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Stress dependence of the binding energy of D^- centers in Si

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Calculations of the binding energy of the outer electron in the ground state of D^- centers in Si as a function of uniaxial stress along the [100] direction show that, for centers associated with group V substitutional donors, the binding is not a monotonic function of stress. As the stress increases from zero, the outer electron becomes localized in the two stress-deepened valleys, which leads to a decrease in binding energy. With further increase in stress the inner electron is gradually forced into the same two valleys, increasing the binding energy. Calculated results for Si:P are compared to experiment. The stress dependence of the binding energy of D^- in Si:Li, which is quite different, is also discussed.

I. INTRODUCTION

A study is presented of the ground state of the D^- ion, a shallow donor with an extra electron attached, as a function of applied uniaxial stress in Si. The purpose of this work is to identify the most important physical aspects of the problem and to treat them in simple models. Our hope is to achieve at least a semiquantitative understanding of the behavior of D^- centers under stress in semiconductors with multivalley conduction bands.

It is well known that the ground-state wave function for a D^- ion in a semiconductor with an isotropic single-valley conduction band can be approximated by the Chandrasekhar variational wave function, given in atomic units by

$$[\exp(-\alpha r_1-\beta r_2)+\exp(-\alpha r_2-\beta r_1)](1+Cr_{12}) \quad , \quad (1)$$

where $r_{12}=|\vec{r}_1-\vec{r}_2|$, $\alpha=1.075$, $\beta=0.478$, and $C=0.312$. This wave function yields a binding energy (BE), here defined as the minimum energy required to free one of the electrons, of $0.0518\,\mathcal{R}$, a value equal to 93% of the exact BE. ($\mathcal{R}$ is the hydrogenic rydberg.) If one neglects correlation in Eq. (1) by setting $C=0$, the calculated BE drops to $0.026\,\mathcal{R}$, only 47% of the exact BE. Notice that since the optimal value of α in Eq. (1) is 1.075 the inner orbital, $\exp(-\alpha r)$, is very nearly the same as the donor ground-state wave function, $\exp(-r)$.[1]

For multivalley semiconductors the D^- problem is much more complicated. A complete treatment must take into account the mass anisotropy (MA) for each valley, which produces different nonspherical envelope functions for electrons in different valleys, valley-orbit (VO) interaction, which profoundly affects the distribution of the electronic wave function over the valleys, as well as correlation and exchange.

An important initial approach to this problem was made by Natori and Kamimura[2] who attempted to estimate the role of MA on the binding of D^- in Si and Ge. Their calculations, which did not include correlation, gave very large effects. For Si those authors found that, in the absence of VO interaction, the BE, ϵ_{ij}, of a D^- ion constructed by putting the two electrons in nonequivalent valleys ("intervalley configuration") was 36% greater than the BE, ϵ_{ii}, arising when both electrons are in the same valley ("intravalley configuration").[3] The physical origin of the difference between ϵ_{ii} and ϵ_{ij} resides in the electrostatic repulsion between the two electrons; the repulsion energy is high when the axes of symmetry of the electron orbitals are the same and low when these axes are perpendicular to each other. When MA is zero the orbitals are spherical and $\epsilon_{ii}=\epsilon_{ij}$.

Subsequent calculations on D^- in Si which include both MA and correlation[4] give only a 10% increase in ϵ_{ij} over ϵ_{ii}. Moreover, ϵ_{ii} calculated with correlation is found to be $\sim 86\%$ greater than the same quantity calculated without. These results suggest that perhaps a better starting point for an approximate description of D^- in Si would be to neglect MA and include correlation.

