ENERGY BAND STRUCTURE IN *P*-TYPE GERMANIUM AND SILICON

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Abstract—Energy-band calculations are made for the three valence bands in silicon and germanium in terms of the cyclotron resonance parameters. The energy in the band measured from $k = 0$ is not assumed small compared to the spin-orbit splitting so that parabolic bands do not result. The above calculation results from considering the first term of a perturbation expansion of the $k \cdot p$ and spin-orbit perturbations. The contributions from higher-order terms are examined and found to be important for germanium but not for silicon. Matrix elements for direct optical transitions between the valence bands are calculated from the cyclotron resonance constants. The free-carrier absorption is computed from the present band-structure calculations, and comparison is made with recent experimental data of R. NEWMAN for germanium. A correction to the split-off valence-band calculations is estimated, using the experimental data. Formulae are derived for degenerate perturbation theory with two perturbations of different orders acting.

1. INTRODUCTION

CONSIDERABLE progress has been made recently in understanding the band structure of silicon and germanium. This progress has resulted chiefly from cyclotron resonance measurements[1, 2, 3] and free-carrier absorption[4, 5] measurements. The theoretical discussion of degenerate bands near an energy extremum has been given by SHOCKLEY[6]. SHOCKLEY'S treatment has been extended to include the effects of spin-orbit coupling by DRESSELHAUS and others[1, 7, 8]. The analysis of free-carrier absorption in *p*-germanium by KAHN[9] has confirmed the interpretation of cyclotron resonance measurements and determined the spin-orbit splitting of the valence bands.

The general second-order perturbation equation for the energy bands including spin-orbit splitting has been given as a sixth-order determinant by DRESSELHAUS, KIP and KITTEL[1]. Explicit expressions for the energy bands have only been given for the case where the spin-orbit splitting is large compared to the energy in *k*-space measured from $k = 0$. KAHN'S[9] analysis also makes this approximation. In the present paper, the general secular equation is explicitly written as a cubic equation in Section 2. Numerical calculations are made for specific directions in silicon and germanium.

The sixth-order secular equation of reference one is derived as the leading term of a perturbation expansion of two perturbations of different orders. General expressions for the fourth-order terms are obtained in the appendix and are used in Section 3 to estimate the accuracy of the energies obtained from the leading term.

Matrix elements for direct optical transitions between the valence bands are calculated in Section 4 from the cyclotron resonance constants. The free carrier absorption is computed in Section 5 from the present band-structure calculations and comparison is made to recent experimental data of R. NEWMAN[10].

Many references will be made in this paper to the work of DRESSELHAUS, KIP and KITTEL[1]. Subsequently this paper will be referred to as DKK.

2. BAND STRUCTURE

The holes in the valence band of germanium and silicon are now known to possess wave functions which are in many respects similar to atomic *p* functions and may be thought to arise from such functions as we decrease the lattice constant of a fictitious germanium crystal from infinity to the actual value. The overlap of the individual atomic

p functions is, of course, large at the actual lattice constant and a very considerable modification of the atomic wave function naturally results so that the atomic approximation must not be taken too literally.

The holes of minimum energy lie at $k = 0$ in the Brillouin zone and in the absence of spin-orbit splitting would be six-fold degenerate, corresponding to the three *p* functions times the two spin functions, spin up and spin down. Spin-orbit splitting partially removes this degeneracy by lowering the two $j = 1/2$ bands with respect to the four $j = 3/2$ bands.

SHOCKLEY[6] derives the form of the energy surfaces in the neighborhood of $k = 0$ by a perturbation approach. In a periodic lattice the one electron wave functions can always be written as the well-known Bloch functions.

$$\psi_k = e^{ik \cdot r} u_k(r) \tag{1}$$

where $u_k(r)$ is cell periodic. The Schroedinger equation can then be written

$$[(p^2/2m) + V + (\hbar/m)k \cdot p] u_k(r)$$
$$= \{E_k - (\hbar^2/2m)k^2\} u_k(r). \tag{2}$$

The term $(\hbar/m)k \cdot p$ is treated as a perturbation for determining u_k and E_k in the vicinity of $k = 0$ in terms of the complete set of cell periodic wave functions and energy eigenvalues at $k = 0$, which are assumed known. It is convenient to define an eigenvalue E'_k to simplify the form of eq. (2).

$$E'_k = E_k - (\hbar^2/2m)k^2. \tag{3}$$

In a lattice such as the diamond lattice where the inversion is a symmetry operation, the first-order matrix elements of the $k \cdot p$ perturbation vanish when the zero-order wave functions are taken at $k = 0$. If the band at $k = 0$ is nondegenerate, the surfaces of constant energy are spherical and the energy varies parabolically with the magnitude of k. If the band is degenerate at $k = 0$, the surfaces of constant energy may have more complicated shapes. The energy will still vary parabolically with the magnitude of k along a given direction in k space. SHOCKLEY[6] has analysed the form of the energy surfaces for cubic crystals using degenerate second-order perturbation theory. We repeat his derivation in more detail.

Consider a complete orthonormal set $|u_{Ji}\rangle$ of cell-periodic wave functions at $k = 0$ where J indexes different energies and i refers to degenerate functions for a given energy. The degenerate functions $|u_{Ji}\rangle$ for a given energy define a finite vector space where the vector c whose components are $c_1, c_2, \ldots c_n$ represents the function $[c_1 u_{Ji} + c_2 u_{J2} + \ldots c_n u_{Jn}]$. Then the second-order energies and the correct zeroth-order wave functions are found by determining the eigenvalues and eigenvectors of the finite matrix equation

$$H_{kp} c = E'_k c \tag{4}$$

where the elements of H_{kp} are given by

$$\langle u_{Ji} | \mathcal{H}_{kp} | u_{Jk} \rangle$$
$$= \sum_{L,n}' \frac{\langle u_{Ji} | (\hbar/m)k \cdot p | u_{Ln} \rangle \langle u_{Ln} | (\hbar/m)k \cdot p | u_{Jk} \rangle}{E_J - E_L} \tag{5}$$

The prime on the summation means that the term $L = J$ is excluded. The eigenvalue E'_k is related to the actual energy E_k by the definition (3).

The valence band wave functions at $k = 0$ in germanium and silicon transform according to the representation ϵ^+ in the notation of *DKK*. With respect to the basis functions $|\epsilon_1^+\rangle$, $|\epsilon_2^+\rangle$, $|\epsilon_3^+\rangle$ the Hamiltonian of eq. (4) may be written

$$H_{kp} =$$
$$\begin{bmatrix} Lk_x^2 + M(k_y^2 + k_z^2) & Nk_x k_y & Nk_x k_z \\ Nk_x k_y & Lk_y^2 + M(k_x^2 + k_z^2) & Nk_y k_z \\ Nk_x k_z & Nk_y k_z & Lk_z^2 + M(k_x^2 + k_y^2) \end{bmatrix}$$
$$\tag{6}$$

Symmetry arguments have been used to replace the sums over matrix elements in eq. (5) by the three constants L, M, and N. The quantities L, M, and N can be determined from cyclotron resonance measurements as discussed by DKK. Two sign ambiguities give four possible sets of L, M, N of which the two with positive N are easily discarded. In germanium the choice between the two remaining sets seems clearly to be the set selected by DKK. For silicon at the present time an ambiguity remains, although DKK state a preference.

