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October 1985

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-20489 c.1

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EFFECT OF COMPRESSIVE UNIAXIAL STRESS ON THE BINDING ENERGIES OF D^- CENTERS IN Si:P AND Si:As

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ABSTRACT

The binding energies of D^- states in P and As doped silicon crystals are calculated as functions of uniaxial compressive stress along the [100] direction within a variational scheme in the effective-mass approximation and with a Chandrasekhar-type variational function. A model Hamiltonian which takes into account valley-orbit corrections, electron-electron interaction and stress effects is proposed. Our calculation shows that as the stress is applied, the outer electron orbital is driven readily into the two stress-deepened valleys, which leads to a strong decrease in the D^- binding energy. With further increase in stress, the inner electron orbital changes gradually from a function almost evenly distributed among the six conduction valleys into one in which the two stress-deepened valleys are dominant, and the D^- binding energy increases. Our results agree qualitatively with previous theoretical calculations and are in good agreement with far infrared photoconductivity measurements in Si:P.

I. INTRODUCTION

The existence of a D^- negative donor state in semiconductors, the analogue of the H^- hydrogen negative ion, was first suggested by Lampert[1] many years ago. The free H^- ion, observed experimentally by Smith and Burch[2], has a binding energy of 0.75 eV. This value is in good agreement with theoretical studies[3-5] which yield one bound ^1S state with an energy close to $-1.0555\ R_H$, where R_H is the H-atom Rydberg. A crude estimate of the binding energy of a D^- center in Si and Ge can then be obtained by considering an effective Rydberg $R_H^*=m^*e^4/2\varepsilon^2\hbar^2$ where m^* and ε are an average effective mass and the semiconductor dielectric constant respectively. The estimated D^- binding energies[6] would therefore be roughly 1.74 meV for Si (R_H^*=31.27 meV), and 0.54 meV for Ge (R_H^*=9.81 meV). However, Dean et al.[7], who were the first to report the observation of D^- centers in Si and Ge, estimated the binding energies of the D^- second electron as ~ 4 meV for Si and ~ 1.5 meV for Ge, which are about three times as large as the predicted values. The direct observation of D^- centers in Si and Ge were first reported by Gershenzon et al.[8] who determined the D^- binding energy directly from the long-wavelength photoconductivity band at sufficiently low temperatures (T-1.5-4.2 K) and reported values of 2.2 meV for Si:P, and 0.95 meV for Ge:Sb, 1.2 meV for Ge:P and 1.55 meV for Ge:As. Since then, a great deal of interest has been raised in the study of both the D^- donors and A^+ acceptors in semiconductors and considerable experimental work has recently been reported.[9-18] Although many experimental results[7-9] associated with impurity states in semiconductors have been ascribed to isolated D^- centers, Narita[14,18] suggested that some of the large binding energies reported were in fact associated with complex-formation. Therefore it is important to prepare the semiconductor sample with very small donor and acceptor

concentrations in order to study isolated D^- centers.

The present experimental situation with respect to the binding energy of D^- centers can be illustrated by looking at the data on P and As doped Si crystals: the reported D^- binding energies for Si:P are 2.2 meV (Gershenzon et al.[8]), 1.73 meV (Narita et al.[15]) and 1.7 meV (Norton[11]) while for Si:As the binding energy of the D^- extra electron is reported to be 2.05 meV (Narita et al.[15]) and 1.7 meV (Norton[11]). These measurements are in good qualitative agreement with the effective Rydberg theoretical estimate of 1.74 meV mentioned above. Of course, there are considerable differences between the problem of the D^- center in multivalley semiconductors and the free H^- ion. For a complete study of the D^- state in these semiconductors, one should take into account the anisotropy of the electron mass, valley-orbit (VO) effects, as well as electron-electron correlation effects.[19,20]

This paper is essentially concerned with the effect of [100] compressive uniaxial stress on the binding energy of D^- centers in P and As doped Si crystals. By applying a [100] uniaxial compressive stress, the D^- electrons in Si:P and Si:As are driven into the two valleys that have their principal axes of the energy spheroid along the [100]-direction. Recent far infrared photoconductivity measurements in Si:P by Narita and collaborators[12,15,18] show a large D^- binding energy decrease with stress from a zero stress value of ~ 1.7 meV to ~ 0.7 meV at a stress of 2×10^8 dyn cm^{-2}. They found that above 2.5×10^8 dyn cm^{-2} the photo-response becomes too small to be detected[12]. It recovers[15] however with further increase in stress and the D^- binding energy is ~ 1.1 meV at a stress of 1.8×10^9 dyn cm^{-2}. In the case of Si:As, Narita et al.[15] report a zero stress D^- binding energy of 2.05 meV and a value of ~ 1.1 meV at a stress of 1.8×10^9 dyn cm^{-2}.

A qualitative explanation for the observed experimental data was given by

Larsen[20], who used a Chandrasekhar-type variational function for the D^- state, neglected mass anisotropy by considering an effective-mass Rydberg associated with the light m_t mass (R_H^*=20 meV), and also assumed that the VO interaction only affects the inner orbital of the two electrons in the D^- center, which in turn is assumed to respond to this interaction as if the orbital were identical to the donor D° 1s ground-state wavefunction. Although Larsen's results account qualitatively for the stress behavior of the experimental D^- binding energies, his theoretical value[21] for the zero stress D^- binding energies is 1.0 meV for both Si:P and Si:As, a result which is a factor of two smaller than the experimental measurements[8,11,15] and which does not account for the observed differences[15] between the zero stress D^- binding energies in Si:P and Si:As. In addition, Larsen's theoretical approach[20] applied to the A_1 ground state of the donor D° in Si:P and Si:As would yield 31 meV and 39 meV, respectively, to be compared with the experimental results[22] of 45.59 meV and 53.76 meV.

In this work a model Hamiltonian which takes into account electron-electron interaction, stress effects and VO corrections for <u>both</u> the inner and the outer orbitals of the D^- state in doped Si is proposed. We use a variational scheme in the effective mass approximation with m^* and ε such that an effective Rydberg of 31.27 meV (equal to Faulkner's ground-state value[6]) is obtained. Electron-electron correlation is taken into account[20] through a Chandrasekhar-type variational wavefunction for the two-electron D^- state.

In Section II we present the D° and D^- model Hamiltonians for substitutional P and As in doped silicon and describe the basic assumptions of the present calculations; results and discussion are presented in Section III; the conclusions are in Section IV.