In this paper a simple model of the D^- center in Si is proposed for calculating the stress dependence of the BE. For group V substitutional donors, MA is ignored, for ease of calculation, but correlation is included. The VO interaction is assumed to affect only the inner orbital, which, in turn, is assumed to respond to this interaction as if the orbital were identical to the donor 1s ground-state wave function. The calculation is carried out in the effective-mass approximation so that increased screening of the donor ion by the inner electron due to drawing in of the envelope function of the inner orbital by the short-range central cell potential[5] is ignored. Further, effects of the VO interaction on the outer orbital, which is only weakly penetrating, are neglected.[6]

II. GROUP V SUBSTITUTIONAL IMPURITIES

For group V substitutional donors like P and As, the donor ground state has A_1 symmetry (the donor electron distributes itself with equal probability over all six valleys), and, assuming, as an approximation, that at zero stress the lowest lying T_1 and E states are degenerate, then the VO splitting, $6\Delta_c$, and the stress splitting of the valleys, S, completely define the splitting of the $1s$ donor levels under stress along [100].[7] Since the VO splitting for P or As donors is large compared to the observed D^- BE, the inner D^- orbital can be taken in the donorlike form (not normalized)

$$\phi(r)=\exp(-1.075r)\sum_{j=1}^{6}\alpha_j u_j(r)\ ,\qquad \alpha_1=\alpha_2=1,\ \ \alpha_3=\alpha_4=\alpha_5=\alpha_6=B\ , \tag{2}$$

where u_j is the Bloch function for valley j, B has the same value as it would for the corresponding donor ground state,[7] and the valleys are numbered such that band edges associated with valleys 1 and 2 are lowered in energy by [100] compressive stress. At zero stress $B=1$, whereas $B\to 0$ as $S\to\infty$. The outer orbital, denoted by a prime, is given by

$$\phi'(r)=\exp(-\xi r)\sum \beta_j u_j(r)\ ,\qquad \beta_1=\beta_2=1,\ \ \beta_3=\beta_4=\beta_5=\beta_6=A\ , \tag{3}$$

where ξ and A are variational parameters. Combining Eqs. (2) and (3) and adding correlation we obtain for the final trial function, in analogy to Eq. (1),

$$\psi=[\phi'(r_1)\phi(r_2)+\phi'(r_2)\phi(r_1)](1+Cr_{12})\ , \tag{4}$$

where C is an additional variational parameter.[8]

If Eq. (4) is expanded in products of pairs of Bloch functions, one obtains

$$\psi=\frac{1}{2}\sum_{i=1}^{6}\sum_{j=1}^{6}u_i(r_1)u_j(r_2)\,(D_{ij}^{(+)}\Phi_+ + D_{ij}^{(-)}\Phi_-)\ , \tag{5}$$

where

$$D_{ij}^{(\pm)}=\alpha_i\beta_j \pm \alpha_j\beta_i\ , \tag{6}$$

and

$$\Phi_\pm=[\exp(-1.075r_1-\xi r_2) \pm \exp(-\xi r_1-1.075r_2)](1+Cr_{12})\ . \tag{7}$$

The functions Φ_+ and Φ_- play the role of the bonding and antibonding states, respectively, discussed in Ref. 2. Antibonding states are high-energy configurations, and their admixture into ψ, due to the application of stress, causes the D^- binding energy to be smaller in the presence of stress than at zero stress in the model proposed here.

The model Hamiltonian employed in the present calculations is given by

$$H=H_{\mathrm{EM}}+H_S(1)+H_S(2)+H_{\mathrm{VO}}(1)+H_{\mathrm{VO}}(2)\ , \tag{8}$$

where, with lengths in units of the effective Bohr radius and energy in units of $\mathcal{R}$,

$$H_{\mathrm{EM}}=-\nabla_1^2-\nabla_2^2-2/r_1-2/r_2+2/r_{12}\ . \tag{9}$$

Matrix elements of H_{EM} are evaluated in the effective-mass approximation, which means that H_{EM} is assumed diagonal in band index pairs. The stress energy operators, H_S in Eq. (8), have the properties

$$H_S(i)u_j(r_i)=\begin{bmatrix}-2S/3\,(i=1,2)\\ S/3\,(i=3-6)\end{bmatrix}u_j(r_i)\ , \tag{10}$$

H_S is assumed to operate only on the Bloch functions. H_{VO} is defined by

$$\begin{aligned} H_{\mathrm{VO}}(i)(1+Cr_{12})e^{-1.075r_i}u_j(r_i) &= -(1+Cr_{12})e^{-1.075r_i}\Delta_c\sum_{k\neq j}u_k(r_i)\ ,\\ H_{\mathrm{VO}}(i)(1+Cr_{12})e^{-\xi r_i}u_j(r_i) &= 0\ . \end{aligned} \tag{11}$$

In postulating Eq. (11) we are assuming that ξ will be sufficiently small that the valley-orbit interaction will have negligible effect on the outer orbital.

