure Ge crystals has recently been characterized. These involve two atoms, one a substitutional atom such as C, Si, or O, and the other a hydrogen atom which is bound to, and tunnels around, the substitutional atom.[1-5] The complexes [H,C] and [H,Si] are shallow acceptors, whereas [H,O] is a shallow donor. The shallow-level spectra of these complexes exhibit two remarkable features: They are associated with *two* series of shallow hydrogenic spectral lines, and these lines do not split under uniaxial stress. A major issue is the nature of the physical mechanisms controling whether these complexes behave as acceptor, donor, or neutral impurities for a given choice of substitutional atom.

It is interesting to observe that atomic H alone in crystalline Ge is believed to be a rapidly diffusing interstitial neutral deep donor with a single relatively tightly bound electron.[6] Furthermore, the isoelectronic atoms C and Si in crystalline Ge are neutral substitutional impurities. Yet two facts are suggested by experiment: H is attracted to substitutional C or Si, and, in addition, the neighborhood of the two atoms is affected in such a way that an extra electron is localized nearby. This, in turn, leads to the shallow binding of a hole. Alternatively, H can become bound to what is believed to be (in conjunction with H) substitutional O with the result that one electron is delocalized from the neighborhood and goes, instead, into a large shallow orbit.

To focus on one issue we ask why the proximity of the two individually neutral impurities, for instance, H and C in the semiconducting host, leads to binding of the extra electron. Somewhat secondary, for now, is the issue of dynamics of the H atom. We concentrate on the cases of H in pure Ge, and the complexes [H, C] and [H, O]. For purposes of an initial study whose goal is the elucidation of the basic physical mechanisms involved rather than quantitativeness, we utilize a minimal-basis Bethe-cluster approach.[7]

We point out that a significant aspect of any H-related state is the role of the local Coulomb repulsion at the H "site." Roughly speaking, this tends to favor only a single electron being present at the H site. Indeed, in the case of normal muonium in Ge, it is the net spin density at the muon which is detected in muon-spin-rotation (μSR) spectroscopy.[8] The large local correlation effect is also evident in a comparison of the total energies of H and H^- in vacuum. The additional electron in H^- is bound by only 0.7 eV, not the 13.6 eV characteristic of noninteracting electrons. This specifies a correlation energy of ~ 1 Ry. Introduction of H into the semiconductor would be expected to somewhat reduce the correlation energy from this value.

The important local correlation effect is included in our model via a Hubbard-type term at the H site. This many-body effect is treated in the Hartree-Fock approximation. The self-consistent occupations for spin-up and -down electrons at the H site are calculated as function of the H-site position, restricted to the region of the so-called "large hole." The goal of this paper is to clarify the charge state near the H atom as a function of H-atom position and also as a function of the choice of substitutional atom.

Section II describes the model, while Sec. III presents a number of formal results for the H-site local self-energy and cluster-site Green's functions appropriate to the one-body part of the problem. These results simplify compu-

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tational aspects associated with varying the position of the H site. The self-consistent solution procedure, now with H present, as well as a new approach for remedying the problem of overly large gap in the Bethe-lattice approach, is discussed in Sec. IV. General principles promoting a given charge character within our model are given in Sec. V. Tight-binding parameters are discussed in Sec. VI. Section VII presents results for charge character for H at the tetrahedral cage center and for H near the substitutional atom. Also considered are results for continuous variation of the H position and the question of total energy as a function of H position.

II. MODEL

The experimental shallow-level spectra for these complexes are consistent with the assumption that the *net* charge within the vicinity of the center is independent of the "position" of the H atom as it tunnels. Therefore it is acceptable to investigate the charge state for some limited number of (fixed) H-site positions likely to be encountered in the H "trajectory." We are presuming here that during tunneling the local electron density adiabatically follows the proton. Note that this seems likely as the H tunneling frequency [$\sim 10^{13}$ sec^{-1} (Ref. 4)] is much smaller than the plasmon frequency ($\sim 10^{16}$ sec^{-1}).

The Ge lattice with a substitutional atom is modeled as a Bethe-cluster with a ten-atom cluster comprising the tetrahedral "big cage," i.e., the cage of atoms bounding the central region of the diamond-structure face-centered cube (see Fig. 1). Connected to each site of the cluster are one or two sites (depending on the cluster site) to which, in turn, a fourfold-coordinated Bethe lattice is connected.[7] The Bethe-lattice modeling of the periodic lattice preserves certain aspects of the local environment (e.g., proper coordination), and includes long-range coherence effects (leading to bands of states), but does not include effects of closed rings of bonds. The substitutional site is chosen at the top of the cage, i.e., at the $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ site relative to the cube enclosing the cage. Four sp^3 hybrid orbitals are taken at each site. The H site with a single 1*s* orbital is located within the big cage. The net charge near the H site is considered as a function of the H-site position within a central region in the interior of the tetrahedral cage.

Within the Ge lattice (including substitutional atom) we allow only nearest-neighbor coupling, but among all possible pairs of orbitals. Intrasite matrix elements among all orbitals are also included. The H site is coupled to the ten atoms of the cage.

The Hamiltonian for each spin σ is given by

$$\hat{H}_{\sigma}=\hat{H}_{0\sigma}+\hat{H}_{1\sigma}+\hat{H}_{2\sigma}\ , \tag{1a}$$

$$\begin{aligned}\hat{H}_{0\sigma}\equiv{}&E_{\mathrm{H}}a^{\dagger}_{\mathrm{H}\sigma}a_{\mathrm{H}\sigma}+\sum_{\alpha,\beta}E_{S\alpha\beta}a^{\dagger}_{S\alpha\sigma}a_{S\beta\sigma}+\sum_{i}\sum_{\alpha,\beta}E_{G\alpha\beta}a^{\dagger}_{i\alpha\sigma}a_{i\beta\sigma}\\&+\sum_{j}\sum_{\alpha,\beta}V_{S\alpha j\beta}a^{\dagger}_{S\alpha\sigma}a_{j\beta\sigma}+\text{H.c.}\\&+\sum_{i,i'}{}'\sum_{\alpha,\beta}V_{i\alpha i'\beta}a^{\dagger}_{i\alpha\sigma}a_{i'\beta\sigma}+\text{H.c.}\ ,\end{aligned} \tag{1b}$$

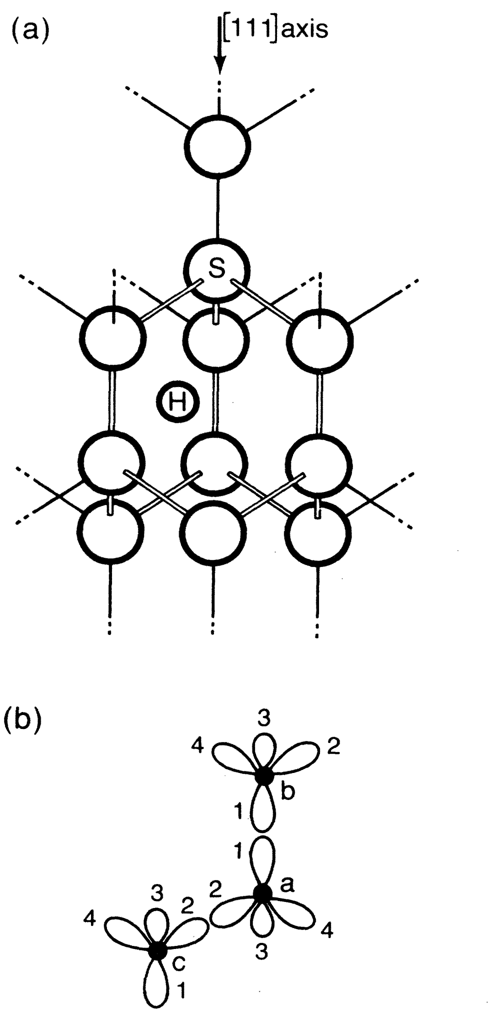

FIG. 1. (a) Projection of tetrahedral cage onto $(\bar{1}\bar{1}1)$ plane. Double lines connect atoms of cage. The substitutional site (S) forms the top of the cage. Solid lines and dashes indicate how fourfold Bethe lattices are connected to cage. The hydrogen site (H) is located within the volume of the cage. (b) Orbital notation for sp^3 hybrids. There are four bonding "directions" in the Bethe lattice, labeled here by 1, 2, 3, and 4. At a given site, orbitals are labeled according to the bond direction to which they are collinear.

