account for this anomaly and it was hoped, at the outset, that the neutron diffraction results might decide which of these was correct. There are, however, a number of uncertainties which limit the accuracy of the method and rule out the possibility of a precise measurement of the individual moments of the ions on A and B sites. As has been noted, the nuclear and magnetic Bragg reflections are superimposed. Thus, any errors in the determination of the parameters which fix the chemical unit cell are reflected in the magnetic scattering pattern, which is obtained by difference. Furthermore, the magnetic scattering has a form factor dependence which cannot be determined independently and must therefore be treated as a parameter in the analysis. In addition there are uncertainties in the stoichiometry. An over-all estimate of these errors rules out the possibility of deciding any

subtle questions such as partial oxidation-reduction of Mn^{+2}-Fe^{+3} which would account for the anomalous moment.

SUMMARY

The neutron diffraction data are in good agreement with the Néel model of ferrimagnetism. The large difference in the coherent scattering amplitudes of iron and manganese enables one to fix the cation distribution rather precisely. The observed magnetic scattering is consistent with the measured saturation magnetization at both room temperature and liquid helium temperature.

Scattering of Holes by Phonons in Germanium*

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The lattice scattering of holes within and between the two valence bands of germanium, degenerate at $k=0$, is calculated. Scattering by both acoustical and optical modes is considered. The electron-lattice interaction Hamiltonian is seen to be separable into two parts: the first, associated with acoustical modes, arises from vibrations of the unit cells as a whole and the other, associated with both acoustical and optical modes, arises from the relative motion of the two atoms in the unit cell of the germanium lattice. The matrix elements for scattering are expressible in terms of two constants, C_1 and C_4, associated respectively with the two parts of the interaction Hamiltonian. The wave functions used to calculate the matrix elements are determined by $k \cdot p$ and spin-orbit perturbations and assume spherical surfaces of constant energy in k-space and a parabolic relation between energy and wave number. For the terms in C_1 the scattering is treated using both the deformable and rigid ion models. The angular distributions for scattering are such that heavy holes are scattered predominantly in the forward direction and light holes in the backward direction for the deformable ion model, whereas the opposite is true for the rigid ion model. The scattering resulting from transverse and longitudinal phonons is about equally important for deformable ions; for rigid ions scattering by transverse modes is less significant. The matrix elements depending on C_4 are obtained from the rigid ion model alone. The transition probabilities for scattering are presented in a form which can be applied readily to the transport properties of germanium.

1. INTRODUCTION

THE temperature dependence of the lattice scattering mobility of holes in germanium has been determined experimentally[1] as about $T^{-2.3}$, in a range of temperatures, extending roughly between 100°K and

300°K, for which the lattice vibrations are the dominant mechanism for scattering. This result is in disagreement with the theoretically predicted temperature dependence of $T^{-1.5}$, obtained by assuming that conduction takes place in a single valence band whose wave functions and energy surfaces near the band edge, at $k=0$, have spherical symmetry.[2]

Because of this disagreement, it is necessary to reconsider the problem of the lattice-scattering mobility of holes in the light of the information concerning the valence band structure that is now available. The

* Preliminary accounts of this material are given in the following references: H. Ehrenreich and A. W. Overhauser, Phys. Rev. **98**, 1533(A) (1955); H. Ehrenreich, Bull. Am. Phys. Soc. Ser. II, **1**, 48 (1956).

† This work was begun at Cornell University and is based in part on a section of a thesis submitted (by H.E.) in partial fulfillment of the requirements for the Ph.D. degree.

[1] F. J. Morin, Phys. Rev. **93**, 62 (1953); M. B. Prince, Phys. Rev. **92**, 681 (1953); F. J. Morin and J. P. Maita, Phys. Rev. **94**, 1525 (1954).

[2] F. Seitz, Phys. Rev. **73**, 549 (1948); J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

cyclotron resonance experiments,[3] and the calculations of Herman,[4] have demonstrated that the model of the valence band used in earlier mobility calculations is too simple. It has been established that the upper band edge does occur at $\mathbf{k}=0$, but that the energy surfaces are multiply sheeted in this region. Two bands with associated effective masses of 0.33 and 0.042 electron masses are degenerate at the center of the Brillouin zone. A third band, split off from the degenerate pair by spin-orbit coupling, is lower in energy by about 0.3 ev. It is clear that both degenerate bands must take part in the conduction process. The third band however is energetically too far removed in germanium to contribute significantly.

The electron-phonon interaction Hamiltonian employed in the earlier calculations also requires generalization. In addition to the expression used previously, two further terms arise that result from the fact that there are two atoms per unit cell. One of these terms is associated with optical modes and the other arises from acoustical modes as a result of small phase differences in the vibration of the two atoms of the unit cell.

In this paper we shall derive expressions proportional to the differential cross sections for scattering of holes in the valence bands of germanium by acoustical and optical phonons. Section 2 is concerned with the calculation of wave functions describing holes in the valence bands near $\mathbf{k}=0$. The electron-phonon interaction Hamiltonian is developed in Sec. 3 and applied to the germanium lattice. In Sec. 4 the matrix elements and transition probabilities for lattice scattering are derived. The application of these results to the mobility will be deferred to a subsequent paper.

2. CALCULATION OF THE WAVE FUNCTIONS

The theory of the energy surfaces in the valence bands of germanium and silicon has been treated by Dresselhaus, Kip, and Kittel[3] and others.[5] In this section, an extension of the arguments of reference 3 will be used to obtain the correct wave functions at $\mathbf{k}=0$ corresponding to these energy surfaces.

When spin is neglected, the Schrödinger equation to be solved approximately is

$$[H_0+(\hbar^2k^2/2m)+(\hbar/m)\mathbf{k}\cdot\mathbf{p}]v_k(r)=E(k)v_k(r),\quad(2.1)$$

where the periodic potential $V(r)$ is included in the unperturbed Hamiltonian, H_0, and $v_k(r)$ is the cell-periodic part of the wave function.

The correct valence band wave functions $|\epsilon_1\rangle$, $|\epsilon_2\rangle$, $|\epsilon_3\rangle$ at $\mathbf{k}=0$ belong to the symmetry group representation Γ_{25}^+ and satisfy the unperturbed Schrödinger equation $H_0|\epsilon_s\rangle=E_0|\epsilon_s\rangle$ ($s=1$, 2, 3) exactly. The wave functions at $\mathbf{k}=0$ belonging to other bands will be denoted $|s\alpha\lambda\rangle$, the index s labeling the state belonging to the representation α in band λ, and together with the $|\epsilon_s\rangle$ form a complete orthonormal set.

The functions $|\epsilon_s\rangle$ are degenerate at $\mathbf{k}=0$. The perturbation $(\hbar/m)\mathbf{k}\cdot\mathbf{p}$ removes the degeneracy in second order. Perturbation theory must be used to find the linear combinations

$$v_0(r)=b_{i1}|\epsilon_1\rangle+b_{i2}|\epsilon_2\rangle+b_{i3}|\epsilon_3\rangle,\quad(2.2)$$

which give the wave function correctly in a small region about $\mathbf{k}=0$.

It was shown by Shockley[6] and by Dresselhaus, Kip, and Kittel[3] for the diamond lattice, that the coefficients b_{i1}, b_{i2}, b_{i3} as well as the second-order energy correction w_i are obtained as solutions of the eigenvalue equation

$$\begin{bmatrix} Lk_x^2+M(k_y^2+k_z^2) & Nk_yk_x & Nk_xk_z \\ Nk_xk_y & Lk_y^2+M(k_x^2+k_z^2) & Nk_yk_z \\ Nk_xk_z & Nk_yk_z & Lk_z^2+M(k_x^2+k_y^2) \end{bmatrix}\begin{bmatrix} b_{i1} \\ b_{i2} \\ b_{i3} \end{bmatrix}=w_i\begin{bmatrix} b_{i1} \\ b_{i2} \\ b_{i3} \end{bmatrix},\quad(2.3)$$

where $i=1$, 2, 3 denotes the three solutions of (2.3) and

$$L=(\hbar^2/m^2)\sum_{s\alpha\lambda}(E_0-E_{\lambda\alpha})^{-1}\langle\epsilon_1|p_x|s\alpha\lambda\rangle\langle s\alpha\lambda|p_x|\epsilon_1\rangle,$$

$$M=(\hbar^2/m^2)\sum_{s\alpha\lambda}(E_0-E_{\lambda\alpha})^{-1}\langle\epsilon_1|p_y|s\alpha\lambda\rangle\langle s\alpha\lambda|p_y|\epsilon_1\rangle,\quad(2.4)$$

$$N=(\hbar^2/m^2)\sum_{s\alpha\lambda}(E_0-E_{\lambda\alpha})^{-1}(\langle\epsilon_1|p_x|s\alpha\lambda\rangle\langle s\alpha\lambda|p_y|\epsilon_2\rangle$$
$$+\langle\epsilon_1|p_y|s\alpha\lambda\rangle\langle s\alpha\lambda|p_x|\epsilon_2\rangle).$$

Equation (2.3) may be written more concisely as

$$Sb_i=w_ib_i.\quad(2.5)$$

The operator S is the Shockley matrix.

When spin is introduced, the degeneracy under consideration becomes sixfold. The extra factor of two arises from the two possible orientations of electron spin. Introduction of spin-orbit coupling reduces this degeneracy since the eigenvalues corresponding to different values of the total angular momentum j are split. A representation of the wave function in terms of the quantum numbers (l,s,j,m_j) is diagonal in the spin-orbit interaction. It is desirable to change to this representation since we wish to include the spin-orbit perturbation in this treatment. It can be shown[3] that the quantities L, M, and N appearing in the Shockley matrix will remain unchanged under the unitary

[3] Dresselhaus, Kip, and Kittel, Phys. Rev. 98, 368 (1955).
[4] F. Herman, Phys. Rev. 93, 1214 (1954); Physica 20, 801 (1954).

