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Effect of free carriers on the elastic constants of *p*-type silicon and germanium*

C. K. Kim,† Manuel Cardona, and Sergio Rodriguez‡
Max-Planck-Institut für Festkörperforschung, Stuttgart, Federal Republic of Germany
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Numerical calculations of the effect of free holes on the elastic constant C_{44} of Ge and Si are presented. The energy of the three top valence bands is obtained by diagonalizing a 6 × 6 deformation-potential Hamiltonian, exact to second order in the components of $\vec{k}$. The numerical calculations underline the shortcomings of previous analytical work performed by angular averaging of the energy bands. Our calculations are extended to obtain the effect of a large [001] stress on the hole contribution to C_{44} mentioned above. This effect is anisotropic: The elastic constants C_{44} and C_{66} become inequivalent. The calculations are shown to be in good agreement with experiment in the low-temperature, low-carrier concentration region. This limitation is a direct consequence of having assumed a Hamiltonian quadratic in $\vec{k}$.

I. INTRODUCTION

The effect of free carriers on the elastic constants of heavily doped semiconductors was first discussed by Keyes.[1,2] Keyes suggestion can be described briefly as follows. The application of a stress to a crystal shifts and distorts the electronic energy bands. The subsequent redistribution of the electrons lowers the total free energy of the crystal and thus lowers the elastic constants. In n-type materials, the experimental results[1,3-7] can be easily interpreted because the theoretical analysis can be carried out with a minimum of approximations. In contrast, the case of p-type Si and Ge is complicated by the nature of the valence bands of these materials.[8-10] We consider in this paper the change with hole concentration of the elastic constant C_{44} which was measured by Fjeldly *et al.*[10] in Si by determining the change in the speed of propagation of the fast transverse-acoustic phonon propagating along a [110] direction. These authors also measured the change in the velocities of shear acoustic waves propagating along one of the cubic directions as functions of stresses along a second cubic direction. In this situation the crystal symmetry is no longer cubic and instead of the elastic constant C_{44}, we must consider two elastic constants, C_{44} appropriate for ultrasonic polarization parallel to the stress and C_{66} for polarization perpendicular to the stress. The free-carrier contributions to these elastic constants are obtained by calculating the electronic contribution to the free energy of the crystal both in the presence and absence of a uniform uniaxial stress. For this purpose it is necessary to carry out sums over the occupied hole states which are often approximated, as in Refs. 8 and 9, by either an angular average or a weighted average of the principal directions. This can, of course, lead to significant errors if the bands are severely warped (e.g., for Si) and cannot be used for the calculation in the presence of stress. The purpose of the present work is to overcome this difficulty. This is done by using an effective Hamiltonian exact to second order in the wave vector and linear in the components of the strain tensor, i.e., within the framework of the deformation-potential approximation. The free-energy changes are calculated using the uniform-mesh method (UMM).[11,12] The nature and limitation of the approximations of our procedure will be discussed at the appropriate places. It is sufficient here to state that the use of the deformation-potential method limits the quantitative validity of our results to relatively low carrier concentrations and temperatures. For example, for Si at 77 K this validity extends only to carrier concentrations below ~6×10^{18} cm^{-3}. At higher concentrations we expect only qualitative agreement between theory and experiment.

II. THEORY

Let us consider a cubic crystal subjected to a uniaxial stress along the [001] axis and, in addition, supporting a shear acoustic wave. The contribution to the elastic constants C_{44} and C_{66} (we remember that in the absence of the constant stress, $C_{44}=C_{66}$) arising from the electrons will be called ΔC_{44} and ΔC_{66}, respectively. The change in the electronic free energy caused by the passage of a shear acoustic wave ($\epsilon_{ii}=0$, $\epsilon_{ij}\neq 0$, for $i\neq j$, where ϵ_{ij} are the components of the strain tensor) is

$$\delta F = 2\Delta C_{44}(\epsilon_{yz}^2+\epsilon_{zx}^2)+2\Delta C_{66}\epsilon_{xy}^2. \tag{1}$$

The free-energy change accurate to second order in the ultrasonic strain is given by[8]

$$\delta F=\sum_k f_k \delta E_k^{(2)}+\frac{1}{2}\sum_k \frac{\partial f_k}{\partial E_k}(\delta E_k^{(1)})^2, \tag{2}$$

where $\delta E_k^{(1)}$ and $\delta E_k^{(2)}$ are the changes in the energy of an electron state of wave vector $\vec{k}$ to first and second order in the ultrasonic strain, respectively. The quantity f_k is the Fermi distribution function for the chemical potential μ. E_k is the energy of the electron state. Equation (2) is also valid if f_k refers to the occupation probability of a hole state in which E_k and μ are to be interpreted as the energy and chemical potential of the holes.

To obtain $\delta E_k^{(1)}$ and $\delta E_k^{(2)}$ we use the deformation-potential Hamiltonian

$$H = Ak^2 + a\sum_i \epsilon_{ii} + 3\sum_i (Bk_i^2 + b\epsilon_{ii})(I_i^2 - \tfrac{1}{3}I^2)$$

$$+ 2\sqrt{3}\sum_{i<j}(Dk_ik_j + d\epsilon_{ij})\{I_iI_j\} + \frac{\Delta}{3}\vec{\sigma}\cdot\vec{\mathrm{I}}, \qquad (3)$$

where I_x, I_y, I_z are the components of the angular momentum matrices for angular momentum unity in the x, y, z representation; $\vec{\sigma}$ is the Pauli spin operator; A, B, and D are the standard constants of the valence band of diamond-structure semiconductors; a, b, and d the deformation potentials of the valence band and Δ the spin-orbit splitting. The operator H is a 6×6 matrix obtained by forming direct products of 3×3 (I) and 2×2 (σ) matrices. In those terms in which these matrices do not explicitly appear, it is understood that the unit 3×3 (or 2×2) matrix is present. The quantity $\{I_iI_j\}$ is defined as $\frac{1}{2}(I_iI_j + I_jI_i)$.

The eigenstates of H are, by virtue of Kramers' theorem, at least doubly degenerate, so that Eq. (3) has, at most, three distinct eigenvalues. To obtain these three eigenvalues, we rewrite Eq. (3) as

$$H = H_d + W, \qquad (4)$$

where

$$H_d = Ak^2 + a\sum_i \epsilon_{ii} \qquad (5)$$

is the completely symmetric component and W the traceless part of H. The eigenvalues of W are obtained by solving the cubic equation

$$\lambda^3 - \tfrac{1}{4}\mathrm{Tr}(W^2)\lambda - \tfrac{1}{6}\mathrm{Tr}(W^3) = 0, \qquad (6)$$

which is derived and discussed in Appendix A. Here

$$\mathrm{Tr}(W^2) = \tfrac{4}{3}\Delta^2 + \alpha, \qquad (7)$$

$$\mathrm{Tr}(W^3) = -\tfrac{4}{9}\Delta^3 - \beta, \qquad (8)$$

where α and β are given by

$$\alpha = \tfrac{2}{3}[(\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + (\alpha_{xx} - \alpha_{yy})^2]$$

$$+ \tfrac{4}{3}(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2), \qquad (9)$$

$$\beta = \tfrac{2}{3}(\alpha_{xx}^3 + \alpha_{yy}^3 + \alpha_{zz}^3) - \tfrac{2}{9}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^3$$

$$+ 4\alpha_{xx}\alpha_{yy}\alpha_{zz} + (4/\sqrt{3})\alpha_{xy}\alpha_{yz}\alpha_{zx}$$

$$- \tfrac{2}{3}[\alpha_{yz}^2(2\alpha_{xx} - \alpha_{yy} - \alpha_{zz}) + \alpha_{zx}^2(2\alpha_{yy} - \alpha_{zz} - \alpha_{xx})$$

$$+ \alpha_{xy}^2(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})]. \qquad (10)$$

α_{ii} and α_{ij} are defined as $\alpha_{ii} = 3(Bk_i^2 + b\epsilon_{ii})$, $\alpha_{ij} = 3(Dk_ik_j + d\epsilon_{ij})$, $i \neq j$. The roots of the cubic equation (6) are given by

$$X_1 = (\mathrm{Tr}W^2/3)^{1/2}\cos(\tfrac{1}{3}\theta),$$

$$X_2 = (\mathrm{Tr}W^2/3)^{1/2}\cos(\tfrac{1}{3}\theta + \tfrac{4}{3}\pi), \qquad (11)$$

$$X_3 = (\mathrm{Tr}W^2/3)^{1/2}\cos(\tfrac{1}{3}\theta + \tfrac{2}{3}\pi),$$

where

$$\theta = \cos^{-1}\left(\sqrt{12}\,\frac{\mathrm{Tr}W^3}{(\mathrm{Tr}W^2)^{3/2}}\right). \qquad (12)$$

The eigenvalues of H are obtained by adding the diagonal part H_d to the eigenvalues of W.

