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Donor complex with tunneling hydrogen in pure germanium

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A shallow donor complex observed by several authors in ultrapure germanium grown in a hydrogen atmosphere is attributed to an oxygen-hydrogen system. Photoconductivity data under stress are presented. An abrupt transition in the spectra at a well-defined stress (2.1×10^8 dyn cm^{-2}) is found. It is explained by a theory which involves dynamic tunneling of the hydrogen in the vicinity of an oxygen center. The comparison with other complex donors and acceptors supports the model.

I. INTRODUCTION

In ultrapure germanium with net acceptor or net donor concentrations $<10^{11}$ cm^{-3} several new shallow levels have been recently discovered.[1-7] A donor, which we label $D(\mathrm{H,O})$ and which is the subject of this paper, is found in rapidly quenched crystals grown in a hydrogen atmosphere[1] from a melt contained in a synthetic quartz crucible. The growth atmosphere proved to be relevant when it was shown that the ground state becomes slightly shallower in crystals grown in a deuterium environment. This isotope shift is a direct proof of the presence of a single hydrogen atom[2] in $D(\mathrm{H,O})$. The donor $D(\mathrm{H,O})$ belongs to a new class of impurity complexes which consist of one substitutional and one interstitial impurity: The substitutional impurity is in this case most probably oxygen, and the interstitial, hydrogen. Recently the existence of three such impurity complexes has been demonstrated in germanium, the donor[8] $D(\mathrm{Li,O})$ and the acceptors[7] $A(\mathrm{H,Si})$ and $A(\mathrm{H,C})$.

In these complexes the interstitials are either lithium or hydrogen. They normally are fast-diffusing donors in germanium, but in these complexes they tunnel around a heavier element (oxygen, silicon, or carbon). We call these latter dynamic tunneling systems.

We present in this paper experimental results on $D(\mathrm{H,O})$ and a theoretical model which explains the striking photoelectric spectra obtained with it. Though similar in nature to the (Li, O) complex, $D(\mathrm{H,O})$ has dramatically different properties due to the much smaller size of the hydrogen atom. The possibility of donors associated with OH complexes has been suggested before by Schoenmakers *et al.*[9]

II. EXPERIMENTS

A. General background

Hall[1] discovered a shallow acceptor-donor pair in rapidly quenched samples of ultrapure germanium. He showed that the two defects were not of simple elemental character and studied their thermal annealing kinetics. Over the past several years various investigators discovered special properties of this novel acceptor-donor pair. Only recently it has become possible to create a comprehensive model of the acceptor. The acceptor $A(\mathrm{H,Si})$ is a substitutional silicon impurity in the germanium lattice which binds a hydrogen atom. Hydrogen tunnels between four equivalent real-space positions.[7] The other member of the pair $D(\mathrm{H,O})$, is the subject of this study.

The following experimental facts have been accumulated over the past several years. The donor contains hydrogen, and most probably only one hydrogen atom, as has been shown by an isotope shift in the donor ground state.[2] The shift is produced when hydrogen is substituted by deuterium. The donor can be created in ultrapure germanium crystals grown in a hydrogen atmosphere from a melt contained in quartz. It cannot be generated in crystals which either do not contain oxygen (crystals grown from a melt contained in graphite) or which contain silicon at a concentration much higher than oxygen[7] (crystals grown from a melt contained in quartz and doped with silicon). The last two findings make it clear that free oxygen is required for the formation of $D(\mathrm{H,O})$.

B. Piezospectroscopy studies

Already the very early photothermal ionization spectra of ultrapure germanium samples showed a special feature of $D(\mathrm{H,O})$. The lines due to transitions of an electron from the ground state to one of the bound excited states were much sharper for $D(\mathrm{H,O})$ than for elemental donors such as phosphorus or arsenic.[5,6] It was not clear to the various experimenters that they all had observed Hall's rapid-quench donor. (This explains the multiplicity of inconsistent notations found in the literature.) The extraordinary sharpness of the $D(\mathrm{H,O})$ lines can readily be understood from our piezospectroscopy studies.

Samples measuring $1 \times 1 \times 6$ mm^3 were cut, lapped, and etched[10] with their long axis parallel to the [111], [110], or [100] direction. All the ultrapure germanium crystals used were n-type. They were grown in a hydrogen atmosphere from a melt contained in a quartz crucible. Two small tin contacts were formed on one long side under argon with the brief injection of dry HCl gas to insure good wetting of the germanium by the tin. After the samples were held for a few minutes at ~620 K, they were dropped in pure water at room temperature. Such a quenching procedure was adequate for the production of a sufficient concentration of $D(\mathrm{H,O})$ $\{[D(\mathrm{H,O})] \gtrsim (N_D - N_A)\}$.