[5] E. N. Adams, Chicago Midway Laboratories Report CML-TN-P8, September 1954 (unpublished); R. J. Elliott, Phys. Rev. 96, 266 (1954).
[6] W. Shockley, Phys. Rev. 78, 173 (1950).

transformation to the new representation if spin-orbit splitting of the excited states is neglected.

The Shockley matrix in the (ϵ_s, m_s) representation is symbolically

$$\begin{bmatrix} S & 0 \\ 0 & S \end{bmatrix}.$$

The column vector of the b's in Eq. (2.3) is then replaced by a vector $\mathbf{b}$ having the six components

$b_{i1}(\uparrow)$, $b_{i2}(\uparrow)$, $b_{i3}(\uparrow)$, $b_{i1}(\downarrow)$, $b_{i2}(\downarrow)$, $b_{i3}(\downarrow)$ where $\uparrow$ and $\downarrow$ denote positive and negative spin, respectively.

The transformation to the (l,s,j,m_j) representation is easily accomplished with the help of the well-known Clebsch-Gordan coefficients.[7] The normalization and phase have been chosen in accordance with Condon and Shortley.[8] Abbreviating the wave functions $|lsjm_j\rangle$ by $|jm_j\rangle$ we have, in matrix form,

$$
\begin{bmatrix}
|\tfrac{1}{2} \quad \tfrac{1}{2}\rangle \\
|\tfrac{1}{2} \ -\tfrac{1}{2}\rangle \\
|\tfrac{3}{2} \quad \tfrac{3}{2}\rangle \\
|\tfrac{3}{2} \quad \tfrac{1}{2}\rangle \\
|\tfrac{3}{2} \ -\tfrac{1}{2}\rangle \\
|\tfrac{3}{2} \ -\tfrac{3}{2}\rangle
\end{bmatrix}
=
\begin{bmatrix}
0 & 0 & -1/\sqrt{3} & -1/\sqrt{3} & -i/\sqrt{3} & 0 \\
-1/\sqrt{3} & i/\sqrt{3} & 0 & 0 & 0 & 1/\sqrt{3} \\
-1/\sqrt{2} & -i/\sqrt{2} & 0 & 0 & 0 & 0 \\
0 & 0 & \sqrt{(2/3)} & -1/\sqrt{6} & -i/\sqrt{6} & 0 \\
1/\sqrt{6} & -i/\sqrt{6} & 0 & 0 & 0 & \sqrt{(2/3)} \\
0 & 0 & 0 & 1/\sqrt{2} & -i/\sqrt{2} & 0
\end{bmatrix}
\begin{bmatrix}
|\epsilon_1\uparrow\rangle \\
|\epsilon_2\uparrow\rangle \\
|\epsilon_3\uparrow\rangle \\
|\epsilon_1\downarrow\rangle \\
|\epsilon_2\downarrow\rangle \\
|\epsilon_3\downarrow\rangle
\end{bmatrix}
\tag{2.6}
$$

or more concisely,

$$\Psi = B\Theta, \tag{2.7}$$

as the relationship between the wave functions in the (ϵ_s, m_s) and the (l,s,j,m_j) representation.

The Shockley matrix in the new representation must now be expressed in terms of S and the unitary transformation matrix B. It is easily shown that S' is given by

$$S' = B^* S \tilde{B}, \tag{2.8}$$

where $\tilde{B}$ is the transpose of the matrix B.

The matrix S' may be schematically written

$$S' = \begin{bmatrix} \sigma(\tfrac{1}{2}) & \sigma(\tfrac{3}{2},\tfrac{1}{2}) \\ \sigma(\tfrac{1}{2},\tfrac{3}{2}) & \sigma(\tfrac{3}{2}) \end{bmatrix}, \tag{2.9}$$

where $\sigma(\tfrac{1}{2})$ and $\sigma(\tfrac{3}{2})$ are the submatrices associated, respectively, with $j=\tfrac{1}{2}$ and $j=\tfrac{3}{2}$ alone. The calculation indicated by (2.8) gives for these submatrices:

$$\sigma(\tfrac{1}{2}) = \begin{bmatrix} \tfrac{1}{3}(L+2M)k^2 & 0 \\ 0 & \tfrac{1}{3}(L+2M)k^2 \end{bmatrix}, \tag{2.10}$$

and

$$
\sigma(\tfrac{3}{2}) =
\begin{bmatrix}
\tfrac{1}{2}(L+M)(k_x{}^2+k_y{}^2)+Mk_z{}^2 & -(1/\sqrt{3})Nk_z(k_x-ik_y) \\
-(1/\sqrt{3})Nk_z(k_x+ik_y) & (1/6)(L+5M)(k_x{}^2+k_y{}^2)+\tfrac{1}{3}(2L+M)k_z{}^2 \\
(1/2\sqrt{3})(M-L)(k_x{}^2-k_y{}^2)-(i/\sqrt{3})Nk_xk_y & 0 \\
0 & (1/2\sqrt{3})(M-L)(k_x{}^2-k_y{}^2)-(i/\sqrt{3})Nk_xk_y
\end{bmatrix}
$$

$$
\begin{bmatrix}
(1/2\sqrt{3})(M-L)(k_x{}^2-k_y{}^2)+(i/\sqrt{3})Nk_xk_y & 0 \\
0 & (1/2\sqrt{3})(M-L)(k_x{}^2-k_y{}^2)+(i/\sqrt{3})Nk_xk_y \\
(1/6)(L+5M)(k_x{}^2+k_y{}^2)+\tfrac{1}{3}(2L+M)k_z{}^2 & (1/\sqrt{3})Nk_z(k_x-ik_y) \\
(1/\sqrt{3})Nk_z(k_x+ik_y) & \tfrac{1}{2}(L+M)(k_x{}^2+k_y{}^2)+Mk_z{}^2
\end{bmatrix}. \tag{2.11}
$$

The surfaces of constant energy in k space are obtained using the approximation, discussed in reference 3 and in more detail by Kane,[9] that it is justifiable to neglect the off-diagonal blocks $\sigma(\tfrac{3}{2},\tfrac{1}{2})$ and $\sigma(\tfrac{1}{2},\tfrac{3}{2})$. The secular determinants to be solved for w_i are then,

$$\sigma(\tfrac{3}{2}) - \mathbf{I}w_i = 0, \quad \sigma(\tfrac{1}{2}) - \mathbf{I}(w_i + \Delta) = 0, \tag{2.12}$$

where Δ denotes the spin-orbit splitting of the states $j=\tfrac{3}{2}$ and $j=\tfrac{1}{2}$ at $\mathbf{k}=0$.

The energies associated with the bands degenerate at $\mathbf{k}=0$ are found to be

$$E_{1,2} = Ak^2 \mp [B^2k^4 + C^2(k_x{}^2k_y{}^2 + k_y{}^2k_z{}^2 + k_z{}^2k_x{}^2)]^{\frac{1}{2}}, \tag{2.13}$$

where

$$
\begin{aligned}
A &= \hbar^2/2m + \tfrac{1}{3}(L+2M), \\
B &= \tfrac{1}{3}(L-M), \\
C^2 &= \tfrac{1}{3}[N^2 - (L-M)^2].
\end{aligned}
\tag{2.14}
$$

For the split-off band,

$$E_3 = -\Delta + Ak^2. \tag{2.15}$$

The quantities A, $|B|$, and $|C|$ are determined experimentally by the cyclotron resonance experiments.[3] The minus solution in Eq. (2.13) should be associated with band 1, having the lighter mass $m_1 \approx 0.042m$ and the positive sign, with band 2, having the heavier mass $m_2 \approx 0.33m$. The effect of a nonzero, positive C^2 is to warp the energy surfaces outward in the [111] direction for the holes of mass m_2, but inward along the same direction for the holes of mass m_1.

The wave functions χ corresponding to bands 1 and 2 are most simply expressed as linear combinations of

[9] E. O. Kane, Int. J. Phys. Chem. Solids (to be published).

[7] E. U. Condon and G. Shortley, The Theory of Atomic Spectra (Cambridge University Press, New York, 1951), second edition, Chap. 3, paragraph 14.

[8] Reference 7, Chap. 3, paragraph 3.

the $|jm_j\rangle$ belonging to $j=\frac{3}{2}$ as defined by Eq. (2.6). It is convenient to introduce the four-component wave function

$$\Psi_{\frac{3}{2}} = \begin{pmatrix} |\frac{3}{2} & \frac{3}{2}\rangle \\ |\frac{3}{2} & \frac{1}{2}\rangle \\ |\frac{3}{2} & -\frac{1}{2}\rangle \\ |\frac{3}{2} & -\frac{3}{2}\rangle \end{pmatrix}. \qquad (2.16)$$

By an argument converse to that used to establish (2.8) a matrix A^* which diagonalizes $\sigma(\frac{3}{2})$, that is, which has the property

$$A^*\sigma(\tfrac{3}{2})\tilde{A} = \begin{pmatrix} E_1 & 0 & 0 & 0 \\ 0 & E_1 & 0 & 0 \\ 0 & 0 & E_2 & 0 \\ 0 & 0 & 0 & E_2 \end{pmatrix}, \qquad (2.17)$$

will also determine the correct linear combinations

$$\chi = A\Psi_{\frac{3}{2}}. \qquad (2.18)$$

$$A = \frac{1}{\Delta\sqrt{2}} \begin{pmatrix} (c+id)e^{-i\theta} & (E_1-a) & i(E_1-a)e^{i(\phi-\theta)} & -i(c+id)e^{i\phi} \\ i(c-id)e^{-i\phi} & i(E_1-a)e^{-i(\phi-\theta)} & (E_1-a) & -(c-id)e^{i\theta} \\ -(E_1-a) & (c-id)e^{i\theta} & i(c-id)e^{i\phi} & i(E_1-a)e^{i(\theta+\phi)} \\ i(E_1-a)e^{-i(\theta+\phi)} & -i(c+id)e^{-i\phi} & -(c+id)e^{-i\theta} & -(E_1-a) \end{pmatrix}, \qquad (2.20)$$

where

$$\Delta^2 = (E_1-a)^2+c^2+d^2,$$

satisfies Eq. (2.17). In writing (2.20) use has been made of the easily verified identity $(E_1-a) = -(E_2-b)$. The even more abbreviated form

$$A = [a_{ij}] \qquad (2.21)$$

will be used in the following section to represent the elements of this matrix.

