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Static nontunneling models for the shallow donors D(H,O) and D(Li,O) in germanium

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Static models are proposed for the shallow donors D(H,O) and D(Li,O) in germanium as alternatives to the tunneling model used by Joós, Haller, and Falicov to interpret the photothermal ionization (PTI) spectra, and a critique of the tunneling model is made for these complexes. In the proposed model for D(H,O) a complex with trigonal symmetry that compresses the neighboring lattice along a threefold crystal axis yields a nondegenerate effective-mass (EM) ground state formed from the conduction-band valley parallel to the defect axis, and this state accounts for a sharp stress-independent PTI spectrum as observed in unstressed samples. As shown also by Broeckx, Clauws, and Vennik, a transition to a second sharp spectrum, as found experimentally, is predicted with this model for [111] uniaxial stress beyond a critical value determined by the electron deformation potential Ξ_u. A similar transition is predicted for [110] stress but not for uniaxial stress along [100]. For D(Li,O) a similar model in which the complex has only C_{1h} symmetry and a single (110) plane of reflection symmetry is shown to account for the stress-independent splitting of the peaks in the high-stress spectrum previously attributed to tunneling by lithium. It is shown for both defects that the tunneling hypothesis imposes unlikely constraints on the model in order to fit the experimental spectra.

I. INTRODUCTION

Unusual features in the photothermal ionization (PTI) spectra of several complexes in germanium that involve the light elements hydrogen or lithium and act as shallow donors or acceptors have been cited by Haller and Falicov[1] and by Joós *et al.*[2,3] as evidence that the light ion tunnels between equivalent positions around a heavier partner such as oxygen, carbon, or silicon. Other evidence of tunneling by hydrogen in semiconductors has been found by Muro and Sievers[4] in the infrared spectrum of the acceptor complex Be-H in silicon and by Kahn *et al.*[5] in the PTI spectrum of $A(\mathrm{Cu,H_2})$ in germanium. While recent experiments by McMurray *et al.*[6] and by Kahn *et al.*[7] have revealed that the acceptor complexes in germanium that involve a single hydrogen are described by a static model with trigonal (C_{3v}) point-group symmetry, the belief that the two donors D(H,O) and D(Li,O) behave as if they had full tetrahedral point-group symmetry and involve tunneling by the light ion remains widely accepted.[8–10] It is the purpose of this paper to challenge this interpretation of D(H,O) and D(Li,O) by showing that static, nontunneling models with less than tetrahedral symmetry are equally capable of accounting for the experimental observations, and by showing also that the tunneling model for these donor complexes requires that certain unlikely physical conditions must be satisfied in order to fit the data. Moreover, it will be shown that the tunneling model still does not, in fact, account for all the reported features of the experimental spectra of these two complexes.

An alternative interpretation of the data for the D(H,O) in terms of a static model has been proposed by Broeckx, Clauws, and Vennik.[11] This interpretation is equivalent to the one described in this paper, although the treatment given here is slightly different in order to exhibit directly the relationship to the tunneling model of Joós *et al.*[2] The connection between this formulation and that of Broeckx *et al.* is made explicit in Sec. III B.

The PTI spectrum of a shallow donor results from light-induced excitation of the bound electron, at temperatures between 4.2 and 10 K, from its initial state to various effective-mass (EM) excited states, whence it is excited thermally to the conduction band and recorded by its contribution to an increase in the crystal's electrical conductivity.[12] The spectrum of D(H,O) reveals a ground-state binding energy very similar to that of the simple donor substitutional phosphorus,[2,13] but the lines in the D(H,O) spectrum, unlike those of P, are very sharp and do not shift under an applied stress. This stress-induced shift in the P spectrum and the corresponding broadening of the lines as a result of random crystal strains occurs because the $1s$ EM state of the P donor in tetrahedral symmetry is split by the valley-orbit interaction into a singlet ground state and a higher triplet state.[13–15] Under stress the singlet interacts with a component of the triplet, and its energy therefore shifts nonlinearly with the stress, whereas the excited $2p,3p,\ldots$ states follow their respective conduction-band valleys and thus shift linearly. The transition energies between the ground state and the excited states accordingly depend on the stress. In order to account for the stress independence of the D(H,O) spectrum at low stress, it was therefore essential for Joós *et al.*[2] to assume in their model a valley-orbit interaction that exactly vanishes. By contrast, in the model proposed here for D(H,O) the valley-orbit interaction may be nonzero, but its effect on the ground state is suppressed by a larger splitting of the 1*s* level caused by a localized asymmetric strain related to the nontetrahedral form of the defect. This proposed model for *D*(H,O) is, in fact, essentially the same in its description of the electronic ground state in zero stress as the model proposed by Haller and Falicov[1] for *D*(Li,O).

The argument was made by Joós *et al.*[2] that the nuclear configuration of lowest energy for *D*(H,O) must have tetrahedral symmetry, since otherwise defects with different orientation would be inequivalent with respect to an applied stress and would therefore give spectral lines that would be distinct and show different behavior once stress is applied. In the model proposed here the nuclear configuration of *D*(H,O) does indeed have a symmetry lower than tetrahedral, but with the EM approximation for the donor states these inequivalent orientations nevertheless contribute to a single spectral line, at least at low stress, because the EM states follow the stress dependence of their respective valleys. Departures from the EM model of the donor states, such as those observed by Stavola *et al.*[16] for the thermal donor in silicon, are probably too small for *D*(H,O) to permit lines corresponding to inequivalent orientations to be resolved.

A striking feature of the experimental spectrum of *D*(H,O) was that at a critical uniaxial stress applied along a [111] direction a second sharp spectrum appeared at lower energy, which persisted unshifted at higher stress while the first one became very weak or disappeared. In the tunneling model[2] this second spectrum is attributed to a component from the higher (Γ_5) tunneling triplet having crossed the singlet (Γ_1) to become the new nuclear ground state at high stress. In the proposed model a similar crossing occurs, but involves the 1*s* electronic state formed from the valley oriented along the stress direction, for those defect orientations that are not in this direction, crossing the state formed from the valley parallel the defect axis. As Broeckx *et al.*[11] have shown, the critical stress for this crossing can be predicted from the known value of the electron deformation potential. Various alternative forms of this model are considered in Sec. III A.

Joós *et al.*[2,12] reported that this second *D*(H,O) spectrum also appears when the crystal was stressed along other directions, including [100]. If this is indeed the same spectrum as that which appears under [111] stress, this observation is a critical one, for a static model based on a defect configuration oriented along $\langle 111 \rangle$ directions cannot account for the occurrence of a similar transition under uniaxial stress directed along [100], as shown in Sec. III C. However, it does predict such a transition for [110] stress (at a somewhat larger critical stress). Moreover, even the tunneling model predicts differences in both the high-stress spectrum and in the value of the critical stress, depending on the stress orientation, as shown in Sec. IV C.

For the lithium-oxygen donor *D*(Li,O) the tunneling model of Haller and Falicov[1] requires that the tunneling by the lithium depends on the electronic state, vanishing when the electron is in one of the excited $2p, 3p, \ldots$ states, as discussed in Sec. V B. In the alternative model for *D*(Li,O) proposed in Sec. V C, the splitting of the low-energy line of the high-stress spectrum, attributed to tunneling in the model of Haller and Falicov, is suggested to be the result of the defect's having a symmetry lower than trigonal and revealing this lower symmetry via a small dependence of the 1*s* intravalley electronic energy on the orientation of the nuclear configuration relative to the electron valley.

II. GENERAL THEORETICAL CONSIDERATIONS FOR A DONOR COMPLEX WITH [111] ORIENTATION

There are four conduction-band valleys in germanium each having axial symmetry about a [111] direction. In the EM theory of Kittel and Mitchell[17] and of Luttinger and Kohn,[18] for an attractive Coulombic potential each such valley gives rise to a full set of hydrogenic states 1*s*, 2*s*, $2p_0$, $2p_\pm$, etc., so that for a defect with tetrahedral symmetry and in the absence of valley-orbit interaction (interaction between valleys caused by departures from the EM approximation near the donor impurity) each energy level of the donor electron is either fourfold or eightfold degenerate. Valley-orbit interaction and a defect symmetry lower than tetrahedral can lift this degeneracy, but such splitting usually is very small for excited states because these states are so extended in space and have such low amplitude close to the defect that they are not very sensitive to the structure of the defect and its immediate neighborhood. In this work it will be assumed that such splitting is negligible for the final states of the PTI spectra. Only the 1*s* states exhibit strong sensitivity to the local structure of the complex and therefore depart significantly from EM theory. In the notation of Joós *et al.*,[2] the 1*s* electronic states associated with the four valleys oriented along $[111]$, $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$ are designated χ_a, χ_b, χ_c, and χ_d, respectively.

It will be assumed tentatively that each complex at a given site has C_{3v} symmetry and four possible orientations, each aligned along one [111] axis and thus energetically equivalent in an unstrained crystal, which represent stable equilibrium nuclear configurations of the complex in the absence of any tunneling or other dynamic behavior. Again in the notation of Joós *et al.*,[2] Φ_a, Φ_b, Φ_c, and Φ_d will designate the nuclear state of the complex in this equilibrium configuration oriented, respectively, along $[111]$, $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$. The Φ_I are assumed sufficiently well localized in the space of the nuclear coordinates about their respective configurations that we may consider the Φ_I nonoverlapping and therefore mutually orthogonal.

There are 16 possible choices for the wave function $\Phi_I \chi_m$ $(I, m = a, b, c, d)$ describing the state of the complex at a given site when the electronic state is derived from the 1*s* EM level. Various linear combinations of these wave functions will represent states of different energy of the donor complex when couplings are introduced that reflect the influence of the local structure on the 1*s* electronic state. In describing these couplings it will suffice for the purposes of this paper to introduce a Hamiltonian which is simpler than that used by Joós *et al.*[2] and also simpler than the most general one allowed by symmetry.