The effects of spin-orbit coupling are most easily considered by regarding the spin orbit coupling interaction energy $\mathcal{H}_{so}$ as a perturbation.

$$\mathcal{H}_{so} = (\hbar/4m^2c^2)[\nabla V \times p] \cdot \sigma. \tag{7}$$

In the form of eq. (7) $\mathcal{H}_{so}$ is an operator on the Bloch function ψ_k. It can also be written in the following form as an operator on the cell periodic function u_k

$$\mathcal{H}'_{so} = (\hbar/4m^2c^2)[\nabla V \times p] \cdot \sigma +$$
$$+ (\hbar^2/4m^2c^2)[\nabla V \times k] \cdot \sigma. \tag{8}$$

The first term is k independent and is analogous to the atomic spin-orbit splitting term. The second term is proportional to k and is the additional spin-orbit energy

coming from the crystal momentum. Rough estimates indicate that the effect of the second term on the energy bands is less than 1 per cent of the effect of the $(\mathbf{k}\cdot\mathbf{p})$ terms. The relatively greater importance of the first term comes essentially from the fact that the velocity of the electron in its atomic orbit is very much greater than the velocity of a wave packet made up of wave vectors in the neighbourhood of k. In subsequent discussion the k-dependent spin-orbit term will be neglected.

When spin-orbit effects are considered we take as our degenerate basis functions $|\epsilon_1{}^+\uparrow\rangle, |\epsilon_2{}^+\uparrow\rangle, |\epsilon_3{}^+\uparrow\rangle, |\epsilon_1{}^+\downarrow\rangle,$ $|\epsilon_2{}^+\downarrow\rangle, |\epsilon_3{}^+\downarrow\rangle$; where $\uparrow$ and $\downarrow$ designate the spin functions spin-up and spin-down or $\binom{1}{0}$ and $\binom{0}{1}$. The Hamiltonian of eq. (4) then becomes a 6×6 matrix which may be written schematically

$$\begin{bmatrix} H_{kp} & 0 \\ 0 & H_{kp} \end{bmatrix}$$

where H_{kp} is the 3×3 matrix of eq. (6). In this representation the k-independent spin-orbit perturbation has the form

$$H_{so} = -\frac{\Delta}{3}\begin{bmatrix} 0 & i & 0 & 0 & 0 & -1 \\ -i & 0 & 0 & 0 & 0 & i \\ 0 & 0 & 0 & 1 & -i & 0 \\ 0 & 0 & 1 & 0 & -i & 0 \\ 0 & 0 & i & i & 0 & 0 \\ -1 & -i & 0 & 0 & 0 & 0 \end{bmatrix}$$

(9)

The symmetry properties of the matrix elements permit one to express all matrix elements in terms of a single constant Δ, the spin-orbit splitting. If we think of a fictitious germanium crystal in which we vary the lattice constant, the spin-orbit interaction Hamiltonian will only change through the multiplicative constant Δ. It is to be expected that in the tight-binding limit the spin-orbit Hamiltonian will be diagonalized by transforming to the Jm_j representation. Since the diagonalization is not affected by the value of Δ, the same transformation will diagonalize the spin-orbit interaction even though tight-binding is not a good approximation. The Jm_j transformation matrix is

$$U =$$

$$\begin{bmatrix} -1/(2)^{\frac12} & 0 & 0 & 0 & 1/(6)^{\frac12} & 1/(3)^{\frac12} \\ -i/(2)^{\frac12} & 0 & 0 & 0 & -i/(6)^{\frac12} & -i/(3)^{\frac12} \\ 0 & (2/3)^{\frac12} & -1/(3)^{\frac12} & 0 & 0 & 0 \\ 0 & -1/(6)^{\frac12} & -1/(3)^{\frac12} & -1/(2)^{\frac12} & 0 & 0 \\ 0 & -i/(6)^{\frac12} & -i/(3)^{\frac12} & i/(2)^{\frac12} & 0 & 0 \\ 0 & 0 & 0 & 0 & (2/3)^{\frac12} & -1/(3)^{\frac12} \end{bmatrix}$$

(10)

The transformed matrix is

$$H'_{so} = U^{-1}H_{so}U$$

$$H'_{so} = \begin{bmatrix} \Delta/3 & 0 & 0 & 0 & 0 & 0 \\ 0 & \Delta/3 & 0 & 0 & 0 & 0 \\ 0 & 0 & -2\Delta/3 & 0 & 0 & 0 \\ 0 & 0 & 0 & \Delta/3 & 0 & 0 \\ 0 & 0 & 0 & 0 & \Delta/3 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2\Delta/3 \end{bmatrix}$$

(11)

The new basis functions φ_i are given in terms of the old basis function ϵ_j by the relation

$$\phi_i = \sum_{j=1}^{6} U_{ji}\epsilon_j.$$

(12)

The phases chosen for the Jm_j functions are not the conventional phases but have been selected to simplify the form of the Hamiltonian in the light of subsequent discussion. The ordering of wave functions implicit in the matrix (10) is

$$|j=3/2; m=3/2\rangle, |j=3/2; m=1/2\rangle,$$
$$|j=1/2; m=1/2\rangle, |j=3/2; m=-3/2\rangle,$$
$$|j=3/2; m=-1/2\rangle, |j=1/2; m=-1/2\rangle.$$

A theorem due to KRAMERS states that for any odd electron system in the absence of an external magnetic field all levels are necessarily doubly degenerate. The proof for a one-electron system consists in showing that the operator

$$K = -i\sigma_y C$$

(13)

commutes with the Hamiltonian including spin-orbit interactions and has the property that $K^2 = -1$. (C is the complex conjugation operator, σ_y is the spin operator $\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$. The assumption $K\psi = a\psi$ then leads to $K^2\psi = a^*a\psi = -\psi$ which is a contradiction. Therefore every state is at least doubly degenerate. When KRAMERS' operator is applied to the Bloch functions of a crystal it leads to the results that wave functions with k and $-k$ are degenerate even when the crystal does not possess inversion symmetry. If the crystal does possess inversion symmetry we consider the operator

$$\mathcal{K} = -i\sigma_y C J$$

(14)

where J is the inversion. (For the diamond lattice J is to be replaced by $(\tau|J)$ where τ is the nonprimitive translation (1/4, 1/4, 1/4). This operator also commutes with the Hamiltonian and has the property $\mathcal{K}^2 = -1$. Furthermore the $\mathcal{K}$ operator leaves $e^{ik\cdot r}$ invariant so that in this case the bands are doubly degenerate. It is

easily seen that $\psi = \begin{bmatrix} W_a \\ W_b \end{bmatrix}$ and $K\psi = \begin{bmatrix} W_b{}^* \\ -W_a{}^* \end{bmatrix}$ are always orthogonal, also $\mathcal{K}\psi$ is normalized if ψ is normalized. If ψ_2 is chosen orthogonal to both ψ_1 and $\mathcal{K}\psi_1$, it is easily seen that $\mathcal{K}\psi_2$ will also be orthogonal to both ψ_1 and $\mathcal{K}\psi_1$. Hence it is always possible to choose a basis of the form $|\psi_1\rangle, |\psi_2\rangle, |\psi_3\rangle, |\mathcal{K}\psi_1\rangle, |\mathcal{K}\psi_2\rangle, |\mathcal{K}\psi_3\rangle$. We note the following identities

$$\langle \mathcal{K}\psi_i | \mathcal{K}\psi_j \rangle = \langle \psi_i | \psi_j \rangle^* \tag{15}$$

$$\langle \mathcal{K}\psi_i | \mathcal{H} | \mathcal{K}\psi_j \rangle = \langle \psi_i | \mathcal{H} | \psi_j \rangle^* \tag{16}$$

$$\langle \psi_i | \mathcal{H} | \mathcal{K}\psi_j \rangle = - \langle \psi_j | \mathcal{H} | \mathcal{K}\psi_i \rangle. \tag{17}$$

As a consequence of these identities the Hamiltonian matrix will take the following form when referred to a Kramers' basis

$$H = \begin{bmatrix} G & \Gamma \\ -\Gamma^* & G^* \end{bmatrix} \tag{18}$$

where Γ has the property $\Gamma^\mathsf{T} = -\Gamma$. In the present 6-dimensional case Γ has the form

$$\Gamma = \begin{bmatrix} 0 & \gamma_1 & \gamma_2 \\ -\gamma_1 & 0 & \gamma_3 \\ -\gamma_2 & -\gamma_3 & 0 \end{bmatrix} \tag{19}$$

The unitary transformation matrix from one Kramers' basis to another has the form

$$U = \begin{bmatrix} S & R \\ -R^* & S^* \end{bmatrix} \tag{20}$$

where $H' = U^{-1}HU$. We will use the standard forms (18) and (20) in order to write 6×6 matrices as two 3×3 matrices. The transformation matrix (10) has the standard form (20). The $\pm m$ values for a given j are Kramers degenerate. This result follows from the fact that Kramers' operator $-i\sigma_y \mathcal{C}$ is a time reversal operator.