$$\begin{aligned}\hat{H}_{1\sigma}\equiv{}&\sum_{\alpha}V_{\mathrm{H}S\alpha}a^{\dagger}_{S\alpha\sigma}a_{\mathrm{H}\sigma}+\text{H.c.}\\&+\sum_{i}\sum_{\alpha}V_{\mathrm{H}i\alpha}a^{\dagger}_{i\alpha\sigma}a_{\mathrm{H}\sigma}+\text{H.c.}\end{aligned} \tag{1c}$$

$$\hat{H}_{2\sigma}\equiv\tfrac{1}{2}Ua^{\dagger}_{\mathrm{H}\sigma}a^{\dagger}_{\mathrm{H}\bar{\sigma}}a_{\mathrm{H}\bar{\sigma}}a_{\mathrm{H}\sigma}\ . \tag{1d}$$

We take all nearest-neighbor orbitals to be orthogonal. The symbol $a^{\dagger}_{\mathrm{H}\sigma}$ ($a_{\mathrm{H}\sigma}$) denotes the creation (destruction) operator for an electron of spin σ at the hydrogen site. Similarly, $a^{\dagger}_{S\alpha\sigma}$ and $a^{\dagger}_{i\alpha\sigma}$ denote the creation operators for spin σ for the αth orbital at, respectively, the substitutional site and the ith Ge site. Sums over α,β run over all four orbitals. The sum over i in the second term of $\hat{H}_{1\sigma}$ is over Ge cage sites, while the sum over i in the third term of $H_{0\sigma}$ runs over all Ge sites. In the fourth term of $H_{0\sigma}$, j runs over the four Ge sites nearest the substitutional; in the fifth term of $H_{0\sigma}$, i,i' run over all distinct Ge nearest-neighbor pairs.

In Eq. (1), E_{H} denotes the hydrogen-site energy. The site-energy matrices for the substitutional and Ge sites are of the form $E_{S\alpha\alpha}=E_{Sd}$ and $E_{S\alpha\beta}=E_{So}$, $\alpha\neq\beta$; and $E_{G\alpha\alpha}=E_{Gd}$ and $E_{G\alpha\beta}=E_{Go}$, $\alpha\neq\beta$.

The H-cage atom couplings $\vec{\mathrm{V}}_{\mathrm{H}S}$ and $\vec{\mathrm{V}}_{\mathrm{H}i}$ are taken to be dependent upon H-site position (in some approximation, discussed below). These quantities are related to the standard Koster-Slater hopping parameters $ss\sigma$ and $sp\sigma$ which involve the 1s hydrogen orbital and, respectively, the valence s and p orbitals of the cage atom.

The form of the nearest-neighbor hopping matrices in the Bethe lattice depends upon the orientation of the bond involved, there being four choices [see Fig. 1(b)].[9] These are connected via appropriate unitary transformations.[9] For bond direction 1 the Ge-Ge hopping matrix $\underline{V}_1$ has the form

$$\underline{V}_1=\begin{bmatrix} v_0 & v_1 & v_1 & v_1 \\ v_1 & v_2 & v_3 & v_3 \\ v_1 & v_3 & v_2 & v_3 \\ v_1 & v_3 & v_3 & v_2 \end{bmatrix} . \tag{2}$$

Note, referring to Eqs. (1b) and (2), that the notational correspondence is, for bond direction 1, $V_{11,11}=v_0$, $V_{12,13}=v_3$, etc.

The corresponding hopping matrix $\underline{V}_{S1}$ involving the substitutional site will, in general, be of a form similar to that of $\underline{V}_1$, but with the 1i and i1 elements, $i=2,3,4$, in general, unequal.

Finally, the last term [Eq. (1d)] contains the hydrogen intrasite local correlation effect, and is proportional to the phenomenological Coulomb integral U. The symbol $\bar{\sigma}$ denotes spin opposite to σ.

III. GREEN'S-FUNCTION FORMALISM AND LOCAL SELF-ENERGY

The Green's operator $\hat{G}$ is given by $\hat{G}=(E-\hat{H})^{-1}$ where $\hat{H}$ is the full Hamiltonian $\sum_\sigma \hat{H}_\sigma$. For now we concentrate on the one-body problem, ignoring the Hubbard term except to note that when this term is treated in the Hartree-Fock approximation (as will be done), the result will be equivalent to two coupled one-body problems, one for each spin. Let us comment that the effective one-body Green's functions involve a spin-dependent effective shift of the hydrogen-site energy parameter. This shift is related to the self-consistently determined hydrogen-site occupation for the opposite spin.[10]

Now for the pure one-body problem we consider the H-site local Green's function G_{HH}. The major component of this is the "local self-energy" at the H site Σ_{H} defined via

$$G_{\mathrm{HH}}(E)=[E+i\eta-E_{\mathrm{H}}-\Sigma_{\mathrm{H}}(E)]^{-1} , \tag{3}$$

where η is a positive infinitesimal. In our model, E_{H} is not assumed to depend upon the position of the H site, whereas $\vec{\mathrm{V}}_{\mathrm{H}S}$ and $\vec{\mathrm{V}}_{\mathrm{H}i}$ do have $\vec{\mathrm{R}}_{\mathrm{H}}$ dependence.

We next obtain a useful explicit form for $\Sigma_{\mathrm{H}}(E)$: The starting point is Dyson's equation,

$$\hat{G}=\hat{G}^0+\hat{G}^0\hat{H}_1\hat{G} , \tag{4}$$

where here $\hat{G}^0$ is the unperturbed Green's operator corresponding to $\hat{H}_0\equiv\sum_\sigma\hat{H}_{0\sigma}$, and where $\hat{H}_1\equiv\sum_\sigma\hat{H}_{1\sigma}$. In the site representation we denote the state at the H site by $|\mathrm{H}\rangle$ and the state for any site of the cage, including the substitutional, by $|m\rangle$. Note that $|m\rangle$ has four components corresponding to the four orbitals. We denote matrix elements $\langle m|\hat{G}|m'\rangle$ by $G_{mm'}$, etc.

Using $\langle m|\hat{G}^0|\mathrm{H}\rangle=0$, we find directly from Eq. (4) the following matrix element relations:

$$G_{\mathrm{HH}}=G^0_{\mathrm{HH}}+G^0_{\mathrm{HH}}\sum_m \tilde{H}_{1\mathrm{H}m}\vec{\mathrm{G}}_{m\mathrm{H}} , \tag{5a}$$

$$\vec{\mathrm{G}}_{m\mathrm{H}}=\sum_n \underline{G}^{\,0}_{mn}\vec{\mathrm{H}}_{1n\mathrm{H}}G_{\mathrm{HH}} . \tag{5b}$$

A printed underline denotes a matrix; an arrow (tilde) denotes a column (row) vector. Using

$$G^0_{\mathrm{HH}}=(E-E_{\mathrm{H}})^{-1} , \tag{6}$$

and Eq. (5b) in Eq. (5a), we find an expression for G_{HH} from which we identify

$$\Sigma_{\mathrm{H}}(E)=\sum_{m,n}\tilde{H}_{1\mathrm{H}m}\underline{G}^{\,0}_{mn}(E)\vec{\mathrm{H}}_{1n\mathrm{H}} . \tag{7}$$

We note that in a calculation in which the H site is moved, the G^0_{mn}'s, being $\vec{\mathrm{R}}_{\mathrm{H}}$ independent, need only be calculated once and for all. The form Eq. (7) thus allows an obvious simplification in the repeated calculation of $\Sigma_{\mathrm{H}}(R_{\mathrm{H}})$.

The Green's-function matrix involving cage sites ν and ν' is now obtained: From Dyson's equation we readily obtain the two matrix element relations,

$$\underline{G}_{\nu\nu'}=\underline{G}^{\,0}_{\nu\nu'}+\sum_j \underline{G}_{\nu j}\vec{\mathrm{H}}_{1j\mathrm{H}}\tilde{G}_{\mathrm{H}\nu'} , \tag{8a}$$

$$\tilde{G}_{\mathrm{H}\nu'}=\sum_\nu G^0_{\mathrm{HH}}\tilde{H}_{1\mathrm{H}\nu}\underline{G}_{\nu\nu'} . \tag{8b}$$

The sums here go over all sites of the cage. Substituting Eq. (8a) into Eq. (8b), we obtain an expression for $G_{\mathrm{H}\nu'}$ which is then used in Eq. (8a) to obtain

$$\underline{G}_{\nu\nu'}=\underline{G}^{\,0}_{\nu\nu'}+G^0_{\mathrm{HH}}\left[\sum_j \underline{G}^{\,0}_{\nu j}\vec{\mathrm{H}}_{1j\mathrm{H}}\right]\left[\sum_i \tilde{H}_{1\mathrm{H}i}\underline{G}^{\,0}_{i\nu'}\right] . \tag{9}$$

The $G^0_{\nu\nu'}$ may be evaluated using a straightforward generalization of the approach used for pure Bethe lattices.[9]

IV. SOLUTION OF HARTREE-FOCK EQUATIONS AND GAP SIMULATION

We consider now the determination of the Hartree-Fock self-consistent occupations at the hydrogen site for up and down spins. We denote these quantities by $\langle n_{\mathrm{H}\uparrow}\rangle$ and $\langle n_{\mathrm{H}\downarrow}\rangle$. A similar type of problem was considered by Anderson for an impurity in a metal,[10] and by Haldane and Anderson for an impurity in a semiconductor.[11] It is necessary to elaborate on these treatments for purposes of the present problem.