For the orientation I of the complex let us assume an intravalley electronic energy $E_{1s}-\Delta_1$ for the 1s state belonging to that valley $(m=I)$ having the same orientation as that of the complex and $E_{1s}-\Delta_0$ for the 1s states from the three other valleys $(m\neq I)$, where E_{1s} denotes the 1s energy[19] (-9.81 meV) relative to the conduction-band edge in the EM approximation. Thus for the intravalley part $\mathcal{H}_d^e(1s)$ of the electronic Hamiltonian for the 1s states, one has matrix elements

$$\langle Im\,|\mathcal{H}_d^e(1s)|\,I'm'\rangle =\delta_{II'}\delta_{mm'}[E_{1s}-\Delta_1\delta_{Im}-\Delta_0(1-\delta_{Im})]\ . \qquad (2.1)$$

For the intervalley electronic (valley-orbit) coupling $\mathcal{H}_{\text{v.o.}}^e(1s)$, it will be assumed for simplicity that matrix elements are independent of the orientation of the complex and are given by

$$\langle Im\,|\mathcal{H}_{\text{v.o.}}^e(1s)|\,I'm'\rangle=-\Delta_{\text{v.o.}}(1-\delta_{mm'})\delta_{II'}\ . \qquad (2.2)$$

Ignoring for now the possibility of tunneling or other interactions between different orientations of the complex, one finds then from Eqs. (2.1) and (2.2) that, in the absence of external stress, for each of the four possible orientations the electronic 1s states are split into two singlets and a doublet. Assuming $\Delta_1-\Delta_0$ positive and $\gg|\Delta_{\text{v.o.}}|$ and ignoring corrections to the energies of order $\Delta_{\text{v.o.}}^2/(\Delta_1-\Delta_0)$, one finds then that the 16 states describing the eigenstates of the complex in an unstrained crystal and formed from the wave functions $\Phi_I\chi_m$ divide into a fourfold-degenerate level at

$$E=E_{1s}+E_N-\Delta_1\ , \qquad (2.3a)$$

another quartet at

$$E=E_{1s}+E_N-\Delta_0-2\Delta_{\text{v.o.}}\ , \qquad (2.3b)$$

and an octet at

$$E=E_{1s}+E_N-\Delta_0+\Delta_{\text{v.o.}}\ . \qquad (2.3c)$$

Here, E_N denotes the energy of one of the nuclear states Φ_I in the unstressed crystal. Under these assumptions the lowest level at $E_{1s}+E_N-\Delta_1$ comprises the four states $\Phi_m\chi_m$ $(m=a,b,c,d)$, while the other 12 states, linear combinations of the $\Phi_I\chi_m$ with $I\neq m$, have their center of gravity at $E_{1s}+E_N-\Delta_0$.

A uniform strain caused by an external stress and given by the strain tensor

$$e_{\alpha\beta}=\frac{1}{2}\left[\frac{\partial u_\alpha}{\partial x_\beta}+\frac{\partial u_\beta}{\partial x_\alpha}\right] \qquad (2.4)$$

changes the energies of the four conduction-band valleys through the electronic deformation potentials Ξ_d,Ξ_u and the coupling[20,21]

$$\mathcal{H}_s^e=\sum_{\alpha,\beta}e_{\alpha\beta}\left[\Xi_d\delta_{\alpha\beta}+\Xi_u\sum_j P_j^e n_\alpha^j n_\beta^j\right]\ . \qquad (2.5)$$

Here, P_j^e denotes the projection operator $|j\rangle\langle j|$ for the jth valley, while n_α^j is the α component of a unit vector pointed along the symmetry axis of the jth valley. It will be assumed that the effect of uniform strain on the electronic energy of all donor states derived from the same valley is identical to that of the band edge as given by Eq. (2.5).

By analogy with Eq. (2.5) we may define strain-coupling coefficients Θ_d and Θ_u that give the linear strain-induced change in energy of the oriented complex described by the Φ_I according to

$$\mathcal{H}_s^N=\sum_{\alpha,\beta}e_{\alpha\beta}\left[\Theta_d\delta_{\alpha\beta}+\Theta_u\sum_I P_I^N n_\alpha^I n_\beta^I\right]\ , \qquad (2.6)$$

where $P_I^N=|\Phi_I\rangle\langle\Phi_I|$ is the projection operator for the nuclear state Φ_I, and n_α^I the α component of the unit vector along the I axis.

An obvious mechanism contributing to the energy difference $\Delta_1-\Delta_0$ between the 1s states χ_m from valleys having inequivalent orientations relative to the configuration Φ_I is that the defect introduces a localized strain in its neighborhood. The electronic EM states are sensitive to strain through the deformation-potential coupling as given by Eq. (2.5), but for a localized strain the energy change of a given state is obtained by averaging over the strain distribution weighted with the probability distribution of the electronic wave function of that state. The energy change for the 1s state is accordingly much larger than for the excited np states, which extend much farther into the lattice and have an amplitude which approaches zero at the defect. This argument is consistent with the lack of any observable splitting of the final states of the PTI spectra associated with the nonsymmetrical form of the defect. Because the deformation potential Ξ_u is positive for Ge,[15,22] we expect $\Delta_1-\Delta_0$ in Eq. (2.1) to be positive if the defect introduces a local uniaxial compression of the neighboring lattice, oriented along the defect's axis. For such a defect, Θ_u in Eq. (2.6) should be negative, since an externally applied compression aligned with the local compression will raise the energy of that orientation of the defect relative to that of its other possible orientations.[23]

III. STRESS DEPENDENCE OF THE PTI SPECTRUM FOR A DONOR COMPLEX WITH [111] ORIENTATION

A. General considerations and response to applied uniaxial stress along [111]

The lowest level of the complex introduced in Sec. II when strain $e_{\alpha\beta}$ is zero is the quartet $\Phi_m\chi_m$ $(m=a,b,c,d)$ at an energy given by Eq (2.3a). There is no valley-orbit splitting of this quartet, according to Eq. (2.2), because of the mutual orthogonality of the Φ_I, and under external stress these four states therefore split linearly and follow exactly their respective valleys. Since optical transitions occur only between EM states from the same valley,[14,15] because of **k** conservation, and since under stress the excited np states also follow their valleys exactly, transition energies

$$\Delta E_{np}(D_1)=E_{np}-E_{1s}+\Delta_1 \qquad (3.1)$$

of peaks in the PTI spectrum originating in states from this lowest quartet are independent of the electronic strain coupling. (These transition energies would depend on the strain, and the resulting peaks would split and shift under an applied stress, if the deformation potentials for the 1s states were different from those of the conduction-band edge, contrary to the assumptions of Sec. II.) Since the nuclear state Φ_i must also be the same in the initial and final states of such an electronic transition, the transition energies of these peaks as given by Eq. (3.1) are also independent of the nuclear strain coupling in Eq. (2.6), so that these transition energies should be entirely unaffected by external stress. We should expect, therefore, that transitions originating in this lowest quartet should contribute a sharp component to the PTI spectrum of an unstressed crystal, which should remain sharp and unshifted when stress is applied. This component of the spectrum will be labeled D_1.

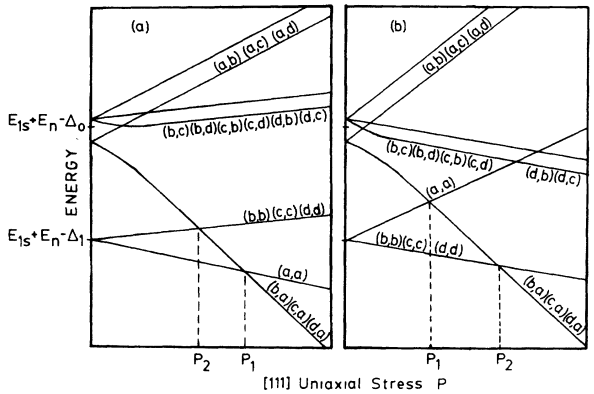

FIG. 1. Relative energies, including that of the nuclear configuration, for the 1s effective-mass states of a donor complex of C_{3v} symmetry oriented along a threefold axis of a Ge crystal, as functions of uniaxial stress P applied along the [111] direction. States are labeled by the appropriate pairs $\Phi_l \chi_m$, using the notation (l,m). The avoided crossing of the states at the critical stress P_2, caused by valley-orbit interaction, is not shown. The figures are drawn for $\Xi_u > 0$, $\Theta_u < 0$ for two cases: (a) $\Xi_u + \Theta_u > 0$; (b) $\Xi_u + \Theta_u < 0$.

In considering how the spectrum may be changed at higher stress, we must determine the relative energies of the various states of the complex when stress is applied, including in the total energy the strain energies of both the electronic and nuclear couplings. Assuming a uniaxial stress P applied along the [111] axis, we have

$$e_{xy}=e_{yz}=e_{zx}=-P/6c_{44} \ , \tag{3.2}$$

where c_{44} is the elastic shear constant of germanium.[24] (P is taken positive for uniaxial compression.) Ignoring the common energy displacement of all levels associated with the dilatation $e_{xx}+e_{yy}+e_{zz}$, we have then, for the energy $E(a,a)$ of the state $\Phi_a \chi_a$ from Eqs. (2.5) and (2.6),

$$E(a,a)=E_{1s}+E_N-\Delta_1-(\Xi_u+\Theta_u)P/3c_{44} \ , \tag{3.3}$$

and, for the energies of the states $\Phi_q \chi_q$ ($q=b,c,d$),

$$E(q,q)=E_{1s}+E_N-\Delta_1+(\Xi_u+\Theta_u)P/9c_{44} \ . \tag{3.4}$$

If $\Xi_u+\Theta_u$ is positive, $\Phi_a \chi_a$ is then the state of lowest energy under [111] uniaxial compression, at least for low stress, as shown in Fig. 1(a). Alternatively, if $\Xi_u+\Theta_u$ is negative, this lowest level is triply degenerate and comprises the states $\Phi_b \chi_b$, $\Phi_c \chi_c$, and $\Phi_d \chi_d$, as shown in Fig. 1(b). The PTI spectrum arising from the states $\Phi_m \chi_m$ ($m=a,b,c,d$) is, in either case, the D_1 spectrum with transition energies given by Eq. (3.1), independent of the stress.

For germanium the electronic deformation potential Ξ_u is positive,[15,22] thus favoring the alignment of the electronic valley along the stress axis (χ_a for stress along [111]). If Θ_u is negative, as we expect for a defect that compresses the neighboring lattice uniaxially along the defect axis,[23] the orientations of the complex favored by stress alone are those not aligned along the stress axis (Φ_q, $q=b,c,d$ for [111] stress). Thus, for $\Theta_u<0$ and for sufficiently high [111] stress the states $\Phi_q \chi_a$ in which both the electronic valley and the complex axis are favorably oriented with respect to the external stress, but not aligned with each other, will have the lowest energy. As shown in Figs. 1(a) and 1(b), as the stress is increased the energies of these states therefore cross those of the mutually aligned states that are the states of lowest energy at low stress. To determine the value of the stress at this crossing, we ignore the valley-orbit coupling (2.2) (as discussed below) to obtain, for the states $\Phi_q \chi_a$ under a large stress,

$$E(q,a)=E_{1s}+E_N-\Delta_0-(\Xi_u-\tfrac{1}{3}\Theta_u)P/3c_{44} \ , \tag{3.5}$$

for $q=b,c,d$. Comparing with Eq. (3.3), we find that these states fall below $\Phi_a \chi_a$ when P exceeds a critical stress P_1 given by

$$\Delta_1-\Delta_0=\tfrac{4}{9}(-\Theta_u)P_1/c_{44} \ . \tag{3.6}$$

Similarly, from Eq. (3.4), these states fall below $\Phi_q \chi_q$ when P exceeds a second critical stress P_2 given by

$$\Delta_1-\Delta_0=\tfrac{4}{9}\Xi_u P_2/c_{44} \ . \tag{3.7}$$

Figure 1(a) shows the case for which $\Xi_u > -\Theta_u$, so that we have $\Xi_u+\Theta_u>0$ and $P_1>P_2$, while in Fig. 1(b) we have $\Xi_u+\Theta_u<0$ and $P_2>P_1$. Θ_u is taken to be negative and Ξ_u positive in both Figs. 1(a) and 1(b).