For each value of S the BE of D^- is determined variationally from Eqs. (2)–(4) and Eqs. (8)–(11) by varying ξ, B, and C. Optimized values of ξ and C turn out to be quite insensitive to S. Details of the calculation can be found in the Appendix. Results for the BE of D^- vs S are given in Fig. 1 for both Si:P and Si:As, the only difference in the calculations of the two curves being the value of Δ_c employed; Δ_c is taken as $0.11\mathcal{R}$ (2.2 meV) for P and $0.19\mathcal{R}$ (3.8 meV) for As donors.[9] The observed zero-stress D^- binding energy in Si:P is 1.7 meV.[10] Experimental points denoted by solid circles in Fig. 1 are calculated from the data of Ref. 10.

It is not difficult to understand qualitatively the variation of the BE with stress depicted in Fig. 1. At zero stress, where A and B are equal, the valley distribution of the inner and outer electrons are the same and $D_{ij}^{(-)}=0$ for all i and j; when the disparity between A and B is large then $|D_{1,2\,j}^{(-)}|^2$ for $j>2$ is also large and a substantial admixture of Φ_-, the high-energy configuration, appears in the ground-state wave function (5), decreasing the BE. Thus, if the disparity between A and B should grow with increasing applied stress then the D^- binding energy will decrease as the stress increases. This is precisely what happens at low stress ($S \ll 6\Delta_c$), for which the relatively strong VO interaction prevents the inner electron from moving readily into valleys 1 and 2. However, the outer electron in our model, feels

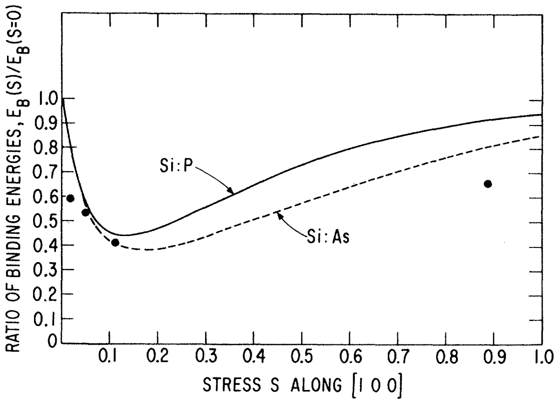

FIG. 1. Variation of the ratio of D^- binding energy at stress S, $E_B(S)$, to the zero-stress D^- binding energy, $E_B(0)$, for P and As impurities in Si. S is the stress splitting of the conduction-band valleys in units of $\mathcal{R}$, the effective-mass donor rydberg associated with the light mass, $m_\perp$. $\mathcal{R}$ is taken as 20 meV; the valley splitting is assumed to be linear in stress and to have the value 8.85 meV at 10^9 dynes/cm^2. The solid circles are computed from experimental data for P centers (Ref. 10).

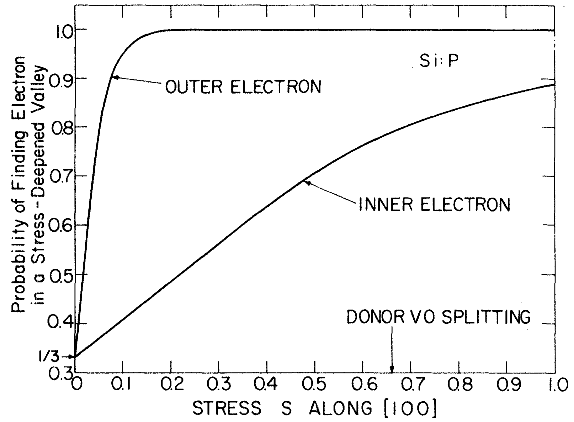

FIG. 2. Variation of the probability of finding an electron in either valley 1 or valley 2 vs uniaxial compressive stress S for P D^- centers. S is defined as in Fig. 1. The vertical arrow indicates the value of S at which, in Si, the stress splitting of the valleys is equal to the VO splitting of P donors. At zero stress each of the six valleys has an equal probability of being occupied.

