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Acceptor complexes in germanium: Systems with tunneling hydrogen

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Experimental data on photothermal ionization spectroscopy of hydrogen-related acceptors in ultrapure germanium are presented. Ground levels do not split under applied uniaxial stresses. A theoretical model based on dynamic tunneling of hydrogen is proposed and analyzed in detail. An overall chemical picture of impurities associated with hydrogen—acceptors and donors—is also presented. It accounts consistently for all known facts related to these complexes: infrared spectra, thermal annealing and quenching, and conditions of crystal growth.

I. INTRODUCTION

Ultrapure germanium with net-acceptor or net-donor concentrations $<10^{11}$ cm^{-3} has recently been developed for use in nuclear radiation detectors. Several new, unknown shallow levels have been discovered in the band gap of this material.[1] The new centers are not related to the well-known acceptors and donors which are due to the presence of substitutional elemental impurities.[2] Experimental and theoretical results on two of these unknown acceptors, which we call A(H,Si) and A(H,C), are presented in this paper. Both acceptors figure in the literature under various labels and changing these to the above names was found to be necessary because it identifies their nature and facilitates a clear description throughout this work.

The acceptor A(H,Si) has been observed by several investigators. Hall[3] found the acceptor when he rapidly quenched small germanium samples from temperatures of around 700 K. He used crystals grown in a *hydrogen-atmosphere* (one atm) from a melt contained in a synthetic *quartz crucible.* The growth atmosphere proved to be relevant when it was shown that the ground state of this acceptor becomes slightly deeper in crystals grown in a deuterium environment.[4] This isotope shift was direct proof of the presence of hydrogen in A(H,Si). Skolnick *et al.*[5] found this acceptor in some of their germanium samples and called it X. After the discovery of several unknown levels, Haller relabeled the same acceptor A_2, for lack of any physically more meaningful name.[1] Only at this point it became clear that all three investigators had observed the same center. Together with A_2 there always appeared a slightly shallower acceptor (labeled by Haller, A_1) in rapidly quenched samples. We show that A_1 and A_2 are due to the one acceptor A(H,Si). A different acceptor A(H,C) has been observed in rapidly quenched samples of germanium crystals grown in a *hydrogen atmosphere* from a melt contained in *graphite.* This center[2] was earlier called Y and later[1] renamed A_6.

The high purity and close-to-ideal crystallographic perfection of these crystals allow the "hydrogenic"[6] bound excited states to develop undisturbed despite their large size. The transition of a hole, in the case of an acceptor, or an electron, in the case of a donor, from the ground state to one of the bound excited states via the absorption of a photon leads to very sharp lines in the far-infrared spectrum. The ir-absorption technique, which was successfully used for lightly doped crystals,[7] is by several orders of magnitude too insensitive to detect acceptor or donor concentrations which are typical for our crystals ($<10^{11}$ cm^{-3}). Photothermal ionization spectroscopy (PTIS), a photoconductivity technique[8] based on the absorption of a photon from an ir source and subsequent absorption of a lattice phonon which transports the hole (electron) into the valence (conduction) band, has been used extensively for the study of shallow centers.[1,4,5,9] Together with a Fourier-transform spectrometer[10] as the ir source, PTIS has sufficient sensitivity and spectral resolution for all our experiments.

An important feature of shallow acceptor spectra is the fact that the spacings between the lines of the "hydrogenic" series are the same for the different acceptors. The change in ground-state energy makes the "hydrogenic" set appear at different energies in the spectrum. This simple situation stems from the large size of the bound-excited-states orbits. These orbits, most of them p like, extend over many crystal lattice sites and are insensitive to the differences in core structure of the different acceptors. The early high-resolution spectra have stimulated a rigorous theoretical treatment of bound excited states of acceptors[11] based on the effective-mass formalism.[12] The excellent agreement between theory and experiment allows the identification of the various transitions up to highly excited states lying very close to the valence band.

II. EXPERIMENTS

A. Thermal-annealing kinetics and chemical composition of *A*(H,Si)

The acceptor *A*(H,Si) appears always and only in rapidly quenched samples of germanium crystals grown in a hydrogen atmosphere (1 atm) from a melt contained in a quartz crucible. Such crystals, grown in this "standard" way, contain, besides the residual electrically active impurities boron, aluminum, and phosphorous, relatively large concentrations of hydrogen (10^{14} cm^{-3}), oxygen ($5-10\times10^{13}$ cm^{-3}), and silicon ($<10^{15}$ cm^{-3}). The latter two impurities are introduced into the germanium melt by the slow reduction of the crucible by the liquid germanium. Only the concentration of oxygen can be determined with good accuracy by the lithium precipitation technique.[13] The hydrogen concentration is estimated by using the experimental results of Frank and Thomas.[14] An upper limit for silicon can be obtained from spark-source mass spectrometry.[15]

Hall[3] recognized in his experiments that the annealing kinetics of *A*(H,Si) varies along the axis of the crystal. Near the "seed" end where the [Si]/[O] ratio is a maximum, because of the opposite direction of segregation of these impurities, the converstion of *A*(H,Si) into a donor labeled *D* is incomplete and slow. Near the "tail" end, where [Si]/[O] is a minimum, the conversion is complete and rapid. Hall suggests in his work[3] that silicon may play a direct role in his observations but he weakens his argument by assigning also an indirect role to silicon.

To clarify the situation we doped several crystals (No. 436, No. 618, and No. 631) with large amounts of silicon ranging from 10^{16} to 3×10^{17} cm^{-3}. The crystals were grown under "standard" conditions.

Analysis of several crystal samples with spark source mass spectroscopy showed that practically all the added silicon was contained in the germanium crystals (i.e., no losses of silicon due to gettering, oxidation, etc. were detectable).

Two major differences were observed in the doped crystals as compared to undoped ones. In Fig. 1 the isochronal annealing curves for *A*(H,Si) in two different samples is shown. No conversion to the donor *D* takes place in samples from silicon-doped crystal No. 436 [Fig. 1(b)]. The other curve [Fig. 1(a)] is taken from work by Hall,[3] and illustrates the cases discussed at the beginning of this section. The second observation concerns the free-oxygen concentration in silicon-doped crystals. The lithium precipitation was extremely slow and the final LiO-donor concentration was undetectable in the intrinsic carrier concentration at the precipitation temperature, 300 K, (Fig. 2). This result compares with results obtained from crystals grown in graphite crucibles and indicates an oxygen concentration much smaller than in