Uniaxial stress was applied parallel to the long axis of a sample using a spring and lever stress rig inside a helium dewar.[11] A Fourier-transform spectrometer with a resolution <8 μeV served as the ir source.[12]

Three photothermal ionization spectra of a sample containing $D(\mathrm{H,O})$ and shallow phosphorus donors are shown in Fig. 1. The "hydrogenic"[13] set of lines of the phosphorus spectrum move with increasing stress (compression) along the [111] direction towards lower energies, as expected.[14] The hydrogenic set of lines of the $D(\mathrm{H,O})$ spectra react totally differently to stress. The lines do not change their positions but at a certain value of stress ($\sim 2 \times 10^8$ dyn cm^{-2}) their intensity starts to decrease rapidly while a new series appears at lower energies. The lines of this new series do not change their positions up to the experimentally limited maximum stress ($\sim 1.5 \times 10^9$ dyn cm^{-2}). This lack of dependence of the line position on stress readily explains their sharpness. Random stress in the crystal produced by dislocations or by the particular mounting of a sample does not affect the linewidth of the $D(\mathrm{H,O})$ spectra. The effect of uniaxial stress can be reversed by increasing the sample temperature. Around $T \gtrsim 9$ K the zero-stress $D(\mathrm{H,O})$ spectrum reappears. All the observed effects are fully reversible in temperature and in uniaxial stress, independent of the orientation. (The choice of the [111] direction for Fig. 1 is arbitrary.)

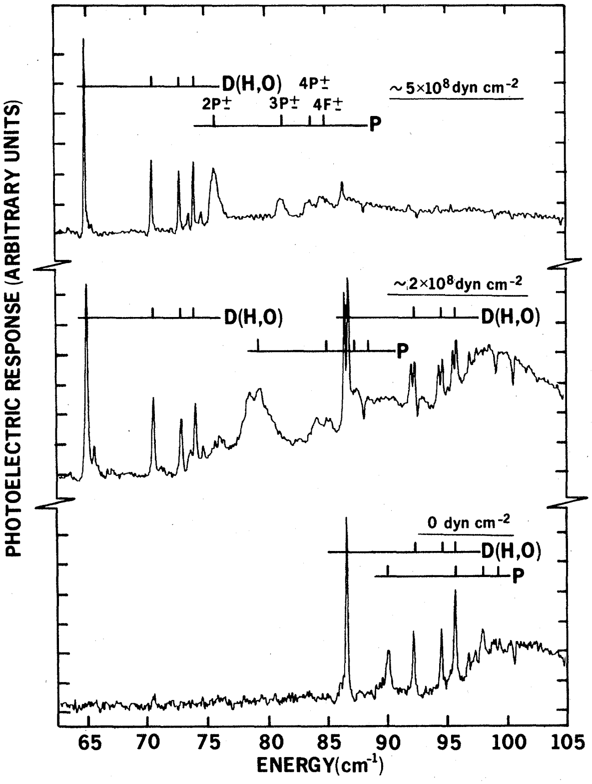

FIG. 1. Photothermal ionization spectra of an ultrapure germanium sample at three different values of compressional stress along [111]. The sample contains phosphorus donors [P] in addition to $D(\mathrm{H,O})$.

This unconventional behavior of a shallow donor spectrum is related to the stress dependence of the lithium-oxygen complex.[8] The tunneling of the lithium atom between equivalent real-space positions modifies the ground-state manifold and leads to a stress-independent set of lines in the photothermal ionization spectrum. In the present system we also assume that tunneling is involved: An interstitial hydrogen is trapped by an oxygen atom.

III. THEORY

A. General considerations

In Fig. 1, many important features of $D(\mathrm{H,O})$ are revealed. First we see that at zero stress the donor electron has an ionization energy E_i very similar to that of substitutional phosphorus: $E_i[D(\mathrm{H,O})] = 12.34$ meV as compared to $E_i[\mathrm{P}] = 12.76$ meV. Therefore $D(\mathrm{H,O})$ as phosphorus is a shallow donor with an ionization energy substantially larger than the pure hydrogenic[13] value of 9.89 meV. In P this deviation is caused mainly by the valley-orbit interaction, and results in large shifts under uniaxial compression.[14] In $D(\mathrm{H,O})$, on the other hand, no shift is observed, which points to a different cause of the ionization energy deviation.

Second, the behavior of the lines under small stress show that $D(\mathrm{H,O})$ must have at least tetrahedral symmetry, T_d. 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.

Third, at a stress of about 2.1×10^8 dyn cm^{-2} a dramatic transition occurs. Over a small stress interval two series coexist, one D_1 at the same energies as the zero stress spectrum, and one D_2 at significantly lower energies. At higher stress the upper series D_1 disappears and the lower one D_2 remains unshifted and as sharp as at the transition stress. Right at the transition the lines in both series are slightly split. The D_2 series, which prevails at higher stress, corresponds to a donor state with an ionization energy of 9.69 meV. If we compare this value with the theoretical value of 9.89 meV, we see that the new series has a negative deviation from the hydrogenic value. We should also note that at larger stress the D_1 series can be repopulated if the temperature is raised sufficiently.