We write the 6×6 $k \cdot p$ Hamiltonian corresponding to eq. (6) in the Jm_j representation. The total Hamiltonian is then the sum of the $k \cdot p$ Hamiltonian and the spin-orbit Hamiltonian of eq. (11). The zero of energy is taken at the top of the valence band so that $\Delta/3$ must be subtracted from the spin-orbit Hamiltonian. The total Hamiltonian is

$$G =$$
$$\begin{bmatrix} \dfrac{H_{11}+H_{22}}{2} & \dfrac{-H_{13}+iH_{23}}{(3)^{\frac{1}{2}}} & \dfrac{H_{13}-iH_{23}}{(6)^{\frac{1}{2}}} \\[2ex] \dfrac{-H_{13}-iH_{23}}{(3)^{\frac{1}{2}}} & \dfrac{H_{11}+H_{22}+4H_{33}}{6} & \dfrac{H_{11}+H_{22}-2H_{33}}{3(2)^{\frac{1}{2}}} \\[2ex] \dfrac{H_{13}+iH_{23}}{(6)^{\frac{1}{2}}} & \dfrac{H_{11}+H_{22}-2H_{33}}{3(2)^{\frac{1}{2}}} & \dfrac{H_{11}+H_{22}+H_{33}}{3}-\Delta \end{bmatrix} \tag{21}$$

$$\Gamma =$$
$$\begin{bmatrix} 0 & \dfrac{-H_{11}+H_{22}+2iH_{12}}{2(3)^{\frac{1}{2}}} & \dfrac{-H_{11}+H_{22}+2i\overline{H_{12}}}{(6)^{\frac{1}{2}}} \\[2ex] \dfrac{H_{11}-H_{22}-2iH_{12}}{2(3)^{\frac{1}{2}}} & 0 & \dfrac{H_{13}-iH_{23}}{(2)^{\frac{1}{2}}} \\[2ex] \dfrac{H_{11}-H_{22}-2iH_{12}}{(6)^{\frac{1}{2}}} & \dfrac{-H_{13}+iH_{23}}{(2)^{\frac{1}{2}}} & 0 \end{bmatrix} \tag{22}$$

The symbols H_{ij} refer to the elements of the matrix given in eq. (6).
We make the definitions

$$Xe^{i\chi} = -H_{11}+H_{22}+2iH_{12} \tag{23}$$

$$Ye^{i\eta} = H_{13}-iH_{23} \tag{24}$$

$$Z = H_{11}+H_{22}-2H_{33}. \tag{25}$$

The number of nonzero terms in Γ can be reduced by making the following unitary transformation

$$S_1 = \frac{1}{(2)^{\frac{1}{2}}}$$
$$\begin{bmatrix} \exp i\left[\dfrac{\chi+\eta}{2}-\dfrac{\pi}{4}\right] & 0 & 0 \\[2ex] 0 & \exp i\left[\dfrac{\chi-\eta}{2}-\dfrac{\pi}{4}\right] & 0 \\[2ex] 0 & 0 & \exp i\left[\dfrac{\chi-\eta}{2}-\dfrac{\pi}{4}\right] \end{bmatrix} \tag{26}$$

$$R_1 = \frac{1}{(2)^{\frac{1}{2}}}$$
$$\begin{bmatrix} -\exp i\left[\dfrac{\chi+\eta}{2}-\dfrac{\pi}{4}\right] & 0 & 0 \\[2ex] 0 & -\exp i\left[\dfrac{\chi-\eta}{2}-\dfrac{\pi}{4}\right] & 0 \\[2ex] 0 & 0 & -\exp i\left[\dfrac{\chi-\eta}{2}-\dfrac{\pi}{4}\right] \end{bmatrix} \tag{27}$$

The transformed Hamiltonian then becomes

$G' =$

$$
\begin{bmatrix}
\dfrac{H_{11}+H_{22}}{2} & \dfrac{-Y+iX/2}{(3)^{\frac{1}{2}}} & \dfrac{Y+iX}{(6)^{\frac{1}{2}}} \\[2ex]
\dfrac{Y-iX/2}{(3)^{\frac{1}{2}}} & \dfrac{H_{11}+H_{22}+4H_{33}}{6} & \dfrac{(Z/3)+iY\cos(\chi-2\eta)}{(2)^{\frac{1}{2}}} \\[2ex]
\dfrac{Y-iX}{(6)^{\frac{1}{2}}} & \dfrac{(Z/3)-iY\cos(\chi-2\eta)}{(2)^{\frac{1}{2}}} & \dfrac{H_{11}+H_{22}+H_{33}}{3}-\Delta
\end{bmatrix}
$$

$$\tag{28}$$

$$
\Gamma' =
\begin{bmatrix}
0 & 0 & 0 \\[2ex]
0 & 0 & \dfrac{Y\sin(\chi-2\eta)}{(2)^{\frac{1}{2}}} \\[2ex]
0 & \dfrac{-Y\sin(\chi-2\eta)}{(2)^{\frac{1}{2}}} & 0
\end{bmatrix}
$$

$$\tag{29}$$

For k-vectors in the $x-y$ plane the quantity Y vanishes; for k in the (111) direction $\chi-2\eta = \pi$ so that for these cases the 6×6 matrix has been factored into two 3×3 matrices. In the general case further transformations are necessary. A brute-force method of making $\Gamma = 0$ in general has been found but will not be given here since G becomes very complicated. It is not difficult to obtain the general secular equation as a product of two cubics directly from the matrix as given in eqs. (28) and (29). The general secular equation can be written

$$H'_{11}H'_{22}H'_{33}+2H_{12}H_{23}H_{13}-H'_{11}H_{23}{}^2-$$

$$-H'_{22}H_{13}{}^2-H'_{33}H_{12}{}^2-(\Delta/3)\{H'_{11}H'_{22}+$$

$$+H'_{11}H'_{33}+H'_{22}H'_{33}-H_{12}{}^2-H_{13}{}^2-H_{23}{}^2\} = 0$$

$$\tag{30}$$

$$H'_{ii} = H_{ii}+(\hbar^2/2m)k^2-E_k.\tag{31}$$

The symbols H_{ij} refer to the elements of the matrix given in eq. (6).

Along the simple directions (100) and (111) the secular equation factors into a quadratic term times a linear term. The linear term corresponds to a band which is unaffected by spin-orbit splitting and hence is parabolic within the limits of the approximations made in this derivation. In germanium the parabolic band is the upper valence band or heavy mass band.

All bands are parabolic in the limit of spin-orbit splitting very large or very small compared to the second-order $k \cdot p$ energy. The limit of $k \cdot p$ energy large compared to spin-orbit energy is not of real interest in germanium because higher-order perturbation terms which have been neglected here become important when the perturbation energy becomes of the order of the band gap. In silicon where $\Delta \simeq 0.04$ eV, the small Δ approximation may be useful for some purposes.