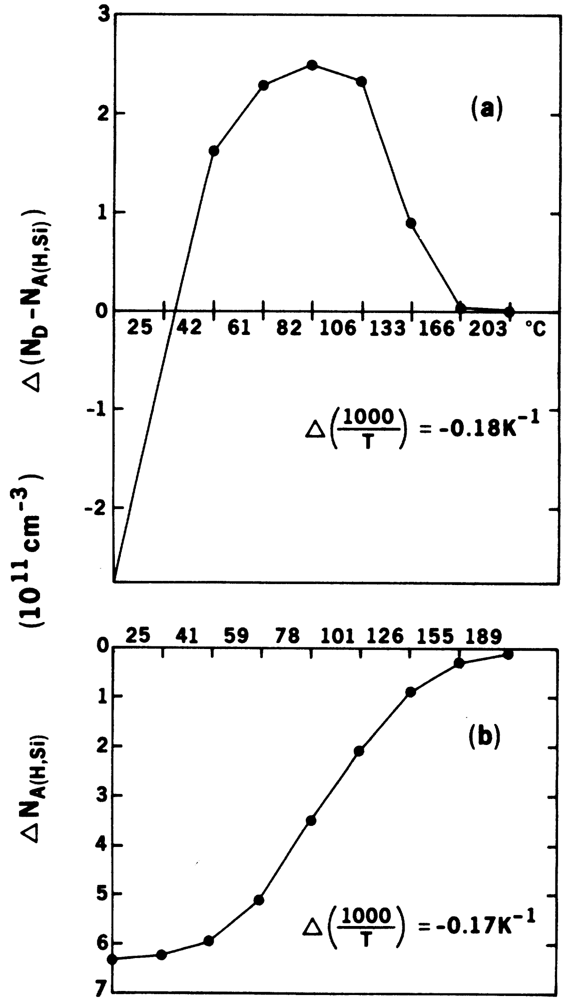

FIG. 1. Isochronal annealing curves for samples containing different amounts of silicon [Fig. 1(a) courtesy of Hall, Ref. 3].

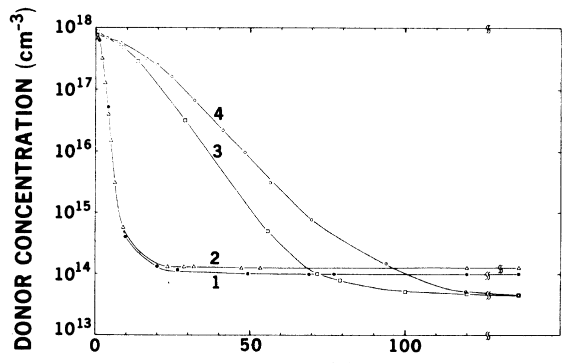

FIG. 2. Li-precipitation curves for four different germanium samples. Samples 1, 2, and 3 were cut from crystals grown under "standard" conditions, but sample 3 contained $[Si]=3\times10^{17}$ cm^{-3}. Sample 4 was cut from a crystal grown out of a graphite crucible.

"standard" crystals. Together with the fact that *A*(H,Si) always and only appears in crystals grown in quartz crucibles, one can draw two conclusions: (i) *A*(H,Si) contains, in addition to the already proven hydrogen,[4] silicon, but no free oxygen; (ii) the donor *D* contains, in addition to hydrogen,[4] free oxygen, but no silicon.

These are further discussed in Sec. IV.

B. Line-intensity studies of *A*(H,Si) and *A*(H,C)

The experimental setup for PTIS is described in detail elsewhere.[16] Briefly, it consists of a Fourier-transform spectrometer with an on-line computer capable of a resolution of $< 8\ \mu$eV. The ir light is guided through a $\frac{1}{2}$-in-diameter brass pipe to the germanium sample. The sample is mounted inside a cavity kept at constant temperature between 2 and 20 K. Cold black polyethylene and Yoshinaga filters[17] shield the sample from any radiation above 125 cm^{-1}.

Germanium samples were cut and lapped to a size of $7 \times 7 \times 2$ mm^3. After removing all mechanical surface damage and impurities by chemically etching,[18] the samples were immersed for 30 min in a lead-bismuth eutectic bath at 700 K. Rapid quenching was achieved with two opposing high-velocity nitrogen jets. Lapping, chemical etching and application of indium-gallium eutectic contacts on two opposing, narrow faces completed the sample preparation. No time constraints in sample preparation[3] had to be considered because silicon-doped crystals were used for the *A*(H,Si) study (see Fig. 1). Two typical PTIS spectra recorded at $T = 9.0$ and 4.2 K of a sample containing *A*(H,Si) are shown in Fig. 3. Due to the thermal part of the two step process in PTIS the intensity of the lines decreases rapidly with decreasing temperature and with increasing energy between the valence-band top and the corresponding bound excited state.

Since different shallow acceptors produce identical sets of "hydrogenic" lines, the *ratios* of intensities of equivalent lines of different acceptors are *independent* of temperature. In Fig. 3 two series can be easily distinguished. We label them $A(\mathrm{H,Si})_1$ and $A(\mathrm{H,Si})_2$. In Fig. 4 the ratios of the intensities of these two series are plotted as functions of temperature: the ratios are not constant but follow precisely a Boltzmann

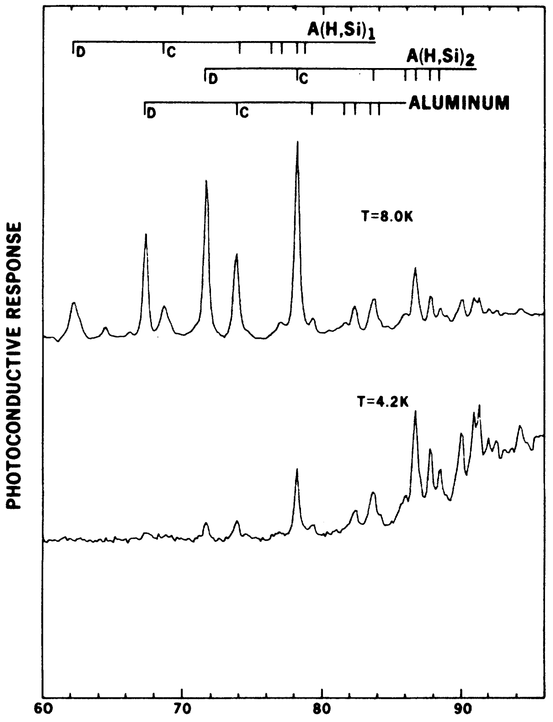

FIG. 3. PTIS spectra of a sample containing *A*(H,Si) and aluminum acceptors.