no VO interaction; it can move much more easily into valleys 1 and 2 under stress. The result is shown in Fig. 2 for Si:P, where it is apparent that for $S \gtrsim 0.15$ the outer electron has been driven almost completely into the stress-deepened valleys ($B \cong 0$). As S increases from 0 to 0.1 the disparity between A and B grows and the D^- binding decreases. As S increases beyond 0.2, the D^- binding *increases* because the inner electron moves more and more into valleys 1 and 2, reducing the disparity between A and B and, therefore, the admixture of antibonding states.

In the limit $S \rightarrow \infty$, the BE should approach ϵ_{ii} since both electrons are in equivalent valleys in that limit. For Si ϵ_{ii} is $\sim 93\%$ of the zero-stress BE, which is given by[4] $(\epsilon_{ii} + 2\epsilon_{ij})/3$. The present model, not distinguishing between ϵ_{ii} and ϵ_{ij} because MA is neglected, predicts equal binding energies at $S = 0$ and $S \rightarrow \infty$.

For the stress along [110], valleys 1–4 are pushed down in energy relative to valleys 5 and 6. Our model predicts in this case a curve of binding energy versus S similar to that in Fig. 1 but with a minimum only half as deep as for the corresponding donor under [100] stress. No variation of binding energy with stress is expected for [111] stress since this stress induces no valley repopulation.

III. Li IMPURITIES

The situation for D^- associated with interstitial Li impurities in Si should be quite different from the cases discussed above due to the inverted structure of the VO split ground-state levels of Li donors.[11] In this case, MA should not be neglected. The D^- ground singlet state at zero stress is expected to be threefold degenerate; an appropriate trial wave function for zero stress might take the form[4]

$$\begin{aligned}\{[F_1(r_1)u_1(r_1) - F_2(r_1)u_2(r_1)][F_3'(r_2)u_3(r_2) - F_4'(r_2)u_4(r_2)]\\ + [F_1'(r_1)u_1(r_1) - F_2'(r_1)u_2(r_1)][F_3(r_2)u_3(r_2) - F_4(r_2)u_4(r_2)] + (r_1 \leftrightarrow r_2)\}(1 + Cr_{12}) \quad , \quad (12)\end{aligned}$$

where F_i and F_i' are anisotropic envelope functions appropriate to valley i for the inner and outer orbital, respectively. Notice that trial function (12) is fundamentally different from Eq. (4) in that Eq. (12) has strong valley correlation whereas in Eq. (4), by contrast, the occupation probability of a valley by one electron is independent of whether or not the other electron is in the same valley. The advantage of choosing Eq. (12) for Li D^- centers is that the binding energy at zero stress is just a pure intervalley energy, ϵ_{ij}. Further, the inner orbitals in Eq. (12) both have T_1 symmetry, which is the symmetry of the ground state of Li donors in Si.[11] Note that if the second + sign inside the curly brackets in Eq. (12) is changed to a − sign the resulting wave function becomes a triplet state which is degenerate with the (singlet) wave function of Eq. (12). This suggests that Si:Li should make an excellent material for D^- magnetospectroscopy experiments at high fields and low temperatures in which the spins of conduction-band electrons are almost entirely aligned and, therefore, singlet D^- states are difficult to observe.