Transition energies under large [111] stress for the PTI spectrum originating in the states $\Phi_q \chi_a$ are obtained by comparing Eq. (3.5) with the energy $E_{np}+E_N-(\Xi_u-\frac{1}{3}\Theta_u)P/3c_{44}$ of the np excited state of the [111] valley and the same nuclear orientation (Φ_q),

$$\Delta E_{np}(D_2)=E_{np}-E_{1s}+\Delta_0 \ . \tag{3.8}$$

This spectrum, which we designate D_2, is shifted relative to that of D_1 [Eq. (3.1)] by

$$\Delta E_{np}(D_1)-\Delta E_{np}(D_2)=\Delta_1-\Delta_0 \ , \tag{3.9}$$

and like D_1, is independent of the stress, at least so long as we can neglect the valley-orbit interaction in obtaining the energies in Eq. (3.5). This neglect is certainly justified if the stress P exceeds the critical stress P_2 by enough to place the states $\Phi_q \chi_a$ ($q=b,c,d$) in Fig. 1(a) and 1(b) below the states $\Phi_q \chi_q$ by an amount large compared to the valley-orbit parameter $\Delta_{\text{v.o.}}$. Accordingly, assuming thermal equilibrium so that the states $\Phi_q \chi_a$ are populated at stresses exceeding the larger of the two critical stresses P_1 and P_2 in Figs. 1(a) and 1(b), we see that we may expect a transition at this critical stress in which the PTI spectrum D_2 replaces the low-stress spectrum D_1. (If reorientation of the complex is frozen out, then both spectra D_1 and D_2 may appear simultaneously above P_2, as discussed below). Depending on which of Fig. 1(a) or 1(b) is appropriate, this critical stress is determined either by the electronic deformation potential Ξ_u or by the nuclear strain-coupling coefficient Θ_u.

At the critical stress P_1, at which the states $\Phi_q \chi_a$ cross $\Phi_a \chi_a$, we would expect no interaction between these states on the basis of the model we have proposed and there would be no unusual structure in the PTI spectrum at this crossing. [If a small tunneling interaction—see Eq. (4.2)—occurs among the nuclear configurations, a fine structure in the spectrum would appear at this crossing.] However, our model does predict a fine structure in both the D_1 and D_2 spectra at the critical stress P_2 at which the states $\Phi_q \chi_a$ cross the states $\Phi_q \chi_q$, since the electronic valley-orbit interaction, Eq. (2.2), now has matrix elements between pairs of the crossing states,

$$\langle \Phi_q \chi_q \,|\, \mathcal{H}^e_{\text{v.o.}}(1s) \,|\, \Phi_q \chi_a \rangle = -\Delta_{\text{v.o.}} \tag{3.10}$$

for $q=b,c,d$. The states from each such pair therefore have an avoided crossing (not shown in Fig. 1), so that transitions from each of the resulting mixed states are allowed to the np excited states of both valleys, thus doubling the peaks of both the D_1 and D_2 spectra. The splitting δE of each of these peaks at precisely the critical stress P_2 is given by

$$\delta E = 2\,|\,\Delta_{\text{v.o.}}\,| \ , \tag{3.11}$$

this difference being the energy separation at the point of closest approach for the two electronic states interacting according to Eq. (3.10). States from different pairs such as $\Phi_b \chi_b$ and $\Phi_c \chi_a$ cross without interaction because they involve different Φ_I, but such crossings add no extra peaks to the spectra since Φ_I must be the same in the initial and final states. If the stress is aligned precisely along [111], all three pairs cross at the same stress and have coincident energy levels, so that each of the peaks of both D_1 and D_2 spectra should simply be split into two peaks. If, however, the stress is misaligned, different pairs will cross at different stresses, so that the transition region will occur over a wider range of stress. The D_1 and D_2 spectra will then be the superposition of those from all three pairs and may therefore have a more complicated structure.

Since the transition from the D_1 to the D_2 spectrum at the critical stress P_2 involves reorienting the electronic valley from χ_b, say, to χ_a, but not the Φ_I, it is clear that this electronic transition can occur rapidly and is independent of the rate at which the complex itself can reorient. Thus thermal equilibrium between the members of each pair of states can easily be established. If nuclear reorientation is slow or effectively frozen out, however, we would expect the state $\Phi_a \chi_a$ (the electronically favorable state for the unfavorable nuclear orientation) to persist even above the critical stress, when its energy is far above the ground state. Since this state contributes to the D_1 spectrum, we would expect in this situation to have the D_1 spectrum present above the critical stress.

An additional possibility, if nuclear reorientation is frozen out, is that in the situation described by Fig. 1(a) we should expect to see the D_2 spectrum appear at the lower critical stress P_2 at which the states $\Phi_q \chi_a$ ($q=b,c,d$) fall below $\Phi_q \chi_q$. Although these states are not close in total energy to the ground state $\Phi_a \chi_a$ until the second critical stress P_1 is reached, it is only the electronic part of their energies that is relevant in establishing thermal equilibrium if nuclear reorientation is prevented. Accordingly, the D_2 spectrum will appear at P_2 as the electronic state of each oriented defect represented by Φ_q assumes the favorable orientation χ_a, and a fine structure should appear in both D_1 and D_2 spectra near P_2 because of the electronic valley-orbit interaction, as described previously in connection with Fig. 1(b). The unsplit D_1 spectrum should nevertheless persist at stresses at and above P_2 because of the continued presence of the state $\Phi_a \chi_a$.

B. Stress response of electronic energies: Model of Broeckx, Clauws, and Vennik

The interpretation of the PTI spectrum of D(H,O) proposed by Broeckx, Clauws, and Vennik[11] considered only the electronic energies of the complexes of different orientation. These electronic energies are plotted in Fig. 2 as functions of uniaxial stress P applied along the [111] axis. It was assumed by Broeckx *et al.* that before the critical stress P_2 was reached, the complexes represented by Φ_a and oriented along [111], being unfavorably oriented with respect to the stress, would reorient "for structural reasons," leaving this state nonexistent for $P > P_2$. The critical stress P_2 is then defined by the crossing of the levels representing $\Phi_q \chi_q$ ($q=b,c,d$) by the levels $\Phi_q \chi_a$, at which point the spectrum shifts from D_1 to D_2. This is just the situation described in Sec. III A by Fig. 1(b).

Broeckx *et al.* pointed out as well that interaction between pairs of states, χ_q and χ_a for Φ_q, as a consequence of the valley-orbit interaction, would split both the D_1 and D_2 peaks at the critical stress P_2, as we have already discussed in Sec. III A. They noted also that, above P_2, raising the temperature would repopulate the upper electronic state of each pair, for each of the three orientations Φ_q, and thus lead to a reappearance of the D_1 spectrum as observed experimentally. It was noted that the intensity ratio of the spectra D_1 and D_2 should approach 1:1 in this situation because of the tendency toward equalizing the populations of the pair of electronic states for each orientation as the temperature is increased.

We may also use Fig. 2 advantageously in the situation

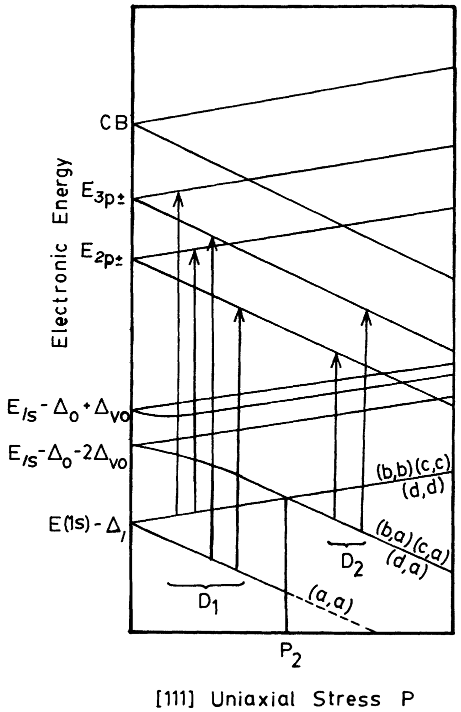

FIG. 2. Electronic energies of effective-mass states and conduction-band minima (CB) as functions of uniaxial stress P along [111], for a donor complex of C_{3v} symmetry oriented along a threefold axis of a Ge crystal. The notation used to identify the lowest $1s$ states for complexes of different orientations is the same as in Fig. 1. Representative electronic transitions contributing to the D_1 and D_2 photothermal ionization spectra are indicated. The state $\Phi_a X_a$ is indicated by a dotted line for high stress to denote the tendency of this complex, for $\Theta_u < 0$ and thermal equilibrium to reorient from Φ_a to another orientation Φ_b, Φ_c, or Φ_d.

when nuclear reorientation is frozen out, so that thermal equilibrium of the nuclear configurations is not achieved during the time of the experimental observations. It is then clear from Fig. 2 that the D_1 spectrum will remain strong at all P, corresponding to the continued occupation of the state X_a for complexes with the orientation Φ_a. Above P_2, complexes with orientations Φ_b, Φ_c, and Φ_d in their lowest state (X_a) will contribute to the D_2 spectrum, but the D_2:D_1 intensity ratio at the lowest temperatures will be reduced from 3:1 if, because of compensation, the Fermi level is deeper than $E_{1s}-\Delta_0$ below the conduction-band edge.

C. Response to uniaxial stress along [100] and [110]

Since for uniaxial stress applied along [100] the strain components e_{xy}, e_{yz}, and e_{zx} are all zero, according to Eqs. (2.5) and (2.6) there should be no effect (apart from that of dilatation) on the conduction-band edges or the electronic or nuclear states. The model proposed here for a donor complex with [111] orientation therefore predicts unambiguously that the D_1 spectrum will be unaffected by applied uniaxial stress along [100] and, in particular, that no critical stress occurs at which a spectrum like D_2 appears.

For uniaxial stress P along [110], we have $e_{yz}=e_{zx}=0$, but

$$e_{xy}=-P/4c_{44} \ . \tag{3.12}$$

The *two* states $\Phi_a X_a$ and $\Phi_d X_d$ now have the same energy,

$$E(a,a)=E(d,d)=E_{1s}+E_N-\Delta_1-(\Xi_u+\Theta_u)P/6c_{44} \ , \tag{3.13}$$

as do $\Phi_b X_b$ and $\Phi_c X_c$,

$$E(b,b)=E(c,c)=E_{1s}+E_N-\Delta_1+(\Xi_u+\Theta_u)P/6c_{44} \ . \tag{3.14}$$

These equations therefore replace Eqs. (3.3) and (3.4) for this direction of stress. Assuming Ξ_u positive and Θ_u negative as in Sec. III A, we have now for the states of lowest energy at high stress $\Phi_b X_a$, $\Phi_c X_a$, $\Phi_b X_d$, and $\Phi_c X_d$ the energies

$$\begin{aligned} E(b,a)=E(c,a)=E(b,d)=E(c,d) \\ =E_{1s}+E_N-\Delta_0 \\ -(\Xi_u-\Theta_u)P/6c_{44} \ , \end{aligned} \tag{3.15}$$

corresponding to Eq. (3.5). Depending on the sign of $\Xi_u+\Theta_u$, the critical stress at which Eq. (3.15) equals the lower of Eqs. (3.13) and (3.14) is now given by

$$\Delta_1-\Delta_0=(-\Theta_u)P_1'/3c_{44} \tag{3.16}$$

or

$$\Delta_1-\Delta_0=\Xi_u P_2'/3c_{44} \ . \tag{3.17}$$

The critical stress P_1' or P_2' for [110] stress is thus simply $\frac{4}{3}$ the corresponding critical stress P_1 or P_2 for [111] stress as given by Eqs. (3.6) and (3.7). In thermal equilibrium this critical stress marks the transition between the low-stress spectrum D_1, with transition energies given by Eq. (3.1), and the high-stress spectrum D_2 as given by Eq. (3.8). However, there is a difference from the situation found with [111] stress in that the states $\Phi_b X_a$ and $\Phi_b X_d$ (or $\Phi_c X_a$ and $\Phi_c X_d$), which have the same energies under [110] stress according to Eq. (3.15), interact via the valley-orbit interaction. Thus each peak of the D_2 spectrum under [110] stress should show a valley-orbit splitting of $2\Delta_{\text{v.o.}}$ at all stress values above the critical stress, in contrast to the simple unsplit peaks found for D_2 with [111] stress. Misalignment of the stress or displacements $\gtrsim \Delta_{\text{v.o.}}$ of the energy levels as a result of random strains will, however, tend to suppress this splitting of the D_2 peaks.