Calculations of the valence-band structure of germanium have been carried out using the values $L = -32.0$ $(\hbar^2/2m)$, $M = -5.30$ $(\hbar^2/2m)$, $N = -32.4$ $(\hbar^2/2m)$ determined from cyclotron resonance constants as given by DKK. The value $\Delta = 0.28$ eV was used. After the calculations were completed, the comparison of theory and experiment indicated that $\Delta = 0.29$ eV was a better value for the spin-orbit splitting. The calculations have not been corrected for this change. The energy and slope have been calculated for all 3 bands and for the (100), (111), (110), and (Y) directions. The direction (Y) makes equal angles with the (100), (111), and (110) directions. The results are plotted in Fig. 1 as E vs. k^2. The slopes, $(2m/\hbar^2)dE/d(k^2)$, are plotted in Fig. 2. In a plot of E vs. k^2 the customary parabolas become straight lines. The surface of the Brillouin zone occurs at $k = 0.51$ atomic units in the (111) direction so that these calculations cover only a small part of the Brillouin zone.

For the (100) and (111) directions the heavy mass-band graphs are straight lines. For the (110) direction the heavy mass-band graph is nearly straight, the departure from a straight line is best seen in the graph of the slope $dE/d(k^2)$. For a larger range of k^2 the curvature of E vs. k^2 in the (110) direction is more noticeable.

For the (100) and (111) directions the light mass-band (band 2) bends up to become asymptotically parallel to band 1. In the (110) direction band 2 bends up appreciably but always remains steeper than band 1. The bending of band 2 is not of great significance to transport problems because the bend occurs at energies appreciably greater than kT. The effect is very noticeable in free carrier absorption, however, because the absorbing holes make vertical transitions from band 1 where the value of k^2 corresponding to thermal energies is much larger.
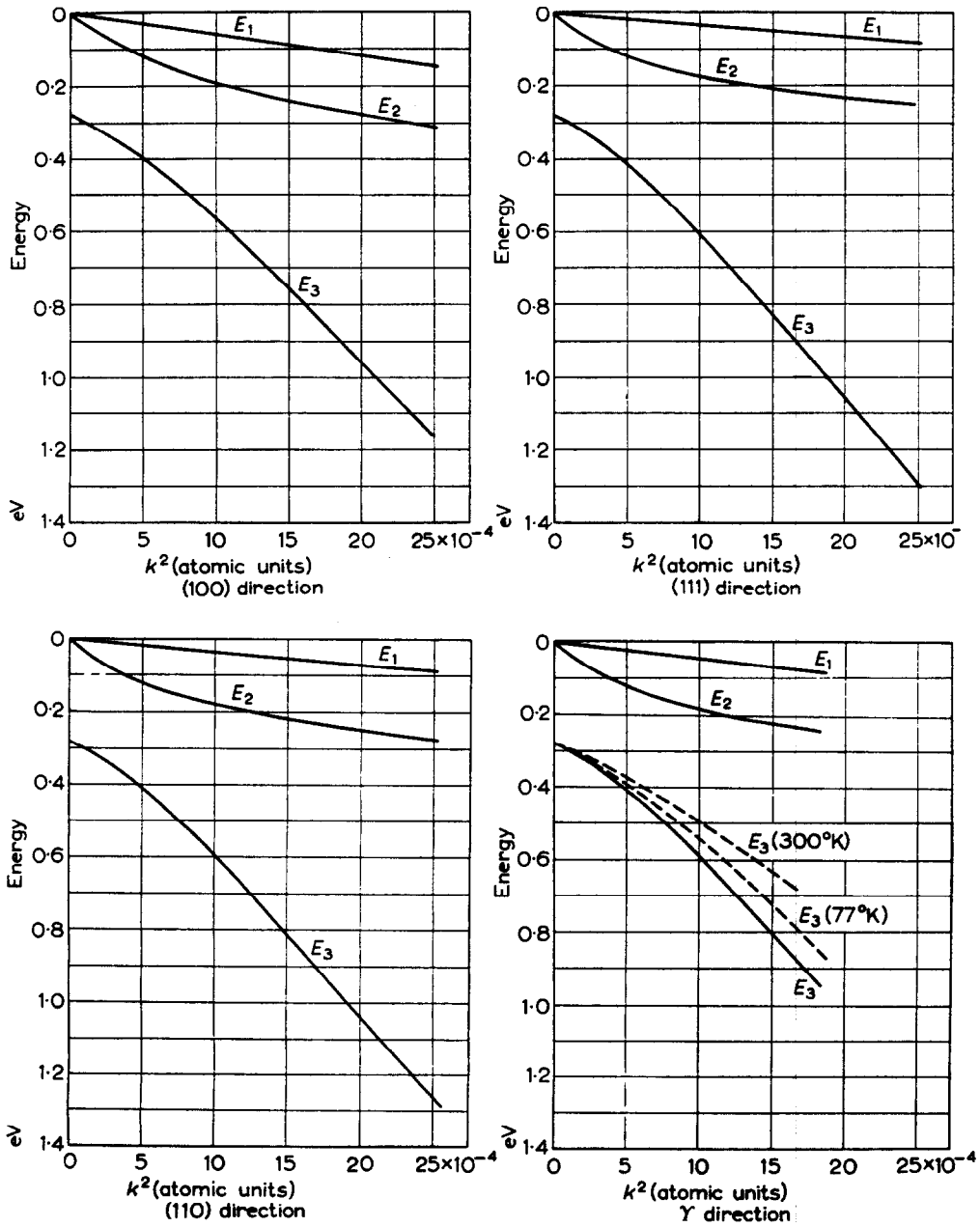
FIG. 1. E vs. k^2 for p-germanium. (Υ) direction shows correction to band 3 to give agreement with free carrier absorption at 300°K and 77°K.
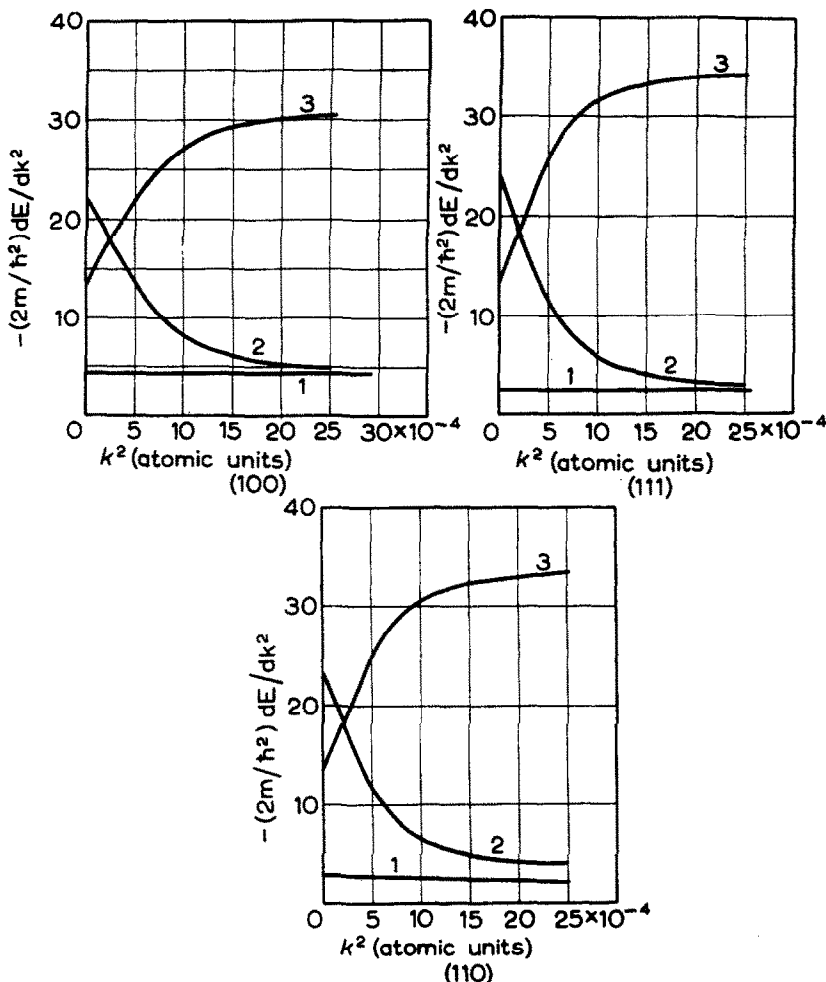
FIG. 2. Slope of E vs. k^2 for p-germanium.