From the above data, it is clear that uniaxial stress alters considerably the structure of the impurity complex. It appears to have two states, two configurations we could say, with different energies and to each corresponds one ionization energy for the donor electron. Uniaxial stress changes the energies of the two configurations producing an inversion of the two at 2.1×10^8 dyn cm^{-2}. The sudden character of the transition and the coexistence of the two series require that the two configurations do not have the same symmetry. Previous considerations[7] have led us to propose that D(H, O) consists of two elements: oxygen and hydrogen. Our preference would be for a system where the diatomic molecule OH lies in a vacancy site and flips (tunnels) between various orientations (see Fig. 2). The specific way in which the bonds between oxygen, hydrogen, and germanium are formed is not clear, but for our study that information is not required. With this physical picture, a more specific explanation can be given for the dramatic transition observed. Let us first note that to have an overall symmetry T_d, the minimum number of equivalent configurations that the impurity complex can have is four: the four states with symmetry axes along the $\langle 111 \rangle$ directions. For simplicity we suppose that this is the case. The fourfold degeneracy, which is then present, is not allowed by the symmetry of the lattice and these states must split into states which belong to the irreducible representations of the symmetry group. As is well known, four tetrahedrally equivalent states can be combined to form a singlet Γ_1 (s type) and a triplet Γ_5 (p type), or in other words, the tunneling of the impurity complex between its four equivalent configurations splits its ground-state manifold into a singlet Γ_1 and a triplet Γ_5. Furthermore, the fact that these donors are shallow makes it unlikely that the envelope of the electronic wave function, which extends over many lattice unit cells, would differ appreciably from the simple hydrogenic model. We therefore expect an electronic contribution of symmetry Γ_1. Hence, the overall symmetry of the states from which the electronic series arise remain Γ_1 and Γ_5. We expect also the central-cell shift in the ionization energy of the Γ_1 state (s-like) to be much larger than that of the Γ_5 states (p-like). The D_1 series appear to arise from the Γ_1 configuration and the D_2 series from the Γ_5 configuration.

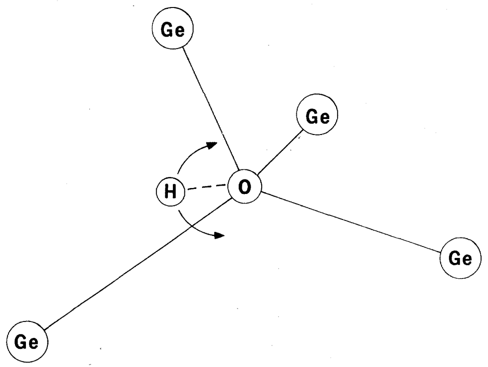

FIG. 2. Schematic representation of the OH complex for a vacancy site (tetrahedral symmetry).

Under a uniaxial stress along a $\langle 111 \rangle$ direction, the symmetry group reduces to C_{3v} and

$$\Gamma_1 \rightarrow \Lambda_1$$

$$\Gamma_5 \rightarrow \Lambda_1 \oplus \Lambda_3 .$$

As stress is applied, the energies of the different configurations change and a crossover occurs if Λ_3 goes below the Λ_1 state arising from Γ_1. We note that the experimental results for D(H, O) are qualitatively different from those for D(Li, O), which seems to be a similar system. The tunneling matrix element for D(Li, O) is small[8,9] and consequently the splitting between the Γ_1 and Γ_5 configurations is also small. The electronic states associated with the two types of configurations are intermingled. This gives rise to the complex spectrum which was observed for that system instead of the hydrogenic series of Fig. 1. For D(H, O), we expect the tunneling matrix element to be substantially larger so that the electronic states associated with each configuration remain distinct.

B. The Hamiltonian without uniaxial stress

We now develop a formalism to study the ground-state manifold of the dynamic donor system. The theory is written for an OH system in a vacancy, but its qualitative features can be applied to other situations as well. The Hamiltonian is the sum of three terms,

$$\mathcal{H}=\mathcal{H}_e+\mathcal{H}_n+\mathcal{H}_{e-n}\,. \tag{3.1}$$

Here $\mathcal{H}_e$ describes the kinetics of an unbound conduction electron in the germanium lattice, $\mathcal{H}_n$ the dynamics of the internal degree of freedom of the impurity complex (e.g., the dynamics of the OH^+ system), and $\mathcal{H}_{e-n}$ the interaction between the two. If we denote by $\vec{r}$ the coordinate of the electron with respect to the center of mass and by $\vec{R}$ the internal degree of freedom coordinate,