We denote the self-consistent Green's functions appropriate to the two coupled one-body Hamiltonians arising in the Hartree-Fock procedure by $G_{\mathrm{H}\sigma}$. In fact, it is well known that the $G_{\mathrm{H}\sigma}$'s have the form

$$G_{\mathrm{H}\sigma}(\omega)=[\omega+i\eta+E_{\mathrm{H}}+U\langle n_{\mathrm{H}\bar{\sigma}}\rangle-\Sigma_{\mathrm{H}}(\omega)]^{-1} . \quad (10)$$

The solution for the case of an isoelectronic substitutional atom is considered first. The $\langle n_{\mathrm{H}\sigma}\rangle$ are self-consistently related to each other via the relations

$$\langle n_{\mathrm{H}\uparrow}\rangle=\mathcal{N}(\langle n_{\mathrm{H}\downarrow}\rangle) , \quad (11a)$$

$$\langle n_{\mathrm{H}\downarrow}\rangle=\mathcal{N}'(\langle n_{\mathrm{H}\uparrow}\rangle) , \quad (11b)$$

where the functions $\mathcal{N}$ and $\mathcal{N}'$ are defined as

$$\mathcal{N}(\langle n_{\mathrm{H}\sigma}\rangle)\equiv\sum_i Z_{i\sigma}-\frac{1}{\pi}\,\mathrm{Im}\int_{\epsilon_{vl}}^{\epsilon_{vu}} G_{\mathrm{H}\sigma}(\omega)d\omega+\sum_j^{\tilde{j}} Z_{j\sigma} , \quad (12a)$$

$$\mathcal{N}'(\langle n_{\mathrm{H}\sigma}\rangle)\equiv\sum_i Z_{i\sigma}-\frac{1}{\pi}\,\mathrm{Im}\int_{\epsilon_{vl}}^{\epsilon_{vu}} G_{\mathrm{H}\sigma}(\omega)d\omega+\sum_j^{\tilde{j}'} Z_{j\sigma} . \quad (12b)$$

In Eqs. (12) the middle terms of the right-hand sides denote the usual contribution from the (essentially) fully occupied valence band; ϵ_{vl} and ϵ_{vu} denote the lower and upper valence-band edges. Now, in general, in the semiconductor, all states below ϵ_{vu} contribute to $\langle n_{\mathrm{H}\sigma}\rangle$. This would include all discrete states in the lower void. Such contributions actually arise from the integral term provided we replace ϵ_{vl} by $-\infty$. The symbol $Z_{i\sigma}$ denotes the residue of the *i*th pole in the lower void for spin σ, and the sum over i is over all lower-void poles.[12]

Such discrete-state contributions to $\langle n_{\mathrm{H}\sigma}\rangle$ also arise from certain, but not all, states in the gap region, depending upon σ. These contributions are represented in the third terms on the right-hand sides of Eqs. (12). The choice of which poles contribute, i.e., the choice of the upper cutoffs $\tilde{j}$ and $\tilde{j}'$, requires some discussion.

We first note that with the H site absent, there are for pure Ge, $2N$ states (for each spin) in both valence and conduction bands, N being the number of sites. Since there are four valence electrons per atom, each of the $2N$ valence-band states is doubly occupied. When one Ge atom is replaced by a different substitutional, the valence-band states are naturally perturbed, and in some cases discrete states are split off the valence band. In what follows, the parameter choices modeling substitutional C and O, however, turn out to be such that no discrete states are split off the valence band into the gap in the absence of H.

We now restore the H site. We first consider $U=0$, $H_1=0$, and take E_{H} to be in the valence band. In this case the H site is doubly occupied. The H atom, however, brings in only a single electron. Since there are now $2N+1$ states for each spin in the valence band region and only $4N+1$ electrons to fill them, we clearly require a hole at the top of the valence band.

We now restore H_1 still with $U=0$. As H_1 increases we expect H-related bonding and antibonding states to eventually split off from the valence band (this is discussed below). For the case of an isoelectronic substitutional atom, when H_1 is such that a discrete nondegenerate H-related state has split off from the valence band into the gap, this state is *singly occupied* (by, for instance, a spin-up electron, taken to be the majority spin in the present calculation); there remain $2N$ states for each spin below the upper valence-band edge, and these accommodate the remaining $4N$ electrons. In this case, $\langle n_{\mathrm{H}\uparrow}\rangle\neq\langle n_{\mathrm{H}\downarrow}\rangle$.

In the more general case where there are m discrete states in the gap having originated from the valence band (assumed singly degenerate), all m states are occupied for spin up, whereas only the lowest-lying $m-1$ states are occupied by spin down. The functionals $\mathcal{N}$ and $\mathcal{N}'$ reflect this asymmetry in the choice of $\tilde{j}$ and $\tilde{j}'$: In general, $\tilde{j}=m$ and $\tilde{j}'=m-1$.

Finally restoring U, the self-consistent occupations are computed using these functionals in the following equation:

$$\langle n_{\mathrm{H}\downarrow}\rangle=\mathcal{N}'(\mathcal{N}(\langle n_{\mathrm{H}\downarrow}\rangle)) . \quad (13)$$

This equation can be solved graphically by finding the intersections of the curve $\mathcal{N}$ vs $\langle n_{\mathrm{H}\downarrow}\rangle$ and the curve plotted "at 90°" of $\mathcal{N}'$ vs $\langle n_{\mathrm{H}\uparrow}\rangle$.[10]

For the case of the nonisoelectronic impurity O, the above discussion needs to be modified. First, O brings in two extra electrons as compared to C. Thus for $U=0$, when H_1 is such that there is one H-related antibonding discrete state in the gap, this state is, unlike the case with C, doubly occupied. The remaining electron goes to the bottom of the conduction band. For this case the self-consistency condition is

$$\langle n_{\mathrm{H}\downarrow}\rangle=\mathcal{N}(\mathcal{N}(\langle n_{\mathrm{H}\downarrow}\rangle)) . \quad (14)$$

If there is more than one discrete state in the gap the self-consistency condition must be modified according to the origin of the gap states.[13]

In general, there are several self-consistent solutions. We, of course, seek the solution with the lowest energy. The calculation of the Hartree-Fock ground-state energy within this type of model and for each self-consistent pair $\langle n_{\mathrm{H}\uparrow}\rangle,\langle n_{\mathrm{H}\downarrow}\rangle$ has been discussed elsewhere.[14] The result discussed in Ref. 14 pertains to a simple Anderson model with a half-filled band and a single orbital per site for each lattice site as well as for the impurity site. That result essentially directly carries over to the present case of a single impurity site with single orbital coupled to ten lattice sites with four orbitals per site. The main modification is that care must be taken in the choice of the upper limit in the energy integral to reflect the presence of discrete states in the gap.

Gap simulation. It has been shown that the gap in the Ge Bethe lattice with nearest-neighbor interactions is, at 2.6 eV, over 3 times larger than the actual crystalline-Ge gap.[15] This large value is significant on the relevant electronic energy scale; indeed, the artifact of such a large gap may affect some of our qualitative conclusions. We observe that a discrete state, at about 0.5 eV above the valence-band edge in the Bethe lattice, presumably would correspond to a resonance within the band of the full lattice at very roughly the same energy. Then in the latter case and in a self-consistent procedure the $\langle n_{\mathrm{H}\sigma} \rangle$'s would be calculated by occupying all states associated with this resonance equally for both spins. This contrasts with the former case, in which for an isoelectronic substitutional atom the discrete state residue is included in $\langle n_{\mathrm{H}\uparrow} \rangle$ but not in $\langle n_{\mathrm{H}\downarrow} \rangle$.