IV. THE DONOR D(H,O)

A. Experimental summary

The PTI spectrum[2] of D(H,O) in zero applied stress reveals a ground-state binding energy of 12.34 meV relative to the conduction-band edge. This spectrum consists of very sharp peaks which remain sharp and unshifted when stress is applied to the crystal. However, under a compressive stress $\sim 2.1\times 10^{7}$ Pa, applied uniaxially along a [111] direction, a second sharp spectrum appears, corresponding to a state with binding energy 9.69 meV, and this spectrum persists sharp and unshifted at higher stress, while the first spectrum reportedly disappears. The high-stress spectrum is reported to appear also for other directions of applied stress.[2,12] Moreover, near the transition stress both spectra appear with their peaks slightly split. Above the transition stress the first spectrum reappears if the temperature is raised sufficiently.

B. Static model

The form of the $D(\mathrm{H,O})$ spectrum in unstressed crystals and its lack of change under applied stress weaker than the transition stress are consistent with the behavior predicted for the D_1 spectrum as given by Eq. (3.1) if only the quartet of states $\Phi_m \chi_m$ is populated at the temperature of the experiment. Under an arbitrary applied stress these four states may have different energies and different relative populations, but all contribute to a single unshifted peak in the spectrum for each $1s \rightarrow np$ transition as long as the deformation potentials Ξ_u and Ξ_d for the $1s$ states are not significantly different from those of the conduction-band edges. If we identify the second spectrum that appears above the critical [111] stress with the D_2 spectrum given by Eq. (3.8), we obtain the difference $\Delta_1-\Delta_0$ from the relative displacement of these spectra as given by Eq. (3.9) to be

$$\Delta_1-\Delta_0=+2.65\ \mathrm{meV}\ . \tag{4.1}$$

The stress independence of the second spectrum above the transition stress is consistent with the expected behavior of the D_2 spectrum.

If we suppose that the transition from D_1 to D_2 occurs at the critical stress P_1 as described by the situation shown in Fig. 1(a), we can then use Eq. (3.6) to evaluate the nuclear strain-coupling coefficient Θ_u from the value of the critical [111] stress $P\sim 2.1\times 10^{7}$ Pa, $\Delta_1-\Delta_0$ as given by Eq. (4.1), and $c_{44}=6.877\times 10^{10}$ Pa,[24] to obtain $\Theta_u \sim -19.5$ eV. This value exceeds in magnitude that of the electronic deformation potential,[22] $\Xi_u=+16.4\pm 0.2$ eV, however, whereas the validity of the situation in Fig. 1(a) requires $\Xi_u > -\Theta_u$. Alternatively, if we suppose that the transition occurs at the critical stress P_2 in Fig. 1(b), we can predict the value of P_2 from Eq. (3.7) and the known value for Ξ_u, obtaining $P_2=2.50\times 10^{7}$ Pa. This predicted value agrees roughly with the reported experimental value $P_2\sim 2.1\times 10^{7}$ Pa, as noted already by Broeckx *et al.*[11] If we take this approximate agreement as supporting the static model, we conclude that the critical stress occurs when the states $\Phi_q \chi_q$ are crossed by $\Phi_q \chi_a$ $(q=b,c,d)$. Assuming the situation shown in Fig. 1(b), we infer then that $-\Theta_u > \Xi_u$ for $D(\mathrm{H,O})$. Moreover, since the states that cross at the critical stress P_2 interact in pairs through the electronic valley-orbit interaction, we expect that the peaks of both the D_1 and D_2 spectra should be split near the critical stress, as has been found experimentally. This splitting at the critical stress appears from the work of Joós *et al.*[2] to be <0.10 meV (see Fig. 1 of Ref. 2), so that from Eq. (3.11) we may estimate the valley-orbit parameter for $D(\mathrm{H,O})$ on the basis of our proposed model to be $|\Delta_{\mathrm{v.o.}}| < 0.05$ meV.

The observation that the D_1 spectrum disappears above the critical stress if the temperature is sufficiently low is consistent with the static model and the situation shown in Fig. 1(b), provided the nuclear configuration can reorient sufficiently rapidly to achieve thermal equilibrium. Otherwise the configuration Φ_a would continue to be present, despite its unfavorable orientation relative to the stress, and the state $\Phi_a \chi_a$ would continue to contribute to the D_1 spectrum at stresses above P_2, with an intensity at least one-third that of D_2. Indeed, occupation of the state $\Phi_a \chi_a$ is energetically favored, as far as the electronic energy alone is concerned, because it is deeper relative to the conduction-band edge by $\Delta_1-\Delta_0$ as compared with $\Phi_q \chi_a$ $(q=b,c,d)$, as seen from Fig. 2. Thus, if the static model as described by Fig. 1(b) is appropriate to $D(\mathrm{H,O})$, we must conclude from the disappearance of the D_1 spectrum above the critical stress that the nuclear configuration can reorient rapidly even at the low temperatures of the PTI experiments.

The static model does not account, however, for the reported observation[2,8,12] that the high-stress spectrum appears when the crystal is stressed uniaxially along [100]. As we have seen in Sec. III C, there should be no departure from the D_1 spectrum in this situation. If the reported result is supported by further experiments and is not the result of inhomogeneity in the applied stress, we will have to conclude that the static model based on defects of trigonal symmetry does not describe $D(\mathrm{H,O})$. As we will show in Sec. IV C, however, the tunneling model as proposed by Joós *et al.*[2] also fails to describe the stress results for [100] stress. Further experiments to test the report of approximate isotropy in the stress results are therefore crucial to distinguish between possible models for this system.

For uniaxial stress along [110] we have seen in Sec. III C that the static model predicts a critical stress at a value $\frac{4}{3}$ that observed for [111] stress, above which a spectrum should appear identical to D_2, except in having its peaks split by $2\Delta_{\mathrm{v.o.}}$. A transition to a spectrum like D_2 has indeed been reported for [110] stress, although at a critical stress said to be approximately the same as for [111] stress, but no splitting of the peaks has been reported. This splitting is very small, however, and it would be sensitive to random strains in the samples or to a sight misalignment of the stress.

Navarro *et al.*[10] have recently observed two additional series of lines, displaced by 2.51 and 2.97 meV with respect to the D_1 series, which appear with increasing temperature in germanium samples with no external stress and which these authors attribute to transitions originating in excited states of the $D(\mathrm{H,O})$ center. If these states are identified with the two excited levels of the static model as given by Eqs. (2.3b) and (2.3c), the energy difference 0.46 meV of the two series yields a value

0.15 meV for the valley-orbit parameter $\Delta_{\text{v.o.}}$, while the center of gravity of their transition energies (weighting the series of lowest frequency by a factor of 2 corresponding to the octet-quartet ratio) as compared to that of the D_1 series given by Eq. (3.1) yields $+2.82$ meV for the difference $\Delta_1-\Delta_0$. This latter value is significantly larger than the value $+2.65$ meV given by Eq. (4.1) from the difference of the D_1 and D_2 series in the stress experiments, while that of $\Delta_{\text{v.o.}}$ is at least 3 times larger than the value $|\Delta_{\text{v.o.}}|<0.05$ meV estimated from the splitting of the peaks at the critical stress.[25] These discrepancies may simply reflect the effects of local strains on the energy levels given by Eqs. (2.3b) and (2.3c), which are much more sensitive to such strains than is the initial state of the D_1 series as given by Eq. (2.3a). A more serious discrepancy with the static model is that the apparent activation energies for these new lines as determined from the temperature dependence of their intensities do not agree with the excitation energies of their initial states as obtained from the differences in their transition energies from those of the D_1 series. Since the static model in thermal equilibrium predicts that the same excitation energies should be obtained in both measurements, Navarro *et al.*[10] cited this difference as evidence supporting the tunneling interpretation. We discuss these results further after describing the tunneling model for D(H,O).

C. Tunneling model

The mathematics of the tunneling model for D(H,O) has been developed by Joós *et al.*[2] and it is the purpose of this subsection to summarize these results in such a way as to make clear the crucial conditions that must be satisfied in order that the model fit the experimental data. Also discussed will be the reasons for regarding certain of these conditions as unlikely on physical grounds. In addition, the treatment given goes beyond that of Joós *et al.* to consider how uniaxial stress along [100] or [110] should affect the tunneling model, and it will be shown that differences in the resulting spectra from those obtained with [111] stress should be apparent.

As in Sec. II, simplifications are again introduced in the treatment of the model as given by Joós *et al.* by assuming the valley-orbit and tunneling matrix elements in the 1s state each to depend on a single parameter, so that the Hamiltonian is simpler in form than the most general one allowed by symmetry. These simplifications in no way affect the essential features of the argument made here.

The tunneling model of Joós *et al.*[2] is built on the same 16 states $\Phi_l\chi_m$ $(l,m=a,b,c,d)$ introduced in Sec. II and augments the electronic intravalley and intervalley couplings with an interaction between the differently oriented nuclear configurations given by

$$\langle lm\,|\,\mathcal{H}_n(1s)\,|\,l'm'\rangle=-t'(1-\delta_{ll'})\delta_{mm'}\ . \tag{4.2}$$

Joós *et al.* make the assumption that the nuclear tunneling rate as given by t' when the donor electron is in one of its 1s EM states χ_m is different from the corresponding rate, which will be denoted by t, when the electron is in any one of its excited np states (or removed entirely from the complex by ionization to the conduction band). The energy of the electronic $1s\rightarrow np$ transition accordingly may depend on the nuclear tunneling rate through the difference $t'-t$.