Explicit expressions for the wave functions to be used in calculating the matrix elements of the electron-phonon interaction are now easily obtained. By definition

$$\chi_{ki} = a_{i1}|\tfrac{3}{2},\tfrac{3}{2}\rangle + a_{i2}|\tfrac{3}{2},\tfrac{1}{2}\rangle + a_{i3}|\tfrac{3}{2},-\tfrac{1}{2}\rangle + a_{i4}|\tfrac{3}{2},-\tfrac{3}{2}\rangle$$
$$\text{for} \quad i=1, 2, 3, 4. \quad (2.22)$$

Using Eq. (2.6) we then obtain

$$\chi_{ki} = -2^{-\frac{1}{2}}(|\epsilon_1\uparrow\rangle + i|\epsilon_2\uparrow\rangle)a_{i1} + (\tfrac{2}{3})^{\frac{1}{2}}|\epsilon_3\uparrow\rangle a_{i2}$$
$$-6^{-\frac{1}{2}}(|\epsilon_1\downarrow\rangle + i|\epsilon_2\downarrow\rangle)a_{i2} + (\tfrac{2}{3})^{\frac{1}{2}}|\epsilon_3\downarrow\rangle a_{i3}$$
$$+6^{-\frac{1}{2}}(|\epsilon_1\uparrow\rangle - i|\epsilon_2\uparrow\rangle)a_{i3} + 2^{-\frac{1}{2}}(|\epsilon_1\downarrow\rangle - i|\epsilon_2\downarrow\rangle)a_{i4}. \quad (2.23)$$

The coefficients a_{ij} contain the dependence on k. When writing final state wave functions, which depend on k', we shall denote the expansion coefficients a_{ij}'.

3. ELECTRON-PHONON INTERACTION

Before proceeding to considerations of the interaction Hamiltonian for electrons and lattice vibrations, it may

Here χ is given by

$$\chi = \begin{pmatrix} \chi_{k1} \\ \chi_{k2} \\ \chi_{k3} \\ \chi_{k4} \end{pmatrix},$$

where the first two elements refer to band 1 and the remaining ones to band 2. The components χ_{ki} depend on the direction, but not the magnitude of k.

Before giving the explicit form of A, let us simplify the notation by introducing quantities a, b, c, d, θ, ϕ such that

$$\sigma(\tfrac{3}{2}) = \begin{pmatrix} a & ce^{i\theta} & de^{i\phi} & 0 \\ ce^{-i\theta} & b & 0 & de^{i\phi} \\ de^{-i\phi} & 0 & b & -ce^{i\theta} \\ 0 & de^{-i\phi} & -ce^{-i\theta} & a \end{pmatrix}. \quad (2.19)$$

The definitions of these new symbols are obtained by direct comparison with Eq. (2.11). One can then verify that the matrix

be well to review some of the features that characterize the current carriers and phonons in p-type germanium. The holes in the valence bands of germanium lie in a small sphere surrounding the origin of the Brillouin zone in k space. The number of holes at room temperature and below, for samples having fewer than 10^{17} acceptors per cm^3, is sufficiently small that Boltzmann statistics can be used to describe their distribution in energy.

A phonon will scatter a hole by being either absorbed or emitted. When dispersion can be neglected, the conservation laws for energy and momentum show that either process can take place as long as the velocity of the hole is larger than the velocity of sound; however, only absorption can occur for hole velocities smaller than the sound velocity. Holes in the heavy mass band can undergo both processes for temperatures greater than about 1°K. The limiting temperature for light holes is about 10°K. It follows that holes in germanium can absorb or emit acoustical phonons throughout the lattice scattering range. The conservation principles show further that a hole can interact only with phonons of wave number q such that $q \leqslant 2k$. Taking k to be the wave number of a hole at room temperature, it is seen that the phonons that can interact with holes have q much smaller than the Debye wave number. This means that dispersion can be neglected for acoustical phonons. The dispersion curve for optical phonons, on the other hand, has zero slope in the region about $q=0$.

Hence the frequency of the optical phonons interacting with holes can be taken to be constant, independent of q.

The energy of an acoustical phonon of polarization P and velocity u_P, is much smaller than that of a hole at room temperature if $q \lesssim 2k$. The phonon energy can be neglected therefore in an emission or absorption process, and the scattering considered as elastic. The number of acoustical phonons of wave number q, polarization P, and velocity u_P, at a temperature T is

$$n_{qP} = (e^{\hbar u_P q / KT} - 1)^{-1} \approx KT / \hbar u_P q. \qquad (3.1)$$

Since $n_{qP} \gg 1$, it follows that $n_{qP} \approx n_{qP} + 1$.

The frequency ω of optical phonons near $q = 0$ is independent of polarization in nonpolar crystals. Defining the optical mode temperature Θ by the relationship $\hbar\omega = K\Theta$, one finds the number of optical phonons of given polarization and wave number to be

$$n = (e^{\Theta/T} - 1)^{-1}. \qquad (3.2)$$

Umklapp processes will be unimportant provided that $k \ll K$, where $2\pi K$ is a reciprocal lattice vector. This condition is well satisfied for the magnitudes of k encountered in the lattice scattering range since $2\pi K \sim 10^8$ cm^{-1}. Therefore, Umklapp processes need not be considered further.

We shall now treat the electron-phonon interaction in a crystal having two atoms per unit cell. The index $l = 0, 1$ will be used to label the atoms in the unit cell. Let the position of the nuclei with respect to a fixed origin be $\mathfrak{g}_l$, where $\mathfrak{g}$ is the index labeling the unit cell. The displacement of a point $\mathbf{r}$ will be written $\mathbf{u}(\mathbf{r})$.

Either of two hypotheses has been commonly made concerning the displacements of various points in the unit cell during lattice vibrations. The first of these, introduced by Bloch,[10] assumes the atoms to be completely deformable while vibrating. The second physically quite different hypothesis of Nordheim[11] supposes the atoms to be totally rigid and displaced as a whole. Concerning these hypotheses, Seitz[2] points out that it is not clear which of them is better for nonpolar crystals like germanium since the degree of polarizability of the electron cloud is uncertain. In the present paper we shall attempt to treat both the deformable-ion (DI) model and the rigid-ion (RI) model simultaneously by adopting the artifice of writing the displacement of a point r in the form $\mathbf{u}[\mathfrak{g}_l + \eta(\mathbf{r} - \mathfrak{g}_l)]$ where η is a parameter having a value $0 \leqslant \eta \leqslant 1$. In the limits of $\eta = 0$ and 1 the displacements reduce to those given by the RI and DI models, respectively. For intervening values of η, there is some displacement in all parts of the atomic cell, with the largest amount occurring at the point $\mathfrak{g}_l$. It seems reasonable to suppose that the actual physical situation will correspond to some value of η in this range, since one would expect the inner cores of the atom to be displaced rigidly, and the outer shells to be deformed.

If we let $U(\mathbf{r} - \mathfrak{g}_l)$ represent the potential at point $\mathbf{r}$ due to the atom centered at $\mathfrak{g}_l$ for the electron configuration with which the atom enters the crystal, then the crystal potential is

$$V(r) = \sum_{\mathfrak{g}, l} U(\mathbf{r} - \mathfrak{g}_l). \qquad (3.3)$$

The interaction Hamiltonian for the electrons and lattice vibrations is

$$H^I = \sum_{\mathfrak{g}l, l} U(\mathbf{r} - \mathfrak{g}_l - \mathbf{u}) - \sum_{\mathfrak{g}l, l} U(\mathbf{r} - \mathfrak{g}_l)$$
$$\approx - \sum_{\mathfrak{g}l, l} \mathbf{u}[\mathfrak{g}_l + \eta(\mathbf{r} - \mathfrak{g}_l)] \cdot \nabla U(\mathbf{r} - \mathfrak{g}_l). \qquad (3.4)$$

The higher order terms in the expansion will be unimportant for small displacements.