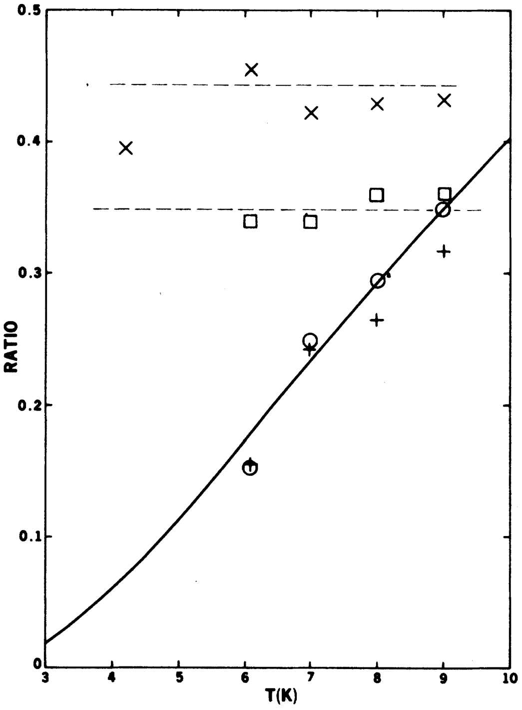

FIG. 4. Ratio of the intensities of the *C* lines in the two series of *A*(H,Si) (circles) and the *D* lines in the same series (plus signs) are proportional to a Boltzmann factor exp(1.1 meV/kT). The ratio of the sum of the intensities of the *C* lines of *A*(H,Si) to the intensity of the aluminum acceptor *C* line is temperature independent (squares). The same holds for the *D* lines (x's).

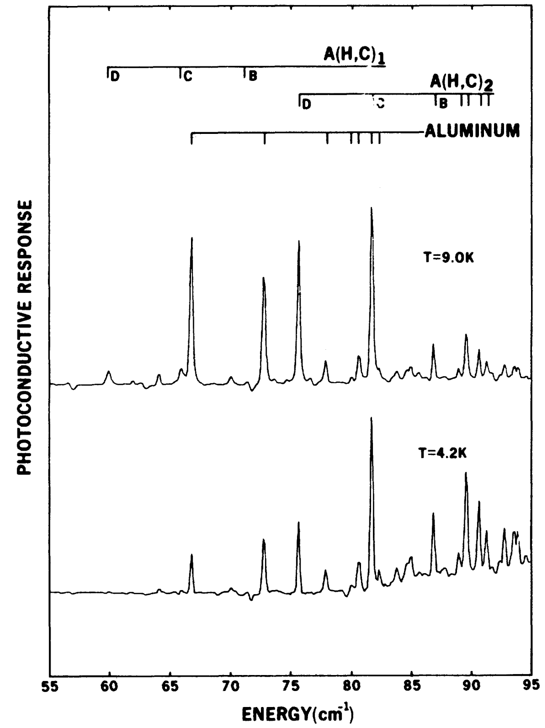

FIG. 5. PTIS spectra of a sample containing A(H,C) and aluminum acceptors.

factor, $\exp(E/k_BT)$, with an energy $E = 1.1$ meV. This is also the separation between equivalent lines. In addition the ratio of the *sum* of the intensities of equivalent $A(\mathrm{H,Si})_1$ and $A(\mathrm{H,Si})_2$ lines to that of the corresponding line in the aluminum acceptor series remains constant, independent of temperature (see Fig. 4). We conclude that $A(\mathrm{H,Si})_1$ and $A(\mathrm{H,Si})_2$ belong to only one acceptor, A(H,Si), which has a ground-state manifold split into two levels separated by 1.1 meV. This is a situation equivalent to donors in germanium[19] and silicon, which exhibit a chemical valley orbit splitting. The assignment of $A(\mathrm{H,Si})_1$ and $A(\mathrm{H,Si})_2$ to the same acceptor is a completely new result, not found in any known simple elemental acceptor.

A similar experimental finding was made for the A(H,C) acceptor with a larger ground-state manifold splitting of $E = 1.9$ meV. The substantially larger splitting leads to a much more rapid depopulation of the upper state with decreasing temperature. To obtain sufficiently intense lines from this higher level one has to choose temperatures so high (> 9 K) that the PTIS signal, because of thermal ionization of the acceptor (Fig. 5), is already substantially reduced. This must be the main reason why the upper-state set of lines has not been observed previously.

C. Piezospectroscopic studies of A(H,Si) and A(H,C)

The behavior of acceptors due to substitutional elemental impurities under uniaxial stress is well understood.[20] A force F parallel to a $\langle 111 \rangle$ direction splits the ground level much more than it does the bound excited levels. This produces a symmetric splitting of all the "hydrogenic" lines in the PTIS spectrum into two components with equal intensity, as can be seen[21] in Fig. 6. In contrast to the normal elemental acceptors no splitting occurs for the two line sets belonging to A(H,Si). Only a very slight shift of equivalent lines of the two series towards each other can be detected. This observation cannot be explained with a center which has a locally built-in stress in the $\langle 111 \rangle$ direction. Any external additional stress would lead to at least two, and in the general case to four, different groups of A(H,Si) acceptors depending on their orientation.

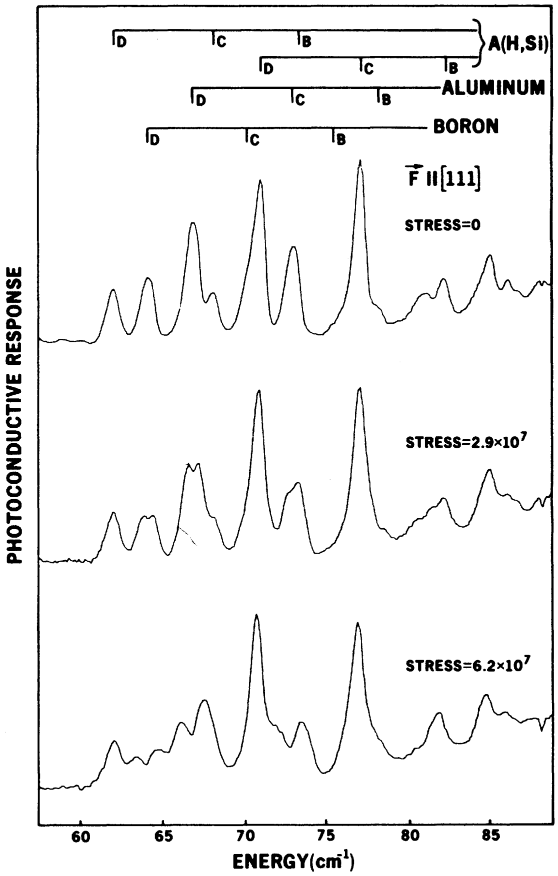

FIG. 6. Uniaxial-stress spectra of a sample containing A(H,Si), boron, and aluminum. The lines of the chemical acceptors split symmetrically with stress. The lines of the two series of A(H,Si) do not split.