For "strong" stress along [100] both electrons are in valleys 1 and 2, and the binding energy should be close to ϵ_{ii} [$\epsilon_{ii} \sim 0.9\epsilon_{ij}$ in Si (Ref. 4)], an intravalley energy corresponding to the trial function

$$\{[F_1(r_1)u_1(r_1) - F_2(r_1)u_2(r_1)][F_1'(r_2)u_1(r_2) - F_2'(r_2)u_2(r_2)] + (r_1 \leftrightarrow r_2)\}(1 + Cr_{12}) \ . \qquad (13)$$

It is hard to see how a trial function of the form (12) could smoothly transform into Eq. (13) with increasing stress. In an abrupt transition between these states the D^- ground-state binding energy should decrease linearly with stress until the stress is high enough that the energies of Eqs. (12) and (13) are equal. At that point a kink would appear in the curve of BE vs S since further increase in stress would have no effect on the binding energy.

For stress along [110] no change in the binding energy of D^- centers associated with Li in Si should be observed since no valley repopulation is expected, Eq. (12) remaining the ground-state wave function at all stress. This follows because Li D^- wave functions of the form (12) are built up from only four valleys (two pairs of equivalent valleys), rather than all six as in the case of P or As. Thus [110] stress, which depresses uniformly valleys 1–4 relative to 5 and 6, will not cause valley repopulation in Eq. (12) but will do so for the trial function (4). (Of course, the threefold degeneracy of the Li D^- ground state at zero stress will be partially lifted by [110] stress, the ground state under stress becoming nondegenerate.)

IV. D^- in Ge

Much of the discussion in Sec. II for Si should apply also to Ge. One might worry, however, about neglecting MA, which is much more pronounced in Ge than in Si. Nevertheless from the experimental data of Ref. 12, which for D^- in Ge:Sb gives a high-stress BE of 0.55 meV and a zero-stress BE of 0.625 meV, it is reasonable to conclude that ϵ_{ij} is only about 20% larger in magnitude than ϵ_{ii}, the calculated results of Ref. 2 notwithstanding.[13] Thus errors introduced by neglecting MA in Ge should be about twice as large as in Si.

V. SUMMARY AND CONCLUSIONS

We have considered the stress dependence of the binding energy of D^- centers in Si associated with two kinds of impurities—those whose donors have A_1 ground states and VO splittings large compared to the D^- BE (e.g., the group V substitutional impurities), and those whose donors have T_1 ground states (e.g., Li).

In the former case, MA can be neglected in a lowest-order theory because the major effect of stress is to admix antibonding configurations into the D^- ground-state wave function due to stress-induced unequal valley repopulation of the inner and outer orbitals. In Si the splitting between bonding and antibonding states is much larger than splittings due to MA, which are the intervalley-intravalley splittings.

The most remarkable prediction of the model is that the D^- binding, as stress increases from zero, first decreases and then recovers. This happens because the biggest disparity between valley distributions of the inner and outer electrons, and hence the weakest binding, occurs at an intermediate-stress value, a stress which is strong enough to drive the outer electron into the stress-deepened valleys but too weak to do the same to the inner electron. The inner electron resists repopulation due to the strong valley-orbit interaction which it feels.

Nonmonotonic variation of D^- BE with stress has recently been confirmed experimentally in Si:P.[10] However, although the theory appears to give a fairly accurate account of the low-stress data, it predicts a too-rapid recovery of the binding at high stress (see Fig. 1). This discrepancy requires more theoretical and experimental study. A check on the theoretical predictions for stress along [110] remains to be made.

For D^- ions associated with Li centers one can place the inner electron into T_1 orbitals, and it is not necessary to admix antibonding configurations when the stress is turned on. Thus only MA can be expected to play a role in the binding of Li D^- centers under stress. We have conjectured that the ground-state binding decreases linearly from the intervalley value, ϵ_{ij}, with stress and then suddenly saturates when it reaches ϵ_{ii}, the intravalley binding strength. Experiments to check this prediction are awaited.

ACKNOWLEDGMENTS

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APPENDIX

The calculation of matrix elements relevant to evaluating the variational energy $\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle$, where ψ is given by Eq. (4) and H by Eq. (8), is outlined here.