Let us consider a uniaxial stress X along the [001] direction. We take into account only the traceless component of the corresponding strain since the hydrostatic part affects only the electronic contributions to C_{44} and C_{66} by changing the band parameters A, B, and D (these changes are negligible unless the gap at $\vec{k}=0$ is very small). The relevant components of the strain are thus $\epsilon_{xx} = \epsilon_{yy} = \epsilon = \frac{1}{3}(S_{12} - S_{11})X$ and $\epsilon_{zz} = -2\epsilon$. (Here S_{ij} are the elastic compliance coefficients.) Only the part Ak^2 of H_d contributes to the eigenvalues. For the three valence bands (heavy hole, light hole, and spin-orbit split), we get, respectively,

$$E_{\mathrm{hh}}(\vec{k}) = Ak^2 + X_1 - \Delta/3, \qquad (13)$$

$$E_{\mathrm{lh}}(\vec{k}) = Ak^2 + X_2 - \Delta/3, \qquad (14)$$

and

$$E_{\mathrm{s-o}}(\vec{k}) = Ak^2 + X_3 - \Delta/3. \qquad (15)$$

The quantity $\Delta/3$ has been subtracted to shift the bottom of the heavy-hole band to zero. Under this static strain ϵ, the change in the energy of a hole state with wave vector $\vec{k}$ due to ultrasonic strains ϵ_{ij} is given by

$$\delta E(\epsilon, \vec{k}) = E(\epsilon, \epsilon_{ij}, \vec{k}) - E(\epsilon, 0, \vec{k}), \quad i \neq j$$

$$= \delta X(\epsilon, \vec{k}).$$

Calculation of δX is detailed in Appendix B.

Substituting these results into Eq. (2), we obtain expressions for the change in the hole free energy due to the ultrasonic strains:

$$\delta F = (\epsilon_{yz}^2 + \epsilon_{zx}^2)\sum_{\vec{k}}(H_1 + H_3 + L_1 + L_3 + S_1 + S_3) + \epsilon_{xy}^2\sum_{\vec{k}}(H_2 + H_4 + L_2 + L_4 + S_2 + S_4); \qquad (16)$$

H_1, H_2, H_3, and H_4 represent contributions from the heavy-hole band:

$$\begin{aligned}H_1 ={}& \frac{-3f_k d^2[X_1+3b\epsilon+(B/2)(k^2-3k_z^2)]}{(X_3-X_1)(X_1-X_2)}\\ &+\frac{18f_k d^2D^2k_z^2}{(X_1-X_2)^3(X_2-X_3)^2(X_3-X_1)^3}\\ &\times (M(X_1M+N)(k_x^2+k_y^2)-(3X_1N+4M^2)\{2\sqrt{3}\,Dk_x^2k_y^2-3b\epsilon(k_x^2+k_y^2)+B[k^2(k_x^2+k_y^2)-6k_x^2k_y^2]\}\\ &+3(X_1M+N)\{3D^2k_x^2k_y^2(k_x^2+k_y^2)+k_y^2[3b\epsilon-B(k^2-3k_x^2)]^2+k_x^2[3b\epsilon-B(k^2-3k_y^2)]^2-2\sqrt{3}\,Dk_x^2k_y^2[6b\epsilon+B(k^2-3k_z^2)]\}),\end{aligned} \tag{17}$$

$$\begin{aligned}H_2 ={}& -\frac{3f_k d^2[X_1-6b\epsilon-B(k^2-3k_z^2)]}{(X_3-X_1)(X_1-X_2)}\\ &+\frac{36f_k d^2D^2k_x^2k_y^2}{(X_1-X_2)^3(X_2-X_3)^2(X_3-X_1)^3}(M(X_1M+N)-(3X_1N+4M^2)[\sqrt{3}\,Dk_z^2+6b\epsilon+B(k^2-3k_z^2)]\\ &+3(X_1M+N)\{3D^2k_z^4+[6b\epsilon+B(k^2-3k_z^2)]^2+2\sqrt{3}\,Dk_z^2[6b\epsilon+B(k^2-3k_z^2)]\}),\end{aligned} \tag{18}$$

$$\begin{aligned}H_3 ={}& \frac{9(\partial f_k/\partial E_k)d^2D^2k_z^2}{(X_3-X_1)^2(X_1-X_2)^2}\{X_1^2(k_x^2+k_y^2)+3D^2k_x^2k_y^2(k_x^2+k_y^2)+k_y^2[3b\epsilon-B(k^2-3k_x^2)]^2+k_x^2[3b\epsilon-B(k^2-3k_y^2)]^2\\ &-2\sqrt{3}\,Dk_x^2k_y^2[6b\epsilon+B(k^2-3k_z^2)]-2X_1[2\sqrt{3}\,Dk_x^2k_y^2-3b\epsilon(k_x^2+k_y^2)\\ &+Bk_y^2(k^2-3k_x^2)+Bk_x^2(k^2-3k_y^2)]\},\end{aligned} \tag{19}$$

and

$$\begin{aligned}H_4 ={}& \frac{18(\partial f_k/\partial E_k)d^2D^2k_x^2k_y^2}{(X_3-X_1)^2(X_1-X_2)^2}\{X_1^2+3D^2k_z^4+[6b\epsilon+B(k^2-3k_z^2)]^2+2\sqrt{3}\,Dk_z^2[6b\epsilon+B(k^2-3k_z^2)]\\ &-2X_1[\sqrt{3}\,Dk_z^2+6b\epsilon+B(k^2-3k_z^2)]\},\end{aligned} \tag{20}$$

where

$$M=\Delta^2/3+\alpha^0/4 \tag{21}$$

and

$$N=\tfrac{2}{9}\Delta^3+\tfrac{1}{2}\beta^0. \tag{22}$$

In the equations above, the quantities X_i are the roots of Eq. (6) in the absence of the ultrasonic strain. Strictly speaking, following the notation of Appendix B, they should have been denoted by X_i^0. To simplify the writing, the superindex has been deleted. The quantities α^0 and β^0 are given by Eqs. (9) and (10) with the understanding that the contributions to α_{ij} arising from the ultrasonic strain are set equal to zero. L_i and S_i ($i=1$, 2, 3, and 4) represent contributions from the light-hole band and from the spin-orbit-split band, respectively, and can be obtained from H_i by cyclically permuting X_1, X_2, and X_3 and replacing E_{hh} by either E_{lh} or $E_{\text{s-o}}$.

The angular averages or weighted directional averages which were employed in previous papers[8-10] yield significant errors in executing the summation of Eq. (16). To overcome this difficulty, we use the uniform-mesh method (UMM),[11,12] which samples the value of a function with cubic symmetry at a uniformly distributed set of points in the irreducible $\frac{1}{48}$th of the Brillouin zone (BZ). The basic UMM integration formula for the fcc structure is given by[12]

$$\delta F=\frac{2}{V_cM^3}\sum_{A,B,C}\mathfrak{M}_{ABC}F^*(\vec{q}_{ABC}), \tag{23}$$

where

$$\vec{q}_{ABC}=(1/M)(A,B,C),$$

$$\mathfrak{M}_{ABC}=2^{Z(A,B,C)}P(A,B,C),$$

$$F^*(\vec{q})=F(2\pi\vec{q}/a)=F(\vec{k}).$$

For the fcc structure $A, B,$ and C are integers of the same parity with the restrictions

$$M\geq A\geq B\geq C\geq 0$$

and

$$A+B+C\leq 3M/2,$$

where M is the number of divisions used, $Z(A,$

B, C) is the number of nonzero elements in the set (A, B, C), and $P(A, B, C)$ the number of distinct permutations of the set. V_c is the volume of the primitive cell and the factor 2 takes the spin degeneracy into account. We neglect in Eq. (23) the surface factors,[12] which arise from the fact that at the zone-boundary sample volumes are shared by the next BZ, since in our calculations the integration does not reach the zone edge.

