

pressure, \bar{Z} and the electronegativity difference being immediately known for a given compound.

Many predictions of polymorphic transitions stem from the present correlations. According to Figs. 4 and 5, MgTe is very similar to CdS and there may be a close similarity in the pressure-induced transitions. Beryllium oxide may be expected to transform to the NaCl structure at only a few hundred kbar. Boron nitride will require considerably higher pressures than is required for the conversion of carbon to a "metallic" form, etc.

Correlations beyond those obtained by Jayaraman, Klement, and Kennedy¹ are not apparent from the yet scanty data for the melting slopes and/or phase boundaries among the several polymorphs common to

these elements and compounds. Likewise, there is no attempt here to examine the behavior under pressure of the I-VII compounds which, in any case, should be considerably simpler because of the generally predominant ionic character of the bonding.

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Deformation Potentials in Silicon. II. Hydrostatic Strain and the Electron-Phonon Interaction*

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The hydrostatic pressure dependence of the energy of $\Gamma_{25'}$, the top of the valence band in Si, is calculated and expressed in terms of the deformation potential constant D_d^v . There are three types of terms which contribute to D_d^v : those involving the valence wave functions explicitly, a term involving the over-all zero of the crystal potential and an exchange and correlation term depending on the average valence charge density. It is shown that to obtain the correct change in the zero of energy with strain one may take the usually arbitrary zero of energy appearing in the Hartree-Fock self-consistent potential to be equal to the total energy of the ions in their equilibrium position divided by the number of electrons. The first term is determined by applying perturbation theory to the wave functions calculated previously by Kleinman and Phillips. The second term is calculated using the Ewald summing technique and the third term is determined from the Bohm-Pines approximation. Our calculated value of the pressure dependence of the $\Gamma_{25'}-L_1$ energy gap in Si is similar to the experimental value obtained in Ge. Our absolute energy shifts lie between those estimated by Herring from transport data, and those of Bagguley *et al.*, who determined the relaxation times appearing in Herring's theory from cyclotron resonance.

I. INTRODUCTION

THE three deformation potential parameters describing the strain dependence of the fourfold degenerate level at the top of the valence band in the covalently bonding semiconductors are the independent components of the hole-phonon coupling tensor for long-wavelength acoustic phonons.¹ Of these, only the parameter D_d^v describing the hydrostatic pressure dependence is not amenable to independent experimental determination. (In I², we calculated the other two parameters; see the references therein for their experimental determination.) If there exists a temperature range low enough for the optical phonon scattering to

be negligible and at the same time high enough for the acoustical phonon scattering to be large compared to impurity scattering, then in principle D_d^v can be determined from a variety of transport properties of the holes; in actual fact, the only experimental estimate of D_d^v is obtained from optical³ determinations of $D_d^v - D_d^c$. D_d^c is the equivalent parameter for the bottom of the conduction band and has been estimated by Herring *et al.*⁴ from a careful study of the transport properties of electrons in Ge. Recently, using cyclotron resonance, Bagguley, Flaxen, and Stradling⁵ have meas-

³ W. Paul and D. M. Worschauer, *J. Phys. Chem. Solids* **4**, 89 (1958).

⁴ C. Herring and E. Vogt, *Phys. Rev.* **101**, 944 (1956); C. Herring, T. H. Geballe, and J. E. Kunzler, *Bell System Tech. J.* **38**, 657 (1959).

⁵ D. M. S. Bagguley, D. W. Flaxen, and R. A. Stradling, *Phys. Letters* **1**, 111 (1962). I should like to thank Dr. S. Koenig for calling this work to my attention.

* Supported in part by the Advanced Research Projects Agency.

¹ G. Bir and G. Picus, *Fiz. Tverd. Tela* **2**, 2287 (1960) [translation: *Soviet Phys.—Solid State* **2**, 2039 (1961)].

² L. Kleinman, *Phys. Rev.* **128**, 2614 (1962). Referred to as I in this paper.

ured the transverse and longitudinal relaxation times appearing in Herring's theory, and obtained results in sharp disagreement with those of Herring. Unfortunately, there exist no data at all for silicon at the present time.

In the early 1930's cohesive energies and elastic constants were calculated for the monovalent metals.^{6,7} The theoretical calculation of the absolute magnitude of D_a^0 is of interest not only because of its importance in hole-phonon interactions, but also because it indicates that those quantities depending on absolute energies which were long ago calculated for the monovalent metals are amenable to calculation in the semiconductors. The relative values of D_a 's calculated throughout the Brillouin zone will be of importance in identifying various peaks in the optical absorption spectra. Thus far, only the L_3-L_1 peak in Ge has been observed to shift with pressure,^{8,9} implying that the shift of this peak is anomalously large. Theoretical estimates of the shifts of all the optical reflection peaks will be the topic of a later paper.¹⁰

In the next section we discuss the deformation potential theory of electron-phonon interactions. The one electron Hartree-Fock crystal potential is arbitrary to within an additive constant; it is shown how the arbitrariness in the change of this constant with strain must be eliminated if a Hartree-Fock potential is to be used in the deformation potential theory of the electron-phonon interaction.

In the third section, we describe the calculation of D_a^0 . Those terms which depend on the valence wave functions are calculated by applying perturbation theory to the wave functions determined previously by Kleinman and Phillips¹¹; this procedure requires only a simple extension of the work in I. These are the only terms needed¹² for calculations of the relative values of the D_a 's. The terms depending on the average charge density consist of a Coulomb and an exchange and correlation contribution. The latter is calculated from the Bohm-Pines approximation. The former is calculated using the Ewald summing technique.

Although relative shifts between levels with applied pressure are well known to be reasonably independent of the semiconductor with which one is dealing,¹³ there is no *a priori* reason to believe that absolute shifts are as well. In the last section we compare our calculated Si results with the experimental data for Ge. Our energy gap dependence is in good agreement with the experi-

mental results and our absolute shifts agree moderately well with those of Bagguley *et al.*⁵ The discrepancy between the experimental results of Herring and Bagguley is much larger than the uncertainties in our calculation, but we are unable to state that Bagguley's results are better because the pressure dependence of individual levels could vary considerably between Si and Ge.