However, within the Bethe-lattice model this effect of doubly occupying these high-lying resonance states in the actual valence band may be approximately modeled by *including* the residue contribution in the calculation of $\langle n_{\mathrm{H}\downarrow} \rangle$ for all discrete states which originate in the valence band and which lie in the region from the Bethe-lattice valence-band top ϵ_{vB} to the periodic-lattice band top ϵ_{vP}. Any discrete state above the periodic-lattice valence-band top and derived from the valence band is, however, still not included. A further modification is to regard any discrete state originating from the valence band and occurring at energy between the periodic-lattice lower conduction-band edge ϵ_{cP} and the Bethe-lattice lower conduction-band edge ϵ_{cB} as an effective conduction-band resonance, and to therefore *not* include its residue contribution in both $\langle n_{\mathrm{H}\downarrow} \rangle$ *and* $\langle n_{\mathrm{H}\uparrow} \rangle$. This last modification would apply to both substitutional C and O. These modifications are referred to here as "gap simulation."

We now give a characterization of acceptor, donor, and neutral complexes in terms of the types of solutions possible for $\langle n_{\mathrm{H}\uparrow} \rangle$ and $\langle n_{\mathrm{H}\downarrow} \rangle$. We consider first the case of [H,C]. The H atom brings in a single electron. Yet [H,C], being an acceptor, must have an extra electron localized nearby. We expect that this additional electron is mainly associated with the H site, i.e., that the 1*s* level at the H site becomes doubly occupied. This corresponds to a nonmagnetic solution $\langle n_{\mathrm{H}\uparrow} \rangle = \langle n_{\mathrm{H}\downarrow} \rangle \approx 1$. Departures of $\langle n_{\mathrm{H}\sigma} \rangle$ from unity reflect the presence of hybridization; some of the net additional electron would be associated with the sites near to the H, principally the C.

Turning next to the case of [H,O], O brings in two extra electrons as compared to an isoelectronic substitutional impurity. Since [H,O] behaves as a shallow donor, one of the two extra electrons becomes localized nearby, and is presumably again strongly associated with the H site. This so far would render the neighborhood of [H,O] singly positively charged. The second extra electron can then fall into a large hydrogenic orbit, thereby giving the donor character. Thus, in our model, we would again associate [H,O] with a symmetric self-consistent solution $\langle n_{\mathrm{H}\uparrow} \rangle = \langle n_{\mathrm{H}\downarrow} \rangle \approx 1$.

Finally, we consider H in pure Ge. Here, the "center" is neutral, and therefore the local occupation of the H level must be such that $\langle n_{\mathrm{H}\uparrow} \rangle \approx 1$ and $\langle n_{\mathrm{H}\downarrow} \rangle \approx 0$. The qualitative characterizations just given would carry over directly with the use of gap simulation.

V. PHYSICAL PRINCIPLES PROMOTING THE SYMMETRIC SOLUTION

We have observed that double occupation of the nominal H levels underlies both the acceptor character of [H,C] and the donor character of [H,O]. We now consider the physical mechanisms which control the double occupation of the nominal H level.

First, an idealized situation is considered in which $U=0$ and $H_1=0$. For the time being we do not consider gap simulation. Clearly for $E_{\mathrm{H}} > \epsilon_{vB}$ the H orbital is singly occupied. For $E_{\mathrm{H}} < \epsilon_{vB}$, this orbital becomes doubly occupied, and for an isoelectronic substitutional impurity, a hole appears at the top of the valence band. When long-range Coulomb effects tied in with the now-present net negative charge at the H site are then added, this hole becomes localized into a shallow hydrogenic orbital. Long-range Coulomb effects are not explicitly included in our model. Their neglect does not, however, significantly affect the issue of double occupation, which is resolved on a much higher energy scale than is operative in the shallow levels. In practice, E_{H} will always be well within the valence band (see below).

Next we consider $H_1=0$ and $E_{\mathrm{H}} < \epsilon_v$, but now at finite U. The range $U>0$ implies a positive cost in energy in attempting to doubly occupy the H level. As a result either the H level is singly occupied or it is doubly occupied, but at a shifted (by U) higher energy. We thus observe that in this simple model ($H_1=0$ and $E_{\mathrm{H}} < \epsilon_{vB}$) double occupation is promoted by a small value of U and/or a low value of the H-site energy parameter.

The effect of turning on H_1 is now considered. We assume $E_{\mathrm{H}} < \epsilon_{vB}$ and take $U=0$. The H-site local density of states (HLDOS) exhibits four qualitatively distinct regimes as functions of H_1. (1) $H_1=0$: HLDOS is a δ function of weight unity centered at $E=E_{\mathrm{H}}$. (2) Small H_1: HLDOS exhibits a sharp resonance centered roughly at $E=E_{\mathrm{H}}$. (3) Intermediate H_1: HLDOS evidences weakening of resonance at $E \approx E_{\mathrm{H}}$ and formation of new resonances near upper and lower valence-band edges (antibonding and bonding resonances). (4) Large H_1: presence of discrete states having split off the lower (bonding) and upper (antibonding) valence-band edges with a corresponding significant weakening of the HLDOS in the valence-band region. Note that in some cases, e.g., E_{H} very near one of the band edges, there may occur a situation intermediate between (3) and (4); for example, the presence of an antibonding discrete state and a bonding resonance in the valence band.

Let us note that when H_1 is large enough that an H-related antibonding discrete state is present for an isoelectronic substitutional (again for $U=0$), this anitbonding state is necessarily singly occupied (again, without gap simulation) with the result that the complex is neutral (this assumes that there are no other discrete gap states). Now when U is turned on for such a large H_1, the self-consistent solution must be such that for spin up, this discrete state has moved up in energy, possibly into the conduction band: The effective spin-up H-site energy $E_{\mathrm{H}} + U\langle n_{\mathrm{H}\downarrow} \rangle$ is greater than E_{H}, implying that all discrete states are shifted up in energy relative to $U=0$. Similarly since $\langle n_{\mathrm{H}\uparrow} \rangle \neq 0$, the effective spin-down H-site energy is shifted up and the (empty) discrete state in the minority-spin HLDOS is, if it has not crossed into the conduction band, at least as high in energy as the corresponding majority-spin discrete state. Assuming that, at most, one state (for each spin) can be present in the gap, the self-consistent solution will be such that the majority-spin discrete state, if it has not moved into the conduction band for the self-consistent $\langle n_{\mathrm{H}\downarrow} \rangle$, is occupied. The minority spins are then all accommodated in the valence band. The result is a neutral complex.

If for $U=0$, H_1 is such that no discrete state has split off into the gap, the self-consistent solution for finite U still may be such that the majority-spin HLDOS has a discrete state in the gap (occupied) with, again, all minority spins accommodated in the valence band. A main point here is that the threshold for the splitting of the discrete state as a function of $U\langle n_{\mathrm{H}\downarrow} \rangle$ depends upon H_1.

In particular, for a given E_{H} well in the valence band, for $U < \epsilon_{vB} - E_{\mathrm{H}}$, and for an isoelectronic substitutional impurity a small value of H_1 will clearly promote acceptor character.

For the case of substitutional O the above discussion needs to be modified. Owing to the presence of two additional electrons contributed by the O, a single antibonding discrete state for the minority spin *is* occupied. It is still the case, however, that double occupation is favored by small H_1. Reducing H_1 will delay the entry of the H-related discrete antibonding state into the conduction band as the effective H-site energy increases.

A fourth component in the promotion of double occupation involves the role of the substitutional site energy E_{Sd}. The basic idea is that if the H site and substitutional site are strongly coupled, then the value of E_{Sd} will have a significant effect upon the energy of any H-related antibonding resonance or discrete state. In particular, lowering E_{Sd} relative to E_{Gd} will tend to lower the energies of resonant features and/or discrete states which are prominant in the upper valence-band region of the HLDOS.

This effect is demonstrated in a simple diatomic example. Consider two sites with single orbitals per site with energy E_1 and E_2 ($E_2 > E_1$) and with coupling V. The local Green's function G_{11}, whose poles determine the energy eigenvalues, is given by

$$G_{11}(E) = [E - E_1 - \Sigma(E)]^{-1} , \tag{15}$$

$$\Sigma(E) = V^2/(E - E_2) . \tag{16}$$

The solution of $E - E_1 = \Sigma(E)$ may be qualitatively understood by visualizing the intersections of the two curves corresponding to the left- and right-hand sides of this equation. Clearly in the case $V \sim E_2 - E_1$, with $E_2 > E_1$, the energies of the antibonding and bonding roots E_A and E_B are significantly lowered as E_2 is lowered. A similar lowering mechanism is clearly operative when sites 1 and 2 are then coupled to a lattice.