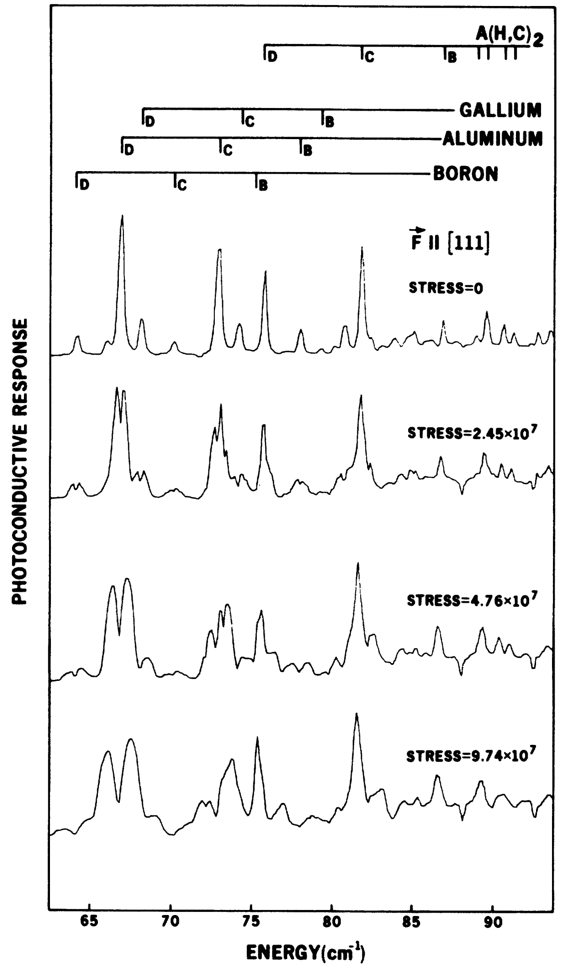

FIG. 7. Uniaxial-stress spectra of a sample containing A(H,C), gallium, aluminum, and boron. The lines of all the chemical acceptors split, the lines of A(H,C) do not.

The situation for A(H,C) is precisely analogous. Both sets of lines do not split under uniaxial stress in the $\langle 111 \rangle$ direction as can be seen in Fig. 7. Again a very slight shift of equivalent lines of the two sets towards each other can be detected.

The results for stress in a $\langle 100 \rangle$ direction show the same lack of ground-level splitting for A(H,Si) and A(H,C). Due to the relatively strong splitting of the bound excited states the spectra are more complex than for the case with F parallel to $\langle 111 \rangle$.

III. THEORY

A. General considerations

The most striking experimental fact in these shallow-acceptor families is that the ground state does not split with stress. All other shallow acceptor levels observed so far have been identified as a Γ_8 symmetry level and they do split under stress.

The top of the valence band in the Ge electronic structure[22,23] is fourfold degenerate and belongs to the Γ_8^+ representation at the point Γ in the Brillouin zone. This representation is isomorphic[24] to the Γ_{8g} of the full cubic group O_h. The ground state of an ordinary shallow acceptor in Ge must have the symmetry corresponding to the direct product of the symmetry of the envelope F and the symmetry of the Bloch function at the top of the valence band.

For a substitutional impurity, the point symmetry is only tetrahedral T_d. In that case since[24]

$$\Gamma_8^+(\text{diamond structure}) \rightarrow \Gamma_8(T_d) \ ,$$

and since the envelope function is of the high-symmetry $1s$ type

$$1s(\text{hydrogen atom}) \rightarrow \Gamma_1(T_d) \ ,$$

the total symmetry of an acceptor state is

$$\Gamma_1 \otimes \Gamma_8 = \Gamma_8 \ ,$$

i.e., a fourfold degenerate level. Any uniaxial stress should lift the degeneracy.

The above result is very general[11] and is independent of the specific approximation used to describe the one-electron impurity state (e.g., effective-mass approximation, simple-product wave function, specific central-cell effects, etc.).

An impurity state with a symmetry lower than tetrahedral cannot explain the observed spectrum because the lower symmetry would produce in the crystal a set of equivalent but not identical sites which would yield different behaviors under uniaxial stress and, therefore, split the spectral lines. For instance, an impurity localized in a Ge—Ge bond gives four equivalent positions and thus, four different signals for an arbitrary uniaxial stress.

The observed experimental spectrum clearly indicates an impurity state of high symmetry (tetrahedral or higher), but whose ground state is either a single level (Γ_1 or Γ_2 in the group T_d) or a Kramers doublet (Γ_6 or Γ_7 in T_d) which cannot be split under a uniaxial lowering of the symmetry. This dramatic change in symmetry of the ground state can be brought about by only two mechanisms: (a) the envelope of the impurity state has a symmetry other than Γ_1; or (b) there is an extra degree of freedom in the system which provides to the wave function a contribution of symmetry other than Γ_1.

In Table I we give the direct product of Γ_8 with the eight irreducible representations of T_d. An inspection of the table shows that in either case the required symmetries which could give rise to a total Γ_1, Γ_2, Γ_6, or Γ_7 symmetry are Γ_3, Γ_4, Γ_5, or Γ_8.

Mechanism (a) is not a very plausible one. The fact that these acceptors are shallow ones makes it unlikely that the envelope of the electronic wave

TABLE I. Direct product of Γ_8 with the eight irreducible representations of T_d.

$$\Gamma_1 \otimes \Gamma_8 = \Gamma_8$$

$$\Gamma_2 \otimes \Gamma_8 = \Gamma_8$$

$$\Gamma_3 \otimes \Gamma_8 = \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8$$

$$\Gamma_4 \otimes \Gamma_8 = \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8 \oplus \Gamma_8$$

$$\Gamma_5 \otimes \Gamma_8 = \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8 \oplus \Gamma_8$$

$$\Gamma_6 \otimes \Gamma_8 = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$$

$$\Gamma_7 \otimes \Gamma_8 = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$$

$$\Gamma_8 \otimes \Gamma_8 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_4 \oplus \Gamma_5 \oplus \Gamma_5$$

function, which extends over very many lattice unit cells, would differ appreciably from the simple hydrogenic model. Therefore an electronic contribution other than Γ_1 (i.e., an envelope very different from a $1s$ function such as a p-type ground state) is not to be expected.

On the other hand the experimental information clearly points out that hydrogen as well as silicon or carbon are involved in these acceptors. This indicates that the acceptor centers must definitely have an internal structure, and therefore mechanism (b) becomes a very likely one. This would also indicate that spin is not essentially involved in this structure[25] and therefore one would expect a Γ_3, Γ_4, or Γ_5 symmetry type in this internal structure degree of freedom, and consequently a Γ_6 or Γ_7 symmetry for the total wave function (electronic plus internal structure) of the whole acceptor.