We proceed in the usual fashion[12,13] by Fourier analyzing $\mathbf{u}$ in terms of the normal modes of vibration

$$u(r) = G^{-\frac{3}{2}} \sum_{q, P, \mu} [a_{qP\mu} e^{i\mathbf{q} \cdot \mathbf{r}} \exp(i\phi_{\mu l}) \hat{e}_{\mu P}(q)$$
$$+ a_{qP\mu}^{\dagger} e^{-i\mathbf{q} \cdot \mathbf{r}} \exp(-i\phi_{\mu l}) \hat{e}_{\mu P}^{*}(q)]. \qquad (3.5)$$

The index μ takes on values 1 and 2 for acoustical and optical modes, respectively. The number of unit cells of mass M (twice the atomic mass) in the crystal volume V is G^3. The quantities $a_{qP\mu}^{\dagger}$ and $a_{qP\mu}$ are the creation and annihilation operators respectively and satisfy the commutation relation

$$[a_{q'P'\mu'}, a_{qP\mu}^{\dagger}] = (\hbar/2M\omega_{\mu P})\delta_{qq'}\delta_{\mu\mu'}\delta_{PP'}. \qquad (3.6)$$

The polarization vectors $\hat{e}_{\mu P}(q)$ may be complex, as will be seen presently. They satisfy

$$\hat{e}_{\mu P}^{*}(q) \cdot \hat{e}_{\mu P'}(q) = \delta_{PP'}. \qquad (3.7)$$

Finally, $e^{i\phi_{\mu l}}$ is a phase factor that distinguishes between acoustical and optical modes, where

$$\phi_{\mu l} = \pi \delta_{\mu 2} \delta_{l2}. \qquad (3.8)$$

For infinite wavelength, the two atoms of the unit cell will then vibrate in phase for acoustical modes and π radians out of phase for optical modes. The phase difference that exists between the two atoms when $q \neq 0$, is included in the polarization vector and will be discussed presently. It should be emphasized however that these terms, arising from nonvanishing phase differences between the atoms of a particular unit cell, will be treated here by means of the RI model only. The DI model is ambiguous for modes of this type, and in any case would require a more complex definition of $\phi_{\mu l}$ than (3.8).

Since we shall want to consider the different vibrational branches and polarizations independently, we

[10] F. Bloch, Z. Physik 52, 555 (1928).
[11] L. Nordheim, Ann. Physik 9, 607 (1931).

[12] A. Sommerfeld and H. Bethe, Handbuch der Physik (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2, p. 509.
[13] A. H. Wilson, The Theory of Metals (Cambridge University Press, New York, 1953), second edition, p. 254.

introduce the notation

$$\mathbf{u}[\mathbf{g}_l+\eta(\mathbf{r}-\mathbf{g}_l)]=\sum_{\mu,P}\mathbf{u}_{\mu P}[\mathbf{g}_l+\eta(\mathbf{r}-\mathbf{g}_l)],$$

$$H^I=\sum_{\mu,P}H_{\mu P}.$$

(3.9)

The wave functions of the electron-phonon system are

$$\Psi_{ki}(\mathbf{r},\{n_{q'P'\mu'}\})=\psi_{ki}(\mathbf{r})\prod_{\mu',q',P'}\varphi(n_{q'P'\mu'}),\quad(3.10)$$

where $\psi_{ki}=G^{-\frac{1}{2}}\chi_{ki}(\mathbf{r})e^{i\mathbf{k}_i\cdot\mathbf{r}}$ is a Bloch function corresponding to a hole having wave number k in band i. The normalized phonon wave function $\varphi(n_{q'P'\mu'})$ describes the field containing $n_{q'P'\mu'}$ phonons of polarization P' and vibrational mode μ' having wave number q', and satisfies the equations

$$a_{qP\mu}{}^\dagger\varphi(n_{qP\mu})=(\hbar/2M\omega_{\mu P})^{\frac{1}{2}}(n_{qP\mu}+1)^{\frac{1}{2}}\varphi(n_{qP\mu}+1),$$
$$a_{qP\mu}\varphi(n_{qP\mu})=(\hbar/2M\omega_{\mu P})^{\frac{1}{2}}(n_{qP\mu})^{\frac{1}{2}}\varphi(n_{qP\mu}-1).$$

(3.11)

The matrix element corresponding to a transition from a state represented by the wave function $\Psi_{kj}(\mathbf{r},n_{qP\mu},\{n_{q'P'\mu'}\})$ to a state $\Psi_{k'i}(\mathbf{r},n_{qP\mu}+1,\{n_{q'P'\mu'}\})$ or $\Psi_{k'i}(\mathbf{r},n_{qP\mu}-1,\{n_{q'P'\mu'}\})$, $(qP\mu\neq q'P'\mu')$, is

$$\langle i,n\mp1|H_{\mu P}|j,n\rangle=\int\Psi_{k'i}{}^*(r,n_{qP\mu}\mp1,\{n_{q'P'\mu'}\})$$
$$\times H_{\mu P}\Psi_{kj}(\mathbf{r},n_{qP\mu},\{n_{q'P'\mu'}\})d\tau,$$

where the upper sign corresponds to an absorption and the lower to an emission process. Evaluating $H_{\mu P}$ using Eq. (3.4), (3.5), and (3.9) and inserting this together with the wave function (3.10) into the preceding expression, we find, with the help of Eq. (3.11), that

$$\langle i,n\mp1|H_{\mu P}|j,n\rangle=G^{-\frac{3}{2}}\sum_q(\hbar n_{\mu P}{}'/2M\omega_{\mu P})^{\frac{1}{2}}$$

$$\times\int\psi_{k'i}{}^*[\sum_{\mathbf{g}_l,l}\exp(\pm i\phi_{\mu l})\hat{e}_{\mu P}{}^{(*)}(q,l)\cdot\nabla U(\mathbf{r}-\mathbf{g}_l)$$

$$\times\exp(\pm i\mathbf{q}\cdot\mathbf{g}_l)\exp[\pm i\eta\mathbf{q}\cdot(\mathbf{r}-\mathbf{g}_l)]]\psi_{kj}d\tau.\quad(3.12)$$

We have introduced $n_{\mu P}{}'$ which equals $n_{\mu P}$ for absorption and $n_{\mu P}+1$ for emission. The asterisk in brackets signifies that the complex conjugate of $e_{\mu P}(q,l)$ is to be taken only for the emission process.

It can be shown that if the solid is sufficiently large and the atomic potential of short range so that surface terms can be neglected,

$$\int_{l'}\psi_{k'i}{}^*[\sum_{\mathbf{g}_l,l}\exp(\pm i\phi_{\mu l})\hat{e}_{\mu P}{}^{(*)}(q,l)\cdot\nabla U(\mathbf{r}-\mathbf{g}_l)$$

$$\times\exp(\pm i\mathbf{q}\cdot\mathbf{g}_l)\exp[\pm i\eta\mathbf{q}\cdot(\mathbf{r}-\mathbf{g}_l)]]\psi_{kj}d\tau$$

$$=\delta_{0,\mathbf{k}\pm\mathbf{q}-\mathbf{k}'}\int_{0,l'}\chi_{k'i}{}^*[\sum_{\mathbf{g}_l,l}\exp(\pm i\phi_{\mu l})\hat{e}_{\mu P}{}^{(*)}(q,l)$$

$$\cdot\nabla U(\mathbf{r}+\mathbf{g}_l)\exp[\pm i(\eta-1)\mathbf{q}\cdot(\mathbf{r}+\mathbf{g}_l)]]\chi_{kj}d\tau$$

$$=\delta_{0,\mathbf{k}\pm\mathbf{q}-\mathbf{k}'}J_{\mu P}{}^\pm(l').\quad(3.13)$$

The subscripts l' or 0, l' on the integral sign define the region of integration as either all of the l'th atomic cells in the crystal, or the l'th atomic cell which is part of the zeroth unit cell, respectively. It will be unnecessary for the present purposes to indicate the dependence of $J_{\mu P}{}^\pm(l)$ on k, k', i, j, and q explicitly.

Thus, for *acoustical* modes where n_{qP} is given by Eq. (3.1), we obtain

$$\langle i,n\mp1|H_{1P}|j,n\rangle=(KT/2MG^3u_P{}^2)^{\frac{1}{2}}$$

$$\times\sum_q q^{-1}\delta_{0,\mathbf{k}\pm\mathbf{q}-\mathbf{k}'}[J_{1P}{}^\pm(1)+J_{1P}{}^\pm(2)].\quad(3.14)$$

The corresponding expression for *optical* modes, assuming n independent of q, is

$$\langle i,n\mp1|H_{2P}|j,n\rangle=(\hbar n'/2MG^3\omega)^{\frac{1}{2}}$$

$$\times\sum_q \delta_{0,\mathbf{k}\pm\mathbf{q}-\mathbf{k}'}[J_{2P}{}^\pm(1)+J_{2P}{}^\pm(2)].\quad(3.15)$$

The present treatment of the electron-phonon interaction will take advantage of the predominance of long vibrational wavelengths. Accordingly the matrix elements will be approximated by including only terms to lowest order in q. Following Born and Huang's treatment of "long waves"[14] we shall write the polarization vector in the form

$$\hat{e}_{\mu P}(q,l)=\hat{e}_P(0)+iqa_0\delta_{\mu P}(l),\quad(3.16)$$

where $2a_0$ is the edge of one of the two interpenetrating face-centered cubes which generate the diamond lattice. The vector $\delta_{\mu P}(l)$ is real. The polarization vector (3.16) need satisfy Eq. (3.7) to first order in q only so that $|e_{\mu P}(q,l)|^2=|e_P(0)|^2$. The meaning of a complex polarization vector for finite wavelengths is simply that the particles no longer vibrate through their centers of mass, as is the case for $q=0$, but in an ellipse thus mixing polarizations slightly. The dependence of (3.16) on l reflects the existence of a phase difference in the vibration of the two atoms of the unit cell along similar ellipses.

Let us now consider in detail the interaction of holes with acoustical phonons. Equation (3.14) can be simplified, as is shown in the appendix, with the help of the notation introduced below. For the sake of simplicity, we shall assume that the atomic potential is large over a single cell only, so that $U(\mathbf{r}-0_l)=V(\mathbf{r})$ for values of r lying in the cell labeled 0_l, and $U(\mathbf{r}-0_l)=0$ for points outside the cell.