With uniaxial stress in the [001] direction, the crystal, and consequently the functions H_i, L_i, and S_i, have tetragonal symmetry. Equation (23) is modified accordingly,

$$\delta F = \frac{2}{V_c M^3} \sum_{A,B,C} \mathfrak{M}_{AB} F^*(\vec{q}_{ABC}), \tag{24}$$

with

$$\mathfrak{M}_{AB} = 2^{Z(A,B)} P(A,B)$$

and

$$M \geq A \geq B \geq 0, \quad M \geq C \geq 0.$$

Except for these modifications, all other conditions following Eq. (23) are retained. The expressions for ΔC_{44} and ΔC_{66} obtained using Eq. (24) are

$$\Delta C_{44} = \frac{4}{M^3 a^3} \sum_{A,B,C} \mathfrak{M}_{AB}(H_1^* + H_3^* + L_1^* + L_3^* + S_1^* + S_3^*) \tag{25}$$

and

$$\Delta C_{66} = \frac{4}{M^3 a^3} \sum_{A,B,C} \mathfrak{M}_{AB}(H_2^* + H_4^* + L_2^* + L_4^* + S_2^* + S_4^*), \tag{26}$$

where a is the lattice parameter, and H_i^* is defined as

$$H_i^*(\vec{q}) = H_i(\vec{k}).$$

III. RESULTS

A. No stress

The various numerical constants used in this work are listed in Table I.[3,13-17] We note that the more recent values of Si valence-band parameters measured by Hensel and Feher[13] (HF) are substantially different from those of Dexter, Zeiger, and Lax (DZL).[14] We believe that HF's values represent more accurately the band shape near the zone center since in their experiment, a large stress was applied to remove the ambiguity arising from the warped band shape. Nevertheless we performed our calculations with both sets of values in order to see which set represents the experimental results better. Unfortunately, difficulties arise in applying our method to the HF parameters, because the corresponding heavy-hole band passes through a maximum in the [110] direction at $|\vec{k}|_{\max} \simeq 1.15 \times 10^7\ \mathrm{cm}^{-1}$, which is about one tenth of the distance from $\vec{k} = 0$ to the zone boundary, and then decreases monotonically, thus causing a divergence in the summation of Eq. (16) for a given μ. It is known that the Si heavy-hole band is extremely flat along the $\langle 110 \rangle$ directions near the zone center and then increases monotonically to approximately 2 eV at the zone boundary.[18,19] This is a limitation of the deformation-potential theory in the form used here, in which the Hamiltonian is defined to order k^2. The validity of the analysis is, thus, limited to the region near the zone center.

To overcome the unphysical divergence obtained with the HF parameters, we divide the BZ into two parts: one, a sphere centered at the zone center with radius $|\vec{k}|_{\max} = 1.15 \times 10^7\ \mathrm{cm}^{-1}$, the other containing the rest of the BZ. ΔC_{44} is calculated by assuming that in the outer region, the valence bands have different band constants A, B, and C

TABLE I. Various numerical constants used in this paper.

	A ($\hbar^2/2m$)	B ($\hbar^2/2m$)	C ($\hbar^2/2m$)	b (eV)	d (eV)	C_{44} (10^{12} dyn/cm^2)	$C_{11}-C_{12}$ (10^{12} dyn/cm^2)
Si	4.28 [a]	−0.75 [a]	−5.25 [a]	−2.1 [c]	−4.85 [c]	0.7951 [d]	
	4.0 [b]	−1.1 [b]	−4.1 [b]			0.802 [e]	1.026 [e]
Ge	13.38 [f]	−8.48 [f]	−13.14 [f]	−2.213 [f]	−4.399 [f]	0.680 [g]	0.812 [g]

[a] Reference 13.
[b] Reference 14.
[c] Reference 15.
[d] At 300 K, Ref. 5.
[e] At 77 K, Ref. 5.
[f] Reference 16.
[g] At 4.2 K, Ref. 17.

than in the inner region. We use for the outer region the values, $A = 4.03\ (\hbar^2/2m)$, $B = -0.88\ (\hbar^2/2m)$, and $C = -4.52\ (\hbar^2/2m)$, which give reasonably behaving band slopes and approximately 2 eV at the zone boundary in the [110] direction. Only the [110] direction of the heavy-hole band is made continuous by matching the outer band to the inner one, since the dominant contribution in the outer region should come from the flat [110] direction of the heavy-hole band. We also compared various sets of values which gave reasonably behaving band shapes, and in the region of interest, all gave similar results. In Table II, our extrapolation scheme is compared in the absence of uniaxial stress, $\epsilon = 0$, with another approximation, in which the angular average with HF's constants is used to calculate the contribution from the outer region. It is obvious that the angular averaging process underestimates the contribution from the outer region. This is not entirely unexpected since the angular average eliminates not only the divergence but also the large contribution of the heavy-hole band along the [110] direction.

DZL's band constants do not pose such difficulties and a straightforward application of Eq. (25) can be carried out. The results are shown in Table II. Table II also shows that at 300 K the theoretical calculations do not agree very well with experiments. To estimate the validity of our extrapolation scheme we define $R \equiv N^{(\mathrm{out})}/N^{(\mathrm{in})}$, which is the ratio of the number of holes in the outer retion to that in the inner region. At 300 K, and carrier concentration $p = 0.22 \times 10^{19}$ cm^{-3}, which is the lowest impurity concentration measured by Fjeldly *et al.*,[10] R has the value of 0.96; hence our scheme should not yield quantitatively correct results. ΔC_{44} was also calculated at 77 K, using both the DZL constants and our extrapolation scheme with the HF parameters. In tables and figures, unless specified otherwise, HF indicates that our extrapolation scheme with HF's constants is used, while DZL means that their parameters were used without an extrapolation scheme. Figure 1 shows the hole concentration vs chemical potential calculated using UMM. Table III shows results of the calculation of ΔC_{44} at 77 K. At low impurity concentration satisfactory agreement with experiment is achieved except at $p = 2.5 \times 10^{18}$ cm^{-3}. We note that for $p = 2.5 \times 10^{18}$ cm^{-3}, ΔC_{44} is smaller than when $p = 1.5 \times 10^{18}$ cm^{-3}. Mason and Bateman attributed this to the fact that the sample with $p = 2.5 \times 10^{18}$ cm^{-3} was doped with boron while for $p = 1.5 \times 10^{18}$ cm^{-3} the dopant was Ga. A difference with dopant can arise from the different covalent radii which place the surroundings of the impurity under tension. This effect is shown in Sec. IV to be two orders of magnitude smaller than the electronic effect. Obviously, in order to confirm the unexplained anomaly, measurements on two series of samples, Ga and B doped, covering a wide range of carrier concentrations are needed. At higher impurity concentration there are no experimental data to compare with our calculations. However, from the calculation of the initial slope of ΔC_{66} vs X in Sec. III B, we expect satisfactory agreement for impurity concentrations up to 6×10^{18} cm^{-3}. At $p = 6 \times 10^{18}$ cm^{-3} the value of R is 0.2.

The above-mentioned difficulty in integrating the approximate energy bands does not arise for Ge, since there is no flat energy band along ⟨110⟩ and

TABLE II. Relative change in the elastic constant C_{44} with doping for p-type Si. $T = 300$ K. HF means that Hensel and Feher's constants (Ref. 13) were used, while the subscript DZL corresponds to use of the constants given by Dexter *et al*. (Ref. 14).

Impurity concentration (10^{19} cm^{-3})	0.22	0.6	1.5	2.6	7	16
$[\Delta C_{44}/C_{44}^i\ (\%)]_{\mathrm{exp}}$ [a]	−0.09	−0.23	−0.74	−1.22	−2.66	−4.53
$[\Delta C_{44}/C_{44}^i\ (\%)]_{\mathrm{HF}}$ [b]	−0.14	−0.37	−0.88	−1.42	−3.08	−5.08
$[\Delta C_{44}/C_{44}^i\ (\%)]_{\mathrm{HF}}$ [c]	−0.15	−0.39	−0.86	−1.23	−1.66	···
$[\Delta C_{44}/C_{44}^i\ (\%)]_{\mathrm{DZL}}$	−0.16	−0.41	−0.94	−1.46	−2.95	−4.54
(Chemical potential $\mu)_{\mathrm{HF}}$ [b] (meV)	−73.6	−46.9	−21.3	−4.8	29.9	69.5
(Chemical potential $\mu)_{\mathrm{DZL}}$ (meV)	−55.4	−27.9	−0.9	16.9	57.4	104.9

[a] Reference 10.

[b] Extrapolation scheme with $A = 4.03(\hbar^2/2m), B = -0.88(\hbar^2/2m), C = -4.52(\hbar^2/2m)$ is used for the outer region.

[c] Angular average is used for the outer region.