II. THEORY OF THE ELECTRON-PHONON INTERACTION

In the usual theory of the electron-phonon interaction in metals,¹⁴ one writes the matrix element of the perturbation $\mathcal{H}' = \sum_l \boldsymbol{\eta}_l \cdot \partial V / \partial \boldsymbol{\eta}_l$ (where $\boldsymbol{\eta}_l$ is the displacement of the l th ion core and V the crystal potential),

$$M(\mathbf{k}, \mathbf{k}') = \langle n_{q_s}, \psi_{\mathbf{k}} | \mathcal{H}' | n_{q_s} - 1, \psi_{\mathbf{k}'} \rangle \\ = A \sum_l e^{-i\mathbf{q} \cdot \mathbf{l}} \int \psi_{\mathbf{k}}^* \hat{e}_{q_s} \cdot \frac{\partial V}{\partial \boldsymbol{\eta}_l} \psi_{\mathbf{k}'} d^3r, \quad (1)$$

where $A = -i(\hbar n_{q_s} / 2Nm\omega_{q_s})^{1/2}$, and where n_{q_s} is the number of phonons of wave vector \mathbf{q} in mode s , \hat{e}_{q_s} is a unit polarization vector of the phonon, ω_{q_s} is its frequency, and the crystal contains N atoms of mass m .¹⁵ Because of the periodicity of the integrand, the origin for each integral may be chosen in the l th cell so that

$$M(\mathbf{k}, \mathbf{k}') = A \sum_l e^{i(\mathbf{k}' - \mathbf{k} - \mathbf{q}) \cdot \mathbf{l}} \int \psi_{\mathbf{k}}^* \hat{e}_{q_s} \cdot \frac{\partial V}{\partial \boldsymbol{\eta}_l} \psi_{\mathbf{k}'} d^3r \\ = A \delta_{\mathbf{K}, \mathbf{k}' - \mathbf{k} - \mathbf{q}} N \int \psi_{\mathbf{k}}^* \hat{e}_{q_s} \cdot \frac{\partial V}{\partial \boldsymbol{\eta}_l} \psi_{\mathbf{k}'} d^3r, \quad (2)$$

where \mathbf{K} is a reciprocal lattice vector. Thus, the scattering process seems to depend only on the change in crystal potential when a single ion is moved. If a Wigner-Seitz model is used (i.e., potential due to l th ion vanishes outside the l th cell), it is found that for small \mathbf{q} , $M(\mathbf{k}, \mathbf{k}') = A \hat{e}_{q_s} \cdot \mathbf{q} (\frac{2}{3} E_F)$. If the Bardeen¹⁶ "self-consistent" model is used $M(\mathbf{k}, \mathbf{k}') = A \hat{e}_{q_s} \cdot \mathbf{q} (\frac{2}{3} E_F)$ for small \mathbf{q} . However, if the "self-consistent" model is used for a semiconductor $M(\mathbf{k}, \mathbf{k}') \sim [\hat{e} \cdot \mathbf{q} / q^2 \epsilon(q)]$ which becomes infinite as $\mathbf{q} \rightarrow 0$ because the dielectric constant $\epsilon(0)$ remains finite. Since the $\mathbf{q} = 0$ phonon implies only a translation of the entire crystal which cannot cause any scattering, this result is patently ridiculous. The theory has broken down, because a truly self-consistent calculation of $\partial V / \partial \boldsymbol{\eta}_l$ is not independent of all the other displacements $\boldsymbol{\eta}_i$. In the metal where each ion is screened from all but a few neighbors, the approximation is probably not too bad. Since the electron-phonon interaction is much more strongly screened in metals than in semiconductors, the results for metals indicate that in

⁶ E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).

⁷ K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935).

⁸ H. R. Philipp, W. C. Dash, and H. Ehrenreich, Bull. Am. Phys. Soc. **7**, 78 (1962).

⁹ R. Zallen, W. Paul, and J. Tauc, Bull. Am. Phys. Soc. **7**, 185 (1962).

¹⁰ I. Goroff and L. Kleinman (to be published).

¹¹ L. Kleinman and J. C. Phillips, Phys. Rev. **118**, 1153 (1960).

¹² This is only true on the assumption that all states see the same zero of energy due to exchange and correlation. This is nearly so for all states near the energy gap.

¹³ W. Paul, J. Appl. Phys. **32**, 2082 (1961).

¹⁴ J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), Chap. 5.

¹⁵ We shall assume only one atom per unit cell to simplify the equations.

¹⁶ J. Bardeen, Phys. Rev. **99**, 1140 (1955).

semiconductors M should approach zero no more rapidly than \mathbf{q} . Note also that in the W-S model $\int_{\text{cell}} \psi_{\mathbf{k}}^* V \psi_{\mathbf{k}} d^3r$ is just the Coulomb contribution to the cohesive energy. We see that, in a better treatment, this Coulomb contribution to the cohesive energy involves all the ion cores and valence electrons and, hence, cannot be determined directly from a one electron potential, but that it still plays an important role in electron-phonon scattering.

In the deformation potential theory of electron-phonon interactions, one usually writes

$$\mathcal{H}C = \mathcal{H}C_e + \mathcal{H}C_L + \mathcal{H}C_{eL},$$

where

$$\mathcal{H}C_e = (\hat{p}_\alpha \hat{p}_\alpha / 2m) + V_0(\mathbf{r}), \quad (3)$$

$$\mathcal{H}C_L = \frac{P_{qs} P_{-qs}}{2M} + \frac{1}{2} M \omega(\mathbf{q}s) \Omega_{qs} \Omega_{-qs}, \quad (4)$$

$$\mathcal{H}C_{eL} = V(\mathbf{r}, \Omega) - V_0(\mathbf{r}). \quad (5)$$

Whitfield¹⁷ has shown that if we use as basis states the orthogonalized deformed Bloch (ODB) functions,¹⁸ the Hamiltonian becomes (in the Bloch representation)