VI. TIGHT-BINDING PARAMETERS

The Ge-Ge hopping parameters are taken to be those of Joannopoulos and Cohen for the fully periodic Ge lattice:[16] $v_0 = -5.0$, $v_1 = -0.2$, $v_2 = 0.6$, $v_3 = 0.4$, and $E_{Go} = -2.0$ eV. The zero of energy is henceforth taken as the sp^3 hybrid energy for Ge, E_{Gd}. The solution for the Ge LDOS for these parameters and with the pure Bethe-lattice topology has been discussed by Rajan and Yńdurain.[15]

A parameter of key significance is the substitutional-atom sp^3 hybrid energy E_{Sd}. The difference $E_{Sd} - E_{Gd}$ is usually estimated from the corresponding difference in atomic-term values in the sp^3 representation.[17] Note that $E_d \equiv \frac{1}{4}(\epsilon_s + 3\epsilon_p)$, where ϵ_s and ϵ_p are the valence s and p atomic-term values, respectively. Hartree-Fock[18] and Hermann-Skillman[19] results for C, Si, Ge, and O are given in Table I. We observe that C and O have sp^3 hybrid energies substantially lower than the value for Ge. We expect that this large difference in site-energy parameter will be of some significance in determining the charge character in the vicinity of [H,C] and [H,O]. Naturally, charge-transfer effects may somewhat offset the magnitude of the difference. Nevertheless, the ultimate difference will likely be of the order of several volts. The specific consequences of a low substitutional-site energy were explored in Sec. V.

Also shown in Table I are the off-diagonal (interorbital, intrasite) parameters $E_o \equiv -\frac{1}{4}(\epsilon_s - \epsilon_p)$. This parameter is basically the same among C, Si, and Ge. The magnitude for O, however, is roughly twice as large.

The estimation of the hopping parameter matrices $\underline{V}_{S1}$

TABLE I. Atomic-term values for valence s and p orbitals in eV. Diagonal and off-diagonal hybrid energies are given by $E_d = (\epsilon_s + 3\epsilon_p)/4$, and $E_o = (\epsilon_s - \epsilon_p)/4$, respectively. Fifth column refers E_d to the E_d value for Ge. F denotes values of Fischer (Ref. 18); HS denotes values of Herman and Skillman (Ref. 19).

		ϵ_s	ϵ_p	E_d	E_o	$E_d - E_d$ (Ge)
C:	F	−19.4	−11.1	−13.2	−2.08	−3.86
	HS	−17.5	−8.97	−11.1	−2.13	−2.74
Si:	F	−14.8	−7.58	−9.38	−1.80	−0.09
	HS	−13.6	−6.52	−8.27	−1.76	0.10
Ge:	F	−15.2	−7.33	−9.29	−1.96	0
	HS	−14.4	−6.36	−8.37	−2.01	0
O:	F	−34.0	−16.7	−21.0	−4.33	−11.8
	HS	−29.1	−14.1	−17.9	−3.76	−9.51

is complicated by the effects of lattice relaxation. Assuming no lattice distortion, we would expect, for substitutional carbon or oxygen, somewhat reduced hopping matrix elements relative to $\underline{V}_1$. This would be associated with the small size of the free C and O as compared to free Ge atom (1.3 and 0.9 vs 1.8 a.u.). On the other hand, lattice relaxation, with the Ge atoms contracting around the C or O, would tend to offset this. It would seem reasonable that $\underline{V}_{S1}$ would be smaller, but comparable to the above given values for $\underline{V}_1$. For our purposes, we take $\underline{V}_{S1}$ for carbon and oxygen to be the same and of magnitude $0.75\underline{V}_1$.

A simple approximation is made for the H-site position dependence of the H-cage-site hopping parameters. They are simply taken as some appropriate scale factor times the corresponding Slater overlap integral. Thus

$$[sl\sigma(\vec{R})]_i = h_l S_{li}(\vec{R}) \ . \tag{17}$$

Here, $S_{li}(\vec{R})$ denotes the Slater overlap integral involving the hydrogen 1*s* orbital and the *l*-symmetry ($l = s,p$) valence orbital for atom of type *i*, with centers of orbitals separated by $\vec{R}$ and with σ orientation.[20] The $sl\sigma$, $l = s,p$, denote the usual Slater-Koster parameters. The choice of the scale factors h_l and of the H-site energy parameter E_H is guided by the results of the calculations of Picket, Cohen, and Kittel[21] (PCK) and of Pandey.[22]

PCK performed a pseudopotential supercell calculation for H at the cage center in pure Ge. This involved the use of an unscreened protonic pseudopotential in addition to screened Ge atomic pseudopotentials with an eight-atom supercell. A prominent feature in the band structure is the presence of a new H-related band at about 7 eV below the upper valence-band edge.

We might expect that in the PCK calculation the position of the H resonance in the valence band would give an indication of the hydrogen-site energy parameter in a tight-binding calculation which neglects the local Coulomb repulsion at the H site. On the other hand, we might expect that this calculation, as it uses superposition of atomic pseudopotentials, would underestimate the effective hopping parameters. Sufficiently increased H-lattice hybridization would cause the single H-like resonance to give way to bonding and antibonding resonances. Furthermore, increased "overlap" may lead to an increase in the effective E_H. Intersite Coulomb effects could also drive E_H upward.

The results of Pandey related to H chemisorption on a Ge surface give an independent rough indication of the hopping parameters. These parameters apply for an H-Ge distance of 1.53 Å and have values of $ss\sigma = -3.30$ eV and $sp\sigma = -2.15$ eV. As they pertain to H saturating a dangling bond, these parameters would be expected to have a larger magnitude than for H at the same distance, but in the antibond direction. In order that our $ss\sigma$ and $sp\sigma$ parameters agree with Pandey's, the scale factors in Eq. (17) must be chosen to be $h_s = -6.35$ eV and $h_p = -3.71$ eV.

The HLDOS for the H site at the cage center for several values of the scale parameters near and below these last values is presented in Fig. 2. The value E_H is, from here on, set at -6 eV. The result in Fig. 2(a), roughly appropriate for the Pandey values, clearly does not correspond to the calculation of PCK: A definite antibonding resonance is evident in the upper valence-band region, and the resonance near $E_H \approx -6$ eV is relatively weak. As is evident in Fig. 2, as the *h*'s are lowered (keeping h_s/h_p equal to roughly the Pandey value) the HLDOS begins to resemble more of what is expected on the basis of PCK, i.e., a dominating single H-like resonance at $E \approx E_H$.

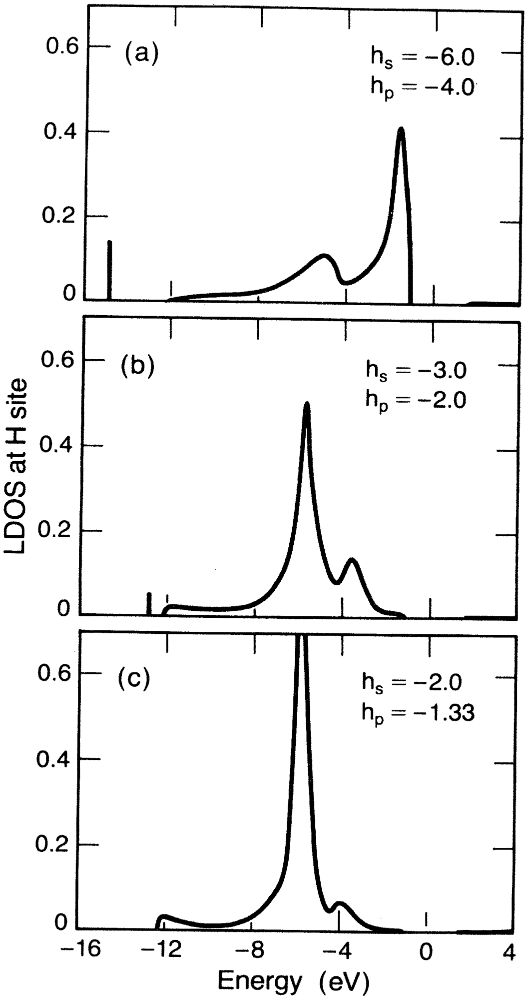

FIG. 2. Dependence of hydrogen-site LDOS's upon H-lattice hybridization strength for H at the cage center. $E_H = -6.0$ eV. Heights of verticle lines denote weight of discrete state at H site. LDOS rises to ~ 1.03 at ≈ -6 eV in (c).

As a compromise we choose the values $h_s = -3.0$ eV and $h_p = -2.0$ eV from here on: These values are qualitatively consistent with the expectation that the Pandey parameters overestimate, while the PCK parameters underestimate, the effective H-lattice coupling appropriate to H within the cage. The HLDOS for this case involves a large H-like resonance at $E \approx E_H$, and, in addition, a discrete state just below the lower valence-band edge.

VII. SOLUTIONS FOR H AT CAGE CENTER AND FOR H NEAR SUBSTITUTIONAL

The expectation of a fairly identifiable H-related resonance for H at the cage center implies that the correlation effect at the H site will be relatively large. We set $U=7$ eV for H at the cage center.