Introducing the symbols

$$\Delta\delta_{1P}=\delta_{1P}(1)-\delta_{1P}(2),$$
$$\partial/\partial s_P=\hat{e}_P(0)\cdot\nabla,$$
$$\partial/\partial s_q=(\mathbf{q}/q)\cdot\nabla,$$
$$\delta_{LP}\equiv\hat{e}_P(0)\cdot\mathbf{q}/q,$$

(3.17)

[14] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), paragraphs 26–27.

and the matrix elements

$$\langle i | F_1{}^P | j \rangle = (\hbar^2/m) \int_0 (\partial \chi_{k'i}{}^* / \partial s_P)(\partial \chi_{kj} / \partial s_q) d\tau, \quad (3.18)$$

$$\langle i | F_2 | j \rangle = \int_0 \chi_{k'i}{}^* \chi_{kj} V(r) d\tau, \quad (3.19)$$

$$\langle i | F_3{}^P | j \rangle = a_0 \int_{1,0} \chi_{k'i}{}^* \chi_{kj} \delta_{1P} \cdot \nabla V d\tau, \quad (3.20)$$

$$\langle i | F_4{}^P | j \rangle = a_0 \int_{1,0} \chi_{k'i}{}^* \chi_{kj} (\partial V / \partial s_P) d\tau, \quad (3.21)$$

we obtain to lowest order in q

$$\langle i, n \mp 1 | H_{1P} | j, n \rangle = \pm i (KT/2u_P{}^2 \rho V)^{\frac{1}{2}} [\langle i | F_1{}^P | j \rangle$$
$$+ (1-\eta) \delta_{LP} \langle i | F_2 | j \rangle + \langle i | F_3{}^P | j \rangle], \quad (3.22)$$

where the density $\rho = MG^3/V$.

The preceding expression for the matrix elements can be evaluated explicitly if $\hat{e}_P(0)$ and δ_{1P} are known. We shall use the general results of Born and Huang[14] as applied to the diamond lattice by Smith.[15] This treatment considers interactions with nearest neighbors without approximation, and interactions with second neighbors assuming that the forces are central. In our notation, the equations of reference 15 giving $\hat{e}_P(0)$ and $\Delta \delta_{1P}$ are

$$\hat{e}_P(0) = (2a_0 \rho \omega_P{}^2)^{-1} S' \hat{e}_P(0), \quad (3.23)$$

and

$$\Delta \delta_{1P} = \frac{1}{2q} \left(\frac{\beta}{\alpha} \right) \begin{bmatrix} 0 & q_z & q_y \\ q_z & 0 & q_x \\ q_y & q_x & 0 \end{bmatrix} \hat{e}_P(0). \quad (3.24)$$

S' is a matrix having the same structure as the Shockley matrix defined by Eq. (2.3), but with q replacing k and the following definitions for L, M and N:

$$L = \alpha + 8\mu,$$
$$M = \alpha - \beta^2/\alpha + 4\mu, \quad (3.25)$$
$$N = \beta(2-\beta/\alpha) + 8\mu.$$

The quantities α, β and μ are functions of the elastic constants to be given explicitly in Sec. 4.

Let us now consider the case of optical modes. In the approximation, used before, that $U(r)$ is of sufficiently short range, we have, to lowest order in q,

$$J_{2P}{}^{\pm}(l) = (-1)^{l-1} \int_{0,l} \chi_{k'i}{}^* (\partial V / \partial s_P) \chi_{kj} d\tau, \quad (3.26)$$

and also that

$$J_{2P}{}^{\pm}(1) = J_{2P}{}^{\pm}(2).$$

Thus, Eq. (3.15) becomes

$$\langle i, n \mp 1 | H_{2P} | j, n \rangle = (2\hbar^2 n'/\rho V K \Theta a_0{}^2)^{\frac{1}{2}} \langle i | F_4{}^P | j \rangle. \quad (3.27)$$

[15] Helen M. J. Smith, Trans. Roy. Soc. (London) A241, 105 (1948).

By applying symmetry arguments to Eqs. (3.18) through (3.21) we arrive at the following conclusions concerning transitions involving acoustical and optical phonons in the diamond lattice. From Eqs. (3.18) and (3.19) we observe that for a cubic lattice, without a basis, there is no coupling between current carriers and transverse phonons if the wave functions have s-symmetry. For carrier wave functions having p-symmetry, however, transverse phonons are effective in scattering. If we now consider the diamond lattice, the preceding statement still holds, but in addition the integrals (3.20) and (3.21) play a part in the transition amplitudes. Interestingly enough, however, these integrals vanish for carrier wave functions having s-symmetry. Thus, in a homopolar semiconductor having the diamond structure, it is impossible for optical modes to contribute to the same order in q if the band has s-symmetry and an extremum occurring at $k=0$. This suggests that a calculation of the temperature dependence of the mobility of n-type InSb, whose conduction band probably satisfies the preceding requirements, would yield an estimate of the polar character of this material, since our remarks concerning the effectiveness of optical modes do not apply to the electron-phonon interaction in polar materials.

In p-type germanium the valence band structure at $k=0$ permits transitions due to all types of phonons within as well as between the two bands degenerate at this point.

4. CALCULATION OF MATRIX ELEMENTS AND RELATED QUANTITIES

This section will develop the explicit quantum-mechanical results needed to calculate the lattice scattering terms of the Boltzmann equation. In addition to the approximations already made, we shall need three further assumptions if tractable expressions for the matrix elements are to be obtained. They are:

(1) The solid will be assumed elastically isotropic, so that longitudinal and transverse sound velocities will be independent of direction, but not necessarily equal to each other. The numerical values of the velocities to be taken as isotropic can be obtained from a suitably weighted average of the measured velocities over crystallographic directions. From these values it is possible to define average elastic constants $\bar{c}_{ij}$ by the relations

$$\bar{c}_{11} = \rho u_L{}^2, \quad \bar{c}_{44} = \rho u_T{}^2. \quad (4.1)$$

The third elastic constant $\bar{c}_{12}$ is determined from the relationship which holds in an elastically isotropic medium,

$$\bar{c}_{11} - \bar{c}_{12} = 2\bar{c}_{44}. \quad (4.2)$$

(2) The surfaces of constant hole energy in k-space will be taken to be spherical. This is achieved by defining a Shockley matrix involving averaged quantities $\bar{L}$, $\bar{M}$, and $\bar{N}$ which satisfy $\bar{N} = \bar{L} - \bar{M}$. In spirit, this approximation is the same as that involving the

elastic constants. In fact, Eq. (4.2) corresponds to precisely the same relationship, $N=L-M$, among the quantities (3.25). This approximation is easily seen to be justified since the warping of the actual energy surfaces is small in comparison to the radius of the best sphere with which one can replace the actual energy surfaces in k space. The energy of the degenerate bands can thus be written $E_s=\hbar^2k^2/2m_s$. The constants m_s are interpreted as the effective masses belonging to bands 1 and 2, and will be given their experimental values: $m_1=0.042$ and $m_2=0.33$ electron masses.

(3) In calculating $F_1{}^P$ and F_2, it will be assumed that ϵ_1, ϵ_2, ϵ_3 transform like x, y, and z, i.e., we shall replace ϵ_1, ϵ_2, and ϵ_3 by functions X, Y, and Z given by $X=xf(r)$, $Y=yf(r)$, $Z=zf(r)$, respectively. The functions $f(r)$, for a particular atomic cell, depend only on the distance r from the center of that cell. Furthermore each atomic cell will be assumed spherical. In effect a Wigner-Seitz approximation is made in treating the *atomic* cell. This manner of treating the wave functions cannot be used in calculating the matrix elements involving $F_3{}^P$ and $F_4{}^P$, since these latter quantities vanish in this approximation.

The first step in calculating the matrix elements consists of finding the polarization vectors $\hat{e}_P$. These are obtained by inserting approximation (1) into (3.23) and solving the resulting equation. Smith[15] shows that coefficients α, β, and μ are related to the elastic constants as follows:

$$2a_0\bar{c}_{11}=\alpha+8\mu,$$
$$2a_0\bar{c}_{44}=\alpha-\beta^2/\alpha+4\mu, \qquad (4.3)$$
$$2a_0\bar{c}_{12}=2\beta-\alpha+4\mu.$$

Use of (4.2) then shows that $\mu=(\beta/2)(\beta/\alpha-1)$ and from (3.25) it follows that $N=L-M$. The secular equation obtained from (3.23) yields the relationship $\omega_P=u_Pq$ between frequency and wave number. The solution for the eigenvectors is

$$\hat{e}_L=(1/q)\begin{bmatrix}q_x\\q_y\\q_z\end{bmatrix},$$

$$\hat{e}_{T1}=(q_x{}^2+q_y{}^2)^{-\frac{1}{2}}\begin{bmatrix}q_y\\-q_x\\0\end{bmatrix}, \qquad (4.4)$$

$$\hat{e}_{T2}=q^{-1}(q_x{}^2+q_y{}^2)^{-\frac{1}{2}}\begin{bmatrix}q_xq_z\\q_yq_z\\-(q_x{}^2+q_y{}^2)\end{bmatrix}.$$

In order to determine $\Delta\hat{\delta}_{1P}$ (to be abbreviated $\Delta\hat{\delta}_P$, since we do not need to consider $\Delta\hat{\delta}_{2P}$ in this treatment) from Eq. (3.25), one needs to know β/α. This is obtained from Eqs. (4.3) which are quadratic in α and β. The physically significant solutions give

$$\delta=\frac{\beta}{\alpha}=\frac{\bar{c}_{11}+2\bar{c}_{44}+3(\bar{c}_{11}\bar{c}_{44})^{\frac{1}{2}}}{\bar{c}_{11}+4\bar{c}_{44}+4(\bar{c}_{11}\bar{c}_{44})^{\frac{1}{2}}}. \qquad (4.5)$$

