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Deformation Potentials in Silicon. I. Uniaxial Strain*

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The rate of splitting with uniaxial strain of the fourfold degenerate ($J=3/2$) valence-band edge of silicon is computed by applying perturbation theory to the Si wave functions calculated previously by Kleinman and Phillips. Based on a "self-consistent" model the calculated values for strain along the [100] and [111] directions are 40% larger than Hensel's experimental values. A primary objective of this calculation was to test the rigid-ion and deformable-ion models often used in the theory of electron-phonon coupling. The rigid-ion model agrees with experiment to within the accuracy of the calculation while the deformable-ion model disagrees with experiment by 300%. For [111] strain the crystal symmetry is so reduced that the separation of the two atoms in each unit cell is not uniquely determined from the macroscopic strain. We have used a model in which the atoms locate themselves in such a way that nearest-neighbor covalent bonds are unchanged in length by shearing strains. This "bond-bending" model is contrasted with a model in which the atomic separation changes with strain like a macroscopic vector. The latter model yields a deformation potential of opposite sign to the experimental one.

I. INTRODUCTION

THE rate of splitting with applied uniaxial strain of the fourfold degenerate ($J=3/2$) valence-band edge of the covalently bonding semiconductors has only recently been measured. The first estimates were made using piezoresistance data[1,2] but because of oversimplifications in the theory, the results for silicon differ by more than an order of magnitude from the latest work.[3] Better results have been obtained (for Ge) by measuring the Hall mobility as a function of strain[4]; the populations and hence the splitting of the two levels are thus determined. Thomas[5] has measured the splitting of the $J=3/2$ valence band in CdTe from the splitting of the exciton peak in the reflection spectra. Price[6] has determined the splitting dependence of the binding energy of acceptor impurities and thus measured the splitting in Ge. Perhaps the most accurate measurements yet are those on Si made by Hensel[3] who measured the effective masses of the split levels by cyclotron resonance. Utilizing the small dependence of the effective masses on the splitting,[7] he was able to determine the splitting as a function of strain.

The effect of a homogeneous strain ϵ_{ij} on the valence band edge has been described by Kleiner and Roth[8] with a Hamiltonian written down from symmetry considerations:

$$\mathcal{H}=\mathcal{H}_0+D_d(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz})+\tfrac{2}{3}D_u[(J_x^2-\tfrac{1}{3}J^2)\epsilon_{xx}+\text{c.p.}]+\tfrac{2}{3}D_{u'}[(J_yJ_z+J_zJ_y)\epsilon_{yz}+\text{c.p.}],\quad(1)$$

where the D's are the deformation potential coefficients, J is the angular momentum of the hole, $\mathcal{H}_0$ describes the situation in the absence of strain, and "c.p." means cyclic permutation. This Hamiltonian is valid in the limit that J is a good quantum number, i.e., the strain splitting is much less than the spin-orbit splitting. D_d is the shift of the band edge per unit dilation. Its value has not been determined experimentally and we shall leave its calculation to a later publication for it depends sensitively on changes in V_{000}, the zeroth Fourier transform of the crystal potential—a quantity difficult to come by.[9] (The difference between D_d for conduction and valence band edges has been measured[10] and could be calculated on the uncertain assumption that conduction and valence states both see the same V_{000}.) The splitting of the band edge per unit extension along the [100] axis is given by $|\tfrac{4}{3}D_u|$ while $|\tfrac{4}{3}D_u'|$ plays the same role for the [111] axis.

Bardeen and Shockley[11] have shown that in simple semiconductors (nondegenerate band edge at $\mathbf{k}=0$) the electron-phonon interaction may be written $D\nabla\cdot\mathbf{u}$, where $\mathbf{u}$ is the displacement of the lattice due to thermal vibrations ($\nabla\cdot\mathbf{u}$ is the dilation) and D is the static deformation potential. Whitfield[12] has derived the deformation potential theorem in its general form (valid for long-wavelength acoustical phonons), and several authors have[13–15] extended it to include degenerate levels. Thus, the constants we here calculate (D_u and D_u') and which were measured in a statically deformed crystal by Hensel[3] are two of the three independent

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[1] G. E. Pikus and G. L. Bir, Fiz. Tverd. Tela 1, 1642 (1959) [translation: Soviet Phys.—Solid State 1, 1502 (1960)].

[2] G. E. Pikus and G. L. Bir, Fiz. Tverd. Tela 1, 1828 (1959) [translation: Soviet Phys.—Solid State 1, 1675 (1960)].

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[4] S. H. Koenig and J. J. Hall, Phys. Rev. Letters 5, 550 (1960).

[5] D. G. Thomas, Conference on Semiconducting Compounds, 1961 [J. Appl. Phys. 32, 2298 (1961)].

[6] P. J. Price, Phys. Rev. 124, 713 (1961).

[7] H. Hasegawa (to be published).

[8] W. H. Kleiner and L. M. Roth, Phys. Rev. Letters 2, 334 (1959).

[9] L. Kleinman and J. C. Phillips, Phys. Rev. 118, 1153 (1960) hereafter called KP.

[10] W. Paul and D. M. Worschauer, J. Phys. Chem. Solids 5, 102 (1958).

[11] J. Bardeen and W. Shockley, Phys. Rev. 80, 72 (1950).

[12] G. D. Whitfield, Phys. Rev. 121, 720 (1961).

[13] G. L. Bir and G. E. Pikus, Fiz. Tverd. Tela 2, 2287 (1960) [translation: Soviet Phys.—Solid State 2, 2039 (1961)].

[14] M. Lax, Application of Group Theory to Solid-State Physics, Notes on Lectures, Bell Telephone Laboratories, 1960–1961 (unpublished).

[15] M. Tiersten, IBM J. Research and Develop. 5, 122 (1961).

components of the hole-phonon coupling tensor in silicon.

Several models (rigid ion,[16] deformable ion,[17] self-consistent[18]) of the change in crystal potential with lattice displacement have been used to calculate electron-phonon couplings. Ehrenreich and Overhauser[19] have calculated the scattering of holes in germanium by acoustical and optical modes. For the acoustical modes they found that with the deformable-ion model scattering by transverse and longitudinal phonons are equally important but with the rigid-ion model only longitudinal phonons play an important role. With a reasonable choice of parameters they were able to fit the experimental $T^{-2.3}$ law of the drift mobility of holes using either model.[20] Hence, the determination of which, if either, of these two models gives the correct static deformation potential would be of considerable importance in the theory of electron-phonon interactions.

In Sec. II we derive the perturbation Hamiltonian $\mathcal{H}'=\mathcal{H}_{\text{deformed}}-\mathcal{H}_{\text{undeformed}}$ which we use in Sec. III to compute the static deformation potential constants from a "self-consistent" model. In the fourth section we compare calculations based on the rigid-ion (R.I.) and deformable-ion (D.I.) models with the "self-consistent" (S.C.) calculation and with the experimental values.[3] The rigid-ion model is shown to be far superior to the deformable-ion model.

Even though our model is nearly self-consistent, an additional assumption is required to calculate D_u'. In a Si crystal strained along the [111] direction the location of the two atoms in the unit cell is not uniquely determined by the macroscopic strain. We use a model in which the atoms move in such a way as to keep all nearest-neighbor bond lengths equal, i.e., a "bond-bending" model. In Sec. IV, we compare this model with one in which the separation between atoms changes with strain as if it were a macroscopic vector. The "bond-bending" model is shown to agree well with experiment while the other model does not. We are also able to show that the "bond-bending" model is compatible with what is known about interatomic force constants.