In the final state of the $1s\rightarrow np$ transition the intravalley and intervalley interactions analogous to Δ_1, Δ_0, and $\Delta_{\text{v.o.}}$ are assumed negligibly small, so that the eigenstates are given by any product of an electronic np EM wave function with a nuclear eigenstate determined in perfect tetrahedral symmetry by the tunneling interaction alone. These nuclear eigenstates are uniquely determined by symmetry to be the singlet (Γ_1) combination

$$\Phi_1=\tfrac{1}{2}(\Phi_a+\Phi_b+\Phi_c+\Phi_d) \tag{4.3}$$

at E_N-3t and the three components

$$\begin{aligned}\Phi_{5x}&=\tfrac{1}{2}(\Phi_a+\Phi_b-\Phi_c-\Phi_d)\ ,\\ \Phi_{5y}&=\tfrac{1}{2}(\Phi_a-\Phi_b+\Phi_c-\Phi_d)\ ,\\ \Phi_{5z}&=\tfrac{1}{2}(\Phi_a-\Phi_b-\Phi_c+\Phi_d)\end{aligned} \tag{4.4}$$

of the degenerate Γ_5 triplet at E_N+t. Unless t is zero (a situation contrary to the assumptions of Joós *et al.* and unlikely if t' is significantly different from zero in the donor ground state), distinct optical transitions to np states built upon *both* Φ_1 and one or more of the Φ_{5i} will occur from any initial state which, because of nonzero values for Δ_0, Δ_1, and $\Delta_{\text{v.o.}}$ in the 1s state, involves any other combination of Φ_a, Φ_b, Φ_c, and Φ_d than those given by Eqs. (4.3) and (4.4). Since there is no such final-state splittings found experimentally in the D(H,O) spectrum at zero stress, we can conclude that the ground state of the $\Phi_l\chi_m$ manifold must to a good approximation involve products of *either* Φ_1 *or* combinations of the Φ_{5i}, but *not both.* Joós *et al.*[2] assumed, consistent with this requirement, that the 1s ground state in zero stress is formed from the Γ_1 tunneling state Φ_1, with no significant mixing with Φ_{5i}, and that it comprises four nearly degenerate states, a Γ_1 singlet,

$$\Psi_{g1}=\Phi_1\chi_1\ , \tag{4.5}$$

and a Γ_5 triplet,

$$\begin{aligned}\Psi_{g5x}&=\Phi_1\chi_{5x}\ ,\\ \Psi_{g5y}&=\Phi_1\chi_{5y}\ ,\\ \Psi_{g5z}&=\Phi_1\chi_{5z}\ .\end{aligned} \tag{4.6}$$

Here, χ_1 and $\chi_{5x},\chi_{5y},\chi_{5z}$ denote symmetrized combinations of the χ_m defined in exactly the same way as in Eqs. (4.3) and (4.4). The energies of these states are easily obtained from their diagonal matrix elements with respect to the Hamiltonian from Eqs. (2.1), (2.2), and (4.2) to be

$$E_g(\Gamma_1)=E_{1s}+E_N-\tfrac{1}{4}\Delta_1-\tfrac{3}{4}\Delta_0-3t'-3\Delta_{\text{v.o.}}\ , \tag{4.7}$$

$$E_g(\Gamma_5)=E_{1s}+E_N-\tfrac{1}{4}\Delta_1-\tfrac{3}{4}\Delta_0-3t'+\Delta_{\text{v.o.}}\ . \tag{4.8}$$

These energies differ by only the valley-orbit splitting $4\Delta_{\text{v.o.}}$.

The transition energies from the $\Gamma_1(\chi_1)$ and $\Gamma_5(\chi_5)$

components of the $1s$ ground state, with wave functions given by Eqs. (4.5) and (4.6) and energies by Eqs. (4.7) and (4.8), to the Φ_1 tunneling component of the np excited state at $E_{np}+E_N-3t$ are accordingly given by the tunneling model of Joós *et al.* to be

$$\Delta E_{np}(1s,\Phi_1{:}\mathcal{X}_1)=E_{np}-E_{1s}+\tfrac{1}{4}\Delta_1+\tfrac{3}{4}\Delta_0+3(t'-t)+3\Delta_{\text{v.o.}}\ , \tag{4.9a}$$

$$\Delta E_{np}(1s,\Phi_1{:}\mathcal{X}_5)=E_{np}-E_{1s}+\tfrac{1}{4}\Delta_1+\tfrac{3}{4}\Delta_0+3(t'-t)-\Delta_{\text{v.o.}}\ . \tag{4.9b}$$

Since each $1s\rightarrow np$ transition occurs as a single very sharp peak in the experimental spectrum and does not shift with applied stress, this interpretation clearly requires a valley-orbit splitting $4\Delta_{\text{v.o.}}$ that is exactly zero so that Eqs. (4.9a) and (4.9b) coincide.

Under an external stress along [111] the four states Φ_1, Φ_{5x}, Φ_{5y}, and Φ_{5z} as given by Eqs. (4.3) and (4.4) are coupled if the stress coupling of the nuclear configurations is as given by Eq. (2.6), and the resulting nonlinear shift of the tunneling states corresponding to the np electronic final states is shown in Fig. 3(a) ($\Theta_u<0$ assumed). A nonlinear shift of the tunneling states also occurs in the $1s$ electronic ground state, but, in general, is quantitatively different from that in the final state, even though the stress-coupling coefficient Θ_u is taken to be the same for both, because the tunneling splitting is $4t'$ in the ground state but $4t$ in the excited state. As a result of this difference the $1s\rightarrow np$ transition energies should shift with applied stress from the value given by Eq. (4.9); the term $3(t'-t)$ in Eq. (4.9) should shift toward $2(t'-t)$, for example. Moreover, it is clear from Fig. 3(a) that with increasing stress there is no point at which the lower nuclear state Λ_3 derived from Φ_5 crosses the nuclear ground state Λ_1 originating in Φ_1, so that there is no reason with this model to anticipate a critical value of the stress at which a sharp change in the $1s\rightarrow np$ spectrum originating in the nuclear ground state occurs. Since the observed low-stress spectrum does *not* shift with applied stress and a critical stress *does* occur, it was therefore essential for Joós *et al.*[2] to assume in their tunneling model an entirely different stress coupling of the nuclear states from that given by Eq. (2.6). In particular, they assumed *no* interaction between the nuclear states Φ_1 and Φ_5 so that the resulting shift in energy of these states could be assumed strictly linear in the stress, as shown in Fig. 3(b). If this linear shift in each nuclear state is taken to be the same for the initial and final electronic states, the transition energy as given by Eq. (4.9) (with $\Delta_{\text{v.o.}}=0$) is then independent of stress, as required to fit the behavior of the experimental spectrum. Moreover, a critical value of the stress now occurs, as shown in Fig. 3(b), at which the Λ_3 component of Φ_5 crosses $\Phi_1(\Lambda_1)$. (Note that we should expect *two* values of the stress at which such a crossing occurs, one for the final electronic state np and one for the $1s$ ground state, because of the different values of the tunneling splitting $4t$ and $4t'$, assuming both t and t' positive.) This Λ_3 component of Φ_5 comprises the two states

$$\Phi_{3\varepsilon}^{\Lambda}=(\Phi_{5x}-\Phi_{5y})/\sqrt{2}=(\Phi_b-\Phi_c)/\sqrt{2}\ ,$$
$$\Phi_{3\theta}^{\Lambda}=(2\Phi_{5z}-\Phi_{5x}-\Phi_{5y})/\sqrt{6}=(2\Phi_d-\Phi_b-\Phi_c)/\sqrt{6}\ . \tag{4.10}$$

The terms in the Hamiltonian given by Eqs. (2.1), (2.2), and (4.2) have diagonal matrix elements with respect to the states $\Phi_{3\varepsilon}^{\Lambda}\mathcal{X}_a$ and $\Phi_{3\theta}^{\Lambda}\mathcal{X}_a$ given by $E_{1s}-\Delta_0+t'$. When this Λ_3 component becomes thermally populated near the critical stress at which the crossing occurs in the ground state, transitions to the Φ_3^{Λ} components of the np final state then occur at a transition energy given by

$$\Delta E_{np}(1s,\Phi_3^{\Lambda}{:}\mathcal{X}_a)=E_{np}-E_{1s}+\Delta_0-(t'-t) \tag{4.11}$$

for the stress-favored electronic state $\mathcal{X}_a$. [It is assumed $4t'$ is large enough so that the $1s$ states derived from $\Phi_5(\Lambda_3)$ have negligible population until near the critical stress.] The change in transition energy between the low-stress and high-stress spectra is accordingly given by the tunneling model of Joós *et al.* as the difference between Eqs. (4.9) ($\Delta_{\text{v.o.}}=0$) and (4.11) to be

$$\Delta E_{np}(1s,\Phi_1{:}\mathcal{X}_{1,5})-\Delta E_{np}(1s,\Phi_3^{\Lambda}{:}\mathcal{X}_a)=4(t'-t)+\tfrac{1}{4}(\Delta_1-\Delta_0)\ . \tag{4.12}$$

This difference must equal 2.65 meV to fit the observed spectra.

Joós *et al.*[2] concluded from Eq. (4.12) [equivalent to their Eq. (3.29), where $\Delta_1'=t'-t$ and $\delta=\tfrac{1}{2}(\Delta_1-\Delta_0)$ in their notation] that whereas $\tfrac{1}{4}(\Delta_1-\Delta_0)$ is a positive quantity of the order 0.5 meV at most, $t'-t$ must therefore be approximately 0.5–0.6 meV in order for the tunneling model to fit the data. Not only does the tunneling model indicate a large value for the tunneling splitting ($4t'\gtrsim 2$ meV), but it also requires this splitting to be at least 2 meV larger when the donor electron is in its $1s$ state than

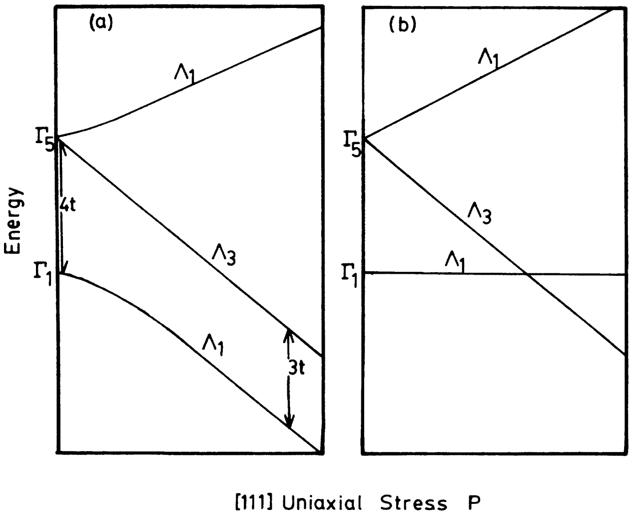

FIG. 3. Splitting of the nuclear tunneling states with [111] uniaxial stress P: (a) according to the interaction given by Eq. (2.6) of the text; (b) according to the assumptions of the tunneling model of Joós *et al.* for D(H,O).

when it is in one of its excited *np* states. The mechanism for such a large electronic contribution to the nuclear tunneling rate is not clear, particularly since EM theory shows that even in its 1*s* state the electron is so spread out as to have only a very small probability of being found within a lattice constant of the defect.