We define, at the outset, the fundamental effective-mass matrix elements $N_\pm$ and $\epsilon_\pm$ by

$$N_\pm=\langle\Phi_\pm|\Phi_\pm\rangle,\quad \epsilon_\pm=\langle\Phi_\pm|H_{\mathrm{EM}}|\Phi_\pm\rangle \ . \tag{A1}$$

These matrix elements can be easily evaluated by the use of Hylleraas coordinates.[1] Notice that by symmetry $\langle\Phi_\pm|\Phi_\mp\rangle=\langle\Phi_\pm|H_{\mathrm{EM}}|\Phi_\mp\rangle=0$.

We can immediately write down from Eqs. (5) and (A1) the relations

$$\langle\psi|\psi\rangle=\sum_{i,j}[(D_{ij}^{(+)})^2N_+ +(D_{ij}^{(-)})^2N_-] \ , \tag{A2}$$

$$\langle\psi|H_{\mathrm{EM}}|\psi\rangle=\sum_{i,j}[(D_{ij}^{(+)})^2\epsilon_+ +(D_{ij}^{(-)})^2\epsilon_-] \ . \tag{A3}$$

From Eqs. (2), (3), and (6) we obtain

$$\begin{aligned}&D_{ij}^{(+)}=1\ \ D_{ij}^{(-)}=0 \text{ for } i\leqslant 2,\ j\leqslant 2 \text{ (4 terms)} \ ,\\&D_{ij}^{(+)}=(A+B)/2\\&D_{ij}^{(-)}=(A-B)/2 \text{ for } i\leqslant 2,\ j>2 \text{ (8 terms)} \ ,\\&D_{ij}^{(+)}=(A+B)/2\\&D_{ij}^{(-)}=-(A-B)/2 \text{ for } i>2,\ j\leqslant 2 \text{ (8 terms)} \ ,\\&D_{ij}^{(+)}=AB\ \ D_{ij}^{(-)}=0 \text{ for } i>2,\ j>2 \text{ (16 terms)} \ .\end{aligned} \tag{A4}$$

From Eqs. (A2), (A3), and (A4) follows

$$\langle\psi|\psi\rangle=4\{[1+(A+B)^2+4A^2B^2]N_+ +(A-B)^2N_-\} \ , \tag{A5}$$

$$\langle\psi|H_{\mathrm{EM}}|\psi\rangle=4\{[1+(A+B)^2+4A^2B^2]\epsilon_+ +(A-B)^2\epsilon_-\} \ . \tag{A6}$$

Let us denote the remaining matrix element to be evaluated,

$$\langle\psi|H_S(1)+H_S(2)+H_{\mathrm{VO}}(1)+H_{\mathrm{VO}}(2)|\psi\rangle \ ,$$

by $\langle H'\rangle+E_D\langle\psi|\psi\rangle$. Observe that from Eqs. (10) and (11)

$$[H_S(1)+H_{\mathrm{VO}}(1)](1+Cr_{12})\phi(r_1)=E_D(1+Cr_{12})\phi(r_1) \ , \tag{A7}$$

where

$$E_D=|\Delta_c|\{-4-x-[(2-3x)^2+32]^{1/2}\}/2$$

with $x=S/(3|\Delta_c|)$, provided that B is chosen to be

$$\{(2-3x)+[(2-3x)^2+32]^{1/2}\}/8 \ .$$

Here E_D is the valley-orbit part of the donor ground-state energy under a stress along [100] which produces the valley splitting S. Our choice of B makes $\phi(r_1)$ an eigenstate of the stress and valley-orbit part of the donor Hamiltonian. In our model the total donor energy is E_D-1. Note that the integers 1 and 2 can be formally interchanged in Eq. (A7).