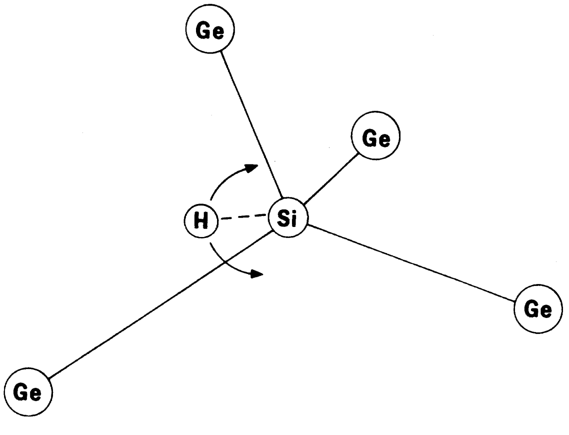

FIG. 8. Schematic representation of the Si–H impurity complex, with Si in a Ge-substitutional position.

The simplest model one can imagine for the sake of definiteness is a Si–H impurity system, with Si at a point in the structure with tetrahedral symmetry (either a Ge site or a "big hole" site equidistant from four Ge neighbors) and a proton dynamically attached to it (see Fig. 8). Haller and Falicov[26] have shown that the Li–O impurity system is a dynamic donor; the systems we include here are in a sense the acceptor counterparts, but the spectra are of course radically different.

B. Hamiltonian

We now develop a formalism which allows us to study the *ground-state manifold* of the dynamic acceptor system. We write the theory in a very general form, but it is useful as a concrete guide to imagine a Si substitutional impurity with a single H^- center attached to it. The Hamiltonian can be written as the sum of three terms

$$H = H_e + H_n + H_{en} \ . \tag{3.1}$$

Here H_e describes the kinetics of an unbound hole in the germanium lattice, H_n the dynamics of the internal degree of freedom of the acceptor complex (e.g., the dynamics of the Si–H^- system), and H_{en} the interaction between the two. If we denote by $\vec{r}$ the coordinate of the hole with respect to the center of mass and by $\vec{R}$ the internal degree of freedom coordinates

$$H_{en} = -\frac{e^2}{\epsilon r} + V(\vec{r}, \vec{R}) \ . \tag{3.2}$$

In Eq. (3.2) the first term describes the electrostatic potential felt by the hole at large distances (i.e., the "hydrogenic" term), and $V(\vec{r}, \vec{R})$ is the "central-cell" potential which depends sensitively on the $\vec{R}$ degrees of freedom. The terms

$$H_a \equiv H_e - \frac{e^2}{\epsilon r} \tag{3.3}$$

correspond to an ordinary isocoric hydrogenic acceptor, whose ground-state manifold yields the fourfold degenerate Γ_8 energy level, which we label E_e. The four functions which comprise that level transform under the operations of the group like the spin $J = \frac{3}{2}$ states of a p level of the hydrogen atom. We denote them as follows:

$$\begin{aligned}
\chi_3 &\equiv |\tfrac{3}{2},\tfrac{3}{2}\rangle \Rightarrow 2^{-1/2}(x+iy)\uparrow \ , \\
\chi_1 &\equiv |\tfrac{3}{2},\tfrac{1}{2}\rangle \Rightarrow 6^{-1/2}[2z\uparrow - (x+iy)\downarrow] \ , \\
\chi_{\bar{1}} &\equiv |\tfrac{3}{2},-\tfrac{1}{2}\rangle \Rightarrow 6^{-1/2}[2z\downarrow + (x-iy)\uparrow] \ , \\
\chi_{\bar{3}} &\equiv |\tfrac{3}{2},-\tfrac{3}{2}\rangle \Rightarrow 2^{-1/2}(x-iy)\downarrow \ .
\end{aligned} \tag{3.4}$$

In Eqs. (3.4) the functions x, y, and z transform according to the Γ_5 representation[24] of T_d (i.e., as p states), and the ↑ and ↓ spinors according to Γ_6.

The eigenstates of H_n require some discussion. If the "mass" attached to the $\vec{R}$ degrees of freedom were infinite, i.e., all kinetic or tunneling effects were to be disregarded, there would be a number of equilibrium positions $\vec{R}_l$ of $\vec{R}$ corresponding to the minima of the potential energy. The number of minima must be compatible with the symmetry of the acceptor and crystal; for T_d symmetry and $\vec{R}_l \neq 0$ the smallest number is four, and so we assume is our case. For nonvanishing but finite "mass", i.e., when dynamic effects must be taken into account, these four positions give rise to four independent ground-state wave functions which we label

$$\begin{aligned} \phi_A &= [111] \Rightarrow \tfrac{1}{2}[S+X+Y+Z] \ , \\ \phi_B &= [1\bar{1}\bar{1}] \Rightarrow \tfrac{1}{2}[S+X-Y-Z] \ , \\ \phi_C &= [\bar{1}1\bar{1}] \Rightarrow \tfrac{1}{2}[S-X+Y-Z] \ , \\ \phi_D &= [\bar{1}\bar{1}1] \Rightarrow \tfrac{1}{2}[S-X-Y+Z] \ . \end{aligned} \tag{3.5}$$

In Eqs. (3.5) we have oriented the four positions $\vec{R}_l$ along the $\langle 111 \rangle$ axes, and the functions S and $\{X,Y,Z\}$ are functions of $\vec{R}$ which transform according to the Γ_1 and Γ_5 representations of T_d. In this representation, and neglecting all other states, H_n can be written as a (4×4) matrix given by

$$H_n = \begin{bmatrix} E_n & t & t & t \\ t & E_n & t & t \\ t & t & E_n & t \\ t & t & t & E_n \end{bmatrix} , \tag{3.6}$$

whose eigenvalues are (E_n+3t), a Γ_1 singlet; and (E_n-t), a Γ_5 triplet. The matrix element t can be thought of as a tunneling contribution.

The total wave function of the complex acceptor can now be written as a linear combination of functions which are direct product functions

$$\{\phi_l\} \otimes \{\chi_m\}; \quad l = A,B,C,D; \quad m = 3,1,\bar{1},\bar{3} \ .$$

There are 16 such functions in our manifold $\phi_A\chi_3$, $\phi_A\chi_1, \ldots, \phi_D\chi_{\bar{3}}$, which for simplicity are denoted by $A3$, $A1, \ldots, D\bar{3}$. We study our problem in this restricted basis and diagonalize the (16×16) matrix obtained from Eq. (3.1) in this set. The matrix elements are of various forms: (i) The diagonal matrix elements

$$\langle lm | H_e + H_n - e^2/\epsilon r | lm \rangle = E_e + E_n \ , \tag{3.7}$$

(ii) the off-diagonal elements of H_n

$$\langle lm | H_n | l'm' \rangle = t\delta_{mm'} \ , \tag{3.8}$$

(iii) the matrix elements of $V(\vec{r},\vec{R})$ can be easily expressed in terms of two reduced matrix elements:

$$\langle lm | V | l'm' \rangle = V_0 C_{l,mm'} \delta_{ll'} + V_1 D_{ll',mm'} (1-\delta_{ll'}) \ . \tag{3.9}$$

In Eq. (3.9) V_0 is the central-cell potential contribution, V_1 is a combined electronic-internal-structure potential, and $C_{l,mm'}$ and $D_{ll',mm'}$ are generalized "Clebsch-Gordan" coefficients corresponding to the T_d group (see Appendix).