The slope of band 3 increases with k^2. Band 3 is accurately isotropic for small k^2 and remains reasonably isotropic for large k^2.

The status of the energy bands in silicon is more uncertain owing to the ambiguity in sign of the cyclotron resonance constants. Furthermore, the limits of error of the constants are larger than in germanium, so that even for a given choice of signs there is considerable uncertainty in the effective mass of the heavy mass band. To illustrate this point, the value of the reciprocal effective mass in the limit of spin-orbit splitting small compared to the $k \cdot p$ energy for the (110) direction will be cited. The set of values $A = -4 \cdot 0$ $(\hbar^2/2m)$,

$B = +1 \cdot 1$ $(\hbar^2/2m)$, $C = -4 \cdot 0$ $(\hbar^2/2m)$ gives a value $+0 \cdot 39$ for $(2m/\hbar^2)dE/d(k^2)$ in the (110) direction for large k. This is the choice of sign preferred by DKK. The other choice of sign $A = -4 \cdot 0$ $(\hbar^2/2m)$, $B = -1 \cdot 1$ $(\hbar^2/2m)$, $C = -4 \cdot 0$ $(\hbar^2/2m)$ gives a value of $-0 \cdot 71$ for $(2m/\hbar^2)$ $dE/d(k^2)$. However, if we take the extreme values of A, B, C in a direction to make the reciprocal effective mass more negative with the DKK choice of sign the slope becomes $-0 \cdot 73$. A positive slope of $+0 \cdot 39$ could rule out the DKK choice of sign because the maxima in the valence band would occur away from $k = 0$. If the cyclotron resonance constants could be determined more
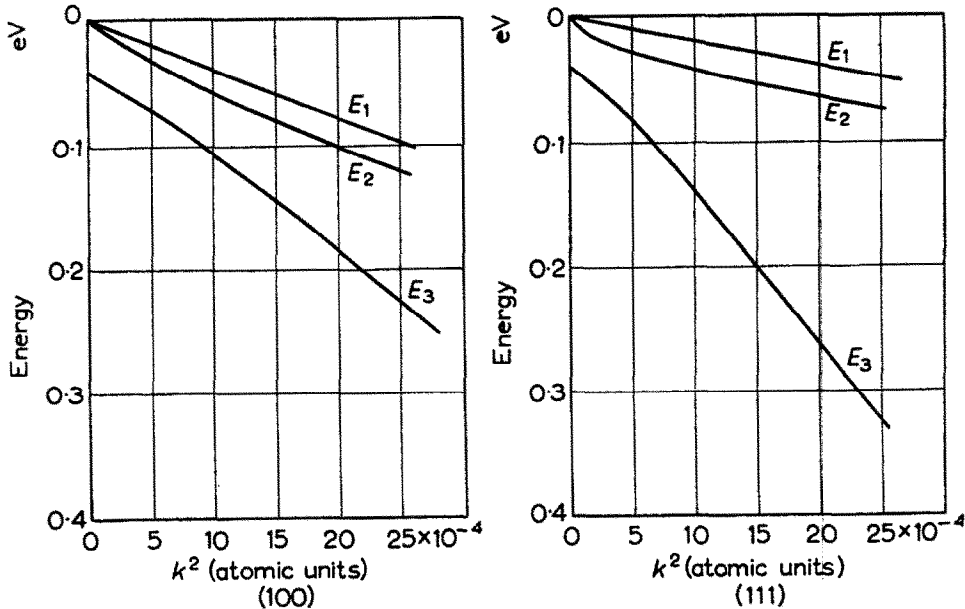
FIG. 3. E vs. k^2 for p-silicon.
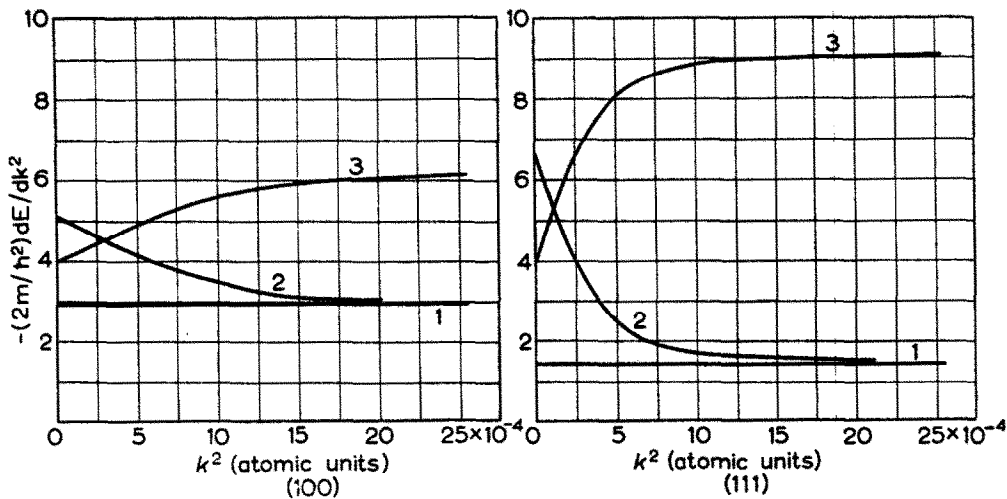
FIG. 4. Slope of E vs. k^2 for p-silicon.

accurately the correct choice of signs might be decidable.

The energy and slope of the valence bands in silicon have been calculated for the (100) and (111) directions. The results are given in Figs. 3 and 4. The values of the parameters used were $L = -7 \cdot 2$ $(\hbar^2/2m)$, $M = -3 \cdot 9$ $(\hbar^2/2m)$, $N = -7 \cdot 7$ $(\hbar^2/2m)$ corresponding to $A = -4 \cdot 0$ $(\hbar^2/2m)$, $B = -1 \cdot 1$ $(\hbar^2/2m)$, $C = -4 \cdot 0$ $(\hbar^2/2m)$. The choice of sign used here makes the silicon band structure qualitatively similar to germanium. This choice of sign is opposite to that given in DKK.

3. HIGHER-ORDER CORRECTIONS

These calculations of band structure have been based on the diagonalization of an interaction Hamiltonian between the triply degenerate valence wave functions at $k = 0$. The Hamiltonian was the sum of two parts: a first-order Hamiltonian of the spin-orbit interaction and a second-order Hamiltonian of the $k \cdot p$ perturbation. The technique of simultaneous diagonalization is clearly the best when both perturbation Hamiltonians are of the same order of magnitude. This procedure is formally indicated by making a perturbation expansion in powers of λ with the $(k \cdot p)$ perturbation multiplied by λ and the spin-orbit perturbation multiplied by λ^2. In nondegenerate perturbation theory the assignment of different powers of λ to different perturbations merely gives a rearrangement of the terms of the perturbation expansion. In degenerate perturbation theory, however, different relative powers in λ result in essentially different series. Convergence is always hastened by arranging powers of λ such that all perturbations act simultaneously to remove the degeneracy. If the degenerate Hamiltonians are of different orders of magnitude the procedure is still formally correct but unnecessary. Formulae for degenerate perturbation theory with two perturbations are developed in the appendix.