$$\mathcal{H}C = \mathcal{H}C_e + \mathcal{H}C_L + \mathcal{H}C' + \mathcal{H}C'', \quad (6)$$

where

$$\mathcal{H}C' = \frac{1}{2} (\mathcal{E}_{\alpha\beta} D_{\beta\alpha} + D_{\beta\alpha} \mathcal{E}_{\alpha\beta}), \quad (7)$$

$$D_{\beta\alpha} = \frac{-\hat{p}_\alpha \hat{p}_\beta}{m} + U_{\beta\alpha}(\mathbf{r}), \quad (8)$$

where the strain in the lattice due to a phonon is $\boldsymbol{\varepsilon}(\mathbf{r}) = -i\hat{e}_{qs} \mathbf{q} \Omega_{qs} e^{-i\mathbf{q}\cdot\mathbf{r}} = -i\mathbf{q} \boldsymbol{\eta}_{qs} e^{-i\mathbf{q}\cdot\mathbf{r}}$, and where $U_{\beta\alpha}(\mathbf{r})$ is the coefficient of the linear term in the expansion of the crystal potential in the strain

$$V(\mathbf{r}) \approx V_0[\mathbf{r} - \boldsymbol{\varepsilon}(\mathbf{r})\mathbf{r}] + U_{\alpha\beta}(\mathbf{r}) \mathcal{E}_{\beta\alpha}(\mathbf{r}). \quad (9)$$

$\mathcal{H}C''$ comes from transforming $\mathcal{H}C_L$ back to the Bloch representation and is $\approx 10^{-3} \mathcal{E}$ eV, and may, therefore, be neglected in comparison with $\mathcal{H}C'$ which is of order $5 \mathcal{E}$ eV. The advantage of the deformation potential theory is that the perturbation $\mathcal{H}C'$ can be calculated self-consistently and since the entire crystal is involved rather than just a single ion, the difficulty inherent in the Bardeen approximation is not present.

Let us examine the scattering matrix element for longitudinal phonons¹⁹ of long wavelength ($q \rightarrow 0$) in the jellium limit, i.e., the limit in which the Bloch functions are single plane waves. It can be shown that because of energy conservation requirements, the phonon wave vector must be nearly perpendicular to the wave vector of the electron which it scatters. Thus, since the

¹⁷ G. Whitfield, Phys. Rev. **121**, 720 (1961).

¹⁸ The ODB basis consists of the original Bloch set which has been deformed with the lattice, re-expressed in the undeformed space and multiplied by a Jacobian to preserve orthogonality.

¹⁹ The restriction to longitudinal phonons is not necessary but simplifies the discussion somewhat. The long-wavelength requirement is necessary so that the expansion (9) of $V(\mathbf{r})$ does not require terms in the derivatives of the strain.

contribution to the scattering of the kinetic energy term of Eq. (8) is of the order $(\mathbf{q}\cdot\mathbf{k})^2/q$, it is negligible. Therefore,

$$M(\mathbf{k}, \mathbf{k}') = A \delta_{0, \mathbf{k}' - \mathbf{k} - \mathbf{q}} V^{-1} \int U_{\mathbf{q}\mathbf{q}}(\mathbf{r}) d^3r, \quad (10)$$

where V is the volume of the crystal.

Because we took the Bloch functions to be plane waves, only the *average* value of the change in potential per unit uniaxial strain in the \mathbf{q} direction enters into the scattering matrix. The average value of $U_{\mathbf{q}\mathbf{q}}(\mathbf{r})$ is zero, because, due to charge neutrality, V_{000} , the average crystal potential is zero in both the strained and unstrained crystal.²⁰ Hence, it appears that in the deformation potential approximation, the electron-phonon matrix element vanishes more rapidly than q which contradicts an inference we drew from the results in metals.²¹

It is interesting to note that if one approximates the crystal by a superposition of spherical charge densities, one finds $V_{000} \sim r_0^2$ where r_0 is a characteristic radius for the spherical charge.²² This apparent discrepancy is due to taking the limit of an infinite crystal differently in the two cases and is simply an example of the fact that the crystal potential is always arbitrary to within an additive constant. Thus, if we can find some condition to fix this previously arbitrary constant and if the condition is such that the constant is different in the strained and unstrained crystals, then the matrix element (10) will be linear in q . We now show that the condition is determined from the requirement that the Hamiltonian be separable into $\mathcal{H}C_e$, $\mathcal{H}C_L$, and $\mathcal{H}C_{eL}$ as given by Eqs. (3), (4), and (5).

The total Hamiltonian is

$$\mathcal{H}C = \sum_i \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i, j; i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_n \frac{P_n^2}{2M} + \frac{1}{2} \sum_{n, m; n \neq m} \frac{1}{|\mathbf{R}_n - \mathbf{R}_m|} + \sum_{i, n} \frac{1}{|\mathbf{r}_i - \mathbf{r}_n|} - \mathcal{U}_{000}^{\text{op}}, \quad (11)$$

where we have added a term $\mathcal{U}_{000}^{\text{op}}$ which when operating on any wave function multiplies it by an arbitrary constant \mathcal{U}_{000} times its charge. This operator has no physical effect since only relative values of energy levels

²⁰ This follows from writing

$$V_{000} = V^{-1} \int V(\mathbf{r}) d^3r = V^{-1} \int \rho(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} d^3r'.$$

Because of the periodicity of $\rho(\mathbf{r}')$, \mathbf{r}' may be taken to lie in the unit cell containing the point $\mathbf{r} = 0$. Thus, expanding $|\mathbf{r} - \mathbf{r}'|^{-1}$ in spherical harmonics outside the first cell,

$$V_{000} = V^{-1} \int_{V_1} d^3r' \rho(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} d^3r' + V^{-1} \int_{V-V_1} d^3r' \rho(\mathbf{r}') d^3r',$$

whence it follows $V_{000} \sim V^{-1}$.

²¹ We have here ignored the nonvanishing exchange contribution to $U_{\mathbf{q}\mathbf{q}}(\mathbf{r}) d^3r$ because exchange is ignored in the calculation for metals.