II. PERTURBING HAMILTONIAN

It is well known that the wave functions of the valence band edge in silicon are at $\mathbf{k}=0$ and (neglecting spin) transform according to the threefold-degenerate representation $\Gamma_{25'}$ i.e., as xy, xz, yz.[9,21] The most satisfactory procedure for determining these wave functions is to expand them in a series of orthogonalized plane waves[22,23]:

$$\psi_\alpha=\sum_i b_i{}^\alpha\chi_i{}^\alpha, \tag{2}$$

$$\chi_i=(N\Omega)^{-1/2}\sum_{\langle\mathbf{k}_i{}^\alpha\rangle}\Big[e^{i\mathbf{k}_i\cdot\mathbf{r}}-\sum_{\nu,n,l}e^{i\mathbf{k}_i\cdot\mathbf{R}_\nu}A_{nl}(k_i)\times U_{nl\mathbf{k}_i}(\mathbf{r}-\mathbf{R}_\nu)\Big], \tag{3}$$

where the sum over $\langle\mathbf{k}_i{}^\alpha\rangle$ means over a symmetrized combination of plane waves transforming according to the irreducible representation of interest, $\mathbf{R}_\nu$ is the νth lattice point in the crystal, U_{nlk} are silicon-core wave functions with quantum numbers n, l, $m=0$ and z axis in direction of $\mathbf{k}_i$, N is the number of unit cells of volume Ω in the crystal, $A_{nl}(k)=\langle U_{nlk},e^{i\mathbf{k}_i\cdot\mathbf{r}}\rangle$, and the expansion coefficients $b_i{}^\alpha$ are determined by minimizing $\langle\psi_\alpha|\mathcal{H}|\psi_\alpha\rangle/\langle\psi_\alpha|\psi_\alpha\rangle$. The one-electron Hamiltonian $\mathcal{H}$ is usually approximated by[24]

$$\mathcal{H}=-\nabla^2+V(\mathbf{r}), \tag{4}$$

where $V(\mathbf{r})$ is a local crystal potential which may be determined self-consistently.[9] It may easily be shown that[25,26] if we write

$$\varphi_\alpha=\frac{1}{(N\Omega)^{1/2}}\sum_i b_i{}^\alpha\sum_{\langle\mathbf{k}_i{}^\alpha\rangle}e^{i\mathbf{k}_i{}^\alpha\cdot\mathbf{r}}, \tag{5}$$

then φ_α obeys the following Schrödinger equation:

$$(\mathcal{H}+V_R)\varphi_\alpha=E\varphi_\alpha, \tag{6}$$

where V_R is a nonlocal repulsive potential such that

$$V_R\varphi(\mathbf{r})=\int V_R(\mathbf{r},\mathbf{s})\varphi(\mathbf{s})d^3s, \tag{7}$$

$$V_R(\mathbf{r}\cdot\mathbf{s})=\sum_\nu\sum_{n,l,m}(E-E_{nl})\times U_{nlm}{}^*(\mathbf{s}-\mathbf{R}_\nu)U_{nlm}(\mathbf{r}-\mathbf{R}_\nu), \tag{8}$$

where the E_{nl} are the eigenvalues of the core eigenfunctions U_{nlm}.

The φ_α's ($\alpha=xy$, xz, or yz) have been computed in KP[9] and we now wish to use first-order perturbation theory and diagonalize the 6×6 matrix $\langle\varphi_\alpha|V'+V_R'+\lambda\mathbf{L}\cdot\mathbf{S}|\varphi_\beta\rangle$, where $\lambda\mathbf{L}\cdot\mathbf{S}$ is the spin-orbit interaction term, and $V'(\mathbf{r})=V^D(\mathbf{r})-V(\mathbf{r})$, where $V^D(\mathbf{r})$ is the potential in a crystal uniaxially strained along one of the two independent axes of Eq. (1). However, as pointed out by Pikus and Bir,[1] in ordinary perturbation theory the wave functions in the perturbed problem are expanded

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[16] L. Nordheim, Ann. Physik 9, 607 (1931); and W. V. Houston, Phys. Rev. 88, 1321 (1952).

[17] F. Bloch, Z. Physik 59, 208 (1930).

[18] J. Bardeen, Phys. Rev. 52, 688 (1937).

[19] H. Ehrenreich and A. W. Overhauser, Phys. Rev. 104, 331 (1956).

[20] H. Ehrenreich and A. W. Overhauser, Phys. Rev. 104, 649 (1956).

[21] G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. 98, 368 (1955).

[22] C. Herring, Phys. Rev. 57, 1169 (1940).

[23] Other expansions either converge too slowly (e.g., plane waves) or require an approximation for the potential which is not justified for the semiconductors (e.g., the muffin-tin potential for the augmented plane-wave expansion).

[24] We use atomic units throughout this paper.

[25] J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).

[26] M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).

in unperturbed functions which satisfy the same boundary conditions as the perturbed function. In the present case of a periodic lattice of infinite extent that periodicity is the boundary condition; hence, both the perturbed and unperturbed functions must have the same periodicity. Thus, following Pikus and Bir,[1] we perform the following transformation of coordinates in order to bring the deformed crystal into coincidence with the undeformed[27]:

$$\mathbf{r}'=(1+\tilde{\epsilon}^{-1})\cdot\mathbf{r}=(1-\tilde{\epsilon})\cdot\mathbf{r}, \tag{9}$$

where $\tilde{\epsilon}$ is the strain tensor whose components appear in (1). Thus

$$\boldsymbol{\nabla}'^2=\boldsymbol{\nabla}^2+2\boldsymbol{\nabla}\cdot\tilde{\epsilon}\cdot\boldsymbol{\nabla}, \tag{10}$$

and

$$\begin{aligned}V^D(\mathbf{r}'+\tilde{\epsilon}\mathbf{r}')&=\sum_{\mathbf{k}} V_{\mathbf{k}}{}^D \exp[i\mathbf{k}\cdot(\mathbf{r}'+\tilde{\epsilon}\mathbf{r}')]\\&=\sum_{\mathbf{k}} V_{\mathbf{k}}{}^D e^{i\mathbf{k}'\cdot\mathbf{r}'}=\sum_{\mathbf{k}'} V_{\mathbf{k}'-\epsilon\mathbf{k}'}{}^D e^{i\mathbf{k}'\cdot\mathbf{r}'},\end{aligned} \tag{11}$$

where $\mathbf{k}'=\mathbf{k}+\tilde{\epsilon}\mathbf{k}$ is the reciprocal lattice vector in the unstrained crystal corresponding to $\mathbf{k}$ in the strained crystal. $V_k{}^D$ is the $\mathbf{k}$th Fourier transform of the potential in the strained crystal and depends on the model chosen. Finally,