We make the convention that the degenerate states we are interested in are labeled by small subscripts j. Other states are labeled by capital subscripts J. For the case of a perturbation P of order λ where all matrix elements P_{ij} are zero and in addition a perturbation Q of order λ^2, we have eq. (A3) for the third-order energy, $E_i^{[3]}$, and eq. (A4) for the fourth-order energy, $E_i^{[4]}$, in the appendix. For our purposes P is the $k \cdot p$ perturbation which only connects states of opposite parity, Q is the spin-orbit interaction which only connects states of like parity. On parity grounds alone all third-order terms are zero and fourth-order terms 6 through 11 in eq. (A4) are zero. The nonzero terms will be repeated here.

$$E_i^{[4]} = \sum_K{}' \frac{Q_{iK}Q_{Ki}}{E_i^0 - E_K^0} - E_i^{[2]} \sum_K{}' \frac{P_{iK}P_{Ki}}{(E_i^0 - E_K^0)^2} +$$

$$+ \sum_{K,L,J}{}' \frac{P_{iL}P_{LK}P_{KJ}P_{Ji}}{(E_i^0 - E_L^0)(E_i^0 - E_K^0)(E_i^0 - E_J^0)} +$$

$$+ 2Re \sum_{K,L}{}' \frac{P_{iL}P_{LK}Q_{Ki}}{(E_i^0 - E_L^0)(E_i^0 - E_K^0)} +$$

$$+ \sum_{K,L}{}' \frac{P_{iK}Q_{KJ}P_{Ji}}{(E_i^0 - E_K^0)(E_i^0 - E_J^0)}. \quad (32)$$
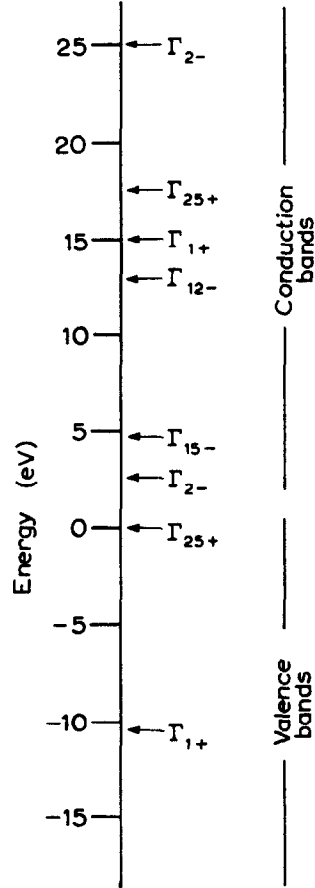
FIG. 5. Energy levels at $k = 0$ based on calculations by F. HERMAN. Reproduced from DRESSELHAUS, KIP, and KITTEL (reference 1).

The magnitude of these fourth-order terms will be discussed for germanium. The estimates refer to the (100) direction calculations but the magnitudes should be comparable for all directions. The energies of bands at $k = 0$ are given in Fig. 5, based on calculations by F. HERMAN[11]. The estimates of corrections to the present calculations from higher order terms are based on these $k = 0$

energies except that we assume that the Γ_2^- band is only 0·88 volts above the valence band as indicated by the optical absorption work of DASH and NEWMAN[12].

The second term is the most important term in eq. (32). The first factor, $E_i^{[2]}$, is the total second-order energy of the *i*th band, hence it contains both spin-orbit and $k \cdot p$ contributions. For small k, $E_i^{[2]}$ is approximately $+\Delta/3$ for bands 1 and 2 and $-2\Delta/3$ for band 3. The summation in term two is very similar to the second-order $k \cdot p$ energy of eq. (5) except that the resonance denominators are squared. The magnitude of the second term is then roughly $E_i^{[2]}(E_i^{[2]}(k) - E_i^{[2]}(0))/(E_i^0 - E_K^0)$ where E_K^0 refers to the band which contributes most to the summation. For band 1, $E_K^0 - E_i^0$ is about 5 volts since the first nonzero term comes from the Γ_{15} band. For bands 2 and 3, $E_K^0 - E_i^0$ is 0·88 volts at nitrogen temperature according to the optical absorption work of DASH and NEWMAN[12]. The lowest conduction band at $k = 0$ is assumed to be the Γ_2^- band. For small k, the second term causes an appreciable error in the calculation of effective masses. The effective mass calculations are about 2 per cent too large for band 1, 10 per cent too large for band 2, and 20 per cent too small for band 3. These estimates are based on the assumption that we have started with the correct values of L, M, N. Since the values used are experimentally derived they essentially include this correction so that we estimate that the correction to band 3 should be about 30 per cent and that bands 1 and 2 are reasonably accurate for small k.

The arguments above do not imply any error in the formula

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

(33)

which has been given in DKK. This is the most general form for the energy surfaces and is perfectly rigorous for small k, except for the possibility that C^2 may be negative. The form follows from the requirements that the secular equation be a quadratic, that E be proportional to k^2, and that the energy surfaces have cubic symmetry. The error arises in relating the quantities L, M, N to A, B, C.

For large k the second term in eq. (32) becomes approximately $-(E_i^{[2]})^2/\Delta E$ where $\Delta E = 0·88$ eV

for band 3, 5 eV for band 1, and some average of 0·88 and 5 eV for band 2. For large k the second term in eq. (32) becomes proportional to k^4. The third term is also proportional to k^4 but appears to be less important than the second term because it involves states further from the valence band which have larger energy denominators.

The first term in eq. (32) is a small correction to the spin-orbit splitting at $k = 0$. The lowest state having a matrix element Q_{iK} with the valence band is the upper Γ_{25}^+ state, about 18 volts above the valence band. If Q_{iK} is of the order of the valence band splitting, the first term in eq. (32) amounts to about 2 per cent of the first order splitting, Δ.

Terms (4) and (5) in eq. (32) are proportional to k^2 times spin-orbit splitting hence they constitute an additional correction to the effective masses near $k = 0$. The largest contribution comes from term (5) and results from the spin-orbit splitting of the Γ_{15}^- band. If the Γ_{15}^- splitting is the same as the valence-band splitting, the fifth term will give a 6 per cent change in the effective mass of of the heavy-mass band. The per cent change will be smaller for bands two and three.

The error in the theoretical procedure should be about 10 times smaller for silicon than for germanium because of the smaller spin-orbit splitting. Unfortunately, the error in the cyclotron resonance constants is still appreciable for silicon and no experimental evidence is yet available which gives the value of the spin-orbit splitting accurately, though an estimate of 0·04 eV from the atomic splitting is probably not far off.

4. OPTICAL MATRIX ELEMENTS

The optical transition probability in free carrier absorption from band *i* to band *j* is proportional to $(e/mc)^2 |\langle u_i | A \cdot p | u_j \rangle|^2$ in the case of direct transitions (i.e. transitions where k is conserved). The k of the light wave is negligible. The quantity A is the vector potential of the light. The momentum operator p has odd parity, hence it has no matrix elements between bands of like parity at $k = 0$. At $k = 0$, parity is a good quantum number in a cubic crystal. The $k \cdot p$ perturbation brings in a first order correction wave function of parity opposite to the $k = 0$ parity of the band. The operator $A \cdot p$ then has a matrix element between bands of like parity which is proportional to k.