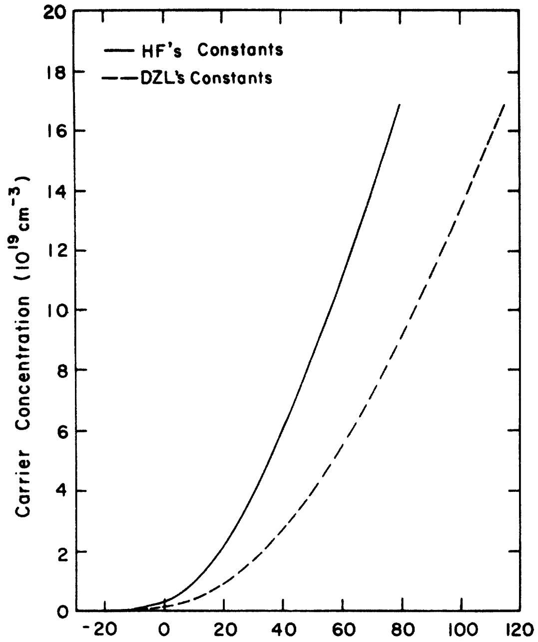

FIG. 1. Carrier concentration vs chemical potential calculated for p-type Si. $T = 77$ K.

there are no significant differences between the earlier valence-band constants and the recent ones.[14,16] We performed calculations at 4.2 K for Ge. Figure 2 shows the relationship between impurity concentration and chemical potential and Fig. 3 shows $\Delta C_{44}/C_{44}^i$ vs chemical potential. C_{44}^i is the value of the elastic constant in the absence of the uniaxial stress. In order to estimate the validity of our results we divide the BZ into two regions in the same way as we did for Si. R is defined in the same way:

$$R \equiv N^{(\mathrm{out})}/N^{(\mathrm{in})},$$

i.e., the ratio of the number of holes in the outer region of the BZ to those in the inner region. At $\mu = 100$ meV, where the impurity concentration is $p = 3.9 \times 10^{19}$ cm^{-3}, we have an R value of 0.1, which suggests that quantitative agreement can be expected for μ at least up to 100 meV at 4.2 K. The radius $|\vec{k}|$ of the inner region was chosen to be 1.15×10^7 cm^{-1}, this choice being to some extent arbitrary.

B. Under [001] uniaxial stress

The traceless part of the strain, associated with the uniaxial stress X along the [001] direction is

$$\overleftrightarrow{\epsilon} = \epsilon \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}, \qquad (27)$$

where

$$\epsilon = -X/3(C_{11} - C_{12}) \qquad (28)$$

has a positive value for compression since $X < 0$. The initial slope of ΔC_{44} vs stress X is

$$\{[\Delta C_{44}(\epsilon) - \Delta C_{44}(0)]/X\}_{\epsilon=0}.$$

The initial slopes of ΔC_{44} and ΔC_{66} can be calculated by simply comparing two values of ΔC_{44} or ΔC_{66}, one at zero stress and the other at very small stress. Calculated values of the initial slope of ΔC_{66} for Si at 77 K are given in Table IV. Comparison with the experiment shows that the agreement, good at low carrier concentration p, becomes poorer at higher concentrations. Our calculations show that the initial slope of ΔC_{66} has a maximum around $p = 2 \times 10^{19}$ cm^{-3}, in agreement with experiment. This maximum was not accounted for by the weighted-average process.[10] Even though both the HF and DZL band constants give poor results at higher impurity concentration, the results obtained with HF's constants are closer to the experiments, thus suggesting that these latter constants plus our extrapolation scheme give a better representation of the flat [110] direction of the heavy-hole band.

It has been shown that both ΔC_{44} and ΔC_{66} tend to zero in the large-stress limit.[10] Our calculation on Si with impurity concentration 6×10^{18} cm^{-3} confirms this, as shown in Fig. 4 together with the corresponding experimental results. It should be noted that the chemical potential varies with varying stress and must be calculated separately for each stress before calculating ΔC_{44} and ΔC_{66}. As an example, for Ge we choose an impurity concentration of 6×10^{18} cm^{-3} and calculate ΔC_{44} and ΔC_{66}

TABLE III. Relative change in the elastic constant C_{44} with doping for p-type Si. $T = 77$ K.

Impurity concentration (10^{19} cm^{-3})	0.05	0.15	0.25	0.6	1.5	2.6	7	16
$[\Delta C_{44}/C_{44}^i\ (\%)]_{\mathrm{exp}}$ [a]	−0.11	−0.27	−0.23	⋯	⋯	⋯	⋯	⋯
$[\Delta C_{44}/C_{44}^i\ (\%)]_{\mathrm{HF}}$	−0.098	−0.281	−0.449	−0.958	−1.898	−2.657	−4.251	−5.671
$[\Delta C_{44}/C_{44}^i\ (\%)]_{\mathrm{DZL}}$	−0.100	−0.272	−0.422	−0.847	−1.628	−2.274	−3.595	−4.846

[a] Reference 3.

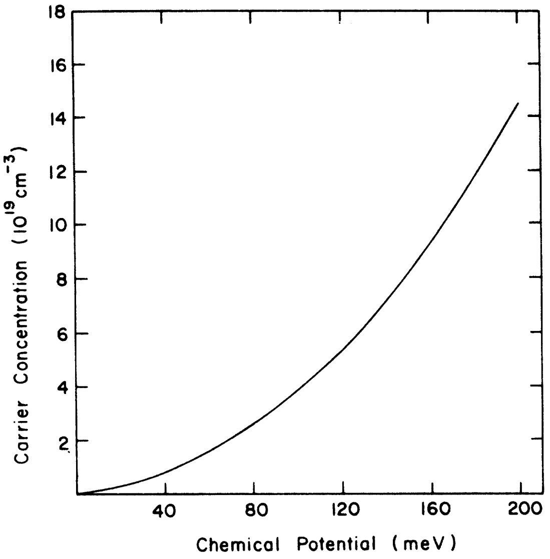

FIG. 2. Carrier concentration vs chemical potential calculated for p-type Ge. $T=4.2$ K.

under [001] stresses up to 9 kbar. The results, shown in Fig. 5, indicate that Ge exhibits the same trend as Si at large stresses, again confirming the results obtained in the large-stress limit.[10]

IV. CONCLUSIONS

A numerical calculation of the effect of free carriers on the elastic constants C_{44} and C_{66} in p-Si and p-Ge under a uniaxial stress along [001] has been performed. We calculated the concentration and stress dependence of ΔC_{44} and ΔC_{66}, and compared them with existing experimental results. Because of the intrinsic limitation of the deformation-potential Hamiltonian, the quantitative validity of our method is limited to relatively low temperatures and impurity concentrations (at 77 K up to $p=6.0\times10^{18}$ cm^{-3}). However, our calculations show all the essential features observed experimentally. We compared the results obtained with two different sets of band parameters for Si, HF's[13] and DZL's.[14] A comparison with experiments at 77 K shows that the HF parameters give results in better agreement with experiments.

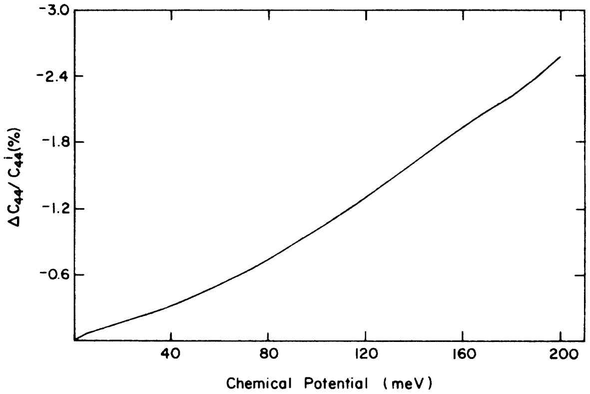

FIG. 3. Electronic contribution to the elastic constant, ΔC_{44}, for p-type Ge as a function of chemical potential. $T=4.2$ K.

We have, so far, neglected direct impurity contributions to the elastic-constant change. The simplest way in which an impurity can affect the elastic constant is through the strain field set up around it, because of the difference in covalent radii. This effect can be estimated from the covalent radii and the Grüneisen constant (~1). For B in Si we find, taking the covalent radii proportional to the lattice constants a_0 of C and Si, respectively:

$$\frac{\delta C_{44}}{C_{44}} \simeq 3\eta \frac{a_0(\mathrm{Si}) - a_0(\mathrm{C})}{a_0(\mathrm{Si})} \simeq \eta,$$

where η is the fractional impurity content. This effect is two orders of magnitude smaller than the pure electronic effects given in Table III.