Joós *et al.*[2] suggested that the small splitting observed in both the high-stress and low-stress spectral peaks at the transition stress could be the result of a small misalignment of the applied stress from the [111] axis, so that a small coupling between the $\Lambda_1(\Phi_1)$ and $\Lambda_3(\Phi_5)$ nuclear states would not be inconsistent with the symmetry of these states. We may note, however, that the presence of such a coupling between the Φ_1 and Φ_5 states, due to a small misalignment, is not consistent with the requirement of the tunneling model as discussed earlier that the coupling between Φ_1 and Φ_5 states due to the Γ_5 strain components e_{xy}, e_{yz}, e_{zx} must vanish in order to account for the absence of any displacement of the low-stress spectrum with increasing stress. Moreover, if such coupling were present, there should be a similar coupling of the $\Lambda_1(\Phi_1)$ and $\Lambda_3(\Phi_5)$ states, due to misalignment, at the lower critical stress (since $t' > t$) at which these states cross in the *final* state (*np*) of the transition (if $t > 0$). This should show up as a splitting of the low-stress spectrum at this final-state crossing.

For the tunneling model to account for a similar transition in the spectrum as reported[2,12] to occur for stress applied along [100], it is necessary to postulate a similar linear splitting of the $\Gamma_5(\Phi_5)$ nuclear states by [100] stress, leading to a similar crossing of the $\Gamma_1(\Phi_1)$ state. Although the theoretical analysis of this case was not discussed by Joós *et al.*,[2] such a splitting is allowed by symmetry but not expected for tunneling states built up from defect orientations Φ_a, Φ_b, Φ_c, and Φ_d oriented along [111] directions, which are equivalent under [100] stress. Nevertheless, if we assume such a splitting of $\Gamma_5(\Phi_5)$ there will be no coupling with $\Gamma_1(\Phi_1)$, since in lowering the symmetry from T_d to D_{2d}, Γ_5 and Γ_1 reduce to different irreducible representations of D_{2d}:

$$\Gamma_5(T_d) \rightarrow \Gamma_4(D_{2d}) + \Gamma_5(D_{2d}) ,$$

$$\Gamma_1(T_d) \rightarrow \Gamma_1(D_{2d}) .$$

Moreover, [100] stress treats all the χ_m equivalently as well. At stresses above the crossing a representative state giving rise to the high-stress spectrum is formed from any of the χ_m and either Φ_{5x}, if the $\Gamma_4(D_{2d})$ component has lower energy under [100] stress, or Φ_{5y} and Φ_{5z} if the $\Gamma_5(D_{2d})$ component is lower. In the former case the transition energy is

$$\Delta E_{np}(1s,\Phi_{5x};\chi_m) = E_{np} - E_{1s} + \tfrac{1}{4}\Delta_1 + \tfrac{3}{4}\Delta_0 - (t'-t) , \tag{4.13}$$

which differs from that of the low-stress spectrum, Eq. (4.9) ($\Delta_{\text{v.o.}} = 0$), by

$$\Delta E_{np}(1s,\Phi_1{:}\chi_{1,5}) - \Delta E_{np}(1s,\Phi_{5x};\chi_m) = 4(t'-t) , \tag{4.14}$$

a different result from that given by Eq. (4.12) for [111] stress. Alternatively, if the $\Gamma_5(D_{2d})$ component of Φ_5 is lower under [100] stress, the interaction $\mathcal{H}_d^e(1s)$ from Eq. (2.1) couples the states $\Phi_{5y}\chi_m$ and $\Phi_{5z}\chi_m$, so that two transitions are predicted in the high-stress spectrum at

$$\Delta E_{np}(1s,\Phi_{5y,z}[1]{:}\chi_m) = E_{np} - E_{1s} + \tfrac{1}{2}(\Delta_1 + \Delta_0) - (t'-t) \tag{4.15a}$$

and

$$\Delta E_{np}(1s,\Phi_{5y,z}[2]{:}\chi_m) = E_{np} - E_{1s} + \Delta_0 - (t'-t) . \tag{4.15b}$$

While the second of these agrees with Eq. (4.11) and thus represents the same spectrum as given for high stress along [111], the first is different unless $\Delta_1 = \Delta_0$. If $\Delta_1 > \Delta_0$, as we expect in agreement with the assumption of Joós *et al.*, Eq. (4.15a) represents the transition from the state of lower energy and thus should be the stronger transition. Regardless of which component $\Gamma_4(D_{2d})$ or $\Gamma_5(D_{2d})$ of Φ_5 has the lower energy under [100] stress, then, the tunneling model predicts a high-stress spectrum different from that found for [111] stress. The experimental spectrum is reported to be the same as for [111] stress.

For uniaxial stress along [110] the splitting of Φ_5 is determined in C_{2v} symmetry to give the states Φ_{5z}, $(\Phi_{5x} + \Phi_{5y})/\sqrt{2}$, and $(\Phi_{5x} - \Phi_{5y})/\sqrt{2}$. Which of these has the lowest energy depends on the relative values of the stress-coupling coefficients for [111] and [100] stress, as does the value of the critical stress at the crossing with Φ_1, but this behavior is predictable from the results for the other stress directions. These three states yield transition energies in agreement, respectively, with Eqs. (4.13), (4.15a), and (4.15b). If the coupling to [111]-type stress is dominant, the last of these should represent the high-stress spectrum, thus agreeing with that found for [111] stress, as reportedly found in the experiments.

The two additional series of lines observed by Navarro *et al.*[10] and attributed to transitions originating from excited levels of *D*(H,O) had activation energies found from the temperature dependence of their intensities to be 1.57 and 1.94 meV. If, following Navarro *et al.*,[10] we identify these excited levels as resulting from association of the 1*s* electronic states χ_m with the excited Γ_5 nuclear tunneling states Φ_{5x}, Φ_{5y}, and Φ_{5z} given by Eq. (4.4), we find from the tunneling model that there should indeed be only two such levels if we stipulate that the valley-orbit interaction $\Delta_{\text{v.o.}}$ be zero, as required by Eqs. (4.7) and (4.8) if the Γ_1 and Γ_5 levels of the nuclear ground state Φ_1 coincide.[26] One of these is fourfold degenerate and combines Γ_1 and Γ_5 states at

$$E_e(\Gamma_1) = E_e(\Gamma_{5a}) = E_{1s} + E_N + t' - \tfrac{3}{4}\Delta_1 - \tfrac{1}{4}\Delta_0 , \tag{4.16}$$

and the other eightfold degenerate and combining Γ_3, Γ_4, and Γ_5 at

$$E_e(\Gamma_3) = E_e(\Gamma_4) = E_e(\Gamma_{5b}) = E_{1s} + E_N + t' - \Delta_0 . \tag{4.17}$$

The energies of the transitions from these levels to the Φ_5 tunneling component of the *np* excited state at $E_{np} + E_N + t$ are accordingly

$$\Delta E_{np}(1s,\Phi_5{:}\Gamma_1)=\Delta E_{np}(1s,\Phi_5{:}\Gamma_{5a}) =E_{np}-E_{1s}+\tfrac{3}{4}\Delta_1+\tfrac{1}{4}\Delta_0-(t'-t)\ , \tag{4.18a}$$

$$\Delta E_{np}(1s,\Phi_5;\Gamma_3)=\Delta E_{np}(1s,\Phi_5;\Gamma_4)=\Delta E_{np}(1s,\Phi_5{:}\Gamma_{5b}) =E_{np}-E_{1s}+\Delta_0-(t'-t)\ . \tag{4.18b}$$

The difference of these equals $\frac{3}{4}(\Delta_1-\Delta_0)$, yielding

$$\Delta_1-\Delta_0=0.61 \text{ meV} \tag{4.19}$$

from the experimental difference in these transition energies [or $\Delta_1-\Delta_0=0.49$ meV from Eqs. (4.16) and (4.17) and the difference in the measured activation energies]. The difference between Eq. (4.16) and Eq. (4.7) or (4.8) ($\Delta_{\text{v.o.}}=0$) yields

$$4t'-\tfrac{1}{2}(\Delta_1-\Delta_0)=1.57 \text{ meV} \tag{4.20}$$

from the activation energy of the first excited state. As Navarro *et al.*[10] noted, therefore, these data provide a direct determination of the tunneling splittings $4t'$ and $4t$. We have, from Eqs. (4.19) and (4.20),

$$4t'=1.88 \text{ meV}\ , \tag{4.21}$$

and from the difference between Eqs. (4.18a) and (4.9) and the corresponding difference in transition energies,

$$4(t'-t)-\tfrac{1}{2}(\Delta_1-\Delta_0)=2.51 \text{ meV}\ , \tag{4.22}$$

whence we obtain with Eqs. (4.19) and (4.21),

$$4t=-0.94 \text{ meV}\ . \tag{4.23}$$

As noted by Navarro *et al.*,[10] this interpretation of the data requires that the sign of the nuclear tunneling splitting be reversed between the 1*s* and *np* electronic states, with the Γ_5 nuclear state below the Γ_1 singlet when the electron is in the *np* state.

The results for the parameters of the tunneling model, as obtained from the data of Navarro *et al.*, can be checked for their consistency with the results of the stress experiments of Joós *et al.*[2] by evaluating the expression given in Eq. (4.12). We obtain from Eqs. (4.19), (4.21), and (4.23) the value 2.97 meV, compared to 2.65 meV from the stress experiments. This discrepancy indicates a significant inconsistency in using the tunneling model to account for both the new lines observed by Navarro *et al.*[10] and the original stress data of Joós *et al.*[2]

V. THE DONOR *D*(Li,O)

A. Experimental summary

The spectrum[1] of *D*(Li,O) contains one set of sharp peaks which are reported to be independent of stress, corresponding to a level with binding energy 10.34 meV, and (at 6.5 K and no applied stress) two sets of broad peaks originating from levels ~9.85 and 9.29 meV below the conduction-band edge. The latter sharpen into two sets of sharp peaks at high uniaxial [111] stress corresponding to levels with binding energies 9.72 and 9.63 meV. The relative intensities of the three sets are in the ratio 1:2:1 at high stress when weighted by suitable Boltzmann factors.

B. Tunneling model

The model proposed by Haller and Falicov[1] to account for the spectrum of *D*(Li,O) is essentially the same as that described in Sec. II for a complex with trigonal symmetry, except that a small tunneling interaction as in Eq. (4.2) was introduced to account for the separation of the peaks in the high-stress spectrum corresponding to the levels at 9.72 and 9.63 meV. Whereas for the tunneling model for *D*(H,O) Joós *et al.*[2] assumed the tunneling splitting large compared to $\Delta_1-\Delta_0$, for *D*(Li,O) Haller and Falicov[1] assumed $\Delta_1-\Delta_0$ large compared to both $4t'$ and $4\Delta_{\text{v.o.}}$, so that the ground state in the unstressed crystal comprises the four states $\Phi_m\chi_m$ ($m=a,b,c,d$) with energy given by Eq. (2.3a). As in Sec. III A, these states shift linearly with stress, each χ_m following its valley, and would be expected to give rise to the stress-independent D_1 spectrum which Haller and Falicov identified with the sharp experimental peaks originating in the 10.34-meV level. Under strong uniaxial stress along [111], the three states $\Phi_q\chi_a$ ($q=b,c,d$) would be expected from the analysis of Sec. III A to contribute to a single series of peaks, the D_2 spectrum, whereas the experimental spectrum exhibits two series (in addition to the D_1 series) with an intensity ratio 2:1. Haller and Falicov[1] concluded that such a structure constituted unambiguous evidence that the equivalent orientations of the complex were coupled by a tunneling interaction, as in Eq. (4.2), to yield singlet and doublet states separated by $3t'$.