$$\mathcal{H}_{e-n}=-(e^2/\epsilon r)+V(\vec{r},\vec{R})\,. \tag{3.2}$$

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

The terms

$$\mathcal{H}_d\equiv\mathcal{H}_e-(e^2/\epsilon r) \tag{3.3}$$

correspond to an ordinary isochoric hydrogenic donor. As is well known, the conduction band of germanium has four equivalent minima located at the L points, i.e., along the $\langle 111\rangle$ directions at the Brillouin zone. If one supposes that there is no valley-orbit interaction, the ground-state manifold of $\mathcal{H}_d$ yields four L_1 states, each with a symmetry axis along one of the $\langle 111\rangle$ directions (L_1 is the invariant representation of the group of the L point[15,16]). The four eigenfunctions can be labeled χ_a, χ_b, χ_c, and χ_d with symmetry axes along $[111]$, $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$, respectively. With the introduction of valley-orbit interaction, $\mathcal{H}_d$ can be written

$$\mathcal{H}_d=\begin{bmatrix} E_e & -\Delta_{vo} & -\Delta_{vo} & -\Delta_{vo}\\ -\Delta_{vo} & E_e & -\Delta_{vo} & -\Delta_{vo}\\ -\Delta_{vo} & -\Delta_{vo} & E_e & -\Delta_{vo}\\ -\Delta_{vo} & -\Delta_{vo} & -\Delta_{vo} & E_e \end{bmatrix}, \tag{3.4}$$

where E_e is the energy of the L_1 state without valley-orbit interaction, and $(-\Delta_{vo})$ is the valley-orbit interaction. The eigenvalues of $\mathcal{H}_d$ are a singlet Γ_1 with energy $(E_e-3\Delta_{vo})$ and a triplet Γ_5 with energy $(E_e+\Delta_{vo})$.

The eigenstates of $\mathcal{H}_n$ 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 $\vec{R}_I$ 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 $\vec{R}_I\neq 0$ 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 (3.5) we have oriented the four positions $\vec{R}_I$ 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, $\mathcal{H}_n$ can be written as a 4×4 matrix given by

$$\mathcal{H}_n=\begin{bmatrix} E_n & -t & -t & -t\\ -t & E_n & -t & -t\\ -t & -t & E_n & -t\\ -t & -t & -t & E_n \end{bmatrix}, \tag{3.6}$$

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 donor can now be written as a linear combination of functions which are direct-product functions:

$$\{\Phi_I\}\otimes\{\chi_m\};\quad I\equiv A,B,C,D;\quad m\equiv a,b,c,d\,. \tag{3.7}$$

There are sixteen such functions in our manifold $\Phi_A\chi_a$, $\Phi_A\chi_b$, ..., $\Phi_D\chi_d$, which for simplicity are denoted Aa, Ab, ..., Dd. We study our problem in this restricted basis set and diagonalize the 16×16 matrix obtained from (3.1).

With $V(\vec{r},\vec{R})=0$, the matrix elements have the form

$$\begin{aligned} \langle Im|(\mathcal{H}_e+\mathcal{H}_n-e^2/\epsilon r)|I'm'\rangle &=(E_e+E_n)\delta_{II'}\delta_{mm'}-\Delta_{vo}\delta_{II'}(1-\delta_{mm'})\\ &\quad-t\delta_{mm'}(1-\delta_{II'})\,. \end{aligned} \tag{3.8}$$

The number of distinct matrix elements contributed by $V(\vec{r},\vec{R})$ can be determined by symmetry considerations. We can write

$$\begin{aligned} \langle Im|V(\vec{r},\vec{R})|I'm'\rangle=&-\delta_{mm'}\{\delta_{II'}[\Delta_1\delta_{Im}+\Delta_0(1-\delta_{Im})]+\Delta_1'(1-\delta_{II'})\}\\ &-(1-\delta_{mm'})\{\delta_{II'}[\Delta_2(\delta_{Im}+\delta_{Im'})+\Delta_3(1-\delta_{Im}-\delta_{Im'})]+(1-\delta_{II'})\Delta_0'\}\,. \end{aligned} \tag{3.9}$$

In (3.9), the six parameters which appear can be separated into two classes: intravalley (i.e., interactions of the state of a given valley with the impurity complex) and intervalley (i.e., interactions between states of different valleys with the impurity complex). The intravalley parameters are Δ_1, Δ_0, and Δ_1'; the intervalley ones are Δ_2, Δ_3, and Δ_0'.

The unprimed terms Δ_1, Δ_0, Δ_2, and Δ_3 are central-cell potential contributions corresponding respectively to the four cases: (1) an intravalley term where the valleys and the molecular complex have the same orientation (Δ_1), (2) an intravalley term where the valleys and the molecular complex do not have the same orientation (Δ_0), (3) an intervalley term where one of the valleys is along the axis of the molecular complex but the other is not (Δ_2), and (4) an intervalley term where none of the two valleys is along the axis of the molecular complex (Δ_3). The two last terms Δ_2 and Δ_3 can be redefined by absorbing into them Δ_{vo}:

$$\begin{aligned} \Delta_2 &\to \Delta_2 + \Delta_{\mathrm{vo}} , \\ \Delta_3 &\to \Delta_3 + \Delta_{\mathrm{vo}} . \end{aligned} \tag{3.10}$$

The primed terms Δ_1' and Δ_0' are combined electronic internal-structure potential terms, the first being an intravalley and the second an intervalley contribution.