²² J. L. Birman, Phys. Rev. **98**, 1863 (1955).

are meaningful. We may write the electronic part of the Hamiltonian in the Hartree-Fock approximation

$$\mathcal{H} = \sum_i \mathcal{H}_i + \mathcal{H}_{\text{ion}} - \mathcal{U}_{000}^{\text{op}}, \quad (12)$$

where

$$\mathcal{H}_i = (p_i^2/2m) + V(\mathbf{r}_i), \quad (13)$$

$$\mathcal{H}_{\text{ion}} = \sum_n \frac{P_n^2}{2M} + \frac{1}{2} \sum_{n,m; n \neq m} \frac{1}{|\mathbf{R}_n - \mathbf{R}_m|} + \sum_{n,i} \int \frac{\rho_i(\mathbf{r}_i)}{|\mathbf{R}_n - \mathbf{r}_i|} d^3r_i. \quad (14)$$

$\rho_i(\mathbf{r}_i)$ is the charge density of the i th electron assumed to be computed self-consistently from (13) and $V(\mathbf{r}_i)$ is an operator which yields just the self-consistent Coulomb and exchange potential energy when operating on $\psi(\mathbf{r}_i)$, but is zero when operating on $\psi(\mathbf{r}_j)$. \mathcal{H}_{ion} operates only on the many ion core wave function, while $\mathcal{U}_{000}^{\text{op}}$ operates on all wave functions. Thus, we obtain a set of equations

$$(\mathcal{H}_i + \mathcal{U}_{000})\psi_i(\mathbf{r}_i) = E_i\psi_i(\mathbf{r}_i), \quad (15)$$

$$(\mathcal{H}_{\text{ion}} - N\mathcal{U}_{000})\Phi(\mathbf{R}_n \cdots \mathbf{R}_m) = E\Phi(\mathbf{R}_n \cdots \mathbf{R}_m). \quad (16)$$

Now if we write $\mathbf{R}_n = \mathbf{R}_n^0 + \boldsymbol{\eta}_n$ and make the usual transformation to normal (phonon) coordinates, we find $\mathcal{H}_{\text{ion}}\Phi = C\Phi(\mathbf{R}_n \cdots \mathbf{R}_m) + \mathcal{H}_L\Phi(\boldsymbol{\eta}_a)$, where C is the self-energy of the ions (at $\mathbf{R}_n = \mathbf{R}_n^0$ for all n). If we write the electronic charge density $\rho(\mathbf{r}) = \rho_0 + \sum_{\mathbf{K}} \rho_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}$, we may write $C = C_0 + \sum_{\mathbf{K}} C_{\mathbf{K}}$, where C_0 is the energy of the ions due to their mutual interaction and the constant background of charge ρ_0 , while $C_{\mathbf{K}}$ is the energy of the ions in a potential $V_{\mathbf{K}} = \rho_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}/K^2$. The calculation of $C_{\mathbf{K}}$ is trivial (assuming $\rho_{\mathbf{K}}$ is known), while C_0 is just the total cohesive energy of a crystal whose electrons form a constant background of charge. (This is because the average value of the crystal potential is zero so the electrons sitting in this potential contribute nothing to the cohesive energy.⁷)

Thus, we see that if we require $\mathcal{U}_{000} = C/N$, we obtain $\mathcal{H} = \mathcal{H}_e + \mathcal{H}_L + \mathcal{H}_{eL}$ where \mathcal{H}_e , \mathcal{H}_L , and \mathcal{H}_{eL} are given by (3), (4), and (5) with $V(\mathbf{r})$ replaced by $V(\mathbf{r}) + \mathcal{U}_{000}$. Had we set $\mathcal{U}_{000} = 0$, Eq. (4) for \mathcal{H}_L would contain the constant C and on transforming to the ODB basis C would contribute to the term \mathcal{H}'' in (6) making it no longer negligible. This many electron-many ion term would, of course, contribute precisely the same thing to the scattering matrix as $\mathcal{U}_{000} = C/N$ does.²³

²³ We wish to emphasize that we have not corrected the deformation potential theory for it is correct as it stands. Rather, we have shown that the separated Hamiltonian of Eqs. (3), (4), and (5) which follows directly from a cellular model also follows for a Hartree-Fock crystal potential when the \mathcal{U}_{000} transformation is made.

TABLE I. Kinetic, potential (excluding V_{000}), and orthogonalization energy contributions in Ry to $\mathcal{H}_{\alpha\alpha'}$ per unit dilation. The wave function φ_{α} has been expanded in symmetrized combinations of plane waves with coefficients b_i ; contributions with coefficients b_1b_1 , $2b_1b_2$ 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 $2b_2b_i$ where $|b_i| > 0.014$.

	T'	V'	$V_{R'}$	$\mathcal{H}_{\alpha\alpha'}$
b_1b_1	-0.517	-0.129	-0.155	-0.801
$2b_1b_2$	0	0.336	-0.254	0.082
b_2b_2	-0.288	-0.037	-0.104	-0.429
Remainder	-0.054	0.150	-0.142	-0.046
Total	-0.859	0.320	-0.655	-1.194

III. CALCULATIONS

In I we obtained satisfactory agreement between theory and experiment using a physically reasonable model for the crystal potential in which the core electrons were considered to be perfectly rigid to any deformation and in which the valence electrons responded self-consistently like a free electron gas to the effective crystal potential. The shift in energy of the top of the valence band by a dilation \mathcal{E} (strain tensor $\boldsymbol{\mathcal{E}} = \frac{1}{3}\mathcal{E}\bar{I}$) is given by applying first-order perturbation theory²⁴ to the undeformed wave functions.