II. THE D° AND D⁻ MODEL HAMILTONIANS

As it is well known, Si presents a multivalley structure[22] of the conduction bands with six equivalent minima along the <100> directions. For substitutional P and As in doped Si the zero-stress D° donor wavefunctions belonging to the 1s ground-state multiplet can be written in the effective-mass approximation (and ignoring the effect of mass anisotropy) as

$$|\phi(D^\circ,\Gamma_i)\uparrow\rangle = F(r)\sum_{j=1}^{6}\gamma_{\Gamma_i,j}\,|u_j\uparrow\rangle \tag{2.1}$$

where $|u_j\uparrow\rangle$ is the Bloch function of spin up at the conduction band minimum of the j-th valley, F(r) is a 1s-like envelope function, Γ_i corresponds to the irreducible representations (A_1, E and T_2) of T_d associated with the s-like states of group V donors in Si, and the $\gamma_{\Gamma_i,j}$ coefficients are as follows:

$$\gamma_{A_1,j} = \frac{1}{\sqrt{6}}\,(1,1,1,1,1,1) \tag{2.2}$$

$$\gamma_{E,j} = \begin{bmatrix} \frac{1}{\sqrt{12}}\,(-1,-1,-1,-1,2,2) \\ \frac{1}{2}\,(1,1,-1,-1,0,0) \end{bmatrix} \tag{2.3}$$

$$\gamma_{T_2,j} = \begin{bmatrix} \frac{1}{\sqrt{2}}\,(1,-1,0,0,0,0) \\ \frac{1}{\sqrt{2}}\,(0,0,1,-1,0,0) \\ \frac{1}{\sqrt{2}}\,(0,0,0,0,1,-1) \end{bmatrix} \tag{2.4}$$

The 1s multiplet of a group V donor in Si splits into a ground state singlet 1s(A_1) and excited triplet 1s(T_2) and doublet 1s(E) components, consistent with the T_d site symmetry of the substitutional donor. The energies of the T_2 and E states are approximately the same (we assumed them

to be degenerate) and in good agreement with effective-mass theoretical calculations.[6,22] The ground-state $1s(A_1)$ level lies below the effective mass value and the energy shift differs for the various group V impurities. The energy separation 6Δ between $1s(E)$ and $1s(A_1)$ is referred to as the "valley-orbit" or "chemical" splitting.

The D° donor model one-electron Hamiltonian in the case of [100] compressive stress is assumed to be

$$\mathcal{H}(D^\circ) = \mathcal{H}_{EM}(D^\circ) + \mathcal{H}_S(D^\circ) + \mathcal{H}_{VO}(D^\circ) , \tag{2.5}$$

where

$$\mathcal{H}_{EM}(D^\circ) = \sum_{k=1}^{6} \sum_{\sigma} H_{EM}(\vec{r}) \, |u_k\sigma\rangle\langle u_k\sigma| \tag{2.6}$$

is the effective-mass Hamiltonian,

$$\mathcal{H}_S(D^\circ) = \sum_{k=1}^{6} \sum_{\sigma} H_S(k) \, |u_k\sigma\rangle\langle u_k\sigma| \tag{2.7}$$

is the stress-dependent term, and

$$\mathcal{H}_{VO}(D^\circ) = \sum_{k,j=1}^{6} \sum_{\sigma} H_{VO}(\vec{r}) \, |u_k\sigma\rangle\langle u_j\sigma| \tag{2.8}$$

is the VO interaction. In the above σ stands for the spin quantum number,

$$H_{EM}(\vec{r}) = -(\hbar^2/2m^*) \, \nabla^2 - (e^2/\varepsilon r), \tag{2.9}$$

$$H_S(k) \, |u_k\sigma\rangle = \begin{Bmatrix} -2S/3 & (k=1,2) \\ S/3 & (k=3-6) \end{Bmatrix} |u_k\sigma\rangle , \tag{2.10}$$

and

$$H_{VO}(\vec{r}) = \begin{cases} -V_\Delta , & r<R , \\ 0 , & r>R , \end{cases} \tag{2.11}$$

with R defining a "central cell region" and V_Δ chosen such that at zero stress the difference in energy between the A_1 and E levels fits the experimental VO splitting[22]. The stress operator H_S acts only on the Bloch functions $|u_k\sigma\rangle$. It shifts the energies[20,23] of the valleys proportionally to

the applied stress: S=1 meV corresponds[12] to a stress of 1.13×10^8 dyn cm^{-2}. The operators $H_{EM}(\vec{r})$ and $H_{VO}(\vec{r})$ act only on the F(r) envelope function; $\mathcal{H}_{EM}(D^\circ)$ is diagonal in band index (effective-mass approximation); $\mathcal{H}_{VO}(D^\circ)$ models the VO interaction, gives no contribution to the energies of the T_2 and E states and is responsible for the chemical shift of the A_1 ground state from the effective-mass[6] result. The average effective mass $m^*=0.2987$ and the dielectric constant $\varepsilon=11.40$ are such that an effective Rydberg equal to Faulkner's[6] ground-state value is obtained.

Under [100] compressive stress, the $1s(A_1)$ ground-state wavefunction takes the general form

$$|\phi(D^\circ,A_1)\uparrow\rangle = (2+4\gamma^2)^{-1/2}\, F(r) \sum_{j=1}^{6} \gamma_j\, |u_j\uparrow\rangle \tag{2.12a}$$

with $\gamma_1 = \gamma_2 = 1$ and $\gamma_3 = \ldots = \gamma_6 = \gamma$. The F(r) wavefunction is assumed to be

$$F(r) = (\xi^3/\pi)^{1/2}\, e^{-\xi r}\ . \tag{2.12b}$$

The D° ground state energy

$$E(D^\circ) = \langle\phi(D^\circ,A_1)\uparrow|\, \mathcal{H}(D^\circ)\,|\phi(D^\circ,A_1)\uparrow\rangle \tag{2.13}$$

can then be calculated as a function of applied compressive stress within a variational scheme, with ξ and γ as variational parameters. One obtains for E(D°) (see Appendix A)

$$E(D^\circ) = \xi^2 - 2\xi - (4S/3)(1-\gamma^2)/(2+4\gamma^2) - \Delta(\xi)(2+4\gamma)^2/(2+4\gamma^2), \tag{2.14a}$$

with

$$\Delta(\xi) = V_\Delta[1-\exp(-2\xi R)(1+2\xi R+2\xi^2R^2)] \tag{2.14b}$$

and ξ and γ to be chosen optimally. In the above expressions, lengths and energies are in units of the effective Bohr radius and effective Rydberg, respectively.

Under [100] compressive stress, the D^- two-electron Hamiltonian is given by

$$\mathcal{H}(D^-) = \mathcal{H}_{EM}(D^-) + \mathcal{H}_S(D^-) + \mathcal{H}_{VO}(D^-) \quad , \tag{2.15}$$

with

$$\mathcal{H}_{EM}(D^-) = \sum_{i=1}^{2} \sum_{k=1}^{6} \sum_{\sigma_i} H_{EM}(\vec{r}_i) \, |u_k\sigma_i\rangle\langle u_k\sigma_i| + \sum_{k,j=1}^{6} \sum_{\sigma_1,\sigma_2} (e^2/\varepsilon r_{12}) \, |u_k\sigma_1\rangle\langle u_k\sigma_1||u_j\sigma_2\rangle\langle u_j\sigma_2| \quad , \tag{2.16}$$

$$\mathcal{H}_S(D^-) = \sum_{i=1}^{2} \sum_{k=1}^{6} \sum_{\sigma_i} H_S(k)|u_k\sigma_i\rangle\langle u_k\sigma_i| \quad , \tag{2.17}$$

and

$$\mathcal{H}_{VO}(D^-) = \sum_{i=1}^{2} \sum_{k,j=1}^{6} \sum_{\sigma_i} H_{VO}(\vec{r}_i)|u_k\sigma_i\rangle\langle u_j\sigma_i|. \tag{2.18}$$