The periodic part of the wave function, correct to first order in the $k \cdot p$ perturbation is

$$u = u_{0i} + \sum_J (\hbar/m) \frac{\langle u_{0J} | k \cdot p | u_{0i} \rangle}{E_i{}^0 - E_J{}^0} u_{0J}. \quad (34)$$

The matrix element of $A \cdot p$ between bands i and j is

$$(e/mc) \langle u_i | A \cdot p | u_j \rangle =$$

$$(e\hbar/m^2 c) \sum_J \frac{\langle u_{0i} | k \cdot p | u_{0J} \rangle \langle u_{0J} | A \cdot p | u_{0j} \rangle + \langle u_{0i} | A \cdot p | u_{0J} \rangle \langle u_{0J} | k \cdot p | u_{0j} \rangle}{E_i{}^0 - E_J{}^0}. \quad (35)$$

The right-hand side of eq. (35) is identical in form with the second-order $k \cdot p$ energy of eq. (5). Hence the matrix for the transition probability may be conveniently obtained by using the $k \cdot p$ part of the Hamiltonian matrix in eq. (21) (set $\Delta = 0$). Eq. (35) indicates that the substitution $k_l A_m + A_l k_m$ should be made for $k_l k_m$ and the matrix should be multiplied by the constant factor $(e/c\hbar)$. The resulting matrix F must then be further transformed to $F' = U^{-1} F U$ by the unitary matrix U which diagonalizes the Hamiltonian of eq. (21). The optical transition probability is proportional to the square of the absolute value of the appropriate matrix element of $A \cdot p$. In a cubic crystal this transition probability will be independent of the direction of A if we average over equivalent cubic directions. We define a quantity W_{ij}

$$W_{ij} = (\hbar^2/m^2) \overline{|\langle u_i | A \cdot p | u_j \rangle|^2} / A^2 k^2 \quad (36)$$

where we have averaged over the direction of A and summed over the two final states which are Kramers degenerate. We have obtained expressions for the matrix elements W_{ij} in the (100), (111) and (110) directions which will be denoted by $W_{ij}{}^{\Delta}$, $W_{ij}{}^{\Lambda}$ and $W_{ij}{}^{\Sigma}$ respectively.

For the (100) direction

$$W_{11}{}^{\Delta} = (4/3)M^2 \quad (37)$$

$$W_{12}{}^{\Delta} = (1/9)\{(2)^{\frac{1}{2}} S_{22}{}^{\Delta} + S_{23}{}^{\Delta}\}^2 N^2 \quad (38)$$

$$W_{13}{}^{\Delta} = (1/9)\{S_{22}{}^{\Delta} - (2)^{\frac{1}{2}} S_{23}{}^{\Delta}\}^2 N^2 \quad (39)$$

$$W_{22}{}^{\Delta} = (4/27)\{L + M + (S_{22}{}^{\Delta})^2 L + (S_{23}{}^{\Delta})^2 M +$$
$$+ 2(2)^{\frac{1}{2}}(L - M) S_{22}{}^{\Delta} S_{23}{}^{\Delta}\}^2 \quad (40)$$

$$W_{23}{}^{\Delta} = (1/27)[9N^2 + 4(L - M)^2 \{S_{22}{}^{\Delta} S_{23}{}^{\Delta} -$$
$$- (2)^{\frac{1}{2}}(S_{22}{}^{\Delta})^2 + (2)^{\frac{1}{2}}(S_{23}{}^{\Delta})^2\}^2] \quad (41)$$

$$W_{33}{}^{\Delta} = (4/27)\{L + M + (S_{23}{}^{\Delta})^2 L + (S_{22}{}^{\Delta})^2 M -$$
$$- 2(2)^{\frac{1}{2}}(L - M) S_{22}{}^{\Delta} S_{23}{}^{\Delta}\}^2 \quad (42)$$

$$S_{22}{}^{\Delta} = \frac{h_{23}{}^{\Delta}}{\{(h_{23}{}^{\Delta})^2 + (E_2{}^{\Delta} - h_{22}{}^{\Delta})^2\}^{\frac{1}{2}}} \quad (43)$$

$$S_{23}{}^{\Delta} = \frac{h_{22}{}^{\Delta} - E_2{}^{\Delta}}{\{(h_{23}{}^{\Delta})^2 + (E_2{}^{\Delta} - h_{22}{}^{\Delta})^2\}^{\frac{1}{2}}} \quad (44)$$

$$h_{23}{}^{\Delta} = -\{(2)^{\frac{1}{2}}/3\}(L - M)k^2 \quad (45)$$

$$h_{22}{}^{\Delta} = (2L + M)k^2/3. \quad (46)$$

In the (100) direction the Hamiltonian of eq. (21) has $\Gamma = 0$. The matrix diagonalizing H is then

$$R^{\Delta} = 0; \quad S^{\Delta} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & S_{22}{}^{\Delta} & S_{23}{}^{\Delta} \\ 0 & -S_{23}{}^{\Delta} & S_{22}{}^{\Delta} \end{bmatrix} \quad (47)$$

The above 3×3 matrices are components of the 6×6 matrix according to eq. (20). The elements $S_{22}{}^{\Delta}$, $S_{23}{}^{\Delta}$ can also be expressed in terms of the energy $E_3{}^{\Delta}$. The energy $E_i{}^{\Delta}$ is the energy of band i in the (100) direction. Similarly, $E_i{}^{\Lambda}$ and $E_i{}^{\Sigma}$ refer to energies in the (111) and (110) directions respectively.

For the (111) direction:

$$W_{11}{}^{\Lambda} = (4/27)(L + 2M - N)^2 \quad (48)$$

$$W_{12}{}^{\Lambda} = (1/27)[2N^2 + 4(L - M)^2 +$$
$$+ \{N^2 - 4N(L - M)\}\{(S_{23}{}^{\Lambda})^2 + 2(2)^{\frac{1}{2}} S_{22}{}^{\Lambda} S_{23}{}^{\Lambda}\}] \quad (49)$$

$$W_{\cdot 3}{}^{\Lambda} = (1/27)[2N^2 + 4(L - M)^2 +$$
$$+ \{N^2 - 4N(L - M)\}\{(S_{22}{}^{\Lambda})^2 - 2(2)^{\frac{1}{2}} S_{22}{}^{\Lambda} S_{23}{}^{\Lambda}\}] \quad (50)$$

$$W_{22}{}^{\Lambda} = (4/27)[L+2M+N\{(S_{22}{}^{\Lambda})^2-$$
$$-2(2)^{\frac{1}{2}}S_{22}{}^{\Lambda}S_{23}{}^{\Lambda}\}]^2 \quad (51)$$

$$W_{23}{}^{\Lambda} = (1/27)[\{2(L-M)+N\}^2+$$
$$+4N^2\{S_{22}{}^{\Lambda}S_{23}{}^{\Lambda}+(2)^{\frac{1}{2}}(S_{22}{}^{\Lambda})^2-(2)^{\frac{1}{2}}(S_{23}{}^{\Lambda})^2\}^2]$$
$$(52)$$

$$W_{33}{}^{\Lambda} = (4/27)[L+2M+$$
$$+N\{(S_{23}{}^{\Lambda})^2+2(2)^{\frac{1}{2}}S_{22}{}^{\Lambda}S_{23}{}^{\Lambda}\}]^2 \quad (53)$$

$$S_{22}{}^{\prime\Lambda} = \frac{h_{23}{}^{\Lambda}}{\{(h_{23}{}^{\Lambda})^2+(E_2{}^{\Lambda}-h_{22}{}^{\Lambda})^2\}^{\frac{1}{2}}} \quad (54)$$

$$S_{23}{}^{\Lambda} = \frac{h_{22}{}^{\Lambda}-E_2{}^{\Lambda}}{\{(h_{23}{}^{\Lambda})^2+(E_2{}^{\Lambda}-h_{22}{}^{\Lambda})^2\}^{\frac{1}{2}}} \quad (55)$$

$$h_{23}{}^{\Lambda} = (2)^{\frac{1}{2}}Nk^2/3 \quad (56)$$

$$h_{22}{}^{\Lambda} = (L+2M+N)k^2/3. \quad (57)$$

In writing the matrix elements for the (110) direction we make the following auxiliary definitions.