$$\begin{aligned}&V_R{}^D(\mathbf{r}'+\tilde{\epsilon}\mathbf{r}',\,\mathbf{s}'+\tilde{\epsilon}\mathbf{s}')\\&\quad=\sum_{\nu,i}\sum_{n,l,m}(E-E_{nl})U_{n,l,m}{}^*((1+\tilde{\epsilon})(\mathbf{s}'-\mathbf{R}_i{}')-\boldsymbol{\tau}_\nu{}^D)\\&\qquad\times U_{nlm}((1+\tilde{\epsilon})(\mathbf{r}'-\mathbf{R}_i{}')-\boldsymbol{\tau}_\nu{}^D),\end{aligned} \tag{12}$$

where $\mathbf{R}_i$ is a vector to the center of the ith cell in the unstrained crystal and where $\boldsymbol{\tau}_\nu{}^D$ is the vector from the center of a cell to one of the atoms in the cell when the crystal has been deformed. Thus, the matrix elements of the perturbing Hamiltonian (neglecting spin-orbit coupling for the time being) in the unstrained coordinates, $\mathcal{H}'(r')=\mathcal{H}^D(r')-\mathcal{H}(r')$, are given by (dropping the primes)

$$\begin{aligned}\mathcal{H}_{\alpha\beta}{}'&=\langle\varphi_\alpha|\mathcal{H}'|\varphi_\beta\rangle\\&=2\langle\varphi_\alpha|\boldsymbol{\nabla}\cdot\tilde{\epsilon}\cdot\boldsymbol{\nabla}|\varphi_\beta\rangle+\sum_{\mathbf{k}}(V_{\mathbf{k}-\epsilon\mathbf{k}}{}^D-V_{\mathbf{k}})\langle\varphi_\alpha|e^{i\mathbf{k}\cdot\mathbf{r}}|\varphi_\beta\rangle\\&\quad+N\sum_{\nu}^{\text{cell}}\sum_{n,l,m}(E-E_{nl})\\&\quad\times\langle\varphi_\alpha(\mathbf{s})|U_{nlm}{}^*(\mathbf{s}+\tilde{\epsilon}\mathbf{s}-\boldsymbol{\tau}_\nu{}^D)U_{nlm}(\mathbf{r}+\tilde{\epsilon}\mathbf{r}-\boldsymbol{\tau}_\nu{}^D)\\&\qquad-U_{nlm}{}^*(\mathbf{s}-\boldsymbol{\tau}_\nu)U_{nlm}(\mathbf{r}-\boldsymbol{\tau}_\nu)|\varphi_\alpha(\mathbf{r})\rangle.\end{aligned} \tag{13}$$

III. CALCULATIONS

Before we can calculate the matrix elements (13), we must decide upon a model for the change in crystal potential with lattice displacement. We choose the following "self-consistent" model. Assume the crystal to be made up of perfectly rigid Si^{4+} ions centered at the lattice cites and an electron gas which responds in a self-consistent manner to the potential due to itself and the Si^{4+} ions. The approximation of perfect rigidity is very nearly self-consistent for the small Si^{4+} ions; the very small redistribution of ionic charge that does take place will be reflected only in the high Fourier components of ionic potential which have little effect on (13) because $\langle\varphi_\alpha|e^{i\mathbf{k}\cdot\mathbf{r}}|\varphi_\beta\rangle$ approaches zero rapidly as $\mathbf{k}$ gets large. Because we assume the ions to be rigid, they remain spherical and we may write[28]

$$\begin{aligned}V_{\mathbf{k}-\epsilon\mathbf{k}}{}^{\text{ion}D}&=V_{0,\mathbf{k}-\epsilon\mathbf{k}}{}^{\text{ion}D}\cos\{(\mathbf{k}-\tilde{\epsilon}\mathbf{k})\cdot\boldsymbol{\tau}^D\}\\&=V_{0,\mathbf{k}-\epsilon\mathbf{k}}{}^{\text{ion}}\cos\{(\mathbf{k}-\tilde{\epsilon}\mathbf{k})\cdot\boldsymbol{\tau}^D\},\end{aligned} \tag{14}$$

where $V_{0,\mathbf{k}-\epsilon\mathbf{k}}{}^{\text{ion}D}$ is the Fourier transform of the (Coulomb+exchange) potential due to a single ion and the $\cos\{(\mathbf{k}-\tilde{\epsilon}\mathbf{k})\cdot\tau^D\}$ is a structure factor arising from the two ions at $\pm\boldsymbol{\tau}^D$ in the unit cell. Note $V_{0,\mathbf{k}-\epsilon\mathbf{k}}{}^{\text{ion}D}=V_{0,\mathbf{k}-\epsilon\mathbf{k}}{}^{\text{ion}}$ follows directly from the R.I. model:

$$V^D(\mathbf{r})=\sum_{n,\nu}v(\mathbf{r}+\boldsymbol{\tau}_\nu{}^D-\mathbf{R}_n-\mathbf{u}_n), \tag{15}$$

where v is the potential due to a single (spherically symmetric) ion and $\mathbf{u}_n=\tilde{\epsilon}\mathbf{R}_n$ is the displacement of the center of the cell located at $\mathbf{R}_n$ in the undeformed crystal. Note further that if $\boldsymbol{\tau}$ deforms normally, i.e., if $\boldsymbol{\tau}_D=\boldsymbol{\tau}+\tilde{\epsilon}\cdot\boldsymbol{\tau}$ then $\cos\{(\mathbf{k}-\tilde{\epsilon}\mathbf{k})\cdot\tau^D\}=\cos(\mathbf{k}\cdot\boldsymbol{\tau})$. Were we to use the D.I. model,

$$V^D(\mathbf{r})=V(\mathbf{r}-\tilde{\epsilon}\mathbf{r}), \tag{16}$$

then $V_{\mathbf{k}-\epsilon\mathbf{k}}{}^D=V_{\mathbf{k}}$ and the potential energy term of (13) would disappear, i.e., the transformation of coordinates (9) transforms the entire D.I. potential-energy term into a kinetic-energy term. We shall see that the R.I. potential energy term is needed in its entirety to give agreement with experiment. We shall also see that the R.I. approximation applied to the valence electrons yields a result not too different from the "self-consistent" model we now discuss.

Cohen and Phillips[29] have pointed out that to first order in the effective ionic potential [the true ionic potential plus V_R of Eq. (6)], one may write

$$V_{\mathbf{k}}{}^{\text{val}}=V_{\mathbf{k}}{}^s+V_{\mathbf{k}}{}^{\text{ex}}, \tag{17}$$

$$V_{\mathbf{k}}{}^s=V_{\mathbf{k}}{}^{\text{ion eff}}\{[1/\epsilon(\mathbf{k})]-1\}, \tag{18}$$

where $V_{\mathbf{k}}{}^s$ is the $\mathbf{k}$th Fourier transform of the Coulomb potential due to the screening (i.e., valence) electrons, $V_{\mathbf{k}}{}^{\text{ex}}$ the $\mathbf{k}$th Fourier transform of the exchange potential due to the valence electrons, and $\epsilon(\mathbf{k})$ is the static dielectric constant of wave number $\mathbf{k}$. Hence, if $\boldsymbol{\tau}$ deforms normally we may write

$$\begin{aligned}V_{\mathbf{k}-\epsilon\mathbf{k}}{}^D-V_{\mathbf{k}}=[&V_{0,\mathbf{k}-\epsilon\mathbf{k}}{}^{\text{ion}}-V_{0,\mathbf{k}}{}^{\text{ion}}\\&+V_{\mathbf{k}-\epsilon k}{}^{\text{val}}-V_{\mathbf{k}}{}^{\text{val}}]\cos(\mathbf{k}\cdot\boldsymbol{\tau}),\end{aligned} \tag{19}$$

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[27] We work only to the first order in $\tilde{\epsilon}$.