Note added in proof: We have also used the band parameters of Si obtained by I. Balslev and P. Lawaetz [Phys. Lett. 19, 6 (1965)]. The results do not differ significantly from those obtained with the HF parameters.

ACKNOWLEDGMENTS

We wish to thank Professor S. Jaswal for useful conversations and Professor A. K. Ramdas for critically reading the manuscript.

APPENDIX A: SECULAR EQUATION

We consider here the nondiagonal part of the Hamiltonian given in Eq. (3):

$$W = 3 \sum_i (Bk_i^2 + b\epsilon_{ii})(I_i^2 - \tfrac{1}{3}I^2) + 2\sqrt{3} \sum_{i<j} (Dk_ik_j + d\epsilon_{ij})\{I_iI_j\} + (\Delta/3)\vec{\sigma}\cdot\vec{\mathrm{I}}. \quad \text{(A1)}$$

Since the eigenvalues of W are doubly degenerate, the secular equation associated with (A1) is of the form

$$\begin{aligned}\det(W_{ij} - \delta_{ij}\lambda) &= (\lambda - w_1)^2(\lambda - w_2)^2(\lambda - w_3)^2 \\ &= [\lambda^3 - (w_1 + w_2 + w_3)\lambda^2 + (w_2w_3 + w_3w_1 + w_1w_2)\lambda \\ &\quad - w_1w_2w_3]^2 = 0. \qquad \text{(A2)}\end{aligned}$$

Since $\mathrm{Tr}W = 0$, $w_1 + w_2 + w_3 = 0$. Thus

$$\begin{aligned}w_2w_3 + w_3w_1 + w_1w_2 &= \tfrac{1}{2}[(w_1 + w_2 + w_3)^2 - w_1^2 - w_2^2 - w_3^2] \\ &= -\tfrac{1}{2}(w_1^2 + w_2^2 + w_3^2) \qquad \text{(A3)}\end{aligned}$$

and

TABLE IV. Initial slope of ΔC_{66} vs X for p-type Si. $T = 77$ K.

Impurity concentration (10^{19} cm^{-3})	0.6	2.6	7	16
$\left(\frac{\Delta C_{66}/C_{44}^{i}}{-X}\right)^{\text{exp a}}_{X=0}$ (% kbar^{-1})	0.130	0.198	0.173	0.155
$\left(\frac{\Delta C_{66}/C_{44}^{i}}{-X}\right)^{\text{HF}}_{X=0}$ (% kbar^{-1})	0.143	0.163	0.105	0.080
$\left(\frac{\Delta C_{66}/C_{44}^{i}}{-X}\right)^{\text{DZL}}_{X=0}$ (% kbar^{-1})	0.099	0.100	0.063	0.035
$\left(\frac{\Delta C_{66}/C_{44}^{i}}{-X}\right)^{\text{ang. av. b}}_{X=0}$ (% kbar^{-1})	0.103	0.067	0.051	0.040

[a] Reference 10.

[b] Angular average combined with weighted average (Ref. 10).

$$w_1 w_2 w_3 = -w_1 w_2 (w_1 + w_2) = -\tfrac{1}{3}[(w_1 + w_2)^3 - w_1^3 - w_2^3]$$
$$= \tfrac{1}{3}(w_1^3 + w_2^3 + w_3^3). \qquad \text{(A4)}$$

Now

$$\operatorname{Tr} W^2 = 2(w_1^2 + w_2^2 + w_3^2) = -4(w_2 w_3 + w_3 w_1 + w_1 w_2) \qquad \text{(A5)}$$

and

$$\operatorname{Tr} W^3 = 2(w_1^3 + w_2^3 + w_3^3) = 6 w_1 w_2 w_3 . \qquad \text{(A6)}$$

Therefore Eq. (A2) reduces to

$$\lambda^3 - \tfrac{1}{4}(\operatorname{Tr} W^2)\lambda - \tfrac{1}{6}\operatorname{Tr} W^3 = 0. \qquad \text{(A7)}$$

We define

$$\alpha_{ii} = 3(B k_i^2 + b\epsilon_{ii})$$

and

$$\alpha_{ij} = 3(D k_i k_j + d\epsilon_{ij}), \quad \text{if } i \neq j.$$

If we further define

$$P = \sum_i \alpha_{ii}(I_i^2 - \tfrac{1}{3}I^2) \qquad \text{(A8)}$$

and

$$Q = \sum_{i<j} \alpha_{ij}\{I_i I_j\}, \qquad \text{(A9)}$$

we have

$$W = P + \frac{2}{\sqrt{3}}Q + \frac{\Delta}{3}\vec{\sigma}\cdot\vec{I}, \qquad \text{(A10)}$$

$$\operatorname{Tr} P^2 = \tfrac{2}{3}[(\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + (\alpha_{xx} - \alpha_{yy})^2], \qquad \text{(A11)}$$

$$\operatorname{Tr} Q^2 = \alpha_{yz}^2 + \alpha_{zx}^2 + \alpha_{xy}^2, \qquad \text{(A12)}$$

and

$$\operatorname{Tr} W^2 = \tfrac{2}{3}[(\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + (\alpha_{xx} - \alpha_{yy})^2]$$
$$+ \tfrac{4}{3}(\alpha_{yz}^2 + \alpha_{zx}^2 + \alpha_{xy}^2) + 4\Delta^2/3. \qquad \text{(A13)}$$

$\operatorname{Tr} W^3$ reduces to

$$\operatorname{Tr} W^3 = \operatorname{Tr}(P^3) + \frac{8}{3\sqrt{3}}\operatorname{Tr}(Q^3) + \frac{\Delta^3}{27}\operatorname{Tr}(\vec{\sigma}\cdot\vec{I})^3 + 4\operatorname{Tr}(PQ^2). \qquad \text{(A14)}$$

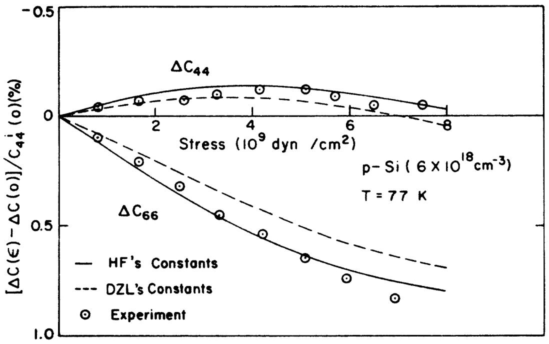

FIG. 4. Stress dependence of ΔC_{44} and ΔC_{66} for a [001] uniaxial stress in Si. Experimental results are taken from Ref. 10.

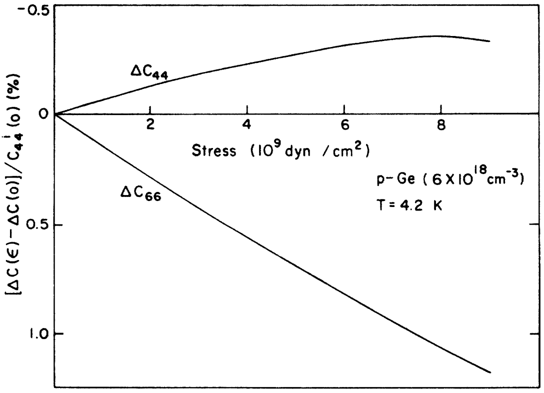

FIG. 5. Stress dependence of ΔC_{44} and ΔC_{66} for a [001] uniaxial stress in Ge.