One finds, if the x, y, z axes are taken along the cubic axes of the crystal, that

$$\Delta\hat{\delta}_L=(\delta/q^2)\begin{bmatrix}q_yq_z\\q_xq_z\\q_xq_y\end{bmatrix},$$

$$\Delta\hat{\delta}_{T1}=(\delta/2q)(q_x{}^2+q_y{}^2)^{-\frac{1}{2}}\begin{bmatrix}-q_xq_z\\q_yq_z\\q_y{}^2-q_x{}^2\end{bmatrix}, \qquad (4.6)$$

$$\Delta\hat{\delta}_{T2}=(\delta/2q^2)(q_x{}^2+q_y{}^2)^{-\frac{1}{2}}\begin{bmatrix}q_y(q_z{}^2-q_x{}^2-q_y{}^2)\\q_x(q_z{}^2-q_x{}^2-q_y{}^2)\\2q_xq_yq_z\end{bmatrix}.$$

The quantities $\langle i|F_1{}^P|j\rangle$ defined by Eq. (3.18) may be evaluated by expressing the operators $(\partial/\partial s_P)$ and $(\partial/\partial s_a)$ in terms of $(\partial/\partial x)$, $(\partial/\partial y)$ and $(\partial/\partial z)$ with the help of Eq. (4.4) and by use of the wave functions (2.23). Of the matrix elements that arise in computing $\langle i|F_1{}^P|j\rangle$, only those of the following type do not vanish:

$$I_1=(\hbar^2/m)\langle\epsilon_1|(\partial/\partial x)(\partial/\partial x)|\epsilon_1\rangle_0,$$
$$I_2=(\hbar^2/m)\langle\epsilon_1|(\partial/\partial y)(\partial/\partial y)|\epsilon_1\rangle_0, \qquad (4.7)$$
$$I_3=(\hbar^2/m)\langle\epsilon_1|(\partial/\partial x)(\partial/\partial y)|\epsilon_2\rangle_0.$$

We have added a subscript 0 to indicate that the integral extends over a single unit cell rather than over all space. Furthermore, we have dropped the explicit dependence on the spins in the bra and ket vectors. We shall assume that the spins involved are always parallel, for only in this case are the quantities (4.7) nonvanishing. The matrix element $\langle i|F_1{}^P|j\rangle$ can thus be expressed in terms of three quantities, which must be considered undetermined since explicit knowledge of the wave functions is lacking. In order, however, to reduce the number of constants for the present purpose, we shall make approximation (3). With this approximation, it can be shown that

$$I_2=I_3, \qquad (4.8)$$

$$2I_3=I_1-I_2. \qquad (4.9)$$

We shall express the integrals (4.7) in terms of the single constant I_2 from which we can henceforth omit the subscript.

The matrix elements $\langle i|F_2|j\rangle$ can be expressed in terms of a single integral

$$C_2=\langle\epsilon_1|V(r)|\epsilon_1\rangle, \qquad (4.10)$$

which will also be treated with the help of approximation (3). This approximation, when considered in conjunction with (1) and (2), permits a choice of the x, y, z, coordinate axes along some arbitrary direction in the crystal, and not just along the cubic axes. Therefore, if the matrix elements depend only on the angle of scattering, and not on the azimuthal angle, it is possible to choose some convenient initial direction of propagation for the hole that is to emit or absorb a phonon.

The quantities $\langle i | F_3{}^P | j \rangle$, $\langle i | F_4{}^P | j \rangle$ can be written as functions of

$$C_3 = (\delta/2) a_0 \langle \epsilon_1 | \partial V / \partial z | \epsilon_2 \rangle_{1,0}, \quad C_4 = (2/\delta) C_3. \quad (4.11)$$

Since symmetry arguments, which depended on the condition that x, y, z coincide with the cubic axes of the crystal had to be used in obtaining the expressions (3.20) and (3.21) and since the quantities (4.11) vanish for spherical unit cells, it is necessary to retain the restriction on the orientation of the x, y, z, axes in the treatment of the scattering terms resulting from the relative motions of the two atoms in a unit cell. In this case, the matrix elements for scattering will therefore depend on the initial direction of propagation of the hole in question.

In evaluating $\langle i | F_1{}^P | j \rangle$ and $\langle i | F_2 | j \rangle$, we may take the initial direction of propagation along the z axis so that $k_x = k_y = 0$ and $k_z = k$.

The coefficients a_{ij} in Eq. (2.21) determine the wave functions corresponding to the initial state. These coefficients may be evaluated with the help of the relationships

$$c = (1/\sqrt{3}) N k_z (k_x{}^2 + k_y{}^2)^{\frac{1}{2}},$$
$$d = (1/2\sqrt{3}) N (k_x{}^2 + k_y{}^2),$$
$$E_1 - a = (1/6) N (k^2 + 3k_z{}^2),$$
$$\sin\theta = -k_y / (k_x{}^2 + k_y{}^2)^{\frac{1}{2}}, \quad (4.12)$$
$$\cos\theta = -k_x / (k_x{}^2 + k_y{}^2)^{\frac{1}{2}},$$
$$\sin\phi = -2k_x k_y / (k_x{}^2 + k_y{}^2),$$
$$\cos\phi = -(k_x{}^2 - k_y{}^2) / (k_x{}^2 + k_y{}^2),$$

which are obtained by using approximations (1) and (2) and Eqs. (2.11) and (2.19).

For this initial direction the quantities (4.12) simplify so that the matrix A of Eq. (2.21) for the *initial* wave functions, becomes

$$A = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & i & 0 \\ 0 & i & 1 & 0 \\ -1 & 0 & 0 & i \\ i & 0 & 0 & -1 \end{bmatrix}. \quad (4.13)$$

It is seen that a hole moving along the z direction in band 1 or 2 is described by a linear combination of the wave functions corresponding to $m_j = \pm\frac{1}{2}$ and $m_j = \pm\frac{3}{2}$, respectively. In forming the probability that a hole in a given band makes a transition to another state within that band or into the other band, we shall average over the initial degenerate states and sum over the final degenerate states. Instead of (4.13), one may take

$$A = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad (4.14)$$

and consider the elements of this matrix as giving the values of the a_{ij} to be used in calculating the matrix elements. The use of (4.14) corresponds only to a different choice of basis functions for treating the initial state.

The same matrix (4.14) will be used to determine the initial state wave functions for calculating $\langle i | F_3{}^P | j \rangle$ and $\langle i | F_4{}^P | j \rangle$. It is thereby assumed that initially the hole is propagating along a [100] direction. In the application to transport theory we shall assume these results to be representative as well of the scattering obtained from other initial directions.

The wave functions describing the final state of a hole propagating in the direction (k_x', k_y', k_z') depend on the a_{ij}' which can be obtained with the help of Eq. (4.12) if primes are added to the k_x, k_y, k_z. In transport theory one is interested in the probabilities, proportional to the absolute squares of the matrix elements, for transitions within and between bands.

The transition probability from band s to band r due to emission or absorption of an acoustical or optical phonon ($\mu = 1, 2$) of polarization P, obtained by averaging over the initial degenerate states and summing over the final degenerate states, is proportional to

$$W_\mu{}^P(r, n\mp 1; s, n)$$
$$= \tfrac{1}{2} \sum_{i(r)} \sum_{j(s)} |\langle i, n\mp 1 | H_{\mu P} | j, n \rangle|^2. \quad (4.15)$$

The notation $j(s)$, $i(r)$ means that we are to sum over the two degenerate states labeled by i and j belonging to bands r and s, respectively. It is seen from Eq. (2.17) that the values of i corresponding to $r = 1$ and 2 are 1, 2 and 3, 4, respectively, and similarly for the j corresponding to $s = 1$ and 2. Since $|\langle i, n\pm 1 | H_{\mu P} | j, n \rangle|^2$ for acoustical phonons is the same for emission and absorption, we can abbreviate the quantity defined by Eq. (4.15) as $W_1{}^P(r, s)$ for $\mu = 1$.

The total transition probability due to transverse phonons is equal to the sum of $W_\mu{}^{T_1}$ and $W_\mu{}^{T_2}$, and will be written

$$W_\mu{}^T = W_\mu{}^{T_1} + W_\mu{}^{T_2}.$$

We can show with Eq. (3.18) that $I = (2/5) C_1$, where C_1 is the kinetic energy at $\mathbf{k} = 0$ if we use the definition

$$C_1 = (\hbar^2/2m) \int_0 |\mathrm{grad}\chi_k|^2 d\tau.$$

C_1 can be considered as the coupling constant for acoustical modes. If we define

$$G_\alpha{}^P(r,s) = \tfrac{1}{2} \sum_{i(r)} \sum_{j(s)} |\langle i | F_\alpha{}^P | j \rangle|^2 / C_\alpha{}^2,$$
$$G_{\alpha\beta}{}^P(r,s) = \tfrac{1}{2} \sum_{i(r)} \sum_{j(s)} (\langle i | F_\alpha{}^P | j \rangle \langle j | F_\beta{}^P | i \rangle \quad (4.16)$$
$$+ \langle i | F_\beta{}^P | j \rangle \langle j | F_\alpha{}^P | i \rangle) / C_\alpha C_\beta,$$

then, from (3.22) and (4.15) we have for acoustical modes

$$W_1{}^P(r,s) = (kT/2u_P{}^2 \rho V) [C_1{}^2 G_1{}^P(r,s)$$
$$+ (1-\eta)^2 \delta_{LP} C_2{}^2 G_2(r,s) + C_3{}^2 G_3{}^P(r,s)$$
$$+ (1-\eta) \delta_{LP} C_1 C_2 G_{12}{}^P(r,s) + C_1 C_3 G_{13}{}^P(r,s)$$
$$+ (1-\eta) \delta_{LP} C_2 C_3 G_{23}{}^P(r,s)]. \quad (4.17)$$