In their analysis of this situation, Haller and Falicov[1] failed to note that tunneling, if present in the 1*s* initial states, would be expected to be significant in the *np* final states as well, corresponding to the tunneling matrix element $-t$ in Sec. IV C. Accordingly, the separation $3(t'-t)$ of the peaks in the high-stress spectrum would be nonzero only if the tunneling is different in the initial and final states. In zero stress, moreover, there should be a splitting $4t$ of the peaks resulting from transitions from the ground states $\Phi_m\chi_m$, because final-state tunneling yields the nuclear states Φ_1 and Φ_5, as given by Eqs. (4.3) and (4.4) and shown in Fig. 3(a), with this separation. Since these states are mixed by strain and therefore shift nonlinearly [Fig. 3(a)], the resulting spectrum should shift with stress and should be broadened by random strain. Since there is no such splitting or stress dependence of the zero-stress spectrum associated with the 10.34-meV level, we conclude that the tunneling matrix element t in the final state would have to be zero despite the nonzero value for t' assumed in the 1*s* state.[27]

C. Static model

A static model for a complex of trigonal symmetry, as in Secs. II and III, fails to account for the appearance of two distinct series of peaks in the high-stress spectrum of *D*(Li,O) corresponding to levels at 9.72 and 9.63 meV, predicting instead the single series of the D_2 spectrum. To explain the observed splitting of these two levels without invoking tunneling, it is proposed that the D(Li,O) complex may have a symmetry lower than trigonal. As will now be shown, it is possible to choose this symmetry to be consistent with a stress-independent splitting of the D_2 transitions in the high-stress spectrum into two peaks with relative intensities 2:1, as found experimentally.

Let us postulate a defect that approximates trigonal symmetry about the [111] axis, but in actuality is invariant under a single symmetry operation, reflection in the $(1\bar{1}0)$ plane (which contains [111]) As in Sec. II, we assume an intravalley electronic energy $E_{1s}-\Delta_1$ for the 1s state χ_a belonging to the [111] valley. Because of the lower symmetry the other three states—χ_b, χ_c, and χ_d—are no longer equivalent, and we assume an energy $E_{1s}-\Delta_{01}$ for the state χ_d belonging to the $[\bar{1}\bar{1}1]$ valley lying in the $(1\bar{1}0)$ reflection plane of the defect. The remaining two states—χ_b and χ_c—belong to valleys that do not lie in this plane but are exchanged by reflection in $(1\bar{1}0)$. Therefore χ_b and χ_c must have equal intravalley energies, which we take to be $E_{1s}-\Delta_{02}$. The states χ_b and χ_c, of course, interact through the valley-orbit interaction, so that eigenstates of the system in the absence of stress are the combinations $(\chi_b \pm \chi_c)/\sqrt{2}$ at energies $E_{1s}-\Delta_{02}\pm\Delta_{\text{v.o.}}$ when valley-orbit interaction with χ_d is ignored.

A mechanism leading to different intravalley energies Δ_{01} and Δ_{02} for χ_d and χ_b,χ_c is the localized strain introduced by the defect, as discussed in Sec. III A. Because of the lower symmetry, the equivalent distributions for the strain components e_{yz} and e_{zx} are no longer related to that for e_{xy}, and the energy shift of χ_d, which depends on strain through $e_{xy}-e_{yz}-e_{zx}$, is therefore different from that of χ_b,χ_c, which depend on $-e_{xy}+e_{yz}-e_{zx}$ and $-e_{xy}-e_{yz}+e_{zx}$, respectively.

The same 1:1:2 splitting of the intravalley energies of the four electronic 1s states (omitting the valley-orbit interaction), occurs, of course, for any of the 12 equivalent orientations of such a lower-symmetry complex in a crystal with no external stress. Under applied uniaxial stress along [111], which lowers the electronic state χ_a, the energy displacements of the 1s states relative to the [111] conduction-band edge for differently oriented complexes again have the same values $E_{1s}-\Delta_1$, $E_{1s}-\Delta_{01}$, and $E_{1s}-\Delta_{02}$ with respective weights 1:1:2, the energy of a particular orientation depending on whether the stress direction is along the preferred axis of the defect or, if not, whether the stress direction lies in the reflection plane of the defect. (Valley-orbit interaction now does not affect these energies.) These energy displacements are independent of the applied stress (at least to a first approximation), since they depend only on the local distortion introduced by the defect. Accordingly, for a defect of this postulated symmetry, peaks in the PTI spectrum at high [111] stress corresponding to defects not aligned with the stress axis should split into two sharp stress-independent peaks with relative intensities 2:1 as found experimentally. This structure should be insensitive to misalignment of the applied stress or to random strain in the crystal. By contrast, the similar structure predicted by the tunneling model should be sensitive to both effects. An experimental test to distinguish which model is appropriate is therefore possible through a delibera misalignment of the applied stress.

From the binding energies of the levels responsible for the sharp peaks in the spectrum observed under stress, we obtain accordingly $\Delta_1=+0.53$ meV, $\Delta_{01}=-0.18$ meV, and $\Delta_{02}=-0.09$ meV. If we approximate the separation of the two series of broad peaks in the zero-stress spectrum by $3\Delta_{\text{v.o.}}$ as in the difference between the levels given by Eqs. (2.3b) and (2.3c), we obtain $|\Delta_{\text{v.o.}}|\sim 0.19$ meV for the valley-orbit interaction. The sign of $\Delta_{\text{v.o.}}$ depends on which of these levels we identify with each set of peaks, but the choice giving the best agreement between the center of gravity of the levels in the zero-stress spectrum and that of the levels under stress yields a negative value for $\Delta_{\text{v.o.}}$. If this interpretation is correct, it would indicate an inverted sense of the valley-orbit interaction for D(Li,O) as found also for the interstitial Li donor in silicon.[28]

The fact that the peaks of the D_1 spectrum remain strong for D(Li,O) at a stress as high as 1.5×10^8 Pa,[1,12] which is 7 times the transition stress for D(H,O), indicates that the D(Li,O) complex does not reorient at the temperatures of the experiment. Either the strain-coupling coefficients giving the relative energies of the differently oriented complexes under stress are very much smaller than for D(H,O) or, more likely, reorientation of the complex is effectively frozen out at these low temperatures.

Assuming no reorientation, we would expect from our model for D(Li,O) that the PTI spectrum should show an effect, not yet reported, corresponding to the splitting of the peaks of both the D_1 and D_2 series in the D(H,O) spectrum at the transition stress. This effect should be evident at a stress $P\sim0.5\times10^7$ Pa along [111] at which the electronic state χ_a crosses the lowest state χ_b, χ_c, or χ_d for any one of the defect orientations having its preferred axis not along the stress axis. However, since the unshifted D_1 spectrum should also be present at this stress for those defect orientations aligned along the stress axis, the splitting of the peaks in the PTI spectrum should be more complicated than the simple doubling reported for D(H,O). A similar effect would be expected for the tunneling model as well.

VI. DISCUSSION

If tunneling is responsible for splitting the peaks of the high-stress spectrum of D(Li,O), as postulated by Haller and Falicov,[1] there should be a corresponding splitting and broadening of the D_1 spectrum at zero stress because of tunneling in the np final state, as has been shown in Sec. V B. This is not observed. The alternative, within the framework of the tunneling model, is that tunneling is negligible in the np final states but significant in the 1s state. This seems a very unlikely situation, but even if it were the case the splitting of the high-stress spectrum should then be sensitive to the effects of random strain and to misalignment of the applied stress, and there is no evidence of such sensitivity. By contrast, we have seen in Sec. V C that a static model involving centers of C_{1h} symmetry can account for the observed behavior, including a split but sharp high-stress spectrum insensitive to random strains and to misalignment. It seems very unlikely, therefore, that tunneling plays a significant role for D(Li,O).

The case against tunneling for D(H,O) also appears very strong. To summarize our conclusions from Sec. IV C, fitting the tunneling model to the observed behavior of D(H,O) necessitates that the valley-orbit interaction be vanishingly small, that the nuclear tunneling rate depend strongly on the electronic state despite the EM nature of those states, and that the splitting of the tunneling states by applied stress be strictly linear and entirely different from that expected for the stress alignment of the oriented configurations on which the tunneling model is based. In addition, we have seen that the tunneling model does not, in fact, account for the splitting of the peaks observed at the transition stress. Moreover, the tunneling model does not account for a transition to a high-stress spectrum for [100] stress that is identical, as reported, to that observed for [111] stress.

The static model for D(H,O) proposed here and by Broeckx *et al.*,[11] by contrast, fits most of the observed behavior very naturally and even predicts approximately the value of the critical [111] stress from the known electron deformation potential. The major failing of this model is its inability to account for the transition to the high-stress spectrum under [100] stress, reported by Joós *et al.*[2,12] While this model does predict such a transition for [110] stress, we showed that the high-stress spectrum in this case should show a small valley-orbit splitting of its peaks (unless suppressed by random strain or by misalignment of the stress), which has not been reported. Clearly, the behavior of the PTI spectrum of D(H,O) for different directions of applied stress needs further clarification.

A further test to distinguish between the static and tunneling models for D(H,O) could be made by using polarized light to study the PTI spectrum under applied stress. With uniaxial compression along [111], in the tunneling model the electronic state χ_a is preferentially populated in thermal equilibrium both above and below the critical stress, so that transitions to $np_\pm$ states should be strongest when the polarization is perpendicular to the stress axis, in both stress regions. In the static model of Fig. 1(b), which we have argued should be appropriate to D(H,O), we find, on the other hand, that the state χ_a is depopulated below the critical stress P_2 if the defect is able to reorient, so that the polarization of the D_1 spectrum below P_2 would be reversed compared to the tunneling model. If reorientation is frozen out and all states $\Phi_m \chi_m$ remain equally populated below P_2, the D_1 spectrum should remain unpolarized. Above P_2 the static model yields the same polarization for the D_2 spectrum (and also for D_1 if it persists in the absence of reorientation) as for the tunneling model.

The new series of lines observed in the recent work of Navarro *et al.*[10] and attributed by these authors to the D(H,O) center should allow the unambiguous determination of the parameters of the tunneling model, including the tunneling splittings in the 1*s* and *np* electronic states, if that model is appropriate. Unfortunately, as we have seen, this determination results in a significant quantitative discrepancy with the interpretation of the stress experiments given by Joós *et al.*[2] An alternative interpretation of the new lines in terms of excited states of the static model leads to a similar though smaller numerical discrepancy with the results of the stress experiments and, in addition, fails to yield the agreement between the thermal activation energies of these states and the transition-energy differences expected on the basis of the static model. The significance of these new lines in discriminating between the models therefore remains unclear.