[28] For typographical convenience the tilde has been dropped from $\tilde{\epsilon}$ in subscripts.

[29] M. H. Cohen and J. C. Phillips, Phys. Rev. **124**, 1818 (1961).

or in differential form

$$V_{\mathbf{k}-\epsilon\mathbf{k}}{}^{D}-V_{\mathbf{k}}=-\cos(\mathbf{k}\cdot\boldsymbol{\tau})\left[\left(\frac{\partial V_{0\mathbf{k}}{}^{\mathrm{ion}}}{\partial\mathbf{k}}\right)_{\mathbf{k}}+\left(\frac{\partial V_{\mathbf{k}}{}^{s}}{\partial\mathbf{k}}\right)_{\mathbf{k}}+\left(\frac{\partial V^{\mathrm{ex}}}{\partial\mathbf{k}}\right)_{\mathbf{k}}\right]\cdot\tilde{\epsilon}\cdot\mathbf{k},\qquad(20)$$

where

$$\left(\frac{\partial V_{\mathbf{k}}{}^{s}}{\partial\mathbf{k}}\right)_{\mathbf{k}}=-\frac{V_{0\mathbf{k}}{}^{\mathrm{ion\ eff}}}{\epsilon^{2}(\mathbf{k})}\left(\frac{\partial\epsilon}{\partial\mathbf{k}}\right)_{\mathbf{k}}-\left(\frac{\partial V_{0\mathbf{k}}{}^{\mathrm{ion\ eff}}}{\partial\mathbf{k}}\right)_{\mathbf{k}}(1-1/\epsilon(\mathbf{k})).\qquad(21)$$

In an Appendix to this paper we derive a formula analogous to (18) for $V_{\mathbf{k}}{}^{\mathrm{ex}}$ using the Slater[30] free-electron and the dielectric-screening[29] approximations. Considering the number of approximations involved in their derivation, Eqs. (17), (18), and (A4) give results in remarkably good agreement with detailed band calculations[9] of the (111) Fourier component of the valence potential (see Appendix). We use them with the knowledge that they contain several 10~20% errors which may not cancel so well for $(\partial V^{\mathrm{val}}/\partial\mathbf{k})_{111}$ as for $V_{111}{}^{\mathrm{val}}$. Higher $V_{\mathbf{k}}{}^{\mathrm{val}}$ are very nearly zero[9] and shall be taken to be exactly zero.

We now can calculate D_u by assuming the crystal to be strained thus:

$$\epsilon_{zz}=\epsilon,\quad\epsilon_{ij}=0\quad\text{for}\quad i,\,j\neq z.\qquad(22)$$

The first thing to notice is that if we take the φ_α's in 13 to be φ_{xy}, φ_{yz}, and φ_{zx}, only diagonal matrix elements exist. With the φ_α's expanded as in (5) the first (kinetic energy) term of (13) is just $-2\epsilon\sum_i b_i^2\sum_{\langle k_i^\alpha\rangle}k_{iz}{}^{\alpha 2}$, where $k_{iz}{}^{\alpha}$ is the z component of $\mathbf{k}_i{}^{\alpha}$. In Table I we list the b_i's which were computed but not listed in reference 9. The first two symmetrized combinations of plane waves for φ_{xy}, φ_{yz}, and φ_{zx} are listed by Herman.[31] In the second column of Table II we list the difference between $2\langle\varphi_{xy}|\nabla_z{}^2|\varphi_{xy}\rangle$ and $2\langle\varphi_{xz}|\nabla_z{}^2|\varphi_{xz}\rangle$ showing explicitly the contributions from the first two symmetrized combinations of plane waves. Note that for the strain in the z direction, $\mathcal{H}'_{xz,xz}=\mathcal{H}'_{yz,yz}$.

TABLE I. Coefficients of symmetrized combinations of plane waves appearing in the state $\Gamma_{25'}$.

SCPW	⟨111⟩	⟨200⟩	⟨220⟩	$\langle 311\rangle_\alpha$	$\langle 311\rangle_\beta$	⟨222⟩
b	0.831	0.537	0.076	−0.099	−0.013	−0.073

TABLE II. Kinetic, potential, and orthogonalization energy contributions in Ry to $\langle xy|\mathcal{H}'|xy\rangle-\langle xz|\mathcal{H}'|xz\rangle$. $\mathcal{H}'$ is the perturbation per unit strain in the [001] direction. The wave functions φ_{xy} and φ_{xz} have been expanded in symmetrized combinations of plane waves with coefficients b_i; contributions with coefficients b_1b_1, $2b_2b_2$, and b_2b_2 are listed separately to show convergence. The row labeled remainder contains all kinetic-energy terms b_i^2 and potential and orthogonalization energy terms $2b_1b_i$ and $2b_2b_i$ where $|b_i|>0.014$.

	T	V	V_R	H_0'
b_1b_1	0	0.376	−0.229	0.147
$2b_1b_2$	0	0.384	−0.176	0.208
b_2b_2	−0.864	0.089	−0.067	−0.842
Remainder	−0.041	0.160	−0.134	−0.015
Total	−0.905	1.009	−0.606	−0.502

The second (potential-energy) term of (13) is calculated using (20). That $\boldsymbol{\tau}$ deforms normally can be seen from symmetry considerations; there are x, y, and z rotation axes passing through the ions which are not destroyed by a uniaxial strain in the z direction. The valence-electron term of (19) is nonzero only for $\mathbf{k}=(2\pi/a)(\pm1,\pm1,\pm1)$; but with $\tilde{\epsilon}$ given by (22), $\mathbf{k}\cdot\tilde{\epsilon}\cdot\mathbf{k}$ is identical for all the $\mathbf{k}=(2\pi/a)(\pm1,\pm1,\pm1)$. Thus, the potential energy due to the valence-electron charge density does not contribute to the difference $\mathcal{H}'_{xy,xy}-\mathcal{H}'_{xz,xz}$ and hence not to $D_u\cdot\partial V_{0,\mathbf{k}}{}^{\mathrm{ion}}/\partial[(a/2\pi)\mathbf{k}]^2$ is listed in Table III.[32] It is obtained by fitting the last column of Table II in KP with an analytical expression and differentiating; it is accurate to the two significant figures listed. The potential-energy contribution to $\mathcal{H}'_{xy,xy}-\mathcal{H}'_{xz,xz}$ is listed in Table II next to the kinetic-energy contribution.

TABLE III. Fourier transforms of potential of Si^{4+} ion for various reciprocal lattice vectors $\mathbf{k}$ and their derivatives with respect to $[(a/2\pi)k]^2$.