The rather complicated (16×16) matrix can be diagonalized by standard group-theoretical techniques. It corresponds to the reduction of

$$(\Gamma_1 \oplus \Gamma_5) \otimes \Gamma_8 \Rightarrow \Gamma_6 \oplus \Gamma_7 \oplus 3\Gamma_8 \ , \tag{3.10}$$

which yields eigenvalues

$$E(\Gamma_6) = E_e + E_n + 2V_0 + \tfrac{1}{3}V_1 - t \ , \tag{3.11}$$

$$E(\Gamma_7) = E_e + E_n + 2V_0 - V_1 - t \ , \tag{3.12}$$

and a (3×3) matrix for the Γ_8 levels

$$\begin{bmatrix} E_e + E_n + \tfrac{1}{2}V_0 - V_1 - t & \tfrac{1}{2}V_0 & \tfrac{1}{2}\sqrt{2}V_0 \\ \tfrac{1}{2}V_0 & E_e + E_n + \tfrac{1}{2}V_0 + \tfrac{1}{3}V_1 - t & \tfrac{1}{2}\sqrt{2}V_0 \\ \tfrac{1}{2}\sqrt{2}V_0 & \tfrac{1}{2}\sqrt{2}V_0 & E_e + E_n + V_0 + V_1 + 3t \end{bmatrix} . \tag{3.13}$$

No simple solution exists for Γ_8 and for arbitrary values of V_0, V_1, and t. The results are, however, very simple if either V_0 or V_1, is zero. The $V_0 = 0$ results are the diagonal elements in (3.13), and the $V_1 = 0$ values are

$$\begin{aligned} E_1(\Gamma_8, V_1 = 0) &= E_e + E_n - t \ , \\ E_\pm(\Gamma_8, V_1 = 0) &= E_e + E_n + V_0 + t \pm (V_0^2 + 4t^2)^{1/2} \ . \end{aligned} \tag{3.14}$$

If both $t = V_1 = 0$, the four l configurations are independent and equivalent. Each one has a C_{3v} symmetry and the Γ_8 electronic level splits into a Λ_4 doublet and a $\Lambda_5 \oplus \Lambda_6$ doublet

$$\begin{aligned} E(\Lambda_4) &= E_e + E_n + 2V_0 \ , \\ E(\Lambda_5, \Lambda_6) &= E_e + E_n \ . \end{aligned} \tag{3.15}$$

The tunneling contribution t couples the four otherwise unrelated configurations yielding four quadruplets: three Γ_8 levels and degenerate Γ_6 and Γ_7 doublets. The mixed electronic-tunneling contribution V_1 removes this accidental degeneracy.

The physics of our system requires that the ground state be a doublet, either Γ_6 or Γ_7. Since these doublets arise only from the direct product of $\Gamma_3 \otimes \Gamma_8$ and not from $\Gamma_1 \otimes \Gamma_8$, it is therefore necessary to have in the H_n eigenstate manifold the triplet with energy lower than the singlet. Examination of Eq. (3.6) and its eigenvalues shows that t must be a positive quantity. This, of course, can also be obtained directly from examination of Eqs. (3.11)–(3.13). This result implies that the nuclear complex (e.g., the dynamic Si–H$^-$ system) is in a p-state configuration. It is instructive to realize that in the Γ_6 state the Si–H$^-$ tends to be located in the plane of the hole orbit, and in the Γ_7 state it lies perpendicular to the hole-orbit plane.

Further examination of the equations above indicates that V_0 must be a negative quantity and that the sign of V_1 determines whether $\Gamma_6(V_1<0)$ or $\Gamma_7(V_1>0)$ is the ground-state doublet.

$$E(\Gamma_6)-E(\Gamma_7)=\tfrac{4}{3}V_1 \ . \tag{3.16}$$

In the case of the A(H,Si) system, the splitting between $A(\text{H,Si})_1$ and $A(\text{H,Si})_2$ is measured to be 1.1 meV, which yields (in meV)

$$|V_1|=0.82 \ .$$

This may appear to be a substantial number for an interaction which involves a nuclear tunneling and an electronic transition. It should be remembered, however, that H is indeed a very light atom and its nuclear wave function is expected to be sufficiently spread out so as to have a sizeable effect on the electronic wave function. A large $|V_1|$ also implies a large value of t, at least of the same order of magnitude.

The values of t and V_0 can only be accurately known if the Γ_8 energy levels are determined; since these have not been observed we can only estimate their values and some upper and lower bounds. The lower bounds arise from the experimental observation that all Γ_8 levels are higher in energy than both Γ_6 and Γ_7. In Fig. 9 we give, in the $t-V_0$ plane, the regions in parameter space for which this condition is satisfied. The basic results are that $V_0 \lesssim -|V_1|$ and that $t \gtrsim (-\frac{1}{4}V_1)$ for $V_1<0$ or that $t \gtrsim V_1$ for $V_1>0$.

Approximate upper bounds can also be found by noting that V_0 is essentially an ordinary central-cell correction, and that the Γ_8 levels are not likely to be at energies very different from the two doublets. In fact, as shown by Eq. (3.15), in the absence of dynamic effects in the nuclei, one quadruplet is degenerate with the (then degenerate) doublet pair. We know that these acceptors are shallow, and the binding energy differs from a pure hydrogenic model by a few meV in each case: ΔE the difference between measured ground-state energy for A(H,Si) and its hydrogenic effective-mass value[1,11] is $\Delta E \sim -2$ meV. This energy should be[27] approximately equal to $2V_0-\frac{1}{3}|V_1|$ if Γ_6 is the ground state, and to $2V_0-|V_1|$ if Γ_7 is lower, as indicated by Eqs. (3.11) and (3.12). It follows from the above that $|V_0|$ cannot be much larger than $|V_1|$, which indicates clearly that the Γ_8 quadruplets must be very close to the upper doublet (see Fig. 9).