$$\begin{aligned} \mathcal{H}_{\alpha\alpha'} = & \frac{2}{3}\mathcal{E}\langle\varphi_{\alpha}|\nabla^2|\varphi_{\alpha}\rangle + \sum_{\mathbf{K}} (V_{\mathbf{K}} - \frac{1}{3}\mathcal{E}K^D - V_{\mathbf{K}}) \\ & \times \langle\varphi_{\alpha}|e^{i\mathbf{K}\cdot\mathbf{r}}|\varphi_{\alpha}\rangle + 2(E - E_{2p}) \sum_{i,j} b_i b_j \\ & \times \sum_{(\mathbf{K}_i^{\alpha}), (\mathbf{K}_j^{\alpha})} [A^{D*}(\mathbf{K}_i - \frac{1}{3}\mathcal{E}\mathbf{K}_i) A^D(\mathbf{K}_j - \frac{1}{3}\mathcal{E}\mathbf{K}_j) \\ & - A^*(\mathbf{K}_i) A(\mathbf{K}_j)] \cos\theta_{ij} \cos[(\mathbf{K}_i - \mathbf{K}_j) \cdot \boldsymbol{\tau}], \quad (17) \end{aligned}$$

where $\varphi_{\alpha} = (N\Omega)^{-1/2} \sum_i b_i \sum_{(\mathbf{K}_i^{\alpha})} e^{i\mathbf{K}_i^{\alpha}\cdot\mathbf{r}}$ is the "smooth" part of one of the degenerate $\Gamma_{25'}^{\alpha}$ ($\alpha = xy, xz, \text{ or } yz$) wave functions at the top of the valence band, Ω is the atomic volume, $\langle\mathbf{K}_i^{\alpha}\rangle$ represents the i th symmetrized combination of plane waves transforming according to α , $A(K) = \Omega^{-1/2} \langle\psi_{2p}, e^{i\mathbf{K}\cdot\mathbf{r}}\rangle$, $V_{\mathbf{K}}$ is the \mathbf{K} th Fourier transform of the crystal potential of reference 11, the superscript D refers to the deformed crystal, θ_{ij} is the angle between \mathbf{K}_i and \mathbf{K}_j , and $\boldsymbol{\tau}$ is the vector $(a/8, a/8, a/8)$. Compare (17) with Eqs. (13) and (23) of I. Calculation of the first (kinetic) term of (17) is straightforward, while that of the second (potential) and third (orthogonalization) terms is similar to their calculation in I with the added complication that the normalizations of $V_{\mathbf{K}}^D$ and $A^D(\mathbf{K})$ as well as the dielectric constant $\epsilon^D(K)$ depend on $\Omega^D \neq \Omega$; this was ignored in I because it does not lead to a splitting of degeneracies. These terms are calculated in the Appendix. From (A1), (A2), (A5), and (A6) we calculate and list in Table I all three terms

²⁴ Because a hydrostatic perturbation does not change the symmetry of the Hamiltonian, it does not mix wave functions of different symmetry; thus first-order nondegenerate perturbation theory is sufficient.

TABLE II. $\mathcal{H}\mathcal{C}_{\alpha\alpha}'$ of Table I plus various contributions to $V_{000}^D - V_{000}$ and $\mathcal{U}_{000}^D - \mathcal{U}_{000}$ in Ry per unit dilation. The values in parenthesis are obtained by reducing V_R' of Table I as discussed in the text.

$\mathcal{H}\mathcal{C}_{\alpha\alpha}'$	$-1.194(-1.108_{+0.03}^{-0.06})$
$\delta V_{000}^{\text{core-val ex}}$	0.039 ± 0.001
$\delta V_{000}^{\text{val-val ex}}$	$0.202_{-0.02}^{+0.04}$
$\delta V_{000}^{\text{val-val corr}}$	0.011 ± 0.01
$\delta \mathcal{U}_{000}^0$	0.700 ± 0.000
$\delta \mathcal{U}_{000}^{\mathbf{K}}$	-0.023 ± 0.02
Total	$-0.265(-0.179_{+0.10}^{-0.11})$

appearing in (17) except that the contribution of the zeroth Fourier transform of the crystal potential to the second term is not included. The convergence of the result in the number of symmetrized combinations of plane waves used to expand φ_{α} is displayed in Table I. It is seen that fair convergence is obtained with just two sets of plane waves. Excellent convergence is obtained with five. In Table II, we list the total $\mathcal{H}\mathcal{C}_{\alpha\alpha}'$ of Table I as well as the terms depending on V_{000} and \mathcal{U}_{000} which we now discuss.

In footnote 20, we showed that because of charge neutrality $V_{000}^{\text{Coul}} = 0$ and, hence, makes no contribution to D_a^p . The exchange interaction of the valence electrons with the ion cores may be written as a one-electron potential. (Core valence correlation is negligible.) The Fourier transforms of this potential are listed under $V_p^{\text{core-val ex}}(K)$ in Table II of reference 11. Thus, we have

$$V_{K-\frac{1}{2}\mathcal{E}K}^D - V_K = V_{000}(\Omega/\Omega^D - 1) \\ = -\mathcal{G}V_p^{\text{core-val ex}}(0) = 0.039\mathcal{E}\text{Ry}$$

as the contribution of $V_{000}^{\text{core-val ex}}$ to D_a^p . The valence-valence exchange and correlation interactions are not so easily approximated by a one-electron potential. We have used the Slater $\rho^{1/3}$ approximation²⁵ for the ($\mathbf{K} \neq 0$) exchange potential. The contribution of exchange to $V_{K \neq 0}$ is included in the first entry of Table II. It has been shown by Phillips²⁶ that the effect of correlation on $V_{K \neq 0}$ is mainly to screen the exchange term. This screening seems to be an inherent part of the Slater exchange hole and calculations of off-diagonal matrix elements of the screened Hartree-Fock exchange operator²⁷ yield results in substantial agreement with those calculated from the Slater approximation. Hence, the best approximation we can make for $V_{K \neq 0}^{\text{corr}}$ is to neglect it. In order to calculate the $\mathbf{K} = 0$ contribution to exchange and correlation, we must separate out their dependence on the average charge density. This may be done because ρ_0 is more than four times larger than any $\rho_{\mathbf{K}}$. Thus, for example, if the exchange is taken to be proportional to $[\rho(\mathbf{r})]^{1/3}$, we may use

$$[\rho(\mathbf{r})]^{1/3} = [\rho_0 + \sum_{\mathbf{K}} \rho_{\mathbf{K}} e^{i\mathbf{K} \cdot \mathbf{r}}]^{1/3} \\ \approx \rho_0^{1/3} + \frac{1}{3} \rho_0^{-2/3} \sum_{\mathbf{K}} \rho_{\mathbf{K}} e^{i\mathbf{K} \cdot \mathbf{r}}. \quad (18)$$

²⁵ J. C. Slater, Phys. Rev. **81**, 385 (1951).