$h^2=[(a/2\pi)k]^2$	$V_{0,k}{}^{\mathrm{ion}}$	$\partial V_0{}^{\mathrm{ion}}/\partial h^2$
3	−0.793	0.22
8	−0.368	0.034
11	−0.294	0.019
16	−0.229	0.0096
19	−0.205	0.0072
24	−0.176	0.0048
27	−0.163	0.0040

The third (repulsive-potential) term of (13) may be calculated in the local approximation used by us in energy-band calculations[9]; this is done by approximating $\varphi(\mathbf{s})$ in (7) by the product of a radial function and a spherical harmonic. This approximation simplifies the calculation greatly and causes only a 5% error in D_u. However, it was felt beforehand that the error might be much larger than this and so the repulsive potential term was calculated exactly by substituting (5) in it, yielding a contribution from the $2p$ core levels[33]

$$V_{R\alpha\alpha}{}'=(E-E_{2p})2\sum_{ij}b_ib_j\times\sum_{\langle\mathbf{k}_i{}^{\alpha}\rangle}\sum_{\langle\mathbf{k}_j{}^{\alpha}\rangle}\{(A^*(k_i{}'')A(k_j{}'')\cos\theta_{i''j''}-A^*(k_i)A(k_j)\cos\theta_{ij})\cos[\boldsymbol{\tau}\cdot(\mathbf{k}_i-\mathbf{k}_j)]\},\qquad(23)$$

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[30] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[31] F. Herman, Phys. Rev. **93**, 1214 (1954).

[32] Since $V_{0,\mathbf{k}}{}^{\mathrm{ion}}$ depends only on the magnitude of $\mathbf{k}$, $\partial V_{0,\mathbf{k}}{}^{\mathrm{ion}}/\partial\mathbf{k}=2\mathbf{k}(a/2\pi)^2\partial V_0{}^{\mathrm{ion}}/\partial[(a/2\pi)k]^2$. Similarly for $A(k)$ and $\epsilon(k)$.

[33] Although $\Gamma_{25'}$ has d-like symmetry about the center of a cell, it is p like about the atoms.

TABLE IV. Orthogonalization coefficients for plane waves appearing in expansion of φ_α and their derivatives with respect to $[(a/2\pi)k]^2$.

$h^2=[(a/2\pi)k]^2$	$A(k)$	$\partial A/\partial h^2$
3	0.0915	0.0081
4	0.0978	0.0050
8	0.1043	−0.0004
11	0.1012	−0.0015
12	0.0997	−0.0016

where $\mathbf{k}''=\mathbf{k}-\tilde{\epsilon}\mathbf{k}$ is a reciprocal lattice vector in the strained crystal corresponding to $\mathbf{k}$ in the unstrained,[34] θ_{ij} is the angle between $\mathbf{k}_i$ and $\mathbf{k}_j$, and we have used the fact that $\boldsymbol{\tau}$ deforms normally. In differential form

$$V_{R\alpha\alpha}'=2(E_{2p}-E)\sum_{ij} b_jb_i \sum_{\langle \mathbf{k}_i\boldsymbol{\alpha}\rangle} \sum_{\langle \mathbf{k}_j\boldsymbol{\alpha}\rangle}\Bigg(\Bigg\{\Bigg[\frac{\mathbf{k}_i\cdot\mathbf{k}_j}{k_ik_j}A^*(k_j)$$

$$\times\left(\frac{\partial A}{\partial\mathbf{k}}\right)_{k_i}+A^*(k_j)A(k_i)\frac{1}{k_i}\left(\frac{\mathbf{k}_j}{k_j}-\frac{\mathbf{k}_i\cdot\mathbf{k}_j}{k_ik_j}\frac{\mathbf{k}_i}{k_i}\right)\Bigg]$$

$$\cdot\tilde{\epsilon}\cdot\mathbf{k}_i+[\ \ ]\cdot\tilde{\epsilon}\cdot\mathbf{k}_j\Bigg\}\cos[\boldsymbol{\tau}\cdot(k_i-k_j)]\Bigg),\quad(24)$$

where the second pair of brackets are identical to the first with i and j interchanged. $A(\mathbf{k})$ and $\partial A/\partial[(a/2\pi)k]^2$ calculated from the $2p$ core functions of KP are listed[31] in Table IV; also from KP, $E-E_{2p}=7.42$ ry. $V_{Rxy,xy}-V_{Rxz,xz}$ is listed in the fourth column of Table II as calculated from (24). The last column of Table II, the sum of the first three, gives $\mathcal{H}'_{xy,xy}-\mathcal{H}'_{xz,xz}$.

We now wish to diagonalize the 6×6 matrix $\langle\varphi_\alpha|\mathcal{H}'+\lambda\mathbf{L}\cdot\mathbf{S}|\varphi_\beta\rangle$. If we choose the φ_α's to diagonalize the spin-orbit term,

$$\begin{aligned}\varphi_{3/2}{}^{3/2}&=(1/\sqrt{2})(\varphi_{xz}+i\varphi_{yz})\alpha,\\ \varphi_{1/2}{}^{3/2}&=(1/\sqrt{6})[(\varphi_{xz}+i\varphi_{yz})\beta-2\varphi_{xy}\alpha],\\ \varphi_{-1/2}{}^{3/2}&=(1/\sqrt{6})[(\varphi_{x\cdot}-i\varphi_{yz})\alpha+2\varphi_{xy}\beta],\\ \varphi_{-3/2}{}^{3/2}&=(1/\sqrt{2})(\varphi_{xz}-i\varphi_{yz})\beta,\\ \varphi_{1/2}{}^{1/2}&=(1/\sqrt{3})[(\varphi_{xz}+i\varphi_{yz})\beta+\varphi_{xy}\alpha],\\ \varphi_{-1/2}{}^{1/2}&=(1/\sqrt{3})[(\varphi_{xz}-i\varphi_{yz})\alpha-\varphi_{xy}\beta],\end{aligned}\quad(25)$$

where α and β denote states of $S_z=1/2$ and $S_z=-1/2$, then note that $\mathcal{H}'$ connects states of different J but is still diagonal within either set of states with the same J. Hence, when the deformation splitting is small compared with the spin-orbit splitting, we need calculate only diagonal elements of the 4×4 $(J=3/2)$ $\mathcal{H}'$ matrix. We find immediately

$$\begin{aligned}\tfrac{4}{3}D_u&=\langle\varphi_{\pm3/2}{}^{3/2}|\mathcal{H}'|\varphi_{\pm3/2}{}^{3/2}\rangle-\langle\varphi_{\pm1/2}{}^{3/2}|\mathcal{H}'|\varphi_{\pm1/2}{}^{3/2}\rangle\\ &=\tfrac{2}{3}(\mathcal{H}'_{xz,xz}-\mathcal{H}'_{xy,xy}),\end{aligned}\quad(26)$$

where we have used the definition of D_u, Eq. (1). Thus from Table II we find $D_u=0.251$ Ry$=3.41$ eV. This is compared with the experimental value in Table VII.