The D^- trial wavefunction is constructed by using a Chandrasekhar-type[3,20] approach

$$|\psi(D^-)\rangle = [|\phi_A(r_1)\phi_B(r_2)\rangle + |\phi_B(r_1)\phi_A(r_2)\rangle](1+\lambda r_{12}) \times (1/\sqrt{2})(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \tag{2.19}$$

where λ takes electron correlation into account and $\phi_A(\phi_B)$ corresponds to the inner (outer) electron orbital of the D^- state, i.e.,

$$|\phi_A(r)\rangle = e^{-\xi_1 r} \sum_{j=1}^{6} \alpha_j \, |u_j\rangle, \tag{2.20a}$$

$\alpha_1 = \alpha_2 = 1$, $\alpha_3 = \ldots = \alpha_6 = \alpha$ for the inner orbital and

$$|\phi_B(r)\rangle = e^{-\xi_2 r} \sum_{j=1}^{6} \beta_j \, |u_j\rangle, \tag{2.20b}$$

$\beta_1 = \beta_2 = 1$, $\beta_3 = \ldots = \beta_6 = \beta$ for the outer orbital. We take $\xi_1 < \xi_2$.

In the above expressions, the parameters ξ_1, ξ_2, α, β and λ are chosen optimally so that the energy

$$E(D^-) = \frac{\langle\psi(D^-)|\,\mathcal{H}(D^-)\,|\psi(D^-)\rangle}{\langle\psi(D^-)|\psi(D^-)\rangle} \tag{2.21}$$

is minimized (see Appendix B for details of the calculation). Of course, at zero stress all the conduction valleys are equivalent and $\alpha = \beta = 1$. Under high compressive stress along the [100] axis, the two conduction valleys having the principal axes of their energy spheroids in the [100]-direction have lower energy than the other four and therefore $\alpha = \beta \to 0$ as $S \to \infty$. It is worth pointing out that all necessary integrals appearing in (2.21) can be performed analytically and that only the minimization requires numerical handling.

III. RESULTS AND DISCUSSION

We calculated the stress dependence of the D^- binding energy of P and As doped Si under the same assumptions considered by Larsen[20], i.e., (i) assume that ξ_2 is sufficiently small so that the VO interaction has negligible effect on the outer orbital; (ii) assume that the VO interaction is delta-function-like, reproduces the experimental value in D° and affects only the inner electron orbital; (iii) the inner-electron orbital envelope function is "frozen" at the zero stress value ξ_1=1.075. In this approximation it is straightforward to show that the VO interaction does not contribute to the zero-stress D^- binding energy since it produces the same energy shift for both $E(D^\circ,A_1)$ and $E(D^-)$.

Table I compares our values at zero stress for the binding energies of the D° ground-state 1s-multiplet and of D^- states in Si:P and Si:As with experiment[8,11,15,22] and Larsen's results[20]. If one takes into account the experimental uncertainty in measuring the zero-stress D^- binding energy, it is apparent from Table I that the results of our model calculation agree well with the experimental data.

The D^- binding energies of P and As doped Si under [100] compressive stress are shown in Fig. 1. Our results agree qualitatively with Larsen's calculations[20] and a minimum in the D^- binding energy as a function of [100]-stress is found for Si:P and Si:As. The measured decrease with stress of the D^- binding energy in Si:P, however, is more pronounced than what the theory predicts. Because of the neglect of the effect of the VO interaction on the outer D^- orbital the same value of 1.62 meV is found for both Si:P and Si:As, in contrast with the more recent experimental measurements by Narita *et al.*[15] which clearly indicate a chemical shift for the zero-stress D^- binding energies in Si:P and Si:As.

In order to investigate the effect of the VO interaction on the D^- outer electron orbital we have modelled the VO interaction by a constant $-V_\Delta$ potential within a central cell region of radius R, with V_Δ such that the experimental valley-orbit splitting between the D° donor levels A_1 and E is reproduced. Also, we have allowed the ξ_1 parameter of the inner-electron envelope function to vary when minimizing the energy of the D^- state. Results for the zero-stress binding energies of the D° ground-state 1s-multiplet and of the D^- state in P doped Si are given in Table II. One should notice the good agreement between the predicted zero-stress D^- binding energy of 2.23 meV and the value of 2.2 meV measured by Gershenzon et al.[5] The zero-stress optimized variational parameters are ξ=1.766 and γ=1.0 for the D° state and ξ_1=1.924, ξ_2=0.597, λ=0.284, α=β=1.0 for the D^- state which should be compared with the values ξ=γ=1.0 and ξ_1=1.075, ξ_2=0.477, λ=0.313, α=β=1.0 obtained by neglecting the effect of the VO interaction on the outer orbital and by assuming it to be delta-function-like when it acts on an unperturbed zero stress ξ_1=1.075 envelope function. It is clear therefore that the effect of the VO interaction on the envelope functions is essentially to decrease their range both in the D° and the D^- centers. The result of this model calculation of the D^- binding energy in Si:P as a function of applied [100] compressive stress is given by the solid curve in Fig. 2. All the essential features of the experimental measurements are well reproduced by our theoretical calculation. The theoretical zero-stress D^- binding energy agrees well with the measured value by Gershenzon et al.[8] and the strong decrease with stress observed by Narita et al.[15] is in good agreement with the theoretical results.

The results for Si:P were obtained by considering R equal to the nearest-neighbor distance in Si, i.e., R=2.35 Å, and V_Δ=0.045 Ry such that

the experimental zero-stress VO splitting[22] between the D° donor levels A_1 and E is reproduced. We have, however, tested the effect of varying R from ~ 1.5 Å to ~ 7.0 Å and at zero stress the theoretical D^- binding energy varied from 2.38 meV to 2.21 meV, which is comparable with the experimental uncertainty at zero stress.

The probability of finding the inner and outer D^- orbitals in one of the stress-deepened valleys, 1 or 2, is shown in Fig. 3 as a function of the applied compressive stress along the [100] direction in Si:P. At zero stress each of the six valleys has an equal probability of being occupied whereas at high stress both the inner and outer D^- orbitals move into the stress-deepened valleys 1 and 2. One can qualitatively understand the behavior of the D^- binding energy with stress as follows[20]: as the stress increases from zero in the low-stress regime ($S \lesssim 7.5\times10^8$ dyn cm^{-2}), the outer D^- electron orbital, which is the least affected by the VO interaction, is easily driven into the two stress-deepened valleys while the inner D^- electron orbital is prevented by the strong VO interaction from increasing readily the contributions of valleys 1 and 2, and is essentially equally distributed over the six valleys. In the low-stress regime, therefore, the contribution of the various valleys to the D^- inner and outer electron orbitals becomes more and more uneven under increasing stress; this leads to an increasingly high admixture of the high-energy antibonding[19,20] configuration and, consequently, to a pronounced decrease in the D^- binding energy. With further increase in stress ($S \gtrsim 7.5\times10^8$ dyn cm^{-2}) the inner D^- electron orbital changes rapidly from a function almost evenly distributed among the six valleys to one in which the stress-deepened valley 1 and 2 have the dominant strength. The outer D^- orbital is already essentially equally distributed over the two stress-deepened valleys and, therefore, the

valley distribution of the inner and outer electron orbitals becomes more alike, with the consequent reduction of the admixture of the high-energy antibonding configuration; this leads to an increase in the D^- binding energy with stress.