²⁶ J. C. Phillips, Phys. Rev. **123**, 420 (1961).

²⁷ J. C. Phillips and L. Kleinman, Phys. Rev. **128**, 2098 (1962).

The error introduced by this separation is probably smaller than the error incurred by using the Slater $\rho^{1/3}$ approximation for exchange in the first place. The fact that the experimentally determined plasma frequency in Si is equal to the value calculated on the free-electron model is a good indication that our simple separation of exchange and correlation into $\mathbf{K} = 0$ and $\mathbf{K} \neq 0$ terms is valid.

The exchange and correlation energy per electron for a free-electron gas is according to the Bohm-Pines approximation²⁸

$$\epsilon_c = -0.916r_s^{-1} + 0.0313 \ln r_s - 0.114 + 0.0005r_s, \quad (19)$$

where r_s is the interelectronic spacing and the error in ϵ_c is estimated²⁸ to be no more than 15% of the correlation energy (last three terms of ϵ_c). If our separation of ρ into $\rho_{\mathbf{K}}$ and ρ_0 is valid, the $\mathbf{K} = 0$ exchange and correlation energy at the top of the valence band must correspond to that at the top of the Fermi sea in a free-electron gas. The energy to remove an electron from the top of the Fermi sea is

$$E^{\text{ex+corr}} = d(n\epsilon_c)/dn = \epsilon_c - \frac{1}{3}d\epsilon_c/d(\ln r_s), \quad (20)$$

$$E^{\text{ex+corr}} = -1.221r_s^{-1} + 0.0313 \ln r_s \\ - 0.124 + 0.0003r_s. \quad (21)$$

Thus, using that under dilation r_s goes to $r_s + \frac{1}{3}\mathcal{E}r_s$, we obtain for the change with dilation of the $\mathbf{K} = 0$ exchange and correlation energy $E^{\text{exD}} - E^{\text{ex}} = 0.407\mathcal{E}r_s^{-1}$ and

$$E^{\text{corrD}} - E^{\text{corr}} = 0.0313 \ln(1 + \frac{1}{3}\mathcal{E}) + 0.0001r_s\mathcal{E} \\ \approx 0.0104\mathcal{E} + 0.0001r_s\mathcal{E}.$$

Using $r_s = 2.006$ we enter these results in Table II. The correlation term is so small that even if the derivative is much less accurate than the term itself, the error is not appreciable. Using the general "exchange hole" arguments of Slater,²⁵ we expect the functional form of the exchange term is correct, hence, the derivative should be as accurate as the term itself.

We now calculate $\mathcal{U}_{000}^{\mathbf{K}} = C_{\mathbf{K}}/N$ and $\mathcal{U}_{000}^0 = C_0/N$. As pointed out in Sec. II, C_0 is just the cohesive energy of a crystal of Si ions in a constant background of electronic charge. As long as the ions do not overlap no error is made by replacing them with point ions. Therefore, we wish to calculate the electrostatic energy per electron of a Si lattice of 4+ point ions with a compensating constant electronic charge density. Wigner and Seitz⁶ have approximated such an electrostatic energy by the electrostatic energy of a single ion surrounded by a uniform sphere of negative charge and radius r_0 where $(4/3)\pi r_0^3 = \Omega$. The energy of the sphere is $-(9/5)Zr_0^{-1} = -2.26$ Ry. Because the atomic cell in Si is so non-spherical (the distances from the atom to the edge of the cell in the $\pm[111]$ directions are in the ratio of 2:1) the W-S approximation should not be expected to be

²⁸ D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, pp. 368.

accurate. A better approximation can be made by displacing the ion in the W-S sphere so that it is $\frac{2}{3}r_0$ from the wall of the sphere making the ratio of the nearest to farthest distance from the wall $2r_0/3:4r_0/3=1:2$. The energy of the displaced W-S sphere is $-(76/45)Zr_0^{-1}=2.12$ Ry. The electrostatic energy of the lattice may be calculated exactly using the Ewald²⁹ summing technique as extended by Fuchs⁷ to nonionic crystals. Fuchs' Eq. (15) written explicitly for the diamond structure is

$$\begin{aligned} \mathcal{U}_{000}^0 = a^{-1} \{ & 32\pi^{-1} \sum_i' h_i^{-2} e^{-\pi^2 h_i^2 / \mu^2} \\ & \times \cos^2[\frac{1}{4}\pi(h_i^{(x)} + h_i^{(y)} + h_i^{(z)})] \\ & + 4 \sum_{l\nu} F(\mu R_{l\nu\nu'}) R_{l\nu\nu'}^{-1} - 8\mu\pi^{-1/2} - 32\pi\mu^{-2} \}, \quad (22) \end{aligned}$$

where the primed sum is over all $\mathbf{h}_i = a(2\pi)^{-1}\mathbf{K}_i \neq 0$, $aR_{l\nu\nu'}$ is the distance from the ν th atom in the 0th cell to the ν th atom in the l th cell, $F(x) = 1 - 2\pi^{-1/2} \int_0^x e^{-t^2} dt$, μ is an arbitrary parameter chosen to optimize the convergence of the two sums, and a is the dimension of the cubic unit cell. Summing (22) we obtain $\mathcal{U}_{000}^0 = -2.10$ Ry. We thus obtain for the change in electrostatic self-energy under dilation $\mathcal{U}_{000}^{0D} - \mathcal{U}_{000}^0 = \mathcal{U}_{000}^0(a/a^D - 1) = -\frac{1}{3}\mathcal{E}\mathcal{U}_{000}^0 = 0.70\mathcal{E}$ Ry and so enter in Table II.