Thus our remaining task is to evaluate $\langle H'\rangle$ where from Eq. (11)

$$\langle H'\rangle=\langle\psi|[H_S(1)\phi'(r_1)\phi(r_2)+1\leftrightarrow 2](1+Cr_{12})\rangle$$

Expanding we obtain

$$\phi'(r_1)\phi(r_2)(1+Cr_{12})=\tfrac{1}{2}(\Phi_+-\Phi_-)\sum_{ij}\beta_i\alpha_ju_i(r_1)u_j(r_2) \ ,$$

$$\phi'(r_2)\phi(r_1)(1+Cr_{12})=\tfrac{1}{2}(\Phi_++\Phi_-)\sum_{ij}\beta_j\alpha_iu_i(r_1)u_j(r_2) \ .$$

Operating with the appropriate stress operators and taking the expectation value using Eqs. (5), (6), and (A4) we obtain after some simple algebra

$$\langle H'\rangle=\tfrac{4}{3}S\{[-2+(A+B)(-2B+A)+4A^2B^2]N_+ +(A-B)(A+2B)N_-\} \ .$$

This completes the computation of matrix elements required for obtaining the total D^- energy in the present model. The binding energy of the D^- is given by

$$|\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle-(E_D-1)+2S/3| \ , \tag{A8}$$

where $-2S/3$ is the energy of a free electron at the bottom of valley 1 or 2 and, as already metioned, E_D-1 is the energy of the donor which remains when an electron is removed from the D^- center.

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[1] H. A. Bethe and E. Salpeter, "Quantum Mechanics of One- and Two-Electron Systems" in *Handbuch Der Physik*, edited by S. Flügge (Springer, Berlin, 1957), Vol. 35.

[2] A. Natori and H. Kamimura, J. Phys. Soc. Jpn. 43, 1274 (1977).

[3] These authors also give a very general discussion of the effects of VO interaction but do not include these effects in explicit numerical calculations.

[4] D. M. Larsen, in *Physics in High Magnetic Fields*, edited by S. Chikazumi and N. Miura (Springer, Berlin, 1981), pp. 120–129.

[5] W. Kohn and J. M. Luttinger, Phys. Rev. 97, 883 (1955).

[6] In Si:P effective-mass theory appears to give a more accurate BE for D^- than for donors. The effective-mass variational calculation of Ref. 4 for group V element D^- centers in stress-free Si gives a BE of 1.61 meV vs the measured value of ~ 1.7 meV for P from Ref. 10. We expect that the variational ansatz of Ref. 4 gives a BE which is less than but close to 93% of the exact D^- effective-mass BE in Si, since for the case of isotropic valleys the same ansatz does give 93% of the correct BE. Thus the agreement between the effective mass and measured BE appears very good in Si:P. This agreement is probably due to a cancellation effect. The increased screening of the central positive charge due to drawing in of the inner electron by the short-range attractive central-cell potential tends to reduce the BE, whereas the attraction of this same potential for the outer electron tends to increase it.

[7] See, for example, D. K. Wilson and G. Feher, Phys. Rev. 124, 1068 (1961), especially Appendix C.

[8] Notice that we do not vary the exponential envelope function of the inner electron in our choice of Eq. (2). Since the valley-orbit splitting of the inner orbital varies with its effective Bohr radius, a stress-induced change in that radius would produce a stress-dependent contribution to the BE, which is not calculable from the effective-mass theory. If we were to ignore this effect on the valley-orbit splitting and vary, with all other parameters, the effective Bohr radius of the inner orbital, we would obtain energy curves which are not substantially different from those in Fig. 1.

[9] R. L. Aggarwal, Solid State Commun. 2, 163 (1964).

[10] M. Taniguchi and S. Narita, Solid State Commun. 20, 131 (1976); S. Narita, J. Phys. Soc. Jpn. Suppl. A 49, 197 (1980).

[11] R. L. Aggarwal, P. Fisher, V. Mourzine, and A. K. Ramdas, Phys. Rev. 138, A882 (1965).

[12] M. Taniguchi and S. Narita, J. Phys. Soc. Jpn. 43, 1262 (1977).

[13] Much the same conclusion is reached in Ref. 2. We would expect that the zero-stress BE could be represented approximately as $\epsilon_{ii}/4+3\epsilon_{ij}/4$, where ϵ_{ii} is the intravalley energy in Ge and ϵ_{ij} the intervalley. The high-stress BE is equal to ϵ_{ii} since both electrons are in the same valley in the high-stress limit. Thus we infer $\epsilon_{ij} \cong 0.65$ meV in Ge.