The optimized values of the variational parameters ξ_1, ξ_2, λ, α and β for D^- centers in P doped Si under stress are shown in Fig. 4. The parameters ξ_1 (inner electron), ξ_2 (outer electron) and λ (electron correlation) are related to the Chandrasekhar-type variational function, whereas α and β are valley-admixture parameters for the inner and outer electron D^- orbitals, respectively. The behavior under stress of the D° variational parameters ξ and γ (not displayed) is very similar to that shown for ξ_1 and α .

So far we have presented a study of the effect of the valley-orbit interaction on both the inner and outer D^- electron orbitals and on the D^- binding energy in P doped Si, for which there are some available stress-dependent data. In the case of Si:As, however, there are no low-stress measurements of the D^- binding energy reported in the literature. As can be seen from the zero-stress experimental data[22] for the D° ground-state $1s(A_1)$ level in Si:As, the chemical shift from the 1s(E) level is 22.5 meV, which is comparable to the ionization energy of the 1s(E) level and about twice the corresponding chemical shift (13.0 meV) for Si:P. Therefore, VO effects and the short-range part of the impurity potential are expected to be particularly important in As doped Si. Our model calculation for Si:As (with the R radius of the central-cell region equal to the nearest-neighbor distance in Si) predicts a zero stress D^- binding energy of 3.93 meV which is about a factor of two larger than the experimental measurement[15] of 2.05 meV. Of course, the modeling of the VO interaction by a constant potential in a central cell region does not account for microscopic details of the

potential in the neighborhood of the impurity and is too crude to account properly for such strong central-cell corrections as those observed in As doped Si.

IV. CONCLUSIONS

We have calculated the [100] stress dependence of the binding energy of the two-electron D^- state in P doped silicon within a variational scheme in the effective-mass approximation. Stress effects, VO corrections, electron-electron interaction and correlation were taken into account by a model Hamiltonian and a Chandrasekhar-type variational wavefunction for the two-electron D^- state. The observed behavior of the D^- binding energy of Si:P under [100] compressive stress is well reproduced by our calculation. The theoretical zero-stress D^- binding energy is in good agreement with experiment. The pronounced decrease followed by a recovery of the D^- binding energy under [100] stress (observed by far infrared photoconductivity measurements in Si:P) is quantitatively reproduced by our theoretical results. The theory shows that as the stress increases from zero, the D^- outer electron orbital is driven into the two stress-deepened valleys, which leads to a strong decrease in the D^- binding energy. With further increase in stress, the D^- inner electron orbital increases its contribution of the two stress-deepened valleys and the D^- binding energy increases with stress.

The VO Hamiltonian was modeled by a constant potential within a central-cell region so that it could account for some corrections to the effective-mass approximation. Of course, such simple model VO interaction does not properly account for microscopic details of the impurity potential in the neighborhood of the substitutional impurity and is expected to be too crude to mimic such strong central-cell corrections as observed for example in As doped Si. For substitutional P in Si, however, a comparison between our calculations and the experimental results for the D^- binding energy under [100] compressive stress is certainly encouraging.

ACKNOWLEDGMENTS

This work was supported at the Lawrence Berkeley Laboratory by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the Department of Energy under contract number DE-AC03-76SF00098. The support of the U.S. National Science Foundation (through Grant NSF-INT83-12951) and the Brazilian CNPq through their cooperative program is also gratefully acknowledged.

One of us (L.E.O.) would like to acknowledge the postdoctoral scholarships of the two Brazilian Agencies CAPES and FAPESP.

APPENDIX A

The D° ground state energy, as expressed by (2.13), (2.5) and (2.12), is given in terms of ξ and γ as

$$E(D^\circ) = E_{EM}(D^\circ,A_1) + E_S(D^\circ,A_1) + E_{VO}(D^\circ,A_1) \tag{A.1}$$

where

$$E_{EM}(D^\circ,A_1) = \langle\phi(D^\circ,A_1)\uparrow|\mathcal{H}_{EM}(D^\circ)|\phi(D^\circ,A_1)\uparrow\rangle = \xi^2 - 2\xi, \tag{A.2}$$

$$\begin{aligned} E_S(D^\circ,A_1) &= \langle\phi(D^\circ,A_1)\uparrow|\mathcal{H}_S(D^\circ)|\phi(D^\circ,A_1)\uparrow\rangle \\ &= -(4S/3)(1-\gamma)^2/(2+4\gamma^2) \end{aligned} \tag{A.3}$$

and

$$\begin{aligned} E_{VO}(D^\circ,A_1) &= \langle\phi(D^\circ,A_1)\uparrow|\mathcal{H}_{VO}(D^\circ)|\phi(D^\circ,A_1)\uparrow\rangle \\ &= -\Delta(\xi)(2+4\gamma)^2/(2+4\gamma^2) \end{aligned} \tag{A.4}$$

with

$$\Delta(\xi) = -\int H_{VO}(\vec{r})F^2(r)d\vec{r} = V_\Delta[1-\exp(-2\xi R)(1+2\xi R+2\xi^2R^2)]. \tag{A.5}$$

The above equations result in (2.14) for E(D°). It is then straightforward to minimize the A_1 energy with respect to γ and ξ for each value of the stress. By evaluating $\partial E(D^\circ)/\partial\gamma=0$, we obtain,

$$\gamma = \{(2-3X) + [(2-3X)^2 + 32]^{1/2}\}/8 \tag{A.6}$$

with $X=S/3\Delta(\xi)$. It can then be shown that $|\phi(D^\circ,A_1)\uparrow\rangle$ is an eigenstate of the stress and VO part of the $\mathcal{H}(D^\circ)$ donor Hamiltonian, i.e.,

$$[\mathcal{H}_S(D^\circ) + \mathcal{H}_{VO}(D^\circ)]|\phi(D^\circ,A_1)\uparrow\rangle = E_{S+VO}(D^\circ,A_1)|\phi(D^\circ,A_1)\uparrow\rangle \tag{A.7}$$

with

$$E_{S+VO}(D^\circ,A_1) = E_S(D^\circ,A_1) + E_{VO}(D^\circ,A_1) =(1/2)\Delta(\xi)\ \{-6-X-[(2-3X)^2 + 32]^{1/2}\}. \tag{A.8}$$

One can now, for each S, numerically minimize

$$E(D^\circ) = \xi^2 - 2\xi + (1/2)\Delta(\xi)\ \{-6-X-[(2-3X)^2 + 32]^{1/2}\} \tag{A.9}$$

with respect to ξ and then obtain the ground-state energy E(D°) as a function of [100] compressive stress.