We now determine D_u' by considering a strain 3ϵ along the [111] axis giving a strain tensor $\epsilon_{11}=3\epsilon$ and $\epsilon_{ij}=0$ for i, $j\neq1$ in a coordinate system with the x axis in the [111] direction and $\epsilon_{ij}=\epsilon$ for all i, j in the crystal-coordinate system. The dilation $\epsilon_{xx}=\epsilon_{yy}=\epsilon_{zz}$ may be set equal to zero to simplify the calculations as it cannot lead to a splitting of the levels. If the φ_α's are now chosen to be $\varphi_A=(\varphi_{xy}+\varphi_{yz}+\varphi_{zx})/\sqrt{3}$, $\varphi_{E1}=(\varphi_{xy}-\varphi_{zx})/\sqrt{2}$, and $\varphi_{E2}=(\varphi_{xy}+\varphi_{zx}-2\varphi_{yz})/\sqrt{6}$ the $\mathcal{H}'$ matrix [Eq. (13)] will be diagonalized with $\mathcal{H}'_{E1,E1}=\mathcal{H}'_{E2,E2}$. The calculation of the kinetic-energy contributions proceeds as before and we list $\mathcal{H}'_{AA}(\mathrm{KE})-\mathcal{H}'_{EE}(\mathrm{KE})$ in the first column of Table VI.

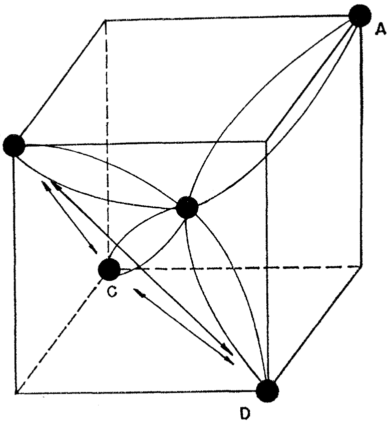

FIG. 1. Covalent bonds showing forces along [1$\bar{1}$0], [10$\bar{1}$], [01$\bar{1}$] directions which bend the three bonds B, C, D but leave the lengths of all four bonds unchanged for $\zeta=1$.

The potential-energy and repulsive-potential terms are a bit more complicated, however, because the location of the ions in the strained unit cell is not known. From symmetry considerations the ions must remain on the threefold axis along which the strain is applied and must be reflection images of each other in the center of the unit cell but their distance apart is not determined, the twofold rotation-inversion axes perpendicular to the strain having been destroyed. We have already divided the strain into a dilation, which we ignore, and a shear. We now choose the following model whose implications will be discussed in the next section: All shears take place through the mechanism of "bond bending." The three shears of which the [111] uniaxial strain is composed are equivalent to three uniaxial strains along the three [110] axes perpendicular to the [111] strain direction. In our model these strains do not change the length of any (nearest-neighbor) bonds but rather bend those bonds not along the [111] strain direction. (See Fig. 1.) With this assumption then $\boldsymbol{\tau}^D=\boldsymbol{\tau}$; thus we can write $V_{\mathbf{k}-\epsilon\mathbf{k}}{}^D-V_{\mathbf{k}}=V_{\mathbf{k}}{}^{0\prime}+V_{\mathbf{k}}{}^{B\prime}$, where $V_{\mathbf{k}}{}^{0\prime}$ is what would be

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[34] Recall that in Eq. (13) we dropped the primes which had previously appeared on all vectors in the unstrained coordinate system.

TABLE V. Quantities appearing in Eqs. (21) and (A5) evaluated at $k=(2\pi/a)(1,1,1)$.

$V_{0,k}{}^{\text{ion eff}}$	$\partial V_0{}^{\text{ion eff}}/\partial h^2$	$\epsilon(k)$	$\partial\epsilon/\partial h^2$	$\partial V^s/\partial h^2$	$\partial V^{\text{ex}}/\partial h^2$
−0.32	0.18	1.97	−0.36	−0.12	0.02

obtained if $\boldsymbol{\tau}$ deformed normally and is given by (20) and

$$V_{\mathbf{k}}{}^{B'}=[V_{0,\mathbf{k}}{}^{\text{ion}}+V_{\mathbf{k}}{}^{s}+V_{\mathbf{k}}{}^{\text{ex}}](\sin\mathbf{k}\cdot\boldsymbol{\tau})\boldsymbol{\tau}\cdot\tilde{\epsilon}\cdot\mathbf{k} \quad (27)$$

is the contribution to the change in potential in the distorted crystal due to bond bending. $\partial V^{\text{ex}}/\partial[(a/2\pi)k]^2$, $\partial V^{s}/\partial[(a/2\pi)k]^2$, and the values of $\epsilon(\mathbf{k})$, $\partial\epsilon/\partial[(a/2\pi)k]^2$, $V_{0,\mathbf{k}}{}^{\text{ion eff}}$, $\partial V_0{}^{\text{ion eff}}/\partial[(a/2\pi)k]^2$ [for $\mathbf{k}=(2\pi/a)(1,1,1)$] used[31] to calculate them are listed in Table V. $V_{0,\mathbf{k}}{}^{\text{ion eff}}$ which is $V_{0,\mathbf{k}}{}^{\text{ion}}$ plus an average[29] of the s and p repulsive potentials was taken from KP whence its derivative was also taken. $\epsilon(\mathbf{k})$ and its derivative were computed from the well-known equation for the static dielectric constant of a free electron gas.[35] This approximation should be satisfactory since the dielectric constant of a semiconductor is similar to that of a free electron gas for large $\mathbf{k}$ where large $\mathbf{k}$ means $\epsilon(\mathbf{k})\ll\epsilon(0)=12$ for silicon. The quantity $V_{0,111}{}^{\text{ion}}+V_{111}{}^{s}+V_{111}{}^{\text{ex}}=0.688$ Ry from KP. $V_{111}{}^{s}$ was also calculated from (18) and $V_{111}{}^{\text{ex}}$ from (A4). This gives $V_{0,111}{}^{\text{ion}}+V_{111}{}^{s}+V_{111}{}^{\text{ex}}=0.685$ Ry (see Appendix). The contributions to $\mathcal{H}'_{AA}-\mathcal{H}'_{EE}$ of $V_{\mathbf{k}}{}^{0'}$ and $V_{\mathbf{k}}{}^{B'}$ are listed separately in Table VI.

Similarly the matrix elements of the repulsive potential are $V_{R\alpha\alpha}{}'=V_R{}^{0'}+V_R{}^{B'}$, where $V_R{}^{0'}$ is given by (24) and

$$V_{R\alpha\alpha}{}^{B'}=2(E-E_{2p})\sum_{ij} b_ib_j \sum_{\langle\mathbf{k}_i\alpha\rangle}\sum_{\langle\mathbf{k}_j\alpha\rangle} \frac{\mathbf{k}_i\mathbf{k}_j}{k_ik_j}A(k_j)A(k_i)$$
$$\times\sin[(\mathbf{k}_i-\mathbf{k}_j)\cdot\boldsymbol{\tau}](\boldsymbol{\tau}\cdot\tilde{\epsilon}\cdot\mathbf{k}_i-\boldsymbol{\tau}\cdot\tilde{\epsilon}\cdot\mathbf{k}_j). \quad (28)$$

$V_{RAA}{}^{0'}-V_{REE}{}^{0'}$ and $V_{RAA}{}^{B'}-V_{REE}{}^{B'}$ are listed in Table VI. The last column of Table VI, the sum of the first five, gives $\mathcal{H}'_{AA}-\mathcal{H}'_{EE}$.

Choosing φ_α's to diagonalize the spin-orbit term as in (25) but with $xy\to A$, $xz\to E1$, $yz\to E2$, we find that (26) holds for $D_u{}'$. Thus from Table VI (remembering our initial strain was 3ϵ this time) we find $D_u{}'=0.232$ Ry $=3.15$ eV.