In Eq. (4.17) the total contribution due to transverse modes has been written

$$G^T = G^{T_1} + G^{T_2}.$$

For optical modes,

$$W_2^P(r, n\pm 1; s, n) = (2\hbar^2 n'/\rho V K\Theta a_0^2) C_4^2 G_3^P(r,s). \quad (4.18)$$

The results of these calculations will be presented by giving explicit expressions for the $G_\alpha^P(r,s)$ and the $G_{\alpha\beta}^P(r,s)$. These expressions simplify considerably if one has introduced conservation of momentum and energy into the calculations since it is possible thereby to eliminate the explicit dependence on q. To distinguish between initial and final states in the two bands, we shall write the wave numbers as k_s and k_r', the subscripts s and r denoting that the hole is in band s before and in band r after having interacted with the phonon. Since $\hbar u_P q \ll KT$, for the temperature range where lattice scattering is the principal scattering mechanism, the equations giving conservation of energy for transitions between the bands by acoustical phonons are

$$\begin{aligned} k_2'^2 &= \alpha k_1^2, \quad (1\rightarrow 2), \\ k_1'^2 &= \alpha^{-1} k_2^2 \quad (2\rightarrow 1), \end{aligned} \quad (4.19)$$

where

$$\alpha = (m_2/m_1). \quad (4.20)$$

For scattering within a band

$$k_s'^2 = k_s^2 \quad (s = 1, 2). \quad (4.21)$$

In the case of optical phonons it is not legitimate to neglect the energy of the phonon in comparison to that of the hole. The principle of conservation of energy is therefore

$$(\hbar^2 k_r'^2/2m_r) = (\hbar^2 k_s^2/2m_s) \pm K\Theta, \quad (4.22)$$

the upper sign being associated with phonon absorption and the lower with emission.

The conditions for conservation of momentum are

$$\mathbf{k}_r' = \mathbf{k}_s \pm \mathbf{q} \quad (4.23)$$

for both acoustical and optical photons. By introducing a polar coordinate system with the polar angle β satisfying

$$\cos\beta = k_{rz}'/k_r' \quad (4.24)$$

and the convenient symbol

$$\sigma = 1 + \alpha - 2\alpha^{\frac{1}{2}} \cos\beta \quad (4.25)$$

the dependence on q can be eliminated.

If the matrix elements are to depend only on the angle of scattering, two further assumptions are necessary in treating those G_α^P and $G_{\alpha\beta}^P$ for which α or β is 3, since they depend on the azimuthal angle even when the initial state is chosen along a [100] direction. We can eliminate the dependence on azimuthal angle in the G_3^P by grouping the quantities corresponding to the three polarizations together into a single scattering term

$$\mathcal{G}_3^P(r,s) = \tfrac{1}{3}[G_3^L(r,s) + G_3^{T_1}(r,s) + G_3^{T_2}(r,s)]$$
$$= \tfrac{1}{3} G_3(r,s) \quad (4.26)$$

depending on an averaged sound velocity

$$\bar{u}^2 = \tfrac{1}{3} u_L^2 + \tfrac{2}{3} u_T^2. \quad (4.27)$$

For the sake of convenience in the application to transport theory, we have divided this resultant scattering term equally among the three polarizations.

We shall neglect those interference terms $G_{\alpha\beta}^P$ for which either α or β is 3. This means that we are ignoring the interference between the term $\delta_{\mu P}$ and the other acoustical terms, and are thereby considering $\mathcal{G}_3^P$ as an independent scattering process. We shall estimate the effect of these neglected terms on the mobility in a subsequent paper. The results for the quantities $G_\alpha^P(r,s)$ and $G_{\alpha\beta}^P(r,s)$ considered in this treatment are:

$$G_1^L(1,1) = (4/25)[(29/18) - (11/6) \cos\beta + 2\cos^2\beta],$$
$$G_1^L(2,2) = (4/25)[(1/2) + (3/2) \cos\beta + 2\cos^2\beta],$$
$$\begin{aligned} G_1^L(1,2) = (4/25)[(7/4) + (7/3\sigma) - (\alpha/\sigma) \\ - (\alpha/\sigma^2) \sin^2\beta] \sin^2\beta. \end{aligned} \quad (4.28)$$

$$G_1^T(1,1) = G_1^T(2,2) = (1/25) \sin^2\beta,$$
$$\begin{aligned} G_1^T(1,2) = (4/25)[(2/3) - \{(\alpha+1)/2\sigma\} \sin^2\beta \\ + (\alpha/\sigma^2) \sin^4\beta]. \end{aligned} \quad (4.29)$$

$$G_2(1,1) = G_2(2,2) = (1/4)(1 + 3\cos^2\beta),$$
$$G_2(1,2) = (3/4) \sin^2\beta. \quad (4.30)$$

$$G_{12}(1,1) = (2/5)[(7/6) - \cos\beta + (5/2) \cos^2\beta],$$
$$G_{12}(2,2) = (2/5)[(1/2) + \cos\beta + (5/2) \cos^2\beta], \quad (4.31)$$
$$G_{12}(1,2) = (2/5) \sin^2\beta[(5/2) + (1-\alpha)/\sigma].$$

$$G_3(1,1) = G_3(2,2) = (1/2) \sin^2\beta,$$
$$G_3(1,2) = (1/6)(1 + 3\cos^2\beta). \quad (4.32)$$

$$G_4^L(r,s) = (1/2) G_3(r,s). \quad (4.33)$$

$$G_4^T(r,s) = G_3(r,s). \quad (4.34)$$

It is a consequence of the dependence of the G's on scattering angle only, and also of the hermiticity of the Hamiltonian matrix, that $G_\alpha^P(r,s) = G_\alpha^P(s,r)$, if we take the left-hand side to refer to a transition from k_s to k_r' and the right-hand side to a transition from k_r to k_s', the initial directions in each case being taken along the z axis.

To facilitate application of the preceding results to transport theory we shall define quantities $\mathcal{W}_\nu^P(r,s)$, such that the probability of a transition from band s to band r due to one of the scattering processes considered here (denoted by the index ν), is

$$(2\pi/\hbar) \mathcal{W}_\nu^P(r,s) \rho_r, \quad (4.35)$$

where ρ_r is the density of states in band r.

Since we have neglected the interference between terms in C_1 and C_4 we may write Eq. (4.17) in the form

$$W_1^P(r,s) = \mathcal{W}_1^P(r,s) + \mathcal{W}_3^P(r,s), \quad (4.36)$$

where

$$\mathcal{W}_1{}^P(r,s) = (KT/2u_P{}^2\rho V)[C_1{}^2G_1{}^P(r,s)$$
$$+ (1-\eta)C_1C_2\delta_{LP}G_{12}{}^P(r,s)$$
$$+ (1-\eta)^2C_2{}^2\delta_{LP}G_2(r,s)], \quad (4.37)$$

and

$$\mathcal{W}_3{}^P(r,s) = (KT/2\bar{u}^2\rho V)C_3{}^2\mathcal{G}_3{}^P(r,s). \quad (4.38)$$

In order to treat the DI and RI models simultaneously in the transport calculations, we shall introduce a parameter

$$\zeta = (1-\eta)(C_2/C_1), \quad (4.39)$$

and also

$$\mathcal{G}_1{}^P(r,s;\eta) = G_1{}^P(r,s) + \zeta\delta_{LP}G_{12}{}^P(r,s)$$
$$+ \zeta^2\delta_{LP}G_2(r,s), \quad (4.40)$$

so that we may write more simply

$$\mathcal{W}_1{}^P(r,s) \equiv \mathcal{W}_1{}^P(r,s;\eta)$$
$$= C_1{}^2(KT/2u_P{}^2\rho V)\mathcal{G}_1{}^P(r,s;\eta). \quad (4.41)$$

We have here introduced explicitly the dependence on η. To obtain a consistent notation we shall also put $W_2{}^P = \mathcal{W}_2{}^P$, and $G_4{}^P = \mathcal{G}_2{}^P$.

We shall now examine the dependence of the $\mathcal{W}_\nu{}^P(r,s)$ on scattering angle. This is of interest, since the transition probabilities are related to $\mathcal{W}_\nu{}^P(r,s)$ through Eq. (4.35). It should be noted, however, that in discussing $\mathcal{W}_\nu{}^P(r,s)$ as a measure of the amount of scattering taking place, we are leaving ρ_r out of consideration. This quantity bears considerable weight in determining the importance of a given scattering process, since the density of states is so different in the two bands.

Let us first consider the effects of $\mathcal{W}_1{}^P(r,s)$ alone. This corresponds to the assumption that $C_3 = C_4 = 0$, which would be the case if there were only one atom per unit cell. The terms involved are analogous to the expressions used to describe lattice-scattering in the theory of monovalent metals[12,13] for nondegenerate conduction bands whose wave functions have s symmetry. In the present treatment these terms, besides taking into account the correct zeroth order wave functions for the germanium valence bands, have been dealt with somewhat more generally in that a quantity η has been introduced which gives the results for the RI and DI models in the limiting cases $\eta = 0$ and 1 respectively.