APPENDIX B

The evaluation of $E(D^-)$ given by (2.21) is outlined here. In what follows, all lengths and energies are in units of the effective Bohr radius $a^* = \hbar^2\varepsilon/m^*e^2$ and effective Rydberg $R_H^* = m^*e^4/2\varepsilon^2\hbar^2$, respectively.

We begin by defining bonding and antibonding[19,20] $\phi_\pm$ functions as

$$\phi_\pm(\vec{r}_1,\vec{r}_2) = [\exp(-\xi_1 r_1 - \xi_2 r_2) \pm \exp(-\xi_2 r_1 - \xi_1 r_2)](1+\lambda r_{12}) \tag{B.1}$$

and one then obtains

$$|\psi(D^-)\rangle = (1/2)\sum_{i,j=1}^{6} [(\alpha_i\beta_j+\alpha_j\beta_i)\phi_+(\vec{r}_1,\vec{r}_2)$$

$$+ (\alpha_i\beta_j-\alpha_j\beta_i)\phi_-(\vec{r}_1,\vec{r}_2)]|u_i u_j\rangle \times \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \tag{B.2}$$

Also, we define effective-mass matrix elements $N_\pm$ and $\varepsilon_\pm$ by[3]

$$N_\pm(\xi_1,\xi_2,\lambda) = \langle\phi_\pm(\vec{r}_1,\vec{r}_2)|\phi_\pm(\vec{r}_1,\vec{r}_2)\rangle, \tag{B.3a}$$

$$\varepsilon_\pm(\xi_1,\xi_2,\lambda) = \langle\phi_\pm(\vec{r}_1,\vec{r}_2)|H_{EM}(\vec{r}_1,\vec{r}_2)|\phi_\pm(\vec{r}_1,\vec{r}_2)\rangle \tag{B.3b}$$

with

$$H_{EM}(\vec{r}_1,\vec{r}_2) = \sum_{i=1}^{2} [-\nabla_i^2 - \frac{2}{r_i}] + \frac{2}{r_{12}} \quad . \tag{B.4}$$

Therefore, it is straightforward to show that[20]

$$\langle\psi(D^-)|\psi(D^-)\rangle = N^{-1} = 4\{[1+(\alpha+\beta)^2+4\alpha^2\beta^2]N_+(\xi_1,\xi_2,\lambda) + (\alpha-\beta)^2 N_-(\xi_1,\xi_2,\lambda)\} \tag{B.5}$$

and

$$\langle\psi(D^-)|\mathcal{H}_{EM}(D^-)|\psi(D^-)\rangle/\langle\psi(D^-)|\psi(D^-)\rangle = E_{EM} \tag{B.6}$$

with

$$E_{EM} = 4N\{[1 + (\alpha+\beta)^2 + 4\alpha^2\beta^2]\varepsilon_+(\xi_1,\xi_2,\lambda) + (\alpha-\beta)^2\varepsilon_-(\xi_1,\xi_2,\lambda)\}. \tag{B.7}$$

For the stress part of the Hamiltonian, we obtain

$$\langle\psi(D^-)|\mathcal{H}_S(D^-)|\psi(D^-)\rangle/\langle\psi(D^-)|\psi(D^-)\rangle = E_S^{(1)} + E_S^{(2)} \tag{B.8}$$

with

$$E_S^{(1)} = (4/3)NS\{[-2 + (\alpha+\beta)(\alpha-2\beta) + 4\alpha^2\beta^2]N_+(\xi_1,\xi_2,\lambda)$$

$$+ (\alpha-\beta)(\alpha+2\beta)N_-(\xi_1,\xi_2,\lambda)\}, \tag{B.9a}$$

$$E_S^{(2)} = (4/3)NS\{[-2 + (\alpha+\beta)(\beta-2\alpha) + 4\alpha^2\beta^2]N_+(\xi_1,\xi_2,\lambda) + (\beta-\alpha)(\beta+2\alpha)N_-(\xi_1,\xi_2,\lambda)\}. \quad (B.9b)$$

The VO contribution to $E(D^-)$ is given by

$$\langle\psi(D^-)|\mathcal{H}_{VO}(D^-)|\psi(D^-)\rangle/\langle\psi(D^-)|\psi(D^-)\rangle = E_{VO}^{(1)} + E_{VO}^{(2)}, \quad (B.10)$$

with

$$E_{VO}^{(1)} = 4N\{[g_+(\xi_1,\xi_2,\lambda) + h_+(\xi_1,\xi_2,\lambda)]f_1(\beta,\alpha) + [g_-(\xi_1,\xi_2,\lambda) + h_-(\xi_1,\xi_2,\lambda)]f_2(\beta,\alpha)\}, \quad (B.11a)$$

$$E_{VO}^{(2)} = 4N\{[g_+(\xi_1,\xi_2,\lambda) - h_+(\xi_1,\xi_2,\lambda)]f_1(\alpha,\beta) + [g_-(\xi_1,\xi_2,\lambda) - h_-(\xi_1,\xi_2,\lambda)]f_2(\alpha,\beta)\}, \quad (B.11b)$$

$$f_1(x_1,x_2) = (1+2x_2)[1 + (1+x_1)(x_1+x_2) + 4x_1^2x_2], \quad (B.12)$$

$$f_2(x_1,x_2) = (1+2x_2)(x_1-x_2)(x_1-1), \quad (B.13)$$

$$g_\pm(\xi_1,\xi_2,\lambda) = \langle\phi_\pm(\vec{r}_1,\vec{r}_2)|H_{VO}(\vec{r}_1) + H_{VO}(\vec{r}_2)|\phi_\pm(\vec{r}_1,\vec{r}_2)\rangle, \quad (B.14)$$

$$h_\pm(\xi_1,\xi_2,\lambda) = \langle\phi_\pm(\vec{r}_1,\vec{r}_2)|H_{VO}(\vec{r}_1) - H_{VO}(\vec{r}_2)|\phi_\mp(\vec{r}_1,\vec{r}_2)\rangle. \quad (B.15)$$

One can show that $E_S^{(1)}$ and $E_{VO}^{(1)}$ correspond to the stress and VO contributions of the inner electron D^- orbital while $E_S^{(2)}$ and $E_{VO}^{(2)}$ are related to the contributions of the outer D^- orbital to $E(D^-)$.

The matrix elements $N_\pm$, $\varepsilon_\pm$, $g_\pm$ and $h_\pm$ can all be evaluated analytically and one then obtains $E(D^-)$ from (2.21) and (B.5) - (B.15). For each value of the stress, $E(D^-)$ is then numerically minimized with respect to ξ_1, ξ_2, α, β and λ. The binding energy of the D^- state as a function of [100] compressive stress is given by

$$BE(D^-) = E(D^\circ) - E(D^-) - (2S/3) \quad , \quad (B.16)$$

with $-2S/3$ being the energy of a free electron at the bottom of valley 1 or 2 of the stress-deepened conduction-band edge.