(Above we dropped all zero-trace terms.)

$$\mathrm{Tr}(P^3) = -\tfrac{4}{9}(\alpha_{xx}^3 + \alpha_{yy}^3 + \alpha_{zz}^3) + \tfrac{2}{3}(\alpha_{xx}\alpha_{yy}^2 + \alpha_{xx}\alpha_{zz}^2 + \alpha_{yy}\alpha_{zz}^2 + \alpha_{yy}\alpha_{xx}^2 + \alpha_{zz}\alpha_{xx}^2 + \alpha_{zz}\alpha_{yy}^2) - \tfrac{8}{3}\alpha_{xx}\alpha_{yy}\alpha_{zz}, \tag{A15}$$

$$\mathrm{Tr}(Q^3) = -\tfrac{3}{2}\alpha_{xy}\alpha_{yz}\alpha_{zx}, \tag{A16}$$

$$\mathrm{Tr}(PQ^2) = \tfrac{1}{6}\alpha_{yz}^2(2\alpha_{xx} - \alpha_{yy} - \alpha_{zz}) + \tfrac{1}{6}\alpha_{zx}^2(2\alpha_{yy} - \alpha_{zz} - \alpha_{xx}) + \tfrac{1}{6}\alpha_{xy}^2(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy}), \tag{A17}$$

$$\mathrm{Tr}[(\vec{\sigma}\cdot\vec{\mathrm{I}})^3] = \mathrm{Tr}(3\vec{\sigma}\cdot\vec{\mathrm{I}} - 2) = -12, \tag{A18}$$

and

$$\begin{aligned}\mathrm{Tr}(W^3) = {}& -\tfrac{4}{9}\Delta^3 - \tfrac{2}{3}(\alpha_{xx}^3 + \alpha_{yy}^3 + \alpha_{zz}^3) + \tfrac{2}{9}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^3 \\ & - 4\alpha_{xx}\alpha_{yy}\alpha_{zz} - (4/\sqrt{3})\alpha_{xy}\alpha_{yz}\alpha_{zx} + \tfrac{2}{3}[\alpha_{yz}^2(2\alpha_{xx} - \alpha_{yy} - \alpha_{zz}) + \alpha_{zx}^2(2\alpha_{yy} - \alpha_{zz} - \alpha_{xx}) + \alpha_{xy}^2(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})].\end{aligned} \tag{A19}$$

We define α and β, respectively,

$$\alpha = \tfrac{2}{3}[(\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + (\alpha_{xx} - \alpha_{yy})^2] + \tfrac{4}{3}(\alpha_{yz}^2 + \alpha_{zx}^2 + \alpha_{xy}^2) + 4\Delta^2/3 \tag{A20}$$

and

$$\begin{aligned}\beta = {}& \tfrac{2}{3}(\alpha_{xx}^3 + \alpha_{yy}^3 + \alpha_{zz}^3) - \tfrac{2}{9}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^3 + 4\alpha_{xx}\alpha_{yy}\alpha_{zz} + (4/\sqrt{3})\alpha_{xy}\alpha_{yz}\alpha_{zx} \\ & - \tfrac{2}{3}[\alpha_{yz}^2(2\alpha_{xx} - \alpha_{yy} - \alpha_{zz}) + \alpha_{zx}^2(2\alpha_{yy} - \alpha_{zz} - \alpha_{xx}) + \alpha_{xy}^2(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})].\end{aligned} \tag{A21}$$

We have

$$\mathrm{Tr}(W^2) = \tfrac{4}{3}\Delta^2 + \alpha \tag{A22}$$

and

$$\mathrm{Tr}(W^3) = -\tfrac{4}{9}\Delta^3 - \beta. \tag{A23}$$

APPENDIX B: SOLUTION OF THE SECULAR EQUATION AND APPROXIMATIONS

The roots X_1, X_2, X_3 of the cubic equation

$$X^3 + a_2 X + a_3 = 0$$

satisfy the conditions

$$\begin{aligned}& X_1 + X_2 + X_3 = 0, \\ & X_1X_2 + X_2X_3 + X_3X_1 = a_2,\end{aligned} \tag{B1}$$

and

$$X_1X_2X_3 = -a_3.$$

We write $X = X^0 + \delta X$, where X^0 denotes a root without ultrasonic perturbation while δX stands for the change of a root caused by the ultrasonic strains. Thus, we can write

$$\begin{aligned}& \delta X_1 + \delta X_2 + \delta X_3 = 0, \\ & X_1^0\delta X_1 + X_2^0\delta X_2 + X_3^0\delta X_3 = -\delta a_2 + (\delta X_1\delta X_2 + \delta X_2\delta X_3 + \delta X_3\delta X_1),\end{aligned} \tag{B2}$$

and

$$a_3\left(\frac{\delta X_1}{X_1^0} + \frac{\delta X_2}{X_2^0} + \frac{\delta X_3}{X_3^0}\right) = \delta a_3 + (X_1^0\delta X_2\delta X_3 + X_2^0\delta X_3\delta X_1 + X_3^0\delta X_1\delta X_2),$$

which in turn give

$$\delta X_1=\frac{1}{(X_3^0-X_1^0)(X_1^0-X_2^0)}[X_1^0\delta a_2-X_1^0(\delta X_1\delta X_2+\delta X_2\delta X_3+\delta X_3\delta X_1)+\delta a_3+X_1^0\delta X_2\delta X_3+X_2^0\delta X_3\delta X_1+X_3^0\delta X_1\delta X_2],$$

$$\delta X_2=\frac{1}{(X_1^0-X_2^0)(X_2^0-X_3^0)}[X_2^0\delta a_2-X_2^0(\delta X_1\delta X_2+\delta X_2\delta X_3+\delta X_3\delta X_1)+\delta a_3+X_1^0\delta X_2\delta X_3+X_2^0\delta X_3\delta X_1+X_3^0\delta X_1\delta X_2],$$

and

$$\delta X_3=\frac{1}{(X_2^0-X_3^0)(X_3^0-X_1^0)}[X_3^0\delta a_2-X_3^0(\delta X_1\delta X_2+\delta X_2\delta X_3+\delta X_3\delta X_1)+\delta a_3+X_1^0\delta X_2\delta X_3+X_2^0\delta X_3\delta X_1+X_3^0\delta X_1\delta X_2]. \tag{B3}$$

The quantities a_2 and a_3 are given by Eqs. (6)–(8):

$$a_2=-\tfrac{1}{4}\operatorname{Tr}(W^2)=-\tfrac{1}{3}\Delta^2-\tfrac{1}{4}\alpha, \tag{B4}$$

$$a_3=-\tfrac{1}{6}\operatorname{Tr}(W^3)=\tfrac{2}{27}\Delta^3+\tfrac{1}{6}\beta, \tag{B5}$$

$$\delta a_2=-\tfrac{1}{4}\delta\alpha, \tag{B6}$$

$$\delta a_3=\tfrac{1}{6}\delta\beta. \tag{B7}$$

We write $\alpha=\alpha^0+\delta\alpha$ and $\beta=\beta^0+\delta\beta$, where α^0 and β^0 represent α and β in the absence of an ultrasonic perturbation.

With a uniaxial stress in the [001] direction, $\epsilon_{xx}=\epsilon_{yy}=\epsilon$, $\epsilon_{zz}=-2\epsilon$, and in the absence of ultrasonic stress α^0 and β^0 are obtained using Eqs. (A20) and (A21). We obtain

$$\alpha^0=108b^2\epsilon^2+36Bb\epsilon(k^2-3k_z^2)+6B^2[(k_x^2-k_y^2)^2+(k_y^2-k_z^2)^2+(k_z^2-k_x^2)^2]+12D^2(k_x^2k_y^2+k_y^2k_z^2+k_z^2k_x^2), \tag{B8}$$

$$\begin{aligned}\beta^0=&-324b^3\epsilon^3-162Bb^2\epsilon^2(k^2-3k_z^2)+54B^2b\epsilon(k_x^4+k_y^4-2k_z^4+2k_z^2k_x^2+2k_y^2k_z^2-4k_x^2k_y^2)-54D^2b\epsilon(k_y^2k_z^2+k_x^2k_z^2-2k_x^2k_y^2)\\&+18B^3(k_x^6+k_y^6+k_z^6)-6B^3k^6+108(B^3+D^3/\sqrt{3})k_x^2k_y^2k_z^2+18BD^2[k_y^2k_z^2(k^2-3k_x^2)+k_z^2k_x^2(k^2-3k_y^2)+k_x^2k_y^2(k^2-3k_z^2)],\end{aligned} \tag{B9}$$

$$\begin{aligned}\delta\alpha=&\,12d^2(\epsilon_{yz}^2+\epsilon_{zx}^2+\epsilon_{xy}^2)\\&+24dD(\epsilon_{yz}k_yk_z+\epsilon_{zx}k_zk_x+\epsilon_{xy}k_xk_y),\end{aligned} \tag{B10}$$

and

$$\begin{aligned}\delta\beta=&\,36\sqrt{3}\,dD^2k_xk_yk_z(\epsilon_{yz}k_x+\epsilon_{zx}k_y+\epsilon_{xy}k_z)-18d^2\epsilon_{yz}^2[3b\epsilon-B(k^2-3k_x^2)]-18d^2\epsilon_{zx}^2[3b\epsilon-B(k^2-3k_y^2)]\\&-18d^2\epsilon_{xy}^2[-6b\epsilon-B(k^2-3k_z^2)]-36dD\epsilon_{yz}k_yk_z[3b\epsilon-B(k^2-3k_x^2)]-36dD\epsilon_{zx}k_zk_x[3b\epsilon-B(k^2-3k_y^2)]\\&-36dD\epsilon_{xy}k_xk_y[-6b\epsilon-B(k^2-3k_z^2)].\end{aligned} \tag{B11}$$