In order to compare the two models one would like to have an explicit value for the ζ of Eq. (4.39). A rough value of ζ can be obtained by use of the virial theorem which relates the average potential energy C_2 to the kinetic energy C_1. Thus,

$$2C_1 \approx -C_2. \quad (4.42)$$

For purposes of comparison it is advantageous to express $\mathcal{W}_1{}^P$ in dimensionless units by taking the ratio of $\mathcal{W}_1{}^P$ to the expression for the absolute square of the matrix element obtained by Sommerfeld and Bethe.[12] Their calculation uses the DI model and shows that

for a single nondegenerate s band the scattering is isotropic and the electrons are coupled only to the longitudinal phonons. The matrix element is

$$\langle k'|H^P|k\rangle = \pm (2/3)iC_1q\delta_{LP}(\hbar n'/2\rho V\omega_q)^{\frac{1}{2}} \quad (4.43)$$

and the quantity with which we wish to compare $\mathcal{W}_1{}^P$ as given by (4.40) may be written

$$W_0 \equiv |\langle k'|H^L|k\rangle|^2 = (2C_1/3)^2(KT/2\rho Vu_L{}^2). \quad (4.44)$$

The results are shown in Figs. 1 and 2. In Fig. 1 the curves giving $\mathcal{W}_1{}^P(r,s)$ as a function of scattering angle β computed from the DI model are shown for transitions due to longitudinal and transverse acoustical phonons within as well as between bands 1 and 2. One observes that longitudinal phonons influence scattering within a given band more than transverse phonons, whereas both types are equally important in the scattering between bands. Further, one notes that the light holes are predominantly scattered backwards, whereas the heavy holes are scattered forward. Figure 2 compares the results for longitudinal modes obtained from the DI and RI models. The two models give the same contribution for transverse modes. It is seen that the relative importance of longitudinal modes compared to transverse modes is much greater for the RI model. In addition, the angular dependence of the intraband scattering obtained from the RI model is opposite to that of the DI model: the light holes are now predominantly scattered forward, and heavy holes backward.

The probability for interband transitions is influenced heavily by the density of final states. Thus, in referring to Fig. 1, it should be remembered that the probability
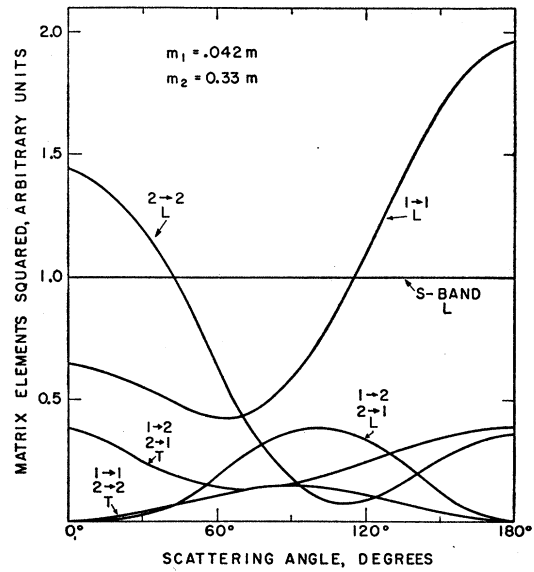

FIG. 1. Matrix elements squared, in arbitrary units, *versus* scattering angle for scattering of holes by longitudinal (L) and transverse (T) phonons, according to the DI model, within and between bands 1 and 2. The horizontal line at 1 represents the spherically symmetric angular distribution for scattering of holes, having s-symmetric wave functions, by longitudinal photons.
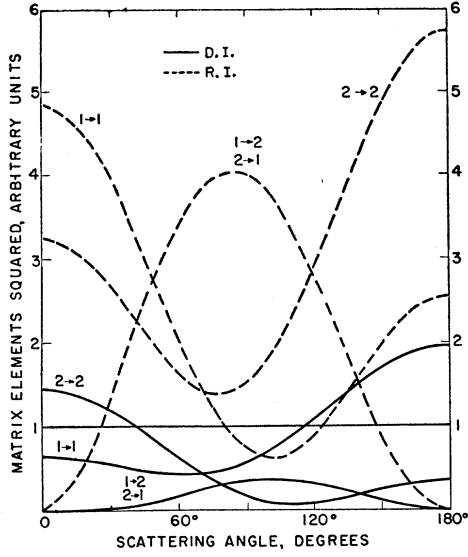
FIG. 2. Matrix elements squared, in arbitrary units, *versus* scattering angle for scattering of holes by longitudinal phonons within and between bands 1 and 2 according to the DI and RI models. Solid curves correspond to the DI model and dashed curves to the RI model. The horizontal line has the same significance as in Fig. 1.

of a transition, say, from band 1 to band 2 produced by a transverse phonon compared to that for a transition within band 1 produced by a longitudinal phonon is larger by a factor of 20 than one would suppose from the graph. Interband scattering therefore plays an important role in transport processes.

Turning now to the angular dependence of the terms involving C_3 and C_4, we see from Eqs. (4.18), (4.38) and (4.32)–(4.34) that it is the same for the terms $\mathcal{W}_2{}^P(r,s)$ and $\mathcal{W}_3{}^P(r,s)$. We note that the scattering is symmetric about $\beta=90°$, and is maximum in the forward and backward directions for interband scattering and zero in these directions for intraband scattering. It should be noted that the angular distributions would be more complicated had we not chosen the initial state along a [100] direction. In each case, transverse modes are twice as effective as longitudinal modes. The relative importance of these terms and $\mathcal{W}_1{}^P(r,s)$ depends on the ratio (C_4/C_1).

These results have been applied to the transport properties of p-type germanium. The calculation of the hole mobility is the subject of a subsequent paper.

5. ACKNOWLEDGMENTS

APPENDIX

We shall show how Eq. (3.15) may be simplified if the atomic potential is of sufficiently short range that $V(r)=U(r)$ for r in the atomic cell 0_1.

From Eqs. (3.8) and (3.13) it follows that

$$J_{1P}{}^\pm(1)+J_{1P}{}^\pm(2)=\int_0 \chi_{k'i}{}^*[\hat{e}_P(0)\cdot\sum_{gl,l}\nabla U(\mathbf{r}+\mathbf{g}_l)$$

$$\times\exp[\pm i(\eta-1)\mathbf{q}\cdot(\mathbf{r}+\mathbf{g}_l)]]\chi_{kj}d\tau$$

$$\pm iqa_0\sum_{l'=1,2}\int_{0,l'}\chi_{k'i}{}^*[\sum_{gl,l}\hat{\delta}_{1P}(l)\cdot\nabla U(\mathbf{r}+\mathbf{g}_l)$$

$$\times\exp[\pm i(\eta-1)\mathbf{q}\cdot(\mathbf{r}+\mathbf{g}_l)]]\chi_{kj}d\tau.$$

We shall not need to make the approximation concerning the range of $U(r)$ in the first term in an expansion to lowest order in q only. Integrating this term by parts yields

$$-\int_0\sum_{gl,l}U(\mathbf{r}+\mathbf{g}_l)\frac{\partial}{\partial s_P}$$

$$\times\{\chi_{k'i}{}^*\chi_{kj}\exp[\pm i(\eta-1)\mathbf{q}\cdot(\mathbf{r}+\mathbf{g}_l)]\}d\tau.$$

The surface terms vanish because of the periodicity of the integrand. We carry out the indicated differentiation and then set $\exp[\pm i(\eta-1)\mathbf{q}\cdot(\mathbf{r}+\mathbf{g}_l)]=1$, since further terms in the series will correspond to higher order terms in q. Using the following identity, proved by Sommerfeld and Bethe,[12]

$$-\int_0 V(r)(\partial/\partial s_P)(\chi_{k'i}{}^*\chi_{kj})d\tau$$

$$=\pm(\hbar^2iq/m)\int_0(\partial\chi_{k'i}{}^*/\partial s_P)(\partial\chi_{kj}/\partial s_q)d\tau$$

and Eq. (3.3), we find, without further approximation, that the first term becomes

$$\pm(i\hbar^2q/m)\int_0(\partial\chi_{k'i}{}^*/\partial s_P)(\partial\chi_{kj}/\partial s_q)d\tau$$

$$\pm i(1-\eta)\delta_{LP}q\int_0\chi_{k'i}{}^*\chi_{kj}V(r)d\tau.$$

If the range of $U(r)$ is limited in the way already described, then the second term becomes

$$\pm iqa_0\sum_{l=1,2}\int_{0,l}\chi_{k'i}{}^*\hat{\delta}_{1P}(l)\cdot\nabla U(r)e^{\pm i(\eta-1)\mathbf{q}\cdot\mathbf{r}}\chi_{kj}d\tau.$$

We observe from the behavior of $\chi_{k'i}$ and χ_{kj} for $k=k'\approx0$ and ∇ under the symmetry operation of the germanium lattice in which a nonprimitive translation $a_0(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is followed by an inversion, that

$$\int_{0,2}\chi_{k'i}{}^*\hat{\delta}_{1P}(l)\cdot\nabla V\chi_{kj}d\tau=-\int_{0,1}\chi_{k'i}{}^*\hat{\delta}_{1P}(l)\cdot\nabla V\chi_{kj}d\tau.$$

Then to lowest order in q, this term may be written

$$\pm iqa_0\int_{0,1}\chi_{k'i}{}^*\Delta\hat{\delta}_{1P}\cdot\nabla V\chi_{kj}d\tau.$$

Insertion of the definitions (3.18)–(3.21) yields

$$J_{1P}{}^\pm(1)+J_{1P}{}^\pm(2)=\pm iq(\langle i|F_1{}^P|j\rangle$$

$$+(1-\eta)\delta_{LP}\langle i|F_2|j\rangle+\langle i|F_3{}^P|j\rangle).$$