Only the zeroth and (111) Fourier transforms of the valence charge density are appreciable in Si.^{2,11} Thus, Eq. (A5) with $\mathbf{K} = (2\pi/a)(1,1,1)$ when multiplied by the structure factor $\cos\mathbf{K}\cdot\boldsymbol{\tau}$ gives the change in the non-constant valence charge-density contribution to the potential in which the ions sit. Since the potential varies spacially as $e^{i\mathbf{K}\cdot\mathbf{r}}$ and the ions sit at $\pm\boldsymbol{\tau}$ in the unit cell, another factor of $\cos\mathbf{K}\cdot\boldsymbol{\tau}$ appears in the energy. Hence $\delta\mathcal{U}_{000}^{\mathbf{K}} = \mathcal{E}(-0.157 + 0.177 + 0.027) \cos^2\mathbf{K}\cdot\boldsymbol{\tau} = 0.023\mathcal{E}$ Ry is the last entry in Table II. Because of the large cancellation in the three terms appearing in (A5) the error in our estimate of $\delta\mathcal{U}_{000}^{\mathbf{K}}$ is probably of the same order as $\delta\mathcal{U}_{000}^{\mathbf{K}}$ itself.

IV. CONCLUSIONS

In Table II are listed the contributions to D_d^v with what we believe are reasonable estimates of the uncertainty in each term. In I, we discussed how the Si energy band calculation¹¹ could be brought into agreement with experiment by reducing $E - E_{2p}$ from 7.42 to 6.42 Ry; the value of $\mathfrak{C}_{\alpha\alpha'}$ listed in the parenthesis contains this correction. In I, we also pointed out that the change in E and E_{2p} caused by the strain affects the repulsive potential and, hence, causes an additional change in E : [Eq. (30) of I]

$$\Delta E = \Delta E_0 + 0.072(\Delta E - \Delta E_{2p}).$$

Now ΔE_{2p} can be broken into two parts: the first due to all the other ions plus a constant background of charge and the second due to the nonconstant part of the electronic charge density. The negative of the

²⁹ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., Appendix A.

TABLE III. Comparison of calculated deformation potential constants in Si (in eV per 10^6 atm) with those determined in Ge by two conflicting experimental methods. The numbers in parenthesis have the estimated spin-orbit contribution subtracted off to facilitate comparison with Si where the spin-orbit contribution is negligible.

	Theory	Transport	Cyclotron res.
D_d^v	1.95	-3.6(-4.04)	3.98(3.54)
D_d^c	6.19	1.4	8.98
gap	4.24	5.0(5.44)	5.0(5.44)

second, we have previously calculated and called $\delta\mathcal{U}_{000}^{\mathbf{K}}$. The negative of the first is just twice what we have previously calculated and called $\delta\mathcal{U}_{000}^0$. Because we are calculating the energy of a single ion in the (Madelung) potential due to all the others, we would if we summed over all ions, count every ion-ion interaction twice. Thus, we get twice the average energy \mathcal{U}_{000}^0 . Therefore, $\Delta E_{2p} = -2\delta\mathcal{U}_{000}^0 - \delta\mathcal{U}_{000}^{\mathbf{K}}$; the change in sign comes about because we are here dealing with negative core electrons rather than positive ion cores. Since E represents the energy of the valence electrons relative to the core electrons, it should not include the average energy term which it was found necessary to include in the electron-phonon interaction. Thus, $\Delta E = D_d^v - \delta\mathcal{U}_{000}^0 - \delta\mathcal{U}_{000}^{\mathbf{K}}$ and

$$D_d^v = D_{d0}^v + 0.072(D_d^v + \delta\mathcal{U}_{000}^0). \quad (23)$$

Thus, we have $D_d^v = -0.179 + 0.072(D_d^v + 0.700)$ which yields $D_d^v = -0.138$ Ry = 1.88 eV (per unit dilation) = 1.95×10^{-6} eV per atmosphere. We have also calculated^{10,30,31} $D_d^c = 6.19 \times 10^{-6}$ eV/atm which gives a calculated gap dependence of 4.24×10^{-6} eV/atm. These results are compared in Table III with experimentally determined data for Ge.

The experimental values of D_d^v are obtained by subtracting the experimental gap dependence³ from the experimental values of D_d^c . D_d^c is obtained from the transport theory of Herring and Vogt.⁴ We are unable to explain the large discrepancy between Herring's⁴ original result in which he uses τ_{11}/τ_1 determined from magnetoresistance data and the recent results of Bagguley *et al.*⁵ in which τ_{11}/τ_1 is determined from cyclotron resonance. The theoretical value for the pressure dependence of the $\Gamma_{25'} - L_1$ energy gap in Si is within 15% of the experimental value in Ge in accord with the fact that the pressure dependence of any given energy gap varies only slightly from semiconductor to semiconductor.¹³ The theoretical values for D_d^v and

³⁰ By D_d^c , we mean the deformation potential constant at L_1 in Si as well as Ge even though L_1 is the bottom of the conduction band in Ge only.

³¹ The strain dependence of $V_{000}^{\text{core-val ex}}$ should be about 0.04 Ry larger in Ge because of the larger core, but $\delta V_{000}^{\text{val-val ex}}$ and $\delta\mathcal{U}_{000}^0$ should decrease by about the same amount due to the 4% larger lattice parameter. The behavior of $\delta\mathcal{U}_{000}^{\mathbf{K}}$ and $\delta V_{000}^{\text{val-val corr}}$ is too complicated to predict, but these are too small to have much effect. However, one cannot conclude that the pressure dependence of $\mathfrak{C}_{\alpha\alpha'}$ is the same in Ge and Si just because the gap dependence is the same.

D_d^c lie between the two sets of experimental values but favor Bagguley's. If, however, one assumes the first term in Table II is the same for Si and Ge when expressed as a function of *pressure* while the remaining terms are the same for Si and Ge when expressed as functions of *strain*,³¹ one finds better agreement with Herring's values. Thus, although the uncertainty in our calculation is only about $\frac{1}{3}$ of the difference between Herring and Bagguley, we are unable to choose between the two. It is interesting to note how important the many-body self-energy term is to the final numerical result. Without \mathcal{U}_{000} , we would have obtained $D_d^v = 10.8$ eV per 10^6 atm.