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

$$(\Gamma_1 \oplus \Gamma_5) \otimes (\Gamma_1 \oplus \Gamma_5) \Rightarrow 2\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_4 \oplus 3\Gamma_5 , \tag{3.11}$$

which yields eigenvalues

$$\begin{aligned} E_{\pm}(\Gamma_1) = {} & E_e + E_n - \Delta_0 - \Delta_3 - \delta - 5\Delta_0' - t' \\ & \pm [(\Delta_3 - \delta + 2\Delta_0' + t')^2 + 3(t' + \Delta_2 + 2\Delta_0')^2]^{1/2} , \end{aligned} \tag{3.12}$$

$$E(\Gamma_3) = E(\Gamma_4) = E_e + E_n - \Delta_0 + \Delta_3 + t' - \Delta_0' \tag{3.13}$$

and a 3×3 matrix for the Γ_5 levels

$$\begin{bmatrix} E_e + E_n - \Delta_1 + \Delta_0' & -\Delta_2 - t' + 2\Delta_0' & \sqrt{2}(-\Delta_2 - t') \\ -\Delta_2 - t' + 2\Delta_0' & E_e + E_n - \Delta_0 + \Delta_0' & \sqrt{2}(-\Delta_3 + t') \\ \sqrt{2}(-\Delta_2 - t') & \sqrt{2}(-\Delta_3 + t') & E_e + E_n - \Delta_0 - \Delta_3 - t' + 3\Delta_0' \end{bmatrix} , \tag{3.14}$$

where $\delta = \frac{1}{2}(\Delta_1 - \Delta_0)$ and $t' = t + \Delta_1'$.

C. Hamiltonian with uniaxial stress

The effect of uniaxial stress on the states of the donor system can be studied by adding the term (3.15) to the Hamiltonian (3.1):

$$K = K_e + K_n , \tag{3.15}$$

where K_e is an electronic part and K_n a term characterizing the changes in the impurity complex. We suppose that the uniaxial stress is applied along the [111] direction, which corresponds to the situation of Fig. 1. With a stress along [111] it is well-known that[14] the energy of the valley along that direction decreases in energy by (-3ϵ) while the other three valleys increase by $(+\epsilon)$. Hence, we have simply,

$$\langle Im | K_e | I'm' \rangle = \delta_{II'} \delta_{mm'} [-3\epsilon \delta_{ma} + \epsilon(1 - \delta_{ma})] , \tag{3.16}$$

where χ_a is the state corresponding to the valley along the direction of the stress and ϵ is a positive quantity proportional to the stress. Figure 3(a) gives the variation of the eigenvalues of $(\mathcal{H}_e + K_e)$ with ϵ. The second term K_n is determined by the symmetry of the basis states of $\mathcal{H}_n$ [see Eq. (3.5)]. Since the states Φ_A consist of a linear combination of Γ_1 and Γ_5 states we can write

$$\langle Im | K_n | I'm' \rangle = \delta_{mm'} S_{II'} , \tag{3.17}$$

where the matrix S is given by

$$S = \begin{bmatrix} \frac{3}{2}\epsilon_p' & \epsilon_s' - \frac{1}{2}\epsilon_p' & \epsilon_s' - \frac{1}{2}\epsilon_p' & \epsilon_s' - \frac{1}{2}\epsilon_p' \\ \epsilon_s' - \frac{1}{2}\epsilon_p' & -\frac{1}{2}\epsilon_p' & \epsilon_s' + \frac{1}{2}\epsilon_p' & \epsilon_s' + \frac{1}{2}\epsilon_p' \\ \epsilon_s' - \frac{1}{2}\epsilon_p' & \epsilon_s' + \frac{1}{2}\epsilon_p' & -\frac{1}{2}\epsilon_p' & \epsilon_s' + \frac{1}{2}\epsilon_p' \\ \epsilon_s' - \frac{1}{2}\epsilon_p' & \epsilon_s' + \frac{1}{2}\epsilon_p' & \epsilon_s' + \frac{1}{2}\epsilon_p' & -\frac{1}{2}\epsilon_p' \end{bmatrix}$$

and where ϵ_s' characterizes the shift of the Γ_1 (s-like) state and ϵ_p' that of the Γ_5 (p-like) states. ϵ_s' is positive if the energy of the Γ_1 state increases with stress; similarly ϵ_p' is positive if the state in Γ_5 with the symmetry axis along the stress rises in energy. A comparison between (3.17) and (3.8) shows that ϵ_s' simply renormalizes t and so does not change the qualitative structure of the Hamiltonian.