TABLE VI. Kinetic, potential, and orthogonalization energy contributions in Ry to $\langle A|\mathcal{H}'|A\rangle-\langle E|\mathcal{H}'|E\rangle$. $\mathcal{H}'$ is the perturbation per unit ϵ for a strain 3ϵ in the [111] direction. The part of the potential and orthogonalization energy which is due to the motion of the atoms within a unit cell is listed separately in columns 4 and 5. The rows are labeled as in Table II.

	T	V	V_R	V^B	$V_R{}^B$	$H_0{}'$
b_1b_1	−2.07	1.13	−0.47	−2.30	1.08	−2.63
$2b_1b_2$	0	2.63	−0.69	−2.33	0.91	0.52
b_2b_2	0	0.94	−0.25	0	0	0.69
Remainder	−0.06	0.68	−0.47	−0.86	0.74	0.03
Total	−2.13	5.38	−1.88	−5.49	2.73	−1.39

IV. DISCUSSION

An examination of Tables II and VI reveals that an expansion of φ_α consisting of just two symmetrized combinations of plane waves is sufficient for determining D_u and $D_u{}'$. The row labeled "remainder" consists of all kinetic-energy contributions with a factor $b_i{}^2$ and potential-energy contributions with a factor $2b_ib_1$ or $2b_ib_2$ where $|b_i|>0.014$; it contributes less than 5% to the total. The contribution from those terms still remaining is quite certainly much smaller yet.

Phillips[36] has pointed out that one can fit all the experimental data of Si by decreasing $E-E_{2p}$ in the KP energy band calculation by about 1.0 Ry which leads to a 13.5% reduction in V_R. While this does not necessarily imply that either $E-E_{2p}$ or V_R is actually in error by this amount, if we assume such an error does exist it leads to $D_u=2.85$ eV and $D_u{}'=3.41$ eV, i.e., it gives a value of $D_u/D_u{}'$ in substantial agreement with the experimental value and reduces the discrepancy between the calculated values of D_u and $D_u{}'$ and experiment to 40%. We list these "corrected" values of D_u and $D_u{}'$ in the third column of Table VII and shall call these our calculated values. It should be pointed out that our corrected values of D_u and $D_u{}'$ do not include the changes in the b_i which must necessarily occur if we recalculated the energy bands, using the corrected V_R. The weaker repulsive potential would cause b_2 to increase and b_1 to decrease, thus reducing the decrease in D_u and the increase in $D_u{}'$.

TABLE VII. Comparison of experimental values[a] of D_u and $D_u{}'$ (in eV) with various calculated values. Column 2 is the "self-consistent" calculation for $\zeta=1$ using $E-E_{2p}=7.42$ Ry. The remaining columns use $E-E_{2p}=6.42$ Ry. Columns 3 and 4 are the "self-consistent" calculation for $\zeta=1$ and $\zeta=0$ [see Eq. (29)]. Column 5 is the rigid-ion model with $\zeta=1$. Column 6 is the deformable-ion model which is independent of ζ.

	Exp	S.C.B.[b]	S.C.B.[b]	S.C.N.[c]	*R.I.*	D.I.
D_u	2.04	3.41	2.85	2.85	2.85	6.15
$D_u{}'$	2.68	3.15	3.41	−3.85	2.09	4.83

[a] See reference 3.
[b] Self-consistent bond bending.
[c] Self-consistent normal.

Other sources of error in the calculation are the $V_{0,\mathbf{k}}$ and the $A(k)$ and their derivatives. Aside from V_{111} and $(\partial V/\partial k^2)_{111}$ which do not enter the calculation of D_u, these depend only on the atomic cores and should not be in error by more than 5%. The errors in V_{111} are due mainly to the uncertainties in the valence-electron exchange terms and the "self-consistent" calculation of the valence potential. Note that the change in $E-E_{2p}$ previously discussed would, if taken properly into account, decrease V_{111} by increasing the self-consistent screening of the valence electrons. In addition, $(\partial V/\partial k^2)_{111}$ suffers from the dielectric screening approximation which does work quite well for V_{111}, how-

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[35] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **28**, 8 (1954).

[36] J. C. Phillips, Phys. Rev. **125**, 1931 (1962).

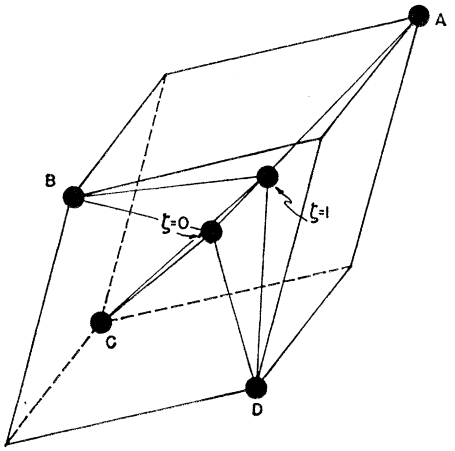

FIG. 2. Location of an atom relative to its nearest neighbors in a crystal strained 3ϵ in the [111] direction. For $\zeta=0$ the atom remains in the center of the strained cube; for $\zeta=1$ all four bonds are of the same length.

ever. In view of these uncertainties in the calculation, the agreement with experiment is as good as can be expected.

We have thus far omitted the correction to the deformation potential due to the change in the repulsive potential caused by the splitting of the valence and core levels. Thus to H' we must add a term

$$N\sum_{\nu}^{\text{cell}}\sum_{n,l,m}(H'-\Delta E_{nl})\times\langle\varphi_\alpha(\mathbf{s})|U_{nlm}^*(\mathbf{s}-\boldsymbol{\tau}_\nu)U_{nlm}(\mathbf{r}-\boldsymbol{\tau}_\nu)|\varphi_\alpha(\mathbf{r})\rangle, \quad (29)$$

where H' is the splitting per unit strain of the top of the valence band and ΔE_{nl} is the splitting of the $2p$ core levels. We thus obtain

$$H'=H_0'+0.07(H'-\Delta E_{nl}). \quad (30)$$

An exact calculation of ΔE_{nl} would be extremely tedious. Just as for H', there are kinetic and potential energy contributions to ΔE_{nl}. The kinetic contributions are of order $\partial E_{2p}/\partial r_s<0.0001$ while the potential energy contributions though larger are still much smaller than the potential energy contributions to H_0', because the change in crystal potential with strain is much smaller in the core region than in the valence region.