REFERENCES

1. M. A. Lampert, Phys. Rev. Lett. 1, 450 (1958).
2. S. J. Smith and D. S. Burch, Phys. Rev. 116, 1125 (1959).
3. H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two-Electron Systems," Springer, Berlin (1957).
4. C. L. Pekeris, Phys. Rev. 112, 1649 (1958); 126, 1470 (1962).
5. R. N. Hill, Phys. Rev. Lett. 38, 643 (1977).
6. R. A. Faulkner, Phys. Rev. 184, 713 (1969).
7. P. J. Dean, J. R. Haymes and W. F. Flood, Phys. Rev. 161, 711 (1967).
8. E. M. Gershenzon, G. N. Gol'tsman and A. P. Mel'nikov, JETP Lett. 14, 185 (1971).
9. M. Taniguchi, M. Hirano and S. Narita, Phys. Rev. Lett. 35, 1095 (1975).
10. S. Narita and M. Taniguchi, Phys. Rev. Lett. 36, 913 (1976).
11. P. Norton, J. Appl. Phys. 47, 308 (1976); Phys. Rev. Lett. 37, 164 (1976).
12. M. Taniguchi and S. Narita, Solid State Commun. 20, 131 (1976).
13. M. Taniguchi and S. Narita, J. Phys. Soc. Japan 43, 1262 (1977).
14. S. Narita, J. Phys. Soc. Japan 49, Suppl. A, 173 (1980).
15. S. Narita, T. Shinbashi and M. Kobayashi, J. Phys. Soc. Japan 51, 2186 (1982).
16. E. E. Haller, R. E. McMurray Jr., L. M. Falicov, N. M. Haegel and W. L. Hansen, Phys. Rev. Lett. 51, 1089 (1983).
17. R. E. McMurray Jr., Solid State Commun. 53, 1127 (1985).
18. S. Narita, Solid State Commun. 53, 1115 (1985).
19. A. Natori and H. Kamimura, J. Phys. Soc. Japan 43, 1270 (1977).
20. D. M. Larsen, Phys. Rev. B 23, 5521 (1981).

21. The theoretical results displayed by Narita and collaborators in Figure 2 of reference 15 and Figure 3 of reference 18 do not correspond, of course, to Larsen's results.

22. A. K. Ramdas and S. Rodriguez, Rep. Prog. Phys. 44, 1297 (1981). See Table 4 and references therein.

23. D. K. Wilson and G. Feher, Phys. Rev. 124, 1068 (1961).

TABLE I

Comparison between theory and experiment for the zero-stress binding energies (meV) of the D° ground state 1s-multiplet and of the D^- states in P and As doped Si. Both theoretical calculations assume that the VO interaction affects only the D^- inner electron orbital.

		$A_1(D^\circ)$	$T_2(D^\circ)$	$E(D^\circ)$	D^-
	Larsen[20]	31	-	-	1.04
Si:P	this work	44.28	31.27	31.27	1.62
	expt	45.59[a]	33.89[a]	32.58[a]	1.7[b],1.73[c],2.2[d]
	Larsen[20]	39	-	-	1.04
Si:As	this work	55.77	31.27	31.27	1.62
	expt	53.76[a]	32.67[a]	31.26[a]	1.7[b],2.05[c]

[a]Ramdas and Rodriguez[22]
[b]Norton[11]
[c]Narita *et al.*[15]
[d]Gershenzon *et al.*[8]

TABLE II

Comparison between theory and experiment for the zero-stress binding energies (meV) of the D° ground-state 1s-multiplet and of the D^- state in P doped Si. This calculation corresponds to modeling the VO interaction for both the inner and outer D^- electron orbitals.

	$A_1(D°)$	$T_2(D°)$	$E(D°)$	D^-
Larsen[20]	31	-	-	1.04
this work	44.28	31.27	31.27	2.23
expt	45.59[a]	33.89[a]	32.58[a]	1.7[b],1.73[c],2.2[d]

[a]Ramdas and Rodriguez[22]
[b]Norton[11]
[c]Narita *et al.*[15]
[d]Gershenzon *et al.*[8]

FIGURE CAPTIONS

Figure 1. Comparison between theoretical and experimental binding energies of D^- centers in (a) Si:P and (b) Si:As as functions of applied [100] compressive stress. Dashed lines represent Larsen's results[20] and solid curves correspond to our results. Both theoretical calculations assume that the VO interaction affects only the D^- inner-electron orbital. Experimental results are as follows: Narita *et al.*[15] (●), Norton[11] (○) and Gershenzon *et al.*[8] (□).

Figure 2. Binding energy of D^- center in P doped Si as a function of applied [100] compressive stress. The dashed line represents the result obtained by Larsen[20]; the solid curve (our calculation) corresponds to modeling the VO interaction for *both* the inner and outer D^- orbitals. Also shown are the experimental results of Narita *et al.*[15] (●), Norton[11] (○) and Gershenzon *et al.*[8] (□).

Figure 3. Probability strength of each of the stress-deepened valleys, 1 or 2, in the inner and outer D^- electron orbitals as functions of the [100] compressive stress in P doped Si. The dashed line represents the result obtained by Larsen[20] while the solid curve (our calculation) corresponds to modeling the VO interaction for *both* the inner and outer D^- electron orbitals.

Figure 4. Optimized values of variational parameters ξ_1, ξ_2, λ, α and β for D^- centers in Si:P [cf. (2.19) and (2.20)] as functions of applied compressive stress along [100].