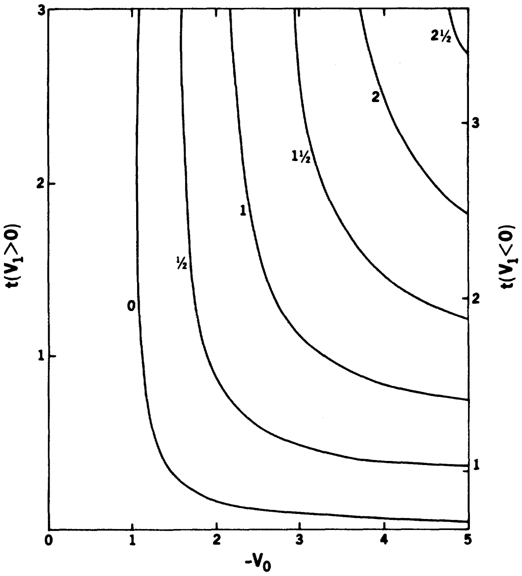

FIG. 9. Region in the $|t/V_1|-|V_0/V_1|$ space for which all Γ_8 quadruplets lie above the Γ_6 and Γ_7 doublets. The numbers in the curves correspond to the difference between the lowest Γ_8 and Γ_6, the upper level when $V_1>0$ (left scale) or between Γ_8 and Γ_7 when $V_1<0$ (right scale). All energies are expressed in units of $|V_1|$.

C. Effect of uniaxial stress

We have made a qualitative calculation of the effect of uniaxial stress on these levels. It is assumed that under such a stress a p-type state with symmetry axis oriented along the stress decreases its energy by an amount 2ϵ for the electronic part H_e, and $2\epsilon'$ for the nuclear components H_n, and the p states with symmetry axis perpendicular to the direction of stress increase their energy by ϵ and ϵ' respectively. The ratio of the energy shifts $s \equiv (\epsilon'/\epsilon)$ is unknown. We concentrate our attention on the two doublets Γ_6 and Γ_7. Under uniaxial stress applied along the [111] direction both Γ_6 and Γ_7 reduce to the Λ_4 representation of the new group of the Hamiltonian C_{3v}. The symmetry of the ground state under stress is therefore independent of its original symmetry and from our calculations so is the shift. Experimentally it was observed that $A(\mathrm{H,Si})_1$ and $A(\mathrm{H,Si})_2$ move slightly toward each other under compressive stress. From our theoretical considerations this occurs when the separation between the Γ_8 levels and the upper doublet (whether Γ_6 or Γ_7) is small and when s is not too large. Typically for a separation between doublet and quadruplet of $\frac{1}{2}|V_1|$, this approaching of the doublets takes place if s is smaller than 6. This result agrees with our previous conclusion.

With stress along [001] the situation is quite different. The symmetry group of the Hamiltonian is now D_{2d} and the two levels remain distinct. The Γ_6 and Γ_7 levels of T_d reduce now to the Γ_6 and Γ_7 levels of D_{2d}, respectively. We therefore expect different behaviors depending on the original symmetry of the ground state. We also find that the results are very sensitive to the value of s. In the limit of small s and when one of the Γ_8 levels is close to the upper doublet, $A(\mathrm{H,Si})_1$ and $A(\mathrm{H,Si})_2$ should move away from one another if Γ_6 is the ground state but significantly towards one another if Γ_7 is the ground state. The rate of change for the latter case is much larger for a stress along [001] than for a stress along [111], a factor of nearly 6 if the separation between the Γ_8 levels and the top doublet is $\frac{1}{2}|V_1|$. This factor, however, decreases quite rapidly with s. Comparison with experimental data becomes very difficult for $\langle 001\rangle$ stresses because of the sizeable splitting of the excited electronic bound states.

IV. OVERALL MODEL AND CONCLUSIONS

In this section we present a general scheme to explain globally the experimental data. We attempt to put together the different pieces of the puzzle in a simple framework. The starting point of our discussion is the theoretical model of Sec. III. We have shown in Sec. III that a shallow acceptor with a ground state constituted of two unsplittable doublets can arise from a dynamical tunneling system with the separation between the two doublets being a measure of the strength of the tunneling. The values of the parameters that reproduce the experimental data appear reasonable and would be characteristic of a hydrogen atom tunneling around an atomic center such as Si. Indeed for $A(\mathrm{H,Si})$ we find that $|V_1| \simeq 0.82$ meV and $t \simeq |V_1|$ (see Fig. 9). This is more than an order of magnitude larger than the value found in Li–O where the tunneling matrix element[26] is $t \simeq 0.027$ meV. But as a simple argument can show the tunneling matrix element associated with the transmission of a particle through a barrier is essentially proportional to $\exp(-\alpha m^{1/2})$, where α is a function of the energy of the particle and the strength of the potential barrier, and m is the mass of the particle.[28] The mass of Li is six or seven times that of H. Hence as one goes from Li to H the tunneling matrix element should increase by at least an order of magnitude. That Si–H is the system giving rise to the $A(\mathrm{H,Si})$ series is also made plausible by chemical arguments. Silicon has a valence of 4. Lying substitutionally in the Ge lattice, it will share its four electrons in covalent bonds with the neighboring Ge and act as an attractive center for hydrogen. The hydrogen-atom electron is, on the other hand, very tightly bound. Hydrogen is known to be "electrically inactive" even at room temperature. Pickett *et al.*[29] have shown that the binding energy of the hydrogen-atom electron in Ge is at least 1 eV, and probably as much as 6 eV. An even more tightly binding orbital is therefore likely to be located between the H and Si atoms, attracted by the positive charge of both centers.

If electron-electron repulsion is not too strong, that orbital could be doubly occupied. The overall Si–H complex thus acts as a neutral single shallow acceptor.

The excited states of the acceptor hole are expected to be very much the same as those of any other shallow acceptor such as B, Al, Ga, or In. The ground state, however, with a large probability in the neighborhood of the central cell, is strongly coupled to the motion of the H^-.

The $A(\mathrm{H,Si})$ acceptor is associated with a donor, D. A candidate for D would be a system obtained from $A(\mathrm{H,Si})$ by adding an external atom to the acceptor complex as suggested by Hall.[3] But the rapid rate of conversion at room temperature requires a very fast diffusing interstitial, and we know that the only difference between D and $A(\mathrm{H,Si})$ is the presence of oxygen, which does not diffuse rapidly. A simpler and more natural choice would be to suppose that D is an O–H complex with oxygen lying substitutionally and hydrogen orbiting around it. This is similar to the Li–O complex, the main differences arising from the very small size and mass of hydrogen. By analogy, the O–H complex is likely to be a shallow donor.