The calculated values of D_u and D_u' are sufficiently accurate to enable us to make several interesting observations about the distorted crystal. The fourth column of Table VII lists D_u' as calculated neglecting the bond-bending contributions, V^B and $V_R{}^B$, of Table VI. If one writes

$$D_{u'}=T+V+V_R+\zeta(V^B+V_R{}^B), \quad (31)$$

then a comparison of the calculated values for $\zeta=0$ and $\zeta=1$ with the experimental value indicates $\zeta>0.9$ or at the worst $\zeta>0.8$, i.e., the "bond-bending" model is about 90% correct. This is consistent with the little that is known about interatomic force constants. In Fig. 2, we show an atom, and its four nearest neighbors in a crystal-strained 3ϵ in the [111] direction. If $\boldsymbol{\tau}$ deforms normally, the [111] bond is of length $(\sqrt{3}a/4)(1+2\epsilon)$ and the other three bonds of length $(\sqrt{3}a/4)(1-2/3\epsilon)$. If we now allow the central atom to move a distance $(a/2)(\epsilon,\epsilon,\epsilon)$, all four bonds attain their natural (unstrained) length $\sqrt{3}a/4$ eliminating the nearest-neighbor central force energy of the system. Opposing this reduction of energy is the increase of nearest-neighbor noncentral force energy (i.e., bond-bending energy) and perhaps far-neighbor energy. According to Herman's[37] fit of the lattice-vibration spectrum of germanium (which should be similar to silicon) the nearest-neighbor force constants are $\alpha=3.7$, $\beta=3.4$; their difference[38] is a measure of the noncentral forces, i.e., about 10% of the central forces. Second and all even neighbors do not effect bond bending since all even neighbors are moved by the same $(a/2)(\epsilon,\epsilon,\epsilon)$. (The diamond lattice may be considered as two interpenetrating fcc lattices. "Bond bending" is a measure of the separation of these two sublattices in the deformed crystal and, thus, cannot involve forces between neighbors on the same sublattice. Of course bonds connecting two atoms on the same sublattice are bent in a strained crystal, but this bending is uniquely determined by the macroscopic strain tensor.) Third and farther neighbor forces are not sufficiently well known to determine whether they aid or oppose bond bending, but in any event, their effect will be of order 10%.

The bond-bending constant should be directly measurable by x-ray scattering. The scattering factor F_{200} in diamond-structure crystals is forbidden because of the structure factor $\cos(\mathbf{k}\cdot\boldsymbol{\tau})$. Unlike other forbidden reflections which fail to vanish[39] (the structure factor assumes the crystal-charge density to be a superposition of atomic-charge densities), F_{200} is rigorously zero from group theoretical considerations. In the strained crystal F_{200} is no longer rigorously zero, but will still be vanishingly small due to the structure factor unless bond bending takes place. We may write for a crystal-strained 3ϵ in the [111] direction

$$F_{200}=f_{200}\cos(\mathbf{k}\cdot\boldsymbol{\tau}-\zeta\mathbf{k}\cdot\tilde{\epsilon}\cdot\boldsymbol{\tau})=\pi\epsilon\zeta f_{200}, \quad (32)$$

where f_{200} is the atomic scattering factor. For $\epsilon=10^{-3}$ we have $F_{200}\sim0.04$ in Si and ~0.08 in Ge. Since x-ray scattering factors are reported to three decimal places,[40] there should be no difficulty in determining ζ.

In the last two columns of Table VII we list D_u and D_u' as computed from the D.I. and R.I. models. Since we have treated the core as rigid in our "self-consistent" model, it is not surprising that the R.I. model varies only slightly from the S.C. calculation. The result

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[37] F. Herman, J. Phys. Chem. Solids **8**, 405 (1959).

[38] Because nearest neighbors lie along [111], all components of their force tensor are equal for central forces.

[39] L. Kleinman and J. C. Phillips, Phys. Rev. **125**, 819 (1962).

[40] S. Göttlicher and E. Wölfel, Z. Electrochem. **63**, 891 (1959).

of treating the valence electrons as rigid is to decrease $\partial V^{\mathrm{val}}/\partial[(a/2\pi)k]^2$ from -0.10 to -0.07, i.e., to make them screen not quite so effectively, which is exactly what was expected. Even though the agreement of the "self-consistent" and rigid-ion models with experiment may be somewhat fortuitous, the disagreement of the deformable-ion model with experiment is real. D_u is in error by 300%. D_u' is only in error by 80%, but if a "bond-bending" contribution were added to it, it would be in error by 400%. Since the D.I. model is independent of both repulsive and Coulomb potentials, the *only* source of error in its calculation is the b_i^2 coefficients of the kinetic-energy terms. These could be in error by as much as 10% not 300%. Furthermore, any attempt to correct the b_i^2 to improve D_u will worsen D_u' and vice versa. Thus, we can flatly state that the deformable-ion model is an extremely poor approximation.

In the near future there will exist digital computer programs which will enable self-consistent energy band calculations to be done with extreme accuracy and ease.[41] A good test of these calculations will be to perform them for strained crystals and thus compute D_u in a truly self-consistent manner. (A truly self-consistent calculation of D_u' would require ζ to be determined by minimizing the total energy of the strained crystal; this however appears to require accuracy beyond present capabilities.) A more immediate use of deformation potentials might be as an aid in identifying optical absorption peaks in a variety of semiconductors.[42] For this reason and because a comparison of deformation potentials at points throughout the Brillouin zone is of interest for its own sake, we are now surveying these.

ACKNOWLEDGMENTS

I wish to express my thanks to Professor J. C. Phillips for helpful and encouraging conversations and to Dr. J. C. Hensel for making his data available to me before publication.

APPENDIX

We here derive the exchange potential due to the valence charge density in the dielectric screening[29] and Slater free electron approximations.[30] From Poisson's equation and (18)

$$\rho_{\mathbf{k}}^{s}=\mathbf{k}^2V_{\mathbf{k}}^{s}/8\pi=-(k^2/8\pi)V_{\mathbf{k}}^{\mathrm{ion\ eff}}\{\epsilon[(\mathbf{k})-1]/\epsilon(\mathbf{k})\},\qquad\text{(A1)}$$

where

$$\rho^{s}(\mathbf{r})=\rho_0^{s}+\sum\nolimits_{\mathbf{k}}\rho_{\mathbf{k}}^{s}e^{i\mathbf{k}\cdot\mathbf{r}},\qquad\text{(A2)}$$

and $\rho_0^s=32/a^3$; there being 32 valence electrons per unit cell of volume $a^3=10.26^3$. In the free-electron approximation

$$V^{\mathrm{ex}}=-6[3\rho(\mathbf{r})/8\pi]^{1/3}=-6(3/8\pi)^{1/3}(32/a^3)^{1/3}\times[1+\tfrac{1}{3}(a^3/32)\sum\nolimits_{\mathbf{k}}\rho_{\mathbf{k}}^{s}e^{i\mathbf{k}\cdot\mathbf{r}}],\qquad\text{(A3)}$$

where we have kept the first two terms in the power series expansion of $\rho^{1/3}$. Thus

$$V_k^{\mathrm{ex}}=-0.411k^2V_k^{s}=0.411k^2V_k^{\mathrm{ion\ eff}}\{[\epsilon(k)-1]/\epsilon(k)\},\qquad\text{(A4)}$$

and

$$\frac{\partial V^{\mathrm{ex}}}{\partial[(a/2\pi)k]^2}=-0.411\left(k^2\frac{\partial V_k^{s}}{\partial[(a/2\pi)k]^2}+0.375V_k^{s}\right).\qquad\text{(A5)}$$

The momentum-dependent[9] Slater approximation is obtained by multiplying (A4) and (A5) by 2/3. Insertion of the values of k, $V_k^{\mathrm{ion\ eff}}$ and $\epsilon(k)$ in (A4) and (18) verifies that $V_{0,111}^{\mathrm{ion}}+V_{111}^{s}+V_{111}^{\mathrm{ex}}=-0.793+0.157-0.049=-0.685$ Ry.

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[41] F. Herman and F. Quelle (private communications).

[42] H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters 8, 59 (1962).