Here we dropped the third-order contributions of the ultrasonic strains. Also terms like $\epsilon_{xy}\epsilon_{yz}k_zk_x$ are neglected since they do not contribute to the final result. We write

$$\delta\alpha=\delta\alpha^{(1)}+\delta\alpha^{(2)}, \tag{B12}$$

$$\delta\beta=\delta\beta^{(1)}+\delta\beta^{(2)}, \tag{B13}$$

where the superscripts (1) and (2) indicate linear and quadratic terms in the ultrasonic strain, respectively. Therefore

$$\delta\alpha^{(1)}=24dD(\epsilon_{yz}k_yk_z+\epsilon_{zx}k_zk_x), \tag{B14}$$

$$\delta\alpha^{(2)}=12d^2(\epsilon_{yz}^2+\epsilon_{zx}^2+\epsilon_{xy}^2), \tag{B15}$$

$$\begin{aligned}\delta\beta^{(1)}=&\,36\sqrt{3}\,dD^2\,k_xk_yk_z(\epsilon_{yz}k_x+\epsilon_{zx}k_y+\epsilon_{xy}k_z)-36dD\{\epsilon_{yz}k_yk_z[3b\epsilon-B(k^2-3k_x^2)]+\epsilon_{zx}k_zk_x[3b\epsilon-B(k^2-3k_y^2)]\\&+\epsilon_{xy}k_xk_y[-6b\epsilon-B(k^2-3k_z^2)]\}\end{aligned} \tag{B16}$$

and

$$\delta\beta^{(2)}=-18d^2\{\epsilon_{yz}^2[3b\epsilon-B(k^2-3k_x^2)]+\epsilon_{zx}^2[3b\epsilon-B(k^2-3k_y^2)]+\epsilon_{xy}^2[-6b\epsilon-B(k^2-3k_z^2)]\}. \tag{B17}$$

$\delta X^{(1)}$ and $\delta X^{(2)}$ can be obtained from the results above and are given by

$$\delta X_1^{(1)}=\frac{1}{(X_3^0-X_1^0)(X_1^0-X_2^0)}\left(-\frac{X_1^0}{4}\delta\alpha^{(1)}+\frac{\delta\beta^{(1)}}{6}\right) \tag{B18}$$

and

$$\begin{aligned}\delta X_1^{(2)} = \frac{1}{(X_3^0 - X_1^0)(X_1^0 - X_2^0)} \Big(& -\frac{X_1^0}{4}\delta\alpha^{(2)} - X_1^0(\delta X_1^{(1)}\delta X_2^{(1)} + \delta X_2^{(1)}\delta X_3^{(1)} + \delta X_3^{(1)}\delta X_1^{(1)}) + \frac{\delta\beta^{(2)}}{6} \\ & + (X_1^0\delta X_2^{(1)}\delta X_3^{(1)} + X_2^0\delta X_3^{(1)}\delta X_1^{(1)} + X_3^0\delta X_1^{(1)}\delta X_2^{(1)})\Big) .\end{aligned} \tag{B19}$$

Equation (B2) can be used to express the second and fourth terms of the right-hand side of Eq. (B19) in terms of α and β.

$$\begin{aligned}&\delta X_1^{(1)}\delta X_2^{(1)} + \delta X_2^{(1)}\delta X_3^{(1)} + \delta X_3^{(1)}\delta X_1^{(1)} \\ &\quad = \frac{1}{(X_1^0 - X_2^0)^2(X_2^0 - X_3^0)^2(X_3^0 - X_1^0)^2}\left[-\frac{(\delta\alpha^{(1)})^2}{16}\left(\frac{\Delta^2}{3} + \frac{\alpha^0}{4}\right)^2 + \tfrac{3}{8}\delta\alpha^{(1)}\delta\beta^{(1)}(\tfrac{2}{27}\Delta^3 + \tfrac{1}{6}\beta^0) - \frac{(\delta\beta^{(1)})^2}{12}\left(\frac{\Delta^2}{3} + \frac{\alpha^0}{4}\right)\right]\end{aligned} \tag{B20}$$

and

$$\begin{aligned}&X_1^0\delta X_2^{(1)}\delta X_3^{(1)} + X_2^0\delta X_3^{(1)}\delta X_1^{(1)} + X_3^0\delta X_1^{(1)}\delta X_2^{(1)} \\ &\quad = \frac{1}{(X_1^0 - X_2^0)^2(X_2^0 - X_3^0)^2(X_3^0 - X_1^0)^2}\left[\tfrac{3}{16}(\delta\alpha^{(1)})^2(\tfrac{2}{27}\Delta^3 + \tfrac{1}{6}\beta^0)\left(\frac{\Delta^2}{3} + \tfrac{1}{4}\alpha^0\right) - \frac{\delta\alpha^{(1)}\delta\beta^{(1)}}{6}\left(\frac{\Delta^2}{3} + \frac{\alpha^0}{4}\right)^2 + \frac{(\delta\beta^{(1)})^2}{4}(\tfrac{2}{27}\Delta^3 + \tfrac{1}{6}\beta^0)\right].\end{aligned} \tag{B21}$$

Combining the above relations, we obtain

$$\begin{aligned}(\delta X_1^{(1)})^2 = {} & 18d^2D^2k_z^2\frac{\epsilon_{yz}^2 + \epsilon_{zx}^2}{(X_3^0 - X_1^0)^2(X_1^0 - X_2^0)^2}\Big[X_1^{0^2}(k_x^2 + k_y^2) + 3D^2k_x^2k_y^2(k_x^2 + k_y^2) + k_y^2[3b\epsilon - B(k^2 - 3k_x^2)]^2 \\ & + k_x^2[3b\epsilon - B(k^2 - 3k_y^2)]^2 - 4\sqrt{3}Dk_x^2k_y^2\left(3b\epsilon + \frac{B}{2}(k^2 - 3k_z^2)\right) \\ & - 4X_1^0\left(\sqrt{3}Dk_x^2k_y^2 - 3b\epsilon(k_x^2 + k_y^2) + \frac{B}{2}[k_y^2(k^2 - 3k_x^2) + k_x^2(k^2 - 3k_y^2)]\right)\Big] \\ & + 36d^2D^2k_x^2k_y^2\frac{\epsilon_{xy}^2}{(X_3^0 - X_1^0)^2(X_1^0 - X_2^0)^2}\{X_1^{0^2} + 3k_z^4 + [6b\epsilon + B(k^2 - 3k_z^2)]^2 + 2\sqrt{3}Dk_z^2[6b\epsilon + B(k^2 - 3k_z^2)] \\ & - 2X_1^0[6b\epsilon + B(k^2 - 3k_z^2) + \sqrt{3}Dk_z^2]\}.\end{aligned} \tag{B22}$$

We define M and N by

$$M = \Delta^2/3 + \alpha^0/4 \tag{B23}$$

and

$$N = \tfrac{2}{9}\Delta^3 + \tfrac{1}{2}\beta^0. \tag{B24}$$

We obtain the expression

$$\begin{aligned}\delta X_1^{(2)} = {} & \frac{-3d^2}{(X_3^0 - X_1^0)(X_1^0 - X_2^0)}\left[(\epsilon_{zx}^2 + \epsilon_{yz}^2)\left(X_1^0 + 3b\epsilon + \frac{B}{2}(k^2 - 3k_z^2)\right) + \epsilon_{xy}^2[X_1^0 - 6b\epsilon - B(k^2 - 3k_z^2)]\right] \\ & + \frac{18d^2D^2k_z^2(\epsilon_{yz}^2 + \epsilon_{zx}^2)}{(X_1^0 - X_2^0)^3(X_2^0 - X_3^0)^2(X_3^0 - X_1^0)^3} \\ & \times\Big\{M(X_1^0M + N)(k_x^2 + k_y^2) - (6X_1^0N + 8M^2)\left(\sqrt{3}Dk_x^2k_y^2 - \tfrac{3}{2}b\epsilon(k_x^2 + k_y^2) + \frac{B}{2}[k^2(k_x^2 + k_y^2) - 6k_x^2k_y^2]\right) \\ & + (X_1^0M + N)\Big[9D^2k_x^2k_y^2(k_x^2 + k_y^2) + 3k_y^2[3b\epsilon - B(k^2 - 3k_x^2)]^2 + 3k_x^2[3b\epsilon - B(k^2 - 3k_y^2)]^2 \\ & - 12\sqrt{3}Dk_x^2k_y^2\left(3b\epsilon + \frac{B}{2}(k^2 - 3k_z^2)\right)\Big]\Big\} + \frac{36d^2D^2k_x^2k_y^2\epsilon_{xy}^2}{(X_1^0 - X_2^0)^3(X_2^0 - X_3^0)^2(X_3^0 - X_1^0)^3} \\ & \times (M(X_1^0M + N) - (X_1^0N + \tfrac{4}{3}M^2)[18b\epsilon + 3B(k^2 - 3k_z^2) + 3\sqrt{3}Dk_z^2] \\ & + (X_1^0M + N)\{9D^2k_z^4 + 3[6b\epsilon + B(k^2 - 3k_z^2)]^2 + 6\sqrt{3}Dk_z^2[6b\epsilon + B(k^2 - 3k_z^2)]\}).\end{aligned} \tag{B25}$$