The electronic structure of oxygen and its smaller size makes the O–H complex considerably more stable than the Si–H system. With the above scheme, the behavior of the two types of states under quenching and annealing can be simply explained. When the temperature is sufficiently high, those hydrogen atoms which were trapped in not too deep potential wells such as Si, O, small defects, or were bound as molecular H_2 are freed and are randomly distributed throughout the crystal. Under fast quenching, their kinetic energy drops abruptly and they are trapped in the nearest potential well. The faster the cooling the more likely they are to remain also on the weaker potential wells, such as the Si centers. Depending therefore upon the relative population of the different impurities and defects and upon the rate of cooling, the crystal may be *p* or *n* type. The experimental data so far reported on the rapidly quenched-in defects in high-purity Ge correspond to one of the three following cases: (i) The density of Si is much larger than that of oxygen and most oxygen atoms are bound as SiO_2 [Fig. 1(b)]. (ii) The density of Si is larger than that of oxygen but there are still "free" oxygen atoms available. (iii) The density of Si is comparable to that of oxygen [Fig. 1(a)]. In all three cases the concentration of A(H,Si) is much smaller than those of oxygen and silicon.

In case (i) no donor can be formed and the rate of decrease in the number of acceptors under annealing is the rate of dissociation of the acceptor complex A(H,Si), i.e., the rate at which the H atoms thermally free themselves from the attractive Si potential [Fig. 1(b)].

In case (iii), the acceptors convert quickly to donors. There is close to every Si–H system an oxygen center and as the temperature is raised the hydrogen hops to the more attractive oxygen and forms a donor. The shape of the variation of $(N_D - N_A)$ as a function of temperature is equal to the rate of dissociation of A(H,Si), plus the rate of formation of D, with enhancements due to interactions between the nearest centers. For these reasons it is a much larger slope than in (i). The initial number of acceptors depends clearly on the rate and temperature of quenching, as mentioned above.

Case (ii) is intermediate between (i) and (iii). Because of the smaller number of available oxygens the conversion is slower. The dip observed in $(N_D - N_A)$ by Hall (Ref. 3, Fig. 3) at the dissociation temperature of the donors is an interesting effect which can be explained by the fact that not all the free hydrogen atoms find an oxygen atom and there is a remaining number of A(H,Si) still present beyond the ~410 K annealing steps.

In all three cases our arguments are supported by the irreversibility of the annealing process. When the temperature is raised again to the quenching temperature T_Q, the hydrogen evolution can be repeated and another quenching and annealing sequence should display a behavior identical to the first. This is precisely what has been observed.

It is also found that in case (iii) the maximum number of acceptors is approximately equal to the maximum number of donors [see Fig. 1(a)]. This means that during the annealing process the number of donors created is equal to the number of A(H,Si) destroyed. At first thought this might appear to be a strong argument in favor of Hall's hypothesis, i.e., that the donors are formed by adding something to the acceptors. It may, however, also be explained within our model. After the quenching the free H have settled on the nearest potential wells be it Si, O, or some defects. Among all the potential wells the Si ones are probably the shallowest and under annealing at the temperatures we are considering they are the first ones (and probably the only ones) from which the hydrogens leave to form the oxygen related donors. The change in $(N_D - N_A)$ is hence essentially due to a conversion of N_A into N_D.

The whole chemical picture presented here, with a complete conversion of acceptors into donors requires a concentration of free hydrogen smaller than the oxygen and silicon concentrations; the hydrogen concentration is the limiting factor throughout.

The other acceptor A(H,C), clearly of the same type as A(H,Si) but with a larger splitting, should be similar. It is formed in crystals grown in graphite crucibles and in quartz crucibles coated with pyrolitic graphite. It is tempting to speculate that sufficient carbon is dissolved in the melt to produce the A(H,C) complex. Germanium and carbon have been shown to be immiscible on a macroscopic scale, but nothing is known about concentrations as small as the ones reported here.

The C–H complex is similar to Si–H but with an even larger tunneling matrix element and a larger dissociation temperature. It does not convert as easily to a donor because crystals grown in a graphite environment contain, typically, two orders of magnitude less oxygen than crystals grown in quartz crystals (see Fig. 2).

The overall picture that we have presented of these systems is, with high probability, a definitive interpretation of the experimental data. Some arguments are supported by hard experimental facts [e.g., the presence of hydrogen in A(H,Si) by isotope shifts, the splitting of the ground-state manifold, and the temperature-dependent Boltzmann factor]. Other arguments are strongly supported by correlation experiments, such as the presence of C or Si in these centers. There is also a not negligible amount of intuition required to blend all this information into a complete, coherent picture. This is altogether very appealing by its simplicity and it is encouraging to note that not one aspect of the experimental data disagrees with our model. It should be kept in mind, when considering these impurity complexes, that the concentrations we are considering are very low (10^{10} to 10^{11} cm^{-3}) and that some usually accepted facts, such as the lack of solubility of carbon in germanium may be quantitatively irrelevant in these circumstances.

As a closing remark we would like to point out that hydrogen is traditionally thought of as a deep donor[29] in which, because of strong correlation effects the hydrogenic electron orbital, deep in the valence band, is only singly occupied. The presence of an isoelectronic impurity (Si or C) in Ge seems to be sufficient to stabilize the occupation by a second electron of the deep orbital, thus converting the system from a deep donor into a shallow acceptor. In this sense the

A(H,Si) and A(H,C) complexes are similar to negatively charged donors: the addition of a second deep electron pushes the electronic energy up in the neighborhood of the center and generates shallow acceptor states at the top of the valence band.

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APPENDIX

The coefficients $C_{l,mm'}$ and $D_{l,mm'}$ of Eq. (3.9) can be easily calculated in the following way. We define

$$\begin{aligned} \vec{r}_A &= \hat{x}+\hat{y}+\hat{z} \;, \quad \vec{r}_B = \hat{x}-\hat{y}-\hat{z} \;, \\ \vec{r}_C &= -\hat{x}+\hat{y}-\hat{z} \;, \quad \vec{r}_D = -\hat{x}-\hat{y}+\hat{z} \;, \end{aligned} \tag{A1}$$

in agreement with the signs of Eq. (3.5). We then have

$$C_{l,mm'} \equiv N_C \langle m | \delta(\vec{r}-\vec{r}_l) | m' \rangle \;, \tag{A2}$$

$$D_{ll',mm'} \equiv N_D \langle m | \delta(\vec{r}-\tfrac{1}{2}\vec{r}_l-\tfrac{1}{2}\vec{r}_{l'}) | m' \rangle \;, \tag{A3}$$

where $l,l' \equiv A,B,C,D$, the functions $|m\rangle$ and $|m'\rangle$ are given in Eq. (3.4), and the normalization coefficients N_C and N_D are such that

$$\sum_m |C_{l,mm'}|^2 = \sum_{m'} |C_{l,mm'}|^2 = 2 \tag{A4}$$

and

$$\sum_{ml} |D_{ll',mm'}|^2 = \sum_{m'l'} |D_{ll',mm'}|^2 = \tfrac{2}{3} \;. \tag{A5}$$

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