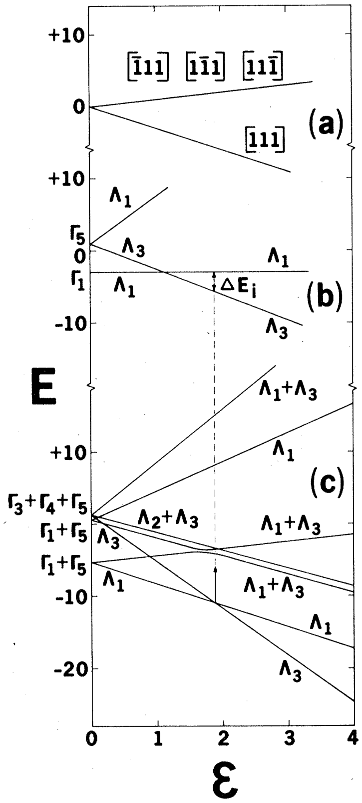

FIG. 3. Stress dependence of the various eigenvalues. (a) The energy of the four valleys in the conduction band of Ge, given by $(\mathcal{H}_e+K_e)$. (b) The states of the internal degrees of freedom $(\mathcal{H}_n+K_n)$, which are also the states of the ionized donor $D(\mathrm{H,O})$. (c) The energy of the fully interacting systems $\mathcal{H}$ in the ground state manifold. The stress is applied along [111]. Values of the parameters are given in the text and all energies are in units of t. The ionization energy of the complex donor is obtained by subtracting the ground-state energy Λ_1 or Λ_3 at a given stress (c) from the sum of the [111] valley energy (a) and the ionic energy (b) of the same Λ symmetry. The energy difference between the two series D_1 and D_2 is given by ΔE_i.

The first point to clarify is under what conditions a sharp transition occurs. For this purpose we note again that since for both small and large stresses simple hydrogenic series have been observed, the OH complex has a tunneling matrix element $(-t)$ which is sufficiently large so as to prevent any significant mixing by the $V(\vec{r},\vec{R})$ interaction of the Γ_1 and Γ_5 states of $\mathcal{H}_n$. We can therefore consider only the variation with stress of the eigenstates of $(\mathcal{H}_n+K_n)$:

$$\mathcal{H}_n+K_n=\begin{bmatrix} E_n & -\tau-\frac{1}{2}\epsilon_p' & -\tau-\frac{1}{2}\epsilon_p' & -\tau-\frac{1}{2}\epsilon_p' \\ -\tau-\frac{1}{2}\epsilon_p' & E_n & -\tau+\frac{1}{2}\epsilon_p' & -\tau+\frac{1}{2}\epsilon_p' \\ -\tau-\frac{1}{2}\epsilon_p' & -\tau+\frac{1}{2}\epsilon_p' & E_n & -\tau+\frac{1}{2}\epsilon_p' \\ -\tau-\frac{1}{2}\epsilon_p' & -\tau+\frac{1}{2}\epsilon_p' & -\tau+\frac{1}{2}\epsilon_p' & E_n \end{bmatrix}, \tag{3.18}$$

where $\tau=t-\epsilon_s'$.

The symmetry of this Hamiltonian is C_{3v} and its eigenstates can be trivially obtained. The diagonalization of (3.18) corresponds to the reduction of

$$\Gamma_1\oplus\Gamma_5\rightarrow 2\Lambda_1\oplus\Lambda_3\,. \tag{3.19}$$

We find that

$$E_n(\Lambda_1)_\pm=E_n+\epsilon_p'-\tau\pm\left|2\tau+\epsilon_p'\right|\,, \tag{3.20}$$

$$E_n(\Lambda_3)=E_n-\epsilon_p'+\tau\,. \tag{3.21}$$

Four cases have to be considered: $(t>0,\epsilon_p'>0)$, $(t>0,\epsilon_p'<0)$, $(t<0,\epsilon_p'>0)$, and $(t<0,\epsilon_p'<0)$. For this analysis we neglect the effect of ϵ_s'. A quick examination shows that only one case leads to a sharp crossover $(t>0,\epsilon_p'>0)$. This corresponds to a situation where at zero stress the impurity complex ground state is Γ_1, and at some critical stress the Λ_3 state (originating from Γ_5) crosses below Γ_1. That $\epsilon_p'>0$ means that the uniaxial stress tries to orient the OH complex in the plane perpendicular to the direction of the applied stress. A positive value of ϵ_s' moves the transition to lower stresses. The variation of the eigenvalues of $(\mathcal{H}_n+K_n)$ as a function of ϵ is given in Fig. 3(b) for $\epsilon_p'=3.5\epsilon$, $\epsilon_s'=0$.