We define H_1, H_2, H_3, and H_4 by

$$\sum_{\vec{k}} f_k \delta X_1^{(2)} = (\epsilon_{yz}^2 + \epsilon_{zx}^2) \sum_{\vec{k}} H_1 + \epsilon_{xy}^2 \sum_{\vec{k}} H_2 \tag{B26}$$

and

$$\frac{1}{2} \sum_{\vec{k}} (\delta X_1^{(1)})^2 \frac{\partial f_k}{\partial E_k} = (\epsilon_{yz}^2 + \epsilon_{zx}^2) \sum_{\vec{k}} H_3 + \epsilon_{xy}^2 \sum_{\vec{k}} H_4 . \tag{B27}$$

Thus

$$\begin{aligned} H_1 = {} & \frac{-3 f_k d^2 [X_1^0 + 3b\epsilon + (B/2)(k^2 - 3k_z^2)]}{(X_3^0 - X_1^0)(X_1^0 - X_2^0)} \\ & + \frac{18 f_k d^2 D^2 k_z^2}{(X_1^0 - X_2^0)^3 (X_2^0 - X_3^0)^2 (X_3^0 - X_1^0)^3} (M(X_1^0 M + N)(k_x^2 + k_y^2) \\ & \qquad - (3X_1^0 N + 4M^2) \{2\sqrt{3} D k_x^2 k_y^2 - 3b\epsilon(k_x^2 + k_y^2) + B[k^2(k_x^2 + k_y^2) - 6k_x^2 k_y^2]\} \\ & \qquad + 3(X_1^0 M + N) \{3D^2 k_x^2 k_y^2 (k_x^2 + k_y^2) + k_y^2 [3b\epsilon - B(k^2 - 3k_x^2)]^2 \\ & \qquad\qquad + k_x^2 [3b\epsilon - B(k^2 - 3k_y^2)]^2 - 2\sqrt{3} D k_x^2 k_y^2 [6b\epsilon + B(k^2 - 3k_z^2)]\}), \end{aligned} \tag{B28}$$

$$\begin{aligned} H_2 = {} & \frac{-3 f_k d^2 [X_1^0 - 6b\epsilon - B(k^2 - 3k_z^2)]}{(X_3^0 - X_1^0)(X_1^0 - X_2^0)} \\ & + \frac{36 f_k d^2 D^2 k_x^2 k_y^2}{(X_1^0 - X_2^0)^3 (X_2^0 - X_3^0)^2 (X_3^0 - X_1^0)^3} (M(X_1^0 M + N) - (3X_1^0 N + 4M^2)[\sqrt{3} D k_z^2 + B(k^2 - 3k_z^2) + 6b\epsilon] \\ & \qquad + 3(X_1^0 M + N)\{3D^2 k_z^4 + [6b\epsilon + B(k^2 - 3k_z^2)]^2 + 2\sqrt{3} D k_z^2 [6b\epsilon + B(k^2 - 3k_z^2)]\}), \end{aligned} \tag{B29}$$

$$\begin{aligned} H_3 = {} & \frac{9(\partial f_k / \partial E_k) d^2 D^2 k_z^2}{(X_3^0 - X_1^0)^2 (X_1^0 - X_2^0)^2} \{X_1^{0^2}(k_x^2 + k_y^2) + 3D^2 k_x^2 k_y^2 (k_x^2 + k_y^2) + k_y^2 [3b\epsilon - B(k^2 - 3k_x^2)]^2 + k_x^2 [3b\epsilon - B(k^2 - 3k_y^2)]^2 \\ & \qquad - 2\sqrt{3} D k_x^2 k_y^2 [6b\epsilon + B(k^2 - 3k_z^2)] \\ & \qquad - 2X_1^0 [2\sqrt{3} D k_x^2 k_y^2 - 3b\epsilon(k_x^2 + k_y^2) + B k_y^2 (k^2 - 3k_x^2) + B k_x^2 (k^2 - 3k_y^2)]\}, \end{aligned} \tag{B30}$$

and

$$\begin{aligned} H_4 = {} & \frac{18(\partial f_k / \partial E_k) d^2 D^2 k_x^2 k_y^2}{(X_3^0 - X_1^0)^2 (X_1^0 - X_2^0)^2} \{X_1^{0^2} + 3D^2 k_z^4 + [6b\epsilon + B(k^2 - 3k_z^2)]^2 + 2\sqrt{3} D k_z^2 [6b\epsilon + B(k^2 - 3k_z^2)] \\ & \qquad - 2X_1^0 [\sqrt{3} D k_z^2 + 6b\epsilon + B(k^2 - 3k_z^2)]\}. \end{aligned} \tag{B31}$$

The contribution to the free-energy change from the heavy-hole band is given by

$$\delta F_{\text{hh}} = (\epsilon_{yz}^2 + \epsilon_{zx}^2) \sum_{\vec{k}} (H_1 + H_3) + \epsilon_{xy}^2 \sum_{\vec{k}} (H_2 + H_4) . \tag{B32}$$

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†Present address: Department of Physics, Purdue University, West Lafayette, Ind. 47907.

‡On sabbatical leave from Department of Physics, Purdue University, West Lafayette, Ind. 47907, Alexander von Humboldt Senior U. S. Scientist.

[1] R. W. Keyes, IBM J. Res. Dev. 5, 226 (1961).

[2] R. W. Keyes, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1967), Vol. 20, p. 37.

[3] W. P. Mason and T. B. Bateman, Phys. Rev. 134, A1387 (1964).

[4] N. G. Einspruch and P. Csavinszky, Appl. Phys. Lett. 2, 1 (1963).

[5] J. J. Hall, Phys. Rev. 161, 756 (1967).

[6] V. M. Beilin, Yu. Kh. Vekilov, and D. M. Krasilinkev, Fiz. Tverd. Tela 12, 684 (1968) [Sov. Phys.-Solid State 12, 531 (1970)].

[7] T. A. Fjeldly, *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972* (P.W.N.—Polish Scientific Publications, Warsaw, 1972), p. 245.

[8] G. L. Bir and A. Tursunov, Fiz. Tverd. Tela 4, 2625 (1962) [Sov. Phys.-Solid State 4, 1925 (1963)].

[9] F. Cerdeira and M. Cardona, Phys. Rev. B 5, 1440 (1972).

[10] T. A. Fjeldly, F. Cerdeira, and M. Cardona, Phys. Rev. B 8, 4723 (1973).

[11] E. W. Kellermann, Philos. Trans. R. Soc. Lond. A 238, 513 (1940).

[12] R. J. Hardy, I. W. Morrison, and S. Bijanki, J. Comput. Phys. 13, 591 (1973).

[13] J. C. Hensel and G. Feher, Phys. Rev. 129, 1041 (1963).

[14] R. N. Dexter, H. J. Zeiger, and B. Lax, Phys. Rev. 104, 637 (1956); B. Lax, Rev. Mod. Phys. 30, 122 (1958).

[15] L. D. Laude, F. H. Pollak, and M. Cardona, Phys. Rev. B 3, 2623 (1971).

[16] J. C. Hensel and K. Suzuki, Phys. Rev. B 9, 4219 (1974).

[17] L. J. Bruner and R. W. Keyes, Phys. Rev. Lett. 7, 55 (1966).

[18] F. Cerdeira, T. A. Fjeldly, and M. Cardona, Solid State Commun. 13, 325 (1973).

[19] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 10, 5095 (1974).