The interpretation of these new lines with the tunneling model makes very clear, as noted by Navarro *et al.*,[10] that when the electron is in the *np* state the ordering of the nuclear tunneling states must place the Γ_5 triplet *below* the Γ_1 singlet. Since the electron in an *np* state is too spread out to affect the nuclear tunneling process, we would be forced to conclude from this result that the nuclear ground state is a Γ_5 triplet when there is no electron on the defect. We expect, however, on very general grounds that the ground state of a particle (the proton) trapped in a potential well or group of wells to have a ground-state wave function without nodes,[29] and this requirement is compatible only with the symmetric representation (Γ_1) of the symmetry group of the system. While the ground state of a system with additional degrees of freedom, such as systems with electronic degeneracy subject to the Jahn-Teller effect, can have ground states belonging to another representation than Γ_1,[30] it is difficult to see how such a situation could be appropriate to the proton in the D(H,O) center. There is therefore a fundamental difficulty in interpreting the new data of Navarro *et al.* according to the tunneling model. A similar difficulty arises with the tunneling model in interpreting the stress data, since according to the interpretation of Joos *et al.*[2] the nuclear ground state ceases to belong to the symmetric representation of the symmetry group of the stress-distorted defect site as soon as the split component of the triplet state Φ_5 ($\Lambda_3(C_{3v})$ for [111] stress as shown in Fig. 3(b), Γ_4 or $\Gamma_5(D_{2d})$ for [100] stress) crosses the singlet Φ_1 at the critical stress.

Evidence that may support the low-symmetry configuration which we have suggested for D(Li,O) is found in studies by Corbett, McDonald, and Watkins[31] of the stress-induced dichroism of the infrared-absorption band due to oxygen in solution in germanium, which indicates that oxygen occupies the interstitial configuration, as it does in silicon. In this configuration an oxygen atom interrupts a normal Ge—Ge bond to form a bent Ge—O—Ge molecular unit that is aligned approximately with one of the [111] crystal axes. The equilibrium configuration of the defect does not have trigonal symmetry, however, because of the off-axis position of the oxygen. If the equilibrium position of the oxygen lies in one of the three (110) reflection planes that contain the axis of the original Ge—Ge bond, there are six equivalent oxygen sites for each of the possible bond orientations. [Since the bond midpoint is a point of inversion symmetry in the diamond lattice, there are two equivalent positions in each (110) plane, related to each other by inversion through the midpoint.] Such a configuration for interstitial oxygen would therefore in itself have the same symmetry as that we postulate for the D(Li,O) complex. In silicon, however, the infrared-vibrational-absorption studies of Bosomworth *et al.*[32] show that the barriers separating equivalent oxygen sites around a given bond axis are small and that the oxygen acts much like a two-dimensional harmonic oscillator in the plane normal to the bond. The corresponding information is not available for oxygen in germanium and, of course, it is not known how the presence of Li changes the oxygen bonding. But if the Li somehow were to increase the barriers between equivalent oxygen positions or otherwise inhibit the reorientation of the oxygen about the bond direction, such behavior would be consistent with the postulated lower symmetry for the D(Li,O) complex.

We have seen in Sec. IV B at the static model for D(H,O) requires that the complex must be able to reorient rapidly from one [111] axis to another in order to explain a nearly complete disappearance of the D_1 spectrum above the critical stress. This conclusion is incompatible with the observation of Corbett *et al.*[31] that the stress-induced dichroism of oxygen in germanium is stable already at room temperature, if oxygen in D(H,O) is in the same interstitial bond-centered position that it occupies as an isolated impurity. The concentration of D(H,O) is much lower than the total oxygen content of the crystal,[9,12] however, so that it is possible that in D(H,O) the oxygen occupies a different, symmetrical site and that the rapid reorientation of the complex in the PTI studies reflects a high low-temperature mobility for the proton. Such a symmetrical site for the oxygen would be compatible with the assumption of Joós *et al.*[2] and of Oliva and Falicov[33,34] that in D(H,O) the oxygen is substitutional.

By contrast, our proposed reinterpretation of D(Li,O) indicates no reorientation of this complex. This conclusion is compatible with the stability of the dichroism found by Corbett *et al.*[31] if the oxygen remains in its interstitial configuration. Since the formation of D(Li,O) by precipitation of Li is used as a means to determine the oxygen content of a germanium crystal,[35] we would expect the configuration of oxygen in D(Li,O) to be closely related to that of isolated oxygen. Our proposed model is consistent with this expectation.

Electron-paramagnetic-resonance (EPR) studies[1] of D(Li,O) reveal a g factor with axial symmetry about a [111] axis, and this result has been cited by Haller and Falicov[1] as proof that the complex has this symmetry. The g factor is determined by the electronic part of the wave function, however, and in EM theory χ_m has the axial symmetry of its valley,[14,15] whether or not the defect actually shares this symmetry. The measured values for D(Li,O), $g_{\parallel}=0.8585\pm0.0010$ and $g_{\perp}=1.9040\pm0.0010$, indeed are in good agreement with g factors for individual valleys obtained by Wilson[36] from EPR studies of As and P donors in Ge samples subjected to an applied stress. Departures from EM theory for D(Li,O) are probably too small to affect the g factor enough to reveal the true symmetry of the defect.

Haller[37] has shown that substitution of deuterium for hydrogen causes an isotope shift of -0.051 meV in the PTI spectrum of D(H,O). If the tunneling model were correct and the transition energy of the low-stress spectrum contained the term $3(t'-t)$ as in Eq. (4.9), we would expect the strong dependence of the tunneling rate on the mass of the particle to cause an isotope shift in this spectrum by a large fraction of the value of $3(t'-t)\sim1.5$ meV estimated for hydrogen by Joós *et al.*[2] That the experimental value is smaller by at least an order of magnitude thus fails to support the argument[8–10] that the existence of the isotope shift is evidence for the tunneling model. Indeed, a H-D isotope shift of similar magnitude $(+0.021)$ meV was found[37] for the acceptor A(H,Si), which has been shown by Kahn *et al.*[7] to be a static complex with C_{3v} symmetry. In our proposed static model for D(H,O) we suggest that the isotope shift has a more conventional explanation in a small difference between initial and final states in the zero-point energy of vibration of hydrogen. A calculation of this difference for a static model of a shallow donor containing hydrogen has been outlined by Kogan,[38] yielding results of the order of magnitude of that observed.

Apart from the lower symmetry postulated for D(Li,O), our proposed static models for D(H,O) and D(Li,O) are very similar. In both cases we identify the sharp series of peaks in the zero-stress spectrum with the D_1 spectrum and conclude that the intravalley energy difference $\Delta_1-\Delta_0$ must be large compared to the valley-orbit splitting. However, whereas for D(H,O) we have $\Delta_1-\Delta_0=2.65$ meV and in the work of Joós *et al.* only the lowest quartet $\Phi_m\chi_m$ from the 1s states is populated at the temperature of the PTI experiment, for D(Li,O) we have $\Delta_1-\Delta_{02}=0.62$ meV, $\Delta_1-\Delta_{01}=0.71$ meV, and higher 1s states $\Phi_I\chi_m$ with $m\neq I$ are appreciably populated. For D(Li,O) additional peaks corresponding to these initial states therefore appear in the zero-stress spectrum, but because these levels are close together $(\Delta_{02}-\Delta_{01}=0.09$ meV) and interact through the valley-orbit interaction $\Delta_{\text{v.o.}}$, these additional peaks are broadened by random strain. With applied stress along [111] strong enough to separate χ_a from χ_b,χ_c,χ_d by an amount large compared to $\Delta_{\text{v.o.}}$, these peaks sharpen into the D_2 spectrum, but with a splitting corresponding to $\Delta_{01}-\Delta_{02}$. There is no sharp transition between D_1 and D_2 at a critical stress for D(Li,O) because all the 1s levels are populated even at zero stress. Moreover, since the nuclear configuration of D(Li,O) evidently does not reorient at the experimental temperature, the D_1 spectrum remains at high stress corresponding to defects aligned with the [111] axis. Nevertheless, it should be possible for D(Li,O) to identify the critical stress P_2 at which χ_a crosses the state χ_b, χ_c, or χ_d for those defects aligned with $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, or $[\bar{1}\bar{1}1]$ axis, from a splitting of the peaks of the D_1 spectrum caused by the valley-orbit interaction, as found for D(H,O) at the critical stress.

VII. CONCLUSION

We have seen that the tunneling model can be fitted to the experimental data for D(H,O) only if a number of unlikely constraints are imposed on the physical parameters of the model, and that even then the model does not account completely for what is observed. The alternative static model of a defect with trigonal symmetry describes most of these data more naturally, but still fails to account for a few of the reported observations. At the present time we must conclude that neither of the proposed models for D(H,O) is entirely successful in describing all the experimental data. Either the various observations are not all mutually consistent, or the final form of the theoretical model has not yet been achieved. Clearly, additional experiments are needed, and we have indicated a number of features of the spectra, not yet reported, which should be observable and for which the models make different predictions. In particular, clarification of the stress behavior of the PTI spectrum is essential to a final interpretation.

The situation of the tunneling model as applied to D(Li,O) is also unsatisfactory, for many of the same reasons as for D(H,O), but in this case the alternative static model of a defect with a single (110) plane of reflection symmetry seems to be in accord with all of the experimental results reported to date. Again we have proposed additional experiments to test the models.

Finally, we should note that the models we have considered are entirely phenomenological. While they provide information on the symmetry of each defect, they do not yield a microscopic model that identifies the site of the hydrogen or lithium ion, and even the location of the oxygen remains largely a matter of speculation. The nature of the bonding between the lighter ion and oxygen is evidently not revealed with any clarity by the PTI spectra, despite their extremely high sensitivity and resolution, and remains beyond the scope of our work.

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[25] The two values for $\Delta_{\mathrm{v.o.}}$ could be reconciled if, following Joós *et al.* (Ref. 2), we assume a valley-orbit interaction Δ_3, between those valleys not aligned with the defect axis, different from the value Δ_2 when one of the valleys is thus aligned. We would have then $\Delta_3=0.15$ meV and $|\Delta_2|<0.05$ meV from the experimental results.

[26] If in the tunneling model of Joós *et al.* (Ref. 2) we require only $\Delta_2+\Delta_3=0$, in order to assure the degeneracy of the Γ_1 and Γ_5 components of the nuclear ground state, but allow Δ_2 and Δ_3 to be nonzero but of opposite signs, we find, in general, that there are four distinct levels derived from the Γ_5 nuclear state—one of Γ_1 symmetry, two of Γ_5, and one comprising degenerate Γ_3 and Γ_4 states. However, it seems most likely that Δ_2 and Δ_3 should have the same sign, since they both represent the same electronic valley-orbit–interaction mechanism. Thus we believe that the requirement $\Delta_2+\Delta_3=0$ should be interpreted as requiring that both Δ_2 and Δ_3 are individually zero.

[27] If the valley-diagonal electronic energy corrections analogous

to $\Delta_1-\Delta_0$ were not negligible in the *np* final states but instead satisifed $|(\Delta_1-\Delta_0)| \gg 4t$, tunneling in the final states accessible from $\Phi_m \chi_m$ would be suppressed and the unsplit, stress-independent D_1 spectrum restored. However, this seems an unlikely possibility if $4t$ is significant. While random strain could play the same role in suppressing final-state tunneling in the zero-stress spectrum it would be expected then to eliminate the tunneling splitting in the high-stress spectrum as well if $4t$ and $4t'$ are of the same magnitude.

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