The above results are confirmed when a full solution of the (16×16) complete Hamiltonian is obtained. The diagonalization follows the same procedure as in the absence of uniaxial stress. With stress the symmetry group is reduced to C_{3v} and the representations present in the Hamiltonian follow from (3.11):

$$2\Gamma_1\oplus\Gamma_3\oplus\Gamma_4\oplus3\Gamma_5\Rightarrow 5\Lambda_1\oplus\Lambda_2\oplus5\Lambda_3\,. \tag{3.22}$$

Analytical solutions cannot be obtained for the Λ_1 and Λ_3 representations. But a computer analysis shows that to have the proper behavior Γ_1 should be the zero-stress ground state and Λ_3 is then the ground state at large stress. A crossover is obtained because Γ_1 reduces to Λ_1 in C_{3v}, which is always orthogonal to Λ_3 and therefore does not interact with it. To compare our theory with the experimental results, we need the energy of the Γ_1 state in the absence of stress which is given by (3.11) and the large stress limit of $\Lambda_1(\Gamma_1)$ state and of the new ground state Λ_3. These latter energies can be obtained analytically by noting that in the large stress limit only the valley along the stress is occupied. We find that

$$E(\Lambda_1)=E_e+E_n-3\epsilon-\Delta_0-3t'-\tfrac{1}{2}\delta\,, \tag{3.23}$$

$$E(\Lambda_3)=E_e+E_n-3\epsilon-\Delta_0+t'-\epsilon_p'\,. \tag{3.24}$$

From (3.12), (3.23), and (3.24) it follows that

(a) the ionization energy of the Γ_1 level at large stress is

$$E_{\Lambda_1} = -E_e + \Delta_0 + \tfrac{1}{2}\delta + 3\Delta_1' ; \tag{3.25}$$

(b) the ionization energy of the Λ_3 level is

$$E_{\Lambda_3} = -E_e + \Delta_0 - \Delta_1' ; \tag{3.26}$$

(c) the bending with stress of the Γ_1 level is

$$\begin{aligned} E_{\Lambda_1} - E_{\Gamma_1} = {} & \Delta_3 + \tfrac{1}{2}\delta + 5\Delta_0' - 2t' \\ & + [(\Delta_3 - \delta + 2\Delta_0' + t')^2 \\ & + 3(\Delta_2 + t' + 2\Delta_0')^2]^{1/2} . \end{aligned} \tag{3.27}$$

Also,

$$E_{\Lambda_1} - E_{\Gamma_1} \simeq \tfrac{3}{2}(\Delta_2 + \Delta_3) + 9\Delta_0', \tag{3.28}$$

when $t' = t + \Delta_1' \gg \Delta_2$, Δ_3 and Δ_0'.

We can also add that from the crossover region to any larger value of stress, the shift in the Λ_3 level is essentially zero.

The experimental evidence shown in Fig. 1 shows that the bending of both the Λ_3 and the Λ_1 states is very small. That Λ_3 does not shift with stress follows directly from our model. That Λ_1 does not shift appreciably indicates on the other hand that the valley-orbit interactions are small. To have $E_{\Lambda_1} - E_{\Gamma_1} \simeq 0$, the intervalley constants Δ_2, Δ_3, and Δ_0' should be small [see Eqs. (3.27), (3.28), and (3.9)]. From Eqs. (3.25) and (3.26), and the fact that the separation between the two series D_1 and D_2 is $\Delta E_i = 2.65$ meV, it follows that

$$\Delta_1' = 0.66 \text{ meV} - \tfrac{1}{8}\delta . \tag{3.29}$$

Equation (3.29) sets an upper bound to Δ_1'; $\delta = \frac{1}{2}(\Delta_1 - \Delta_0)$ is a positive number of the order of 1 meV at most. Hence, Δ_1' is approximately 0.5 to 0.6 meV. If we also suppose that $(-E_e)$ is equal to 9.89 meV (the value given by Faulkner[13]) we find that

$$\Delta_0 + \tfrac{1}{2}\delta + 3\Delta_1' \simeq 2.45 \text{ meV}, \tag{3.30}$$

$$\Delta_0 - \Delta_1' \simeq 0.2 \text{ meV}. \tag{3.31}$$

Though we have two equations for three unknowns, some conclusions can be drawn. First, Δ_0 is smaller than Δ_1' by 0.2 meV (i.e., we expect $\Delta_0 \simeq 0.3$ to 0.4 meV.) On the other hand, Δ_1 is very sensitive to the value given to Δ_0 or Δ_1'. Typically, if we suppose $\Delta_0 \simeq 0.4$ meV, then $\Delta_1' \simeq 0.6$ meV and $\Delta_1 \simeq 1.4$ meV, which gives an idea of the order of magnitude of the constants. We note that the separation between the two series D_1 and D_2 is essentially due to Δ_1', the element that describes the combined intravalley electronic internal structure. The separation between the two series has the same origin as the splitting in the ground state[7] of the acceptors A(H, Si) and A(H, C). There is no way to estimate with our present data the tunneling matrix element t, which is not an electronic term. We expect it, however, to be of the same order of magnitude as Δ_1'.

An example of the complete eigenvalues of $\mathcal{H}$ as a function of ϵ is shown in Fig. 3(c) for $\epsilon_s' = 0$, $\epsilon_p' = 3.5\epsilon$ and $\Delta_2 = \Delta_3 = \Delta_0' = 0$, $\Delta_0 = 0.40t$, $\Delta_1 = 1.40t$, and $\Delta_1' = 0.6t$.