The dependence of the HLDOS upon the choice of substitutional should be relatively small for H at the cage center as the substitutional is one of ten roughly equally important neighbors. In what follows, the parameters modeling the substitutionals are (in eV) $E_{Gd}=0$, $E_{Cd}=-4$, $E_{Od}=-8$; $E_{Go}=E_{Co}=-2$, $E_{Oo}=-4$; and $\underline{V}_{C1}=\underline{V}_{O1}=0.75\underline{V}_1$, with $\underline{V}_1$ the Cohen-Joannopoulos parameters.

Self-consistent solutions for the above parameters and for the three substitutionals were obtained for H at the cage center using gap simulation. In all cases, a magnetic solution is found, implying that for this H-site position, H in pure Ge and [H,C] are neutral while [H,O] is a double donor. Underlying this magnetic character is the relatively large value of U appropriate to H in the cage center. The LDOS for spin up and down at the H site, and for spin up at the substitutional site for the three cases, are shown in Fig. 3 (see Table II).

For H in pure Ge, the majority-spin HLDOS exhibits a large resonance at ~ -5.0 eV. The lower-void discrete state has a very small projection onto the H site. The minority-spin HLDOS has very little weight in the valence band; an unoccupied discrete state appears in the upper gap region. The aspect in the HLDOS of a sharp valence-band resonance near ≈ -5 eV for the majority spin and an unoccupied discrete state in the Bethe-lattice gap region for the minority spin is evident in both [H,C] and [H,O]. In addition, new discrete states in the upper Bethe-lattice gap region, derived from the conduction band, appear for majority and minority spins for both [H,C] and [H,O]. For [H,O], a discrete state with main projection on the O site is present very far below the valence-band edge.

We next consider the case of the H site positioned near the substitutional on the [111] axis. A main effect as the H atom is moved closer to the substitutional is that the total hybridization effect between the H site and the lattice tends to increase. This increase in hybridization is evidenced in an upward shift in energy in antibonding resonances and/or gap states in the (one-particle) HLDOS as the H site is moved in.

A further effect when the H site is located near the substitutional site is increased electron overlap. This screening effect will tend to reduce the effective value of U and suggests the use of an R_H-dependent U. We point out that the assumption of R_H-dependent U and R_H-independent E_H are not necessarily incompatible. For E_H there are two competing factors: As the H site is moved in, the stronger the nuclear potential of the substitutional atom; this tends to lower E_H. On the other hand, near the substitutional core, the larger electron overlap tends to increase E_H. The cancellation of these two effects is probably roughly complete; for this reason, and consistent with most tight-binding calculations, the R_H dependence of E_H is ignored here.

We make a preliminary choice of $U=5.0$ eV for $|R_H|=1.93$ a.u. Naturally, the increased proximity of the H and substitutional sites tends to bring in the strong mixing effect related to the stagger of the substitutional site energy with respect to the host (see Sec. V). In fact, the low values of substitutional site energies for C (-4 eV) and O (-8 eV) would suggest a significant lowering of any prominant H-related upper valence-band resonances and/or discrete gap states, thereby tending to favor double occupation.

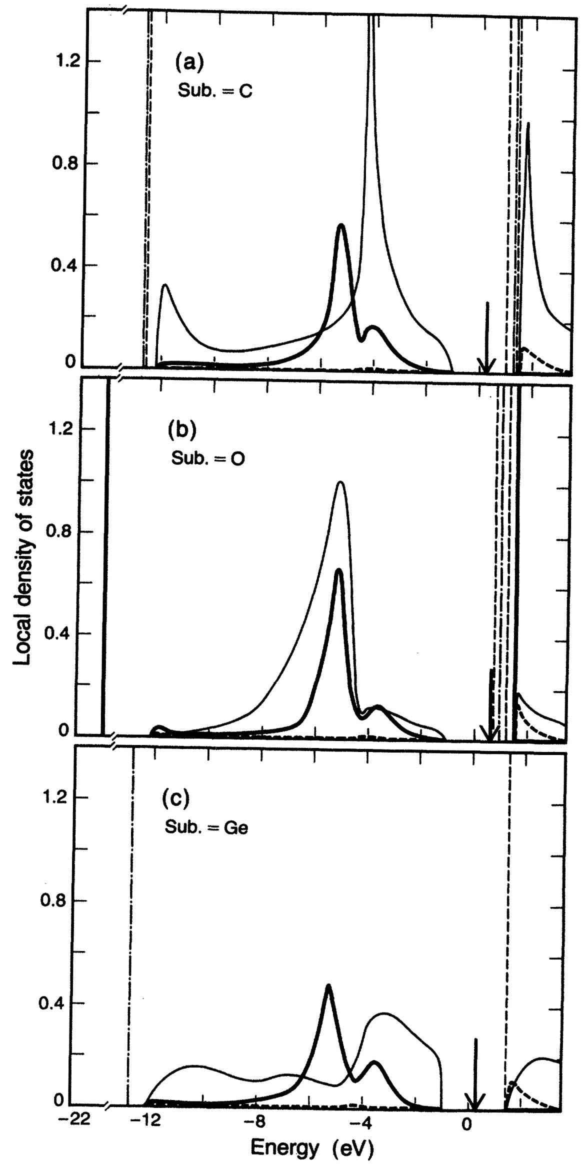

FIG. 3. LDOS's for H at the cage center for three different substitutionals ($R_H=4.63$ a.u.). Thick solid (dashed) lines are LDOS at H site for up (down) spin. Thin solid line is LDOS at substitutional site for spin up. LDOS at substitutional site for spin down is not shown, as this is very close to the result for spin up. Dotted-dashed (dashed) vertical lines give positions of discrete states for spin up (down). Solid vertical lines give positions of almost overlapping spin-up and -down discrete states. Refer to Table II for information pertaining to valence-band occupation and weights of discrete states at H and substitutional sites. Arrow denotes position of effective Fermi level.

Self-consistent solutions at $|\vec{R}_H|=1.93$ a.u. and for the above parameters were carried out. A magnetic solution was found for H in pure Ge, whereas nonmagnetic

TABLE II. Occupation information for the self-consistent solutions $\langle n_{H\uparrow} \rangle$ and $\langle n_{H\downarrow} \rangle$ for the H site [part (a)] and for substitutional site [part (b)]. Gap simulation used in evaluation of total occupations. Pole energies are in eV.

(a)

		Spin up (H site)				Spin down (H site)			
Substitutional	R_H (a.u.)	Pole energy	Residue	Valence-band integral	Total occupation	Pole energy	Residue	Valence-band integral	Total occupation
C	1.93	−12.9	0.017			−12.9	0.017		
		−0.560	0.816			−0.560	0.816		
		1.31	0.008	0.097	0.930	1.31	0.008	0.097	0.930
O	1.93	−21.2	0.007			−21.2	0.007		
		1.08	0.075			1.08	0.075		
		1.49		0.863	0.870	1.49		0.863	0.870
Ge	1.93	−12.9	0.053	0.925	0.978	−12.6	0.019		
						0.018	0.803	0.163	0.182
C	4.63	−12.7	0.010			−12.6	0.006		
		1.25		0.960	0.970	0.995	0.507		
						1.42	0.345	0.056	0.062
O	4.63	−21.0				−21.0			
		0.900				0.644	0.381		
		1.49		0.940	0.940	1.19	0.450		
						1.48		0.063	0.063
Ge	4.63	−12.8	0.046	0.948	0.994	1.40	0.845	0.057	0.057

(b)

		Spin up (substitutional site)				Spin down (substitutional site)			
Substitutional	R_H (a.u.)	Pole energy	Residue	Valence-band integral	Total occupation	Pole energy	Residue	Valence-band integral	Total occupation
C	1.93	−12.9	0.251			−12.9	0.251		
		−0.560	0.105			−0.560	0.105		
		1.31	0.028	2.30	2.65	1.31	0.028	2.30	2.65
O	1.93	−21.2	0.470			−21.2	0.470		
		1.08	0.023			1.08	0.023		
		1.49	0.298	2.41	2.90	1.49	0.298	2.41	2.90
Ge	1.93	−12.9	0.144	1.82	1.96	−12.6	0.106		
						0.018	0.070	1.81	1.91
C	4.63	−12.7	0.159			−12.6	0.217		
		1.25	0.068	2.55	2.71	0.995	0.042		
						1.42		2.48	2.70
O	4.63	−21.0	0.474			−21.0	0.474		
		0.900	0.027			0.644	0.017		
		1.49	0.287	2.39	2.86	1.19	0.032		
						1.48	0.157	2.39	2.86
Ge	4.63	−12.8	0.085	1.93	2.01	1.40	0.015	1.95	1.95

solutions were found for [H,C] and [H,O], implying that for this $\vec{R}_H$ the complexes are, respectively, neutral, acceptor, and donor. The LDOS for spin up and down at the H site and for spin up at the substitutional site are shown in Fig. 4.