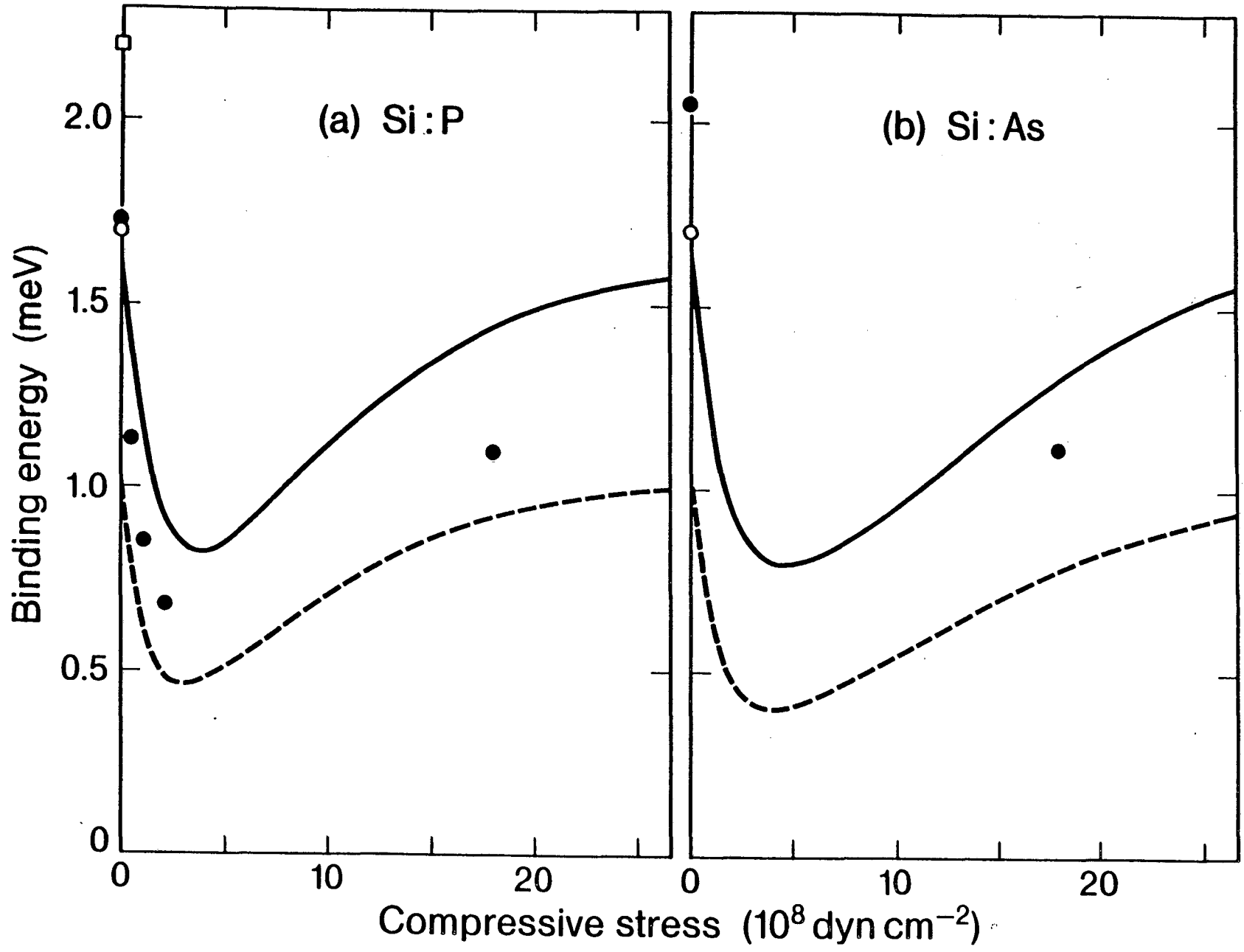
(a) Si : P
(b) Si : As
Binding energy (meV)
2.0
1.5
1.0
0.5
0
0
10
20
0
10
20
Compressive stress (10^8 dyn cm^{-2})

Figure 1

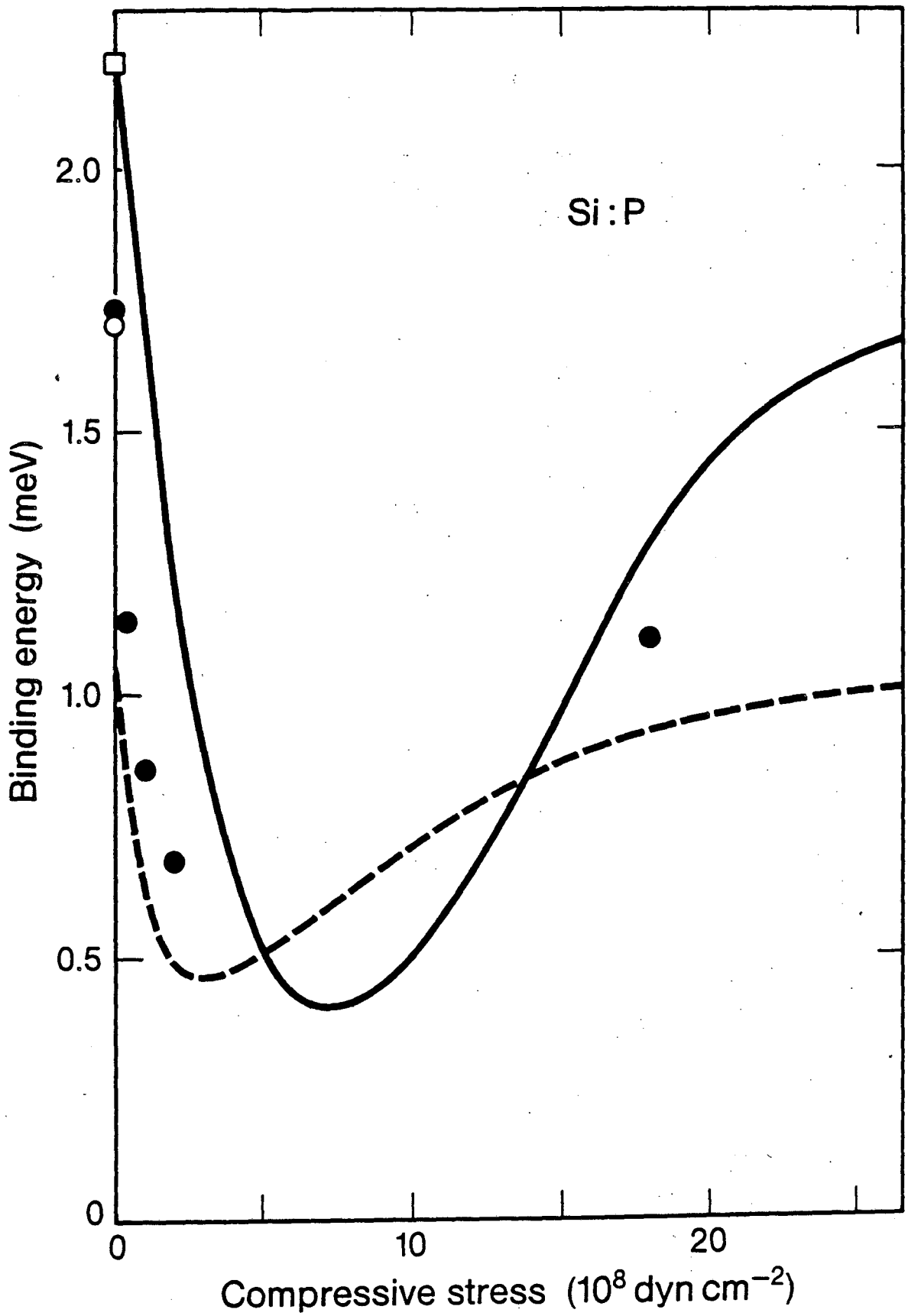
Si : P
Binding energy (meV)
2.0
1.5
1.0
0.5
0
0
10
20
Compressive stress (10^8 dyn cm^{-2})