The ionization energy of the ground state can be obtained by subtracting the value of the ground-state energy at a given stress [Fig. 3(c)] from the sum of the lowest electronic energy (Fig. 3(a), the [111] valley) and the internal degree-of-freedom energy of the same symmetry, i.e., Λ_1 if the ground state is Λ_1, and Λ_3 if the ground state is Λ_3 [Fig. 3(b)]. This can be easily understood if we remember that, upon ionization, the electron performs a transition to the conduction-band state (valley) which makes its wave function in the impurity, and the internal degree of freedom, as given by $\mathcal{H}_n$, is frozen in the transition. The difference between the Λ_1 and Λ_3 levels of $(\mathcal{H}_n + K_n)$ in Fig. 3(b) at the stress corresponding to the ground-state crossover of the total energy [Fig. 3(c)] gives the difference in energy ΔE_i between the ionization energies and between two corresponding lines of the D_1 and D_2 series.

It is, at this point, appropriate to comment on the splitting observed in the series right at the transition stress. Our model has assumed that the stress was perfectly aligned along the [111] direction and that the C_{3v} symmetry is exactly fulfilled. If that is not the case, there is no longer uniaxial symmetry, a coupling (albeit small) between the Λ_1 and Λ_3 states is introduced, and the crossover is no longer sharp. At the crossover point a small splitting appears, with each state being a linear combination of the Λ_1 and Λ_3 symmetries. Transitions to the higher states of either series are possible from each of the split-off states and therefore the lines should all be doubled.

We conclude this section with a brief discussion of the effects of temperature on the two series. We have observed that above the transition stress, the D_1 series can be repopulated by raising the temperature, whereas at zero stress the D_2 series cannot be populated easily. Within our model, which assumes a linear variation with stress, the effect of temperature should be symmetrical with respect to the transition stress. Since we estimate the tunneling matrix element to be of the order of 1 meV, or the separation between the Γ_1, Γ_5 configurations to be of the order of several meV, we do not expect that at zero stress D_2 can be populated by temperatures of 10 K or so. Nor do we expect D_1 to be populated at the same temperature at a stress of $4 \times 10^8 \text{dyn/cm}^2$. That the latter occurs should not be considered as a serious drawback of the theory. It simply indicates that nonlinearities are present even for the relatively small stresses that are involved here.

IV. CONCLUSIONS

We have shown that the complex donor $D(\mathrm{H,O})$ produces photoconductivity spectra which, at a well-defined stress, exhibit an abrupt change in the electronic ionization energy of the ground-state configuration. This behavior can only be explained if the complex has an internal degree of freedom. The uniaxial stress affects differently the different states of the complex and produces the crossover of two orthogonal noninteracting states. In spite of the fact that more than seven parameters are involved in the theory, the qualitative features are reproduced with a minimum number of conditions on their sign and order of magnitude. The required choices show great similarities[7,8] between the donors $D(\mathrm{H,O})$ and $D(\mathrm{Li,O})$ and the acceptors $A(\mathrm{H,Si})$ and $A(\mathrm{H,C})$. First, the tunneling matrix element $|t|$ and the combined electronic internal-structure term appear to be of the same order of magnitude for $D(\mathrm{H,O})$, $A(\mathrm{H,Si})$, and $A(\mathrm{H,C})$, but significantly smaller for $D(\mathrm{Li,O})$. These terms depend essentially on the interstitial atom. The first three complexes involve hydrogen and therefore the constants related to the tunneling of the system between its equivalent configurations should have the same order of magnitude. On the other hand, lithium is a heavier and larger element which tunnels with more difficulty between its equivalent positions and hence the tunneling matrix elements should be much smaller. Second, for both $D(\mathrm{H,O})$ and $D(\mathrm{Li,O})$ the valley-orbit interactions and, in fact, all intervalley terms are negligibly small whereas the intravalley central-cell potential terms appear to be similar for both donors. This is an interesting result which must be related to the presence of O in both donors, more specifically to the polarizations induced by the bonds between oxygen, the interstitial and the germanium atoms. Third, the two acceptors $A(\mathrm{H,Si})$ and $A(\mathrm{H,C})$ have qualitatively the same properties. Finally, the fact that the crossover is between Λ_1 (s-like) and Λ_3 (p-like) states explains qualitatively why the gross features of the spectra are, as experimentally found, roughly independent of the direction of the applied stress; to the first approximation the destruction of cubic symmetry can be thought of as a reduction from a spherical to an axial environment for the internal degree of freedom.

It is worthwhile to remark that a similar crossover does not occur for the two acceptors $A(\mathrm{H,Si})$ and $A(\mathrm{H,C})$, because in those complexes the p-like configuration is already the ground state at zero stress.

We have now identified at least four systems [$A(\mathrm{H,C})$, $A(\mathrm{H,Si})$, $D(\mathrm{H,O})$, and $D(\mathrm{Li,O})$] in which the dynamics of internal degrees of freedom (dynamic tunneling) play an important role in the electronic properties. The phenomenon seems to be of general validity for complex impurity systems which involve the very light elements.

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