For Ge the majority-spin HLDOS is weighted heavily in the upper valence-band region, whereas the minority-spin HLDOS has very little weight anywhere in the valence band. Instead, the minority-spin HLDOS has a significant unoccupied discrete state in the Bethe-lattice gap (residue ≈ 0.80). Both minority- and majority-spin HLDOS's contain discrete states in the lower void with very little projection onto the H site.

For [H,C] with a symmetric solution, the HLDOS has

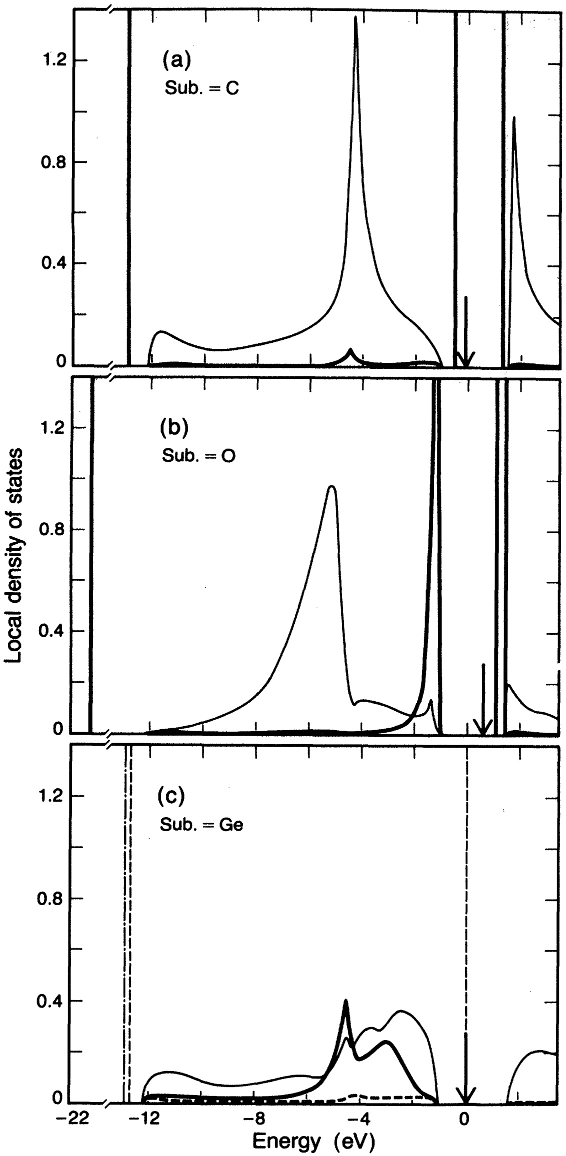

FIG. 4. LDOS's for H near a substitutional site on the [111] axis ($R_{\mathrm{H}}=1.93$ a.u.). Thick solid (dashed) lines are LDOS at H site for up (down) spin. Thin solid line is LDOS at substitutional site for spin up. LDOS at substitutional site for spin down (not shown) is fairly close to result for spin up. Dotted-dashed (dashed) vertical lines give positions of discrete states for spin up (down). Solid vertical lines give positions of overlapping spin-up and spin-down discrete states. For (a) and (b), nonmagnetic solutions are found. Refer to Table II for information pertaining to valence-band occupation and weights of discrete states at H and substitutional sites. Arrow denotes position of effective Fermi level.

very little weight in the valence band and shows three discrete states, two in the Bethe-lattice gap and one in the lower void. Both the void state and the upper gap state have very little projection on the H site. The lower gap state, however, which is treated as being in the effective valence band in gap simulation and hence doubly occupied, does have a major projection on the H site (residue ≈ 0.82). Note that the substitutional-site LDOS evidences significant peaking at $E \approx E_{Sd}$.

In the case of [H,O] the major feature in the HLDOS is a large resonance near the upper valence-band edge. There are three discrete states present, all with small projections on the H site. One very low in the lower void is primarily associated with the O site. The two discrete states in the gap are derived from the conduction band and are above the simulated lower conduction-band edge. A main feature in the substitutional LDOS is a large resonance at ~ -5.5 eV.

We observe that a general feature of the symmetric solutions for these systems is the presence in the HLDOS of either a large resonance near the upper valence-band edge or a (doubly occupied) discrete state in the lower gap region and below the simulated upper valence-band edge.

Empirical facts indicate a clear association of the H with the substitutional C and O atoms in the respective complexes. This strongly suggests that the observed charge states correspond to H being rather near the substitutional atom, e.g., not in the cage center. Our results for this situation correspond to the observed charge character. On the other hand, H in pure Ge is a rapidly diffusing interstitial, and we might expect it to have an equilibrium point nearer the cage center. In any case, our calculations suggest that for a fairly large region with the tetrahedral cage, H in Ge is a neutral impurity.

We point that it would be worth considering the charge character appropriate to positioning the H site in a bond involving the substitutional site. This was not attempted as the tetrahedral cage is not suitable for this geometry and also since the use of a different more suitable cage would have entailed the introduction of systematic errors in comparing results for both cages. In any case, no simple argument can rule out H in the bond.

The charge state for the three substitutional atoms and for a range of H-site positions in the [111] direction within the cage was computed ($R_{\mathrm{H}}=1.93$–5.02 a.u.). The above preliminary choice of parameters was used with an R_{H}-dependent U [$U(R_{\mathrm{H}})=0.74(R_{\mathrm{H}}-1.93)+5$ eV] taken to be the linear interpolate between the two values considered above. As expected in view of the preliminary results, H in pure Ge is neutral for all R_{H}'s considered. For [H,C] we conclude that the complex is an acceptor for $1.93 \lesssim R_{\mathrm{H}} \lesssim 2.70$ a.u. and neutral for $2.70 \lesssim R_{\mathrm{H}} \lesssim 5.02$ a.u. For [H,O] the complex is a donor for $1.93 \lesssim R_{\mathrm{H}} \lesssim 4.25$ a.u. and neutral for $4.25 \lesssim R_{\mathrm{H}} \lesssim 5.02$ a.u. The larger value of the distance R_{H} at crossover from double to single occupation for [H,O] as compared to [H,C] is associated primarily with O having a substantially lower site energy and secondarily with O having a lower strength of hybridization with the H site as compared to C.

The relative role of H-substitutional hybridization and low substitutional-site energy in promoting double occupation for H near substitutional atom was explored for both [H,C] and [H,O] at $R_{\mathrm{H}}=1.93$ and 2.70 a.u. [still using the above value of $U(R_{\mathrm{H}})$]. This was done by setting the H-substitutional atom hopping to the value appropriate to the H-Ge value, i.e., somewhat larger than the H-C and H-O hopping, and keeping all other parameters fixed. For O this increase in hybridization was not sufficient to prevent double occupation, clearly pointing to the intrinsic differences between the site parameters of O and Ge and

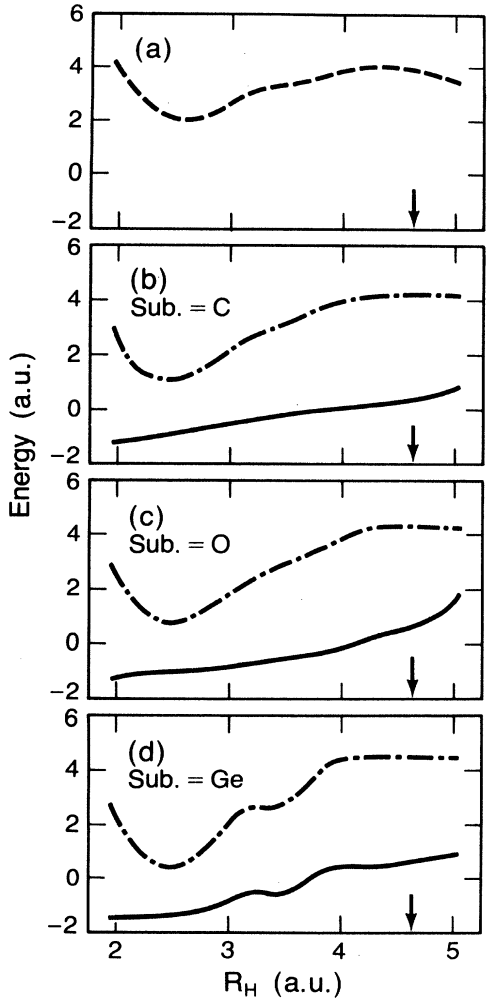

FIG. 5. (a) Falicov-Joós potential energy $\tilde{V}$ for a positive test charge vs distance along the [111] axis in pure Ge (Ref. 24). Frames (b)—(d): Results for total Hartree-Fock electronic energy given by solid line for substitutional C, O, and Ge, respectively. Dotted-dashed line is result of adding Falicov-Joós potential energy (i.e., for H in pure *Ge*) to Hartree-Fock electronic energy. Note, zeros of energies are different in frames (b)—(d); only relative energies as function of R_H are meaningful. Arrow denotes distance to tetrahedral site.

specifically to the effect of the low substitutional site energy of O. For C this change still left a double-occupation solution for $R_H=1.93$ a.u. but a single-occupation solution resulted at $R_H=2.70$ a.u. Overall, we conclude that, for $R_H \lesssim 2.7$ a.u., [H,C] is less strongly in the doubly occupied regime than is [H,O].