We have not calculated the contribution of the spin-orbit coupling to D_d^v ; however, it may be estimated as follows. The difference between the two spin split $L_{3'}$ deformation potentials in Ge has been measured⁹ at 0.8×10^{-6} eV/atm. If we multiply this by the ratio of the unstrained splitting at $\Gamma_{25'}$ to that at $L_{3'}$ and by $\frac{1}{3}$ to account for the fact that the $J = \frac{3}{2}$ level is raised by $\frac{1}{3}$ while the $J = \frac{1}{2}$ level lowered by $\frac{2}{3}$ of the spin-orbit splitting, we should have a good estimate of the spin-orbit contribution to D_d^v . We obtain $0.8 \times 10^{-6} (0.30/0.18) (\frac{1}{3}) = 0.44 \times 10^{-6}$ eV/atm. To obtain an estimate for Si we substitute the Si value for the unstrained $\Gamma_{25'}$ splitting (0.044 eV) and obtain 0.06 eV/atm. If the spin orbit contribution is subtracted from the experimental results for Ge to facilitate comparison with Si, the agreement between theory and Bagguley *et al.*'s results is improved.

I should like to thank Professor J. R. Schrieffer for several interesting discussions about electron-phonon interactions.

APPENDIX A

The orthogonalization (third) term of Eq. (17) may be written

$$V_{R\alpha\alpha'} = \frac{2}{3} \mathcal{E} (E_{2p} - E) \sum_{ij} b_i b_j \sum_{\langle K_i^{\alpha} \rangle} \sum_{\langle K_j^{\alpha'} \rangle} [A^*(K_i) \times \left(\frac{\partial A}{\partial K} \right)_{K_j} K_j + A(K_j) \left(\frac{\partial A^*}{\partial K} \right)_{K_i} K_i + 3A^*(K_i)A(K_j)] \cos \theta_{ij} \cos [\boldsymbol{\tau} \cdot (\mathbf{K}_i - \mathbf{K}_j)]. \quad (\text{A1})$$

The term in $A(K_i)A(K_j)$ arises from $\Omega^D - \Omega = \mathcal{E}\Omega$; such terms were ignored in I because they do not split degeneracies. The potential energy (second) term may

be split as follows:

$$V_{\mathbf{K}-\frac{1}{3}\epsilon\mathbf{K}}^D - V_{\mathbf{K}} = \cos \mathbf{K} \cdot \boldsymbol{\tau} [-\mathcal{E}V_{0K}^{\text{ion}} - \frac{1}{3} \mathcal{E} \left(\frac{\partial V_{0K}^{\text{ion}}}{\partial K} \right)_K K + V_{\mathbf{K}-\frac{1}{3}\epsilon\mathbf{K}}^{sD} - V_{\mathbf{K}}^s + V_{\mathbf{K}-\frac{1}{3}\epsilon\mathbf{K}}^{\text{exD}} - V_{\mathbf{K}}^{\text{ex}}], \quad (\text{A2})$$

where the superscripts s and ex refer to Coulomb and exchange potentials due to the valence electrons and V_{0K}^{ion} is the K th Fourier component of the total (Coulomb+exchange) potential due to a free ion. The first term again arises from $\Omega^D - \Omega = \mathcal{E}\Omega$. We discussed in I how a good approximation to a self-consistent calculation could be made by considering the valence electrons to be like a free-electron gas responding to the (111) Fourier component of the effective ionic potential (true potential plus repulsive potential due to orthogonalization). Thus, in Eq. (18) of I

$$V_{\mathbf{K}}^s = V_{0K}^{\text{ion eff}} [\epsilon^{-1}(K) - 1]$$

and in Eq. (A4) of I

$$V_{\mathbf{K}}^{\text{ex}} = -\frac{2}{3} \times 0.411 K^2 V_{\mathbf{K}}^s,$$

so that

$$V_{\mathbf{K}-\frac{1}{3}\epsilon\mathbf{K}}^{sD} - V_{\mathbf{K}}^s = -\mathcal{E}V_{\mathbf{K}}^s + \frac{1}{3} \mathcal{E} \left(\frac{\partial V_{0K}^{\text{ion eff}}}{\partial K} \right)_K [1 - \epsilon^{-1}(K)] K + V_{0K}^{\text{ion eff}} \left[\frac{1}{\epsilon^D(K - \frac{1}{3}\mathcal{E}K)} - \frac{1}{\epsilon(K)} \right]. \quad (\text{A3})$$

Now the dielectric constant ϵ may be written $\epsilon(K) = 1 + K^{-1}f(K/K_F)$, where K_F is the Fermi momentum and $K_F^D = K_F - \frac{1}{3}\mathcal{E}K_F$, so that

$$\epsilon^D(K - \frac{1}{3}\mathcal{E}K) = (1 - \frac{1}{3}\mathcal{E})^{-1} [\epsilon(K) - 1] + 1. \quad (\text{A4})$$

Thus

$$V_{\mathbf{K}-\frac{1}{3}\epsilon\mathbf{K}}^{sD} - V_{\mathbf{K}}^s = -\mathcal{E}V_{\mathbf{K}}^s + \frac{1}{3} \mathcal{E} \left(\frac{\partial V_{0K}^{\text{ion eff}}}{\partial K} \right)_K [1 - \epsilon^{-1}(K)] K - \frac{1}{3} \mathcal{E} V_{0K}^{\text{ion eff}} \epsilon^{-2}(K) [\epsilon(K) - 1]. \quad (\text{A5})$$

Finally

$$V_{\mathbf{K}-\frac{1}{3}\epsilon\mathbf{K}}^{\text{exD}} - V_{\mathbf{K}}^{\text{ex}} = -\frac{2}{3} \times 0.411 [k^2 (V_{\mathbf{K}-\frac{1}{3}\epsilon\mathbf{K}}^{sD} - V_{\mathbf{K}}^s) - \frac{2}{3} K \mathcal{E} V_{\mathbf{K}}^s]. \quad (\text{A6})$$

All the quantities appearing in these equations are tabulated in I.