Figure 2

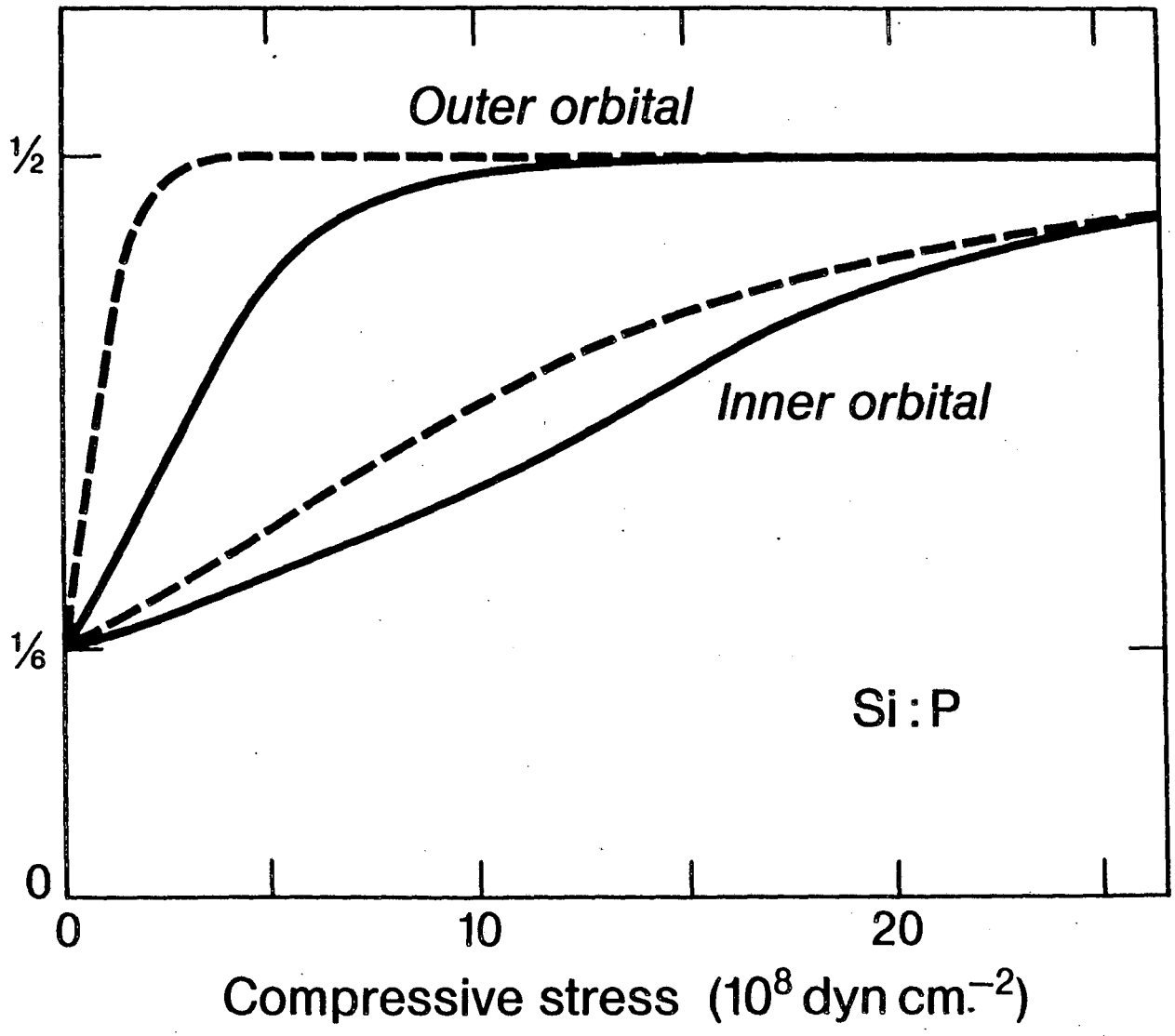
Outer orbital
Inner orbital
Si : P
½
⅙
0
0
10
20
Compressive stress (10⁸ dyn cm⁻²)

Figure 3

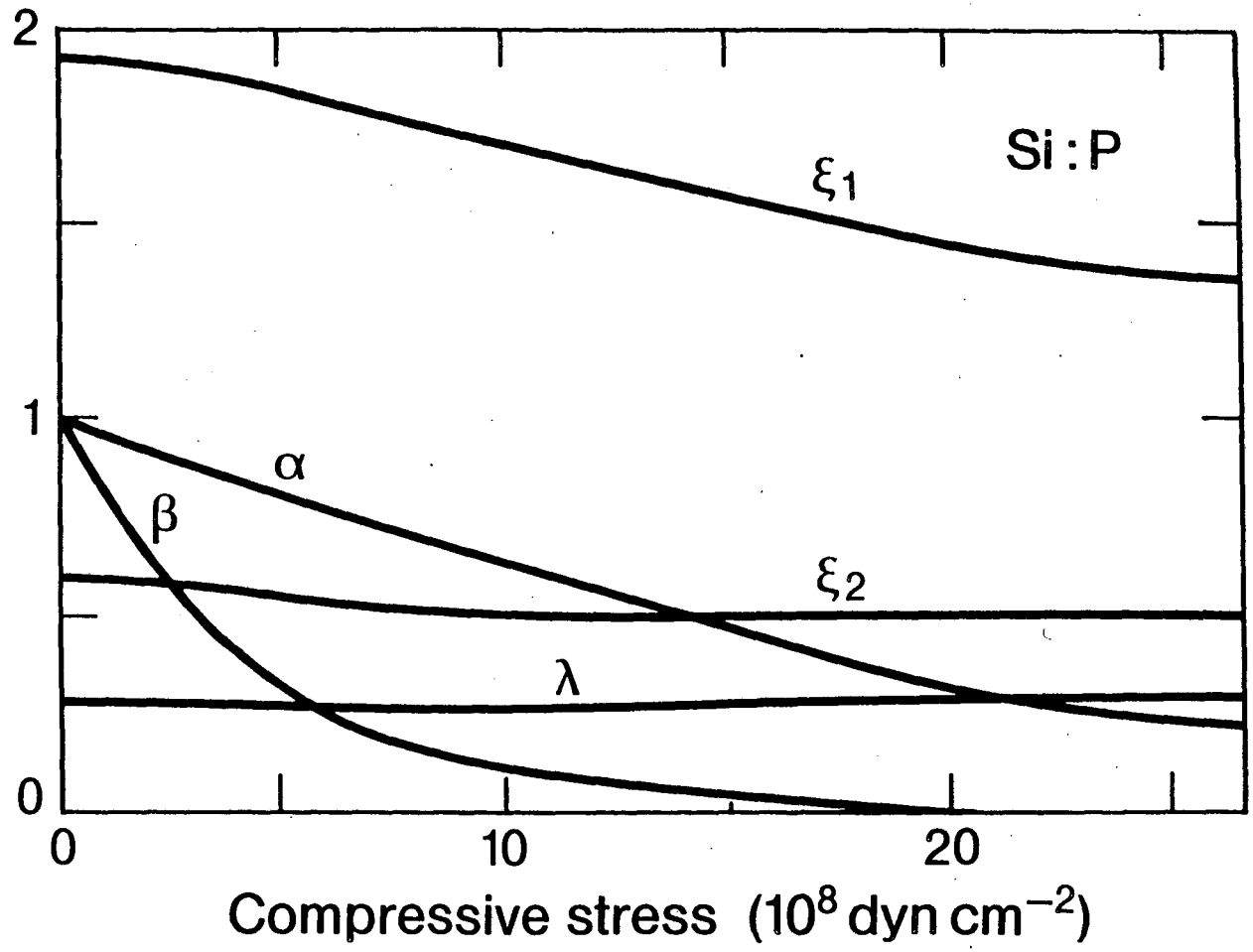

Figure 4

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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