Ideally, it would be very desirable to determine the total energy of the system as function of $\vec{R}_H$. Although, as discussed in Sec. IV, the electronic energy may be readily computed within a Hartree-Fock approximation, the total energy involves also a contribution from the electronically screened ion-ion interaction.[23] As the H site is moved very close to the substitutional atom, this interaction becomes strongly repulsive. At intermediate R_H it may exhibit a minimum. A very rough idea of this interaction is contained in the calculation of Falicov and Joós[24] (Fig. 5). This effective interaction $\tilde{V}(R_H)$ is that appropriate to a positive test charge interacting with an accurately calculated charge density for pure Ge, all treated in linear response. The result of simply adding $\tilde{V}(R_H)$ to the total electronic energy appears in Fig. 5. Given our overall approximation we expect only the relative energies (i.e., in comparing two different $\vec{R}_H$ values) to be significant at best. There is the suggestion in the result for H in pure Ge that the equilibrium H site is actually not at the cage center. The electronic energy and sum of electronic energy and $\tilde{V}$ (the latter appropriate to pure Ge) for substitutional C and O also appears in Fig. 5. Clearly the actual $\tilde{V}$ appropriate to the substitutional C or O will have a minimum at a smaller R_H as compared to that for Ge. In any case, there is an indication of an energy minimum for H relatively near the substitutional atom.

At this stage it is worth observing that, because of the absence of first-principles calculations for H in pure Ge for various R_H values, there is some difficulty in reliably estimating the values of the tight-binding parameters related to the H site. Uncertain parameters which are of some importance are the hopping parameters between the H site and the lattice.

For scale parameters h_s and h_p approximately 50% larger than suggested in Sec. VI, a different, although still consistent, physical scenario for the systematics of charge character versus substitutional emerged. Larger values of h_s and h_p, i.e., closer to Pandey's values, certainly cannot be ruled out at this point. Qualitatively, as h_s and h_p increase, we expect, in the $U=0$ HLDOS, a larger likelihood of their existing split-off bonding states in the lower-void and antibonding states in the gap. Corresponding to the increase of hybridization would be a reduced value of U. It seems possible that U may drop by $\sim$50% for a $\sim$50% increase in h_s and h_p. In this case, even though the prominant H-related resonances in the $U=0$ HLDOS are pushed up in the valence band, the "distance" between these upper valence-band resonances and the upper valence-band edge *in units of U* (with U at its now reduced value) might be comparable to that appropriate for the earlier parameter choice.

Thus the possibility of again obtaining symmetric solutions for [H,C] and [H,O] on account of the effects of the low substitutional-site energy and low H—substitutional-site hopping may be realized for this different range of h_s and h_p. The physical picture would, however, be different from that for the original parameters. Whereas for the original parameters it was the nominal H-like resonance (shifted up by $\sim U$) that tended to appear in the upper valence band in the symmetric solutions for [H,C] and [H,O], it would now be the H-related antibonding resonances (shifted up by the new smaller U) that would be present in the upper valence-band regions in the corresponding symmetric solutions.

Detailed first-principles studies would be relevant here in elucidating the correct picture. We nevertheless feel that, regardless of the specific scenario with respect to the choice of h_s and h_p, the roles of both the substitutional-site—energy stagger and reduced strength of H-substitutional hybridization (relative to Ge) are important in leading to symmetric solutions for [H,C] and [H,O].

VIII. DISCUSSION AND CONCLUSION

We have considered the issue of the charge state of H in pure crystalline Ge, and that of H near substitutional C and O in crystalline Ge. Hydrogen is a rapidly diffusing interstitial in pure Ge, but is bound to substitutional C and to what is believed to be substitutional (in conjunction with H) O. A main issue has been the understanding of the physical mechanisms involved in the facts that, (1) H in pure Ge is neutral, (2) [H,C] is a shallow acceptor, and (3) [H,O] is a shallow donor.

As the H site is moved closer to the substitutional, the following qualitative changes take place: (1) The overall H-lattice hybridization is increased (less so for substitutional C and O than for pure Ge on account of their smaller atomic sizes), which implies (2) the effective U is reduced, and (3) the role of the substantially lower substitutional site energies for C and O with respect to Ge in lowering the energies of the upper valence-band resonances and/or gap states in the HLDOS is increased.

Results for these preliminary, physically consistent, and suggestive choices of parameters were that for $\vec{R}_H$ from the cage center to within ~ 1.9 a.u. (i.e., 40% of the Ge near-neighbor distance) of the substitutional site in the [111] direction, the H site in pure Ge was singly occupied. For [H,C] and [H,O], singly occupied solutions were found for H near the cage center, whereas doubly occupied solutions, corresponding to [H,C] being an acceptor and [H,O] being a donor, were found for H near the substitutional atom (still with $R_H > 1.9$ a.u.).

These conclusions for the charge characters are qualitatively consistent with what is expected on empirical bases: Experiments suggest that H is very near the substitutional atom in the [H,C] and [H,O] complexes, and we have seen that in that case the correct charge character can be understood within our model. On the other hand, H in pure Ge is neutral; this too is implied in our model. It should be emphasized that the conclusions of this calculation should be regarded primarily as suggestive, mainly of the broad mechanisms involved. Indeed, our quantitative results are somewhat sensitive to the specific values of the tight-binding parameters. What has been illustrated, and in a way that elucidates the probable mechanisms involved, is that for parameters which are both individually and mutually (in comparing O, Ge, and C) "reasonable," the empirical facts can be qualitatively accounted for within the simple model utilized.

We should mention that the [H,Si] complex, very analogous to [H,C], has been shown to be an acceptor.[4] However, it was felt that the tight-binding parameters related to Si could not be meaningfully distinguished from those of Ge, and so it was not considered in detail. However, we may observe in view of both the empirical facts and the results of this calculation that H in pure Ge is probably "marginally" neutral, whereas [H,Si] is "marginally" an acceptor.

At this point we might make a preliminary prediction in regard to a possible hydrogen-sulfur complex. It is not unreasonable to expect that S in Ge might behave as does O insofar as going, in conjunction with H, into a tetrahedral site. The atomic site energy parameters for S are $E_{Sd} \approx -5$ eV and $E_{So} \approx -3$ eV. The S-Ge couplings are, moreover, probably comparable to those used in our preliminary model. The H-S hopping is less than that for H-Ge and comparable to that for H-C. Thus, assuming S is substitutional, its parameters fall roughly between those for C and O, both of which are associated with double-occupancy solutions for H near substitutional. It is thus reasonable to expect the [H,S] complex to behave as a shallow donor, mainly as a result of the low value of substitutional site energy.

A number of possibly important effects were not considered in this first study, examples being the effect of going beyond Bethe-cluster topology, charge-transfer and intersite Coulomb effects, next-nearest-neighbor interactions, lattice-relaxation effects, and the effect of locating the H site in a bond. The issues of energetics and H tunneling also remain open. It might be worth considering whether or not the tunneling proceeds by an alternating electronic-state driving mechanism of the type proposed by Baraff *et al.* in connection with diffusion of Al interstitials in Si.[25]

Additional physical questions remain. Why is H attracted to substitutional C, Si, and O? Is, in fact, O substitutional or interstitial (at the cage center) in these complexes, and is the stability of [H,C], [H,O], and [H,Si] relative to diffusing atomic or molecular H in pure Ge?

ACKNOWLEDGMENTS

The author thanks Professor L. M. Falicov for suggesting the problem and for numerous discussions. Thanks also are due Professor E. E. Haller, R. E. McMurray, Jr., and M. O. Robbins for their interest and a number of conversations. Support through IBM and Exxon fellowships and by the National Science Foundation through Grant No. DMR-81-06494 is gratefully acknowledged.

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