$$S_{ij}{}^{\Sigma} = n_{ij}/(n_{1j}{}^2+n_{2j}{}^2+n_{3j}{}^2)^{\frac{1}{2}} \quad (58)$$

$$n_{1j} = h_{12}{}^{\Sigma}h_{23}{}^{\Sigma}-h_{13}{}^{\Sigma}(h_{22}{}^{\Sigma}-E_j{}^{\Sigma})$$
$$n_{2j} = h_{12}{}^{\Sigma}h_{13}{}^{\Sigma}-h_{23}{}^{\Sigma}(h_{11}{}^{\Sigma}-E_j{}^{\Sigma})$$
$$n_{3j} = (h_{11}-E_j)(h_{22}{}^{\Sigma}-E_j{}^{\Sigma})-(h_{12}{}^{\Sigma})^2$$
$$(59)$$

$$h_{11}{}^{\Sigma} = (L+M)k^2/2$$
$$h_{22}{}^{\Sigma} = (L+5M)k^2/6$$
$$h_{12}{}^{\Sigma} = Nk^2/2(3)^{\frac{1}{2}}$$
$$h_{13}{}^{\Sigma} = Nk^2/(6)^{\frac{1}{2}}$$
$$h_{23}{}^{\Sigma} = (L-M)k^2/3(2)^{\frac{1}{2}} \quad (60)$$

where $E_j{}^{\Sigma}$ is the energy of band j in the (110) direction. The quantities $W_{ij}{}^{\Sigma}$ can then be written

$$W_{11}{}^{\Sigma} = (4/3k^4)\{\Delta(S_{31}{}^{\Sigma})^2+E_1{}^{\Sigma}\}^2 \quad (62)$$

$$W_{12}{}^{\Sigma} = (4/3k^4)\{\Delta S_{31}{}^{\Sigma}S_{32}{}^{\Sigma}\}^2+$$
$$+(1/9)(L-M)^2\{S_{11}{}^{\Sigma}S_{22}{}^{\Sigma}-S_{21}{}^{\Sigma}S_{12}{}^{\Sigma}+$$
$$+(2)^{\frac{1}{2}}(S_{11}{}^{\Sigma}S_{32}{}^{\Sigma}-S_{31}{}^{\Sigma}S_{12})\}^2+$$
$$+(1/18)N^2\{(2)^{\frac{1}{2}}(S_{11}{}^{\Sigma}S_{22}{}^{\Sigma}-S_{21}{}^{\Sigma}S_{12}{}^{\Sigma})+$$
$$+(S_{12}{}^{\Sigma}S_{31}{}^{\Sigma}-S_{11}{}^{\Sigma}S_{32}{}^{\Sigma}+$$
$$+(3)^{\frac{1}{2}}(S_{22}{}^{\Sigma}S_{31}{}^{\Sigma}-S_{21}{}^{\Sigma}S_{32}{}^{\Sigma})\}^2 \quad (63)$$

$$W_{13}{}^{\Sigma} = (4/3k^4)(\Delta S_{31}{}^{\Sigma}S_{33}{}^{\Sigma})^2+$$
$$+(1/9)(L-M)^2\{S_{11}{}^{\Sigma}S_{23}{}^{\Sigma}-S_{21}{}^{\Sigma}S_{13}{}^{\Sigma}+$$
$$+(2)^{\frac{1}{2}}(S_{11}{}^{\Sigma}S_{33}{}^{\Sigma}-S_{31}{}^{\Sigma}S_{13}{}^{\Sigma})\}^2+$$
$$+(1/18)N^2\{(2)^{\frac{1}{2}}(S_{11}{}^{\Sigma}S_{23}{}^{\Sigma}-S_{13}{}^{\Sigma}S_{21}{}^{\Sigma})+$$
$$+S_{13}{}^{\Sigma}S_{31}{}^{\Sigma}-S_{11}{}^{\Sigma}S_{33}{}^{\Sigma}+$$
$$+(3)^{\frac{1}{2}}(S_{23}{}^{\Sigma}S_{31}{}^{\Sigma}-S_{21}{}^{\Sigma}S_{33}{}^{\Sigma})\}^2 \quad (64)$$

$$W_{22}{}^{\Sigma} = (4/3k^4)\{\Delta(S_{32}{}^{\Sigma})^2+E_2{}^{\Sigma}\}^2 \quad (65)$$

FIG. 6. Matrix elements for direct optical transitions in *p*-germanium.

$$W_{23} = (4/3k^4)\{\Delta S_{32}{}^{\Sigma}S_{33}{}^{\Sigma}\}^2 +$$
$$+ (1/9)(L-M)^2\{S_{12}{}^{\Sigma}S_{23}{}^{\Sigma} - S_{22}{}^{\Sigma}S_{13}{}^{\Sigma} +$$
$$+ (2)^{\frac{1}{2}}(S_{12}{}^{\Sigma}S_{33}{}^{\Sigma} - S_{32}{}^{\Sigma}S_{13}{}^{\Sigma})\}^2 +$$
$$+ (1/18)N^2\{(2)^{\frac{1}{2}}(S_{12}{}^{\Sigma}S_{23}{}^{\Sigma} - S_{13}{}^{\Sigma}S_{22}{}^{\Sigma}) +$$
$$+ S_{13}{}^{\Sigma}S_{32}{}^{\Sigma} - S_{12}{}^{\Sigma}S_{33}{}^{\Sigma} +$$
$$+ (3)^{\frac{1}{2}}(S_{32}{}^{\Sigma}S_{23}{}^{\Sigma} - S_{33}{}^{\Sigma}S_{22}{}^{\Sigma})\}^2 \quad (66)$$

$$W_{33}{}^{\Sigma} = (4/3k^4)\{\Delta(S_{33}{}^{\Sigma})^2 + E_3{}^{\Sigma}\}^2 \quad (67)$$

Δ is the spin-orbit splitting.

The quantities $W_{13}{}^{\Delta}$, $W_{13}{}^{\Delta}$, $W_{13}{}^{\Sigma}$, $W_{12}{}^{\Sigma}$ have been calculated. The results are plotted in terms of the dimensionless quantities $W_{ij}/(\hbar^2/2m)^2$ in Fig. 6. The value of $W_{23}{}^{\Delta}/(\hbar^2/2m)^2$ was calculated to be 560 for $k = 0$.

5. FREE-CARRIER ABSORPTION

The free-carrier absorption of p germanium has been discussed by KAHN[9]. In his treatment he made the parabolic band approximation. We shall extend his analysis using the band calculations and matrix elements computed in this paper.

The probability per unit time w for absorbing a photon is

$$w = (2\pi/\hbar)H^2\rho(E) \quad (68)$$

where ρ is the density of states per unit energy. The transition probability can be related to the absorption constant, α, by the equation

$$\alpha = 2\pi\hbar^2 cw/nEA^2 \quad (69)$$

where E is the energy of the absorbed quantum and n is the index of refraction. According to eq. (36) the matrix element squared is given by

$$H_{ij}{}^2 = (e/c\hbar)^2 A^2 k^2 W_{ij}. \quad (70)$$

The density of states is determined by the number of possible final states in the energy range $d(E_i - E_j)$ where a hole is to be taken from band i to band j by a direct transition. The number of one electron states per unit volume in this range in band i is

$$k^2/\pi^2[(dE_i/dk) - (dE_j/dk)] \quad (71)$$

for the case of spherical energy bands. To each occupied state in band i there corresponds a final state of the system in which the hole in band i has

been transferred to a state of the same k vector in band j. The density of final states is just the density of states in (71) multiplied by the occupation probability. For Boltzmann statistics the density of states is

$$\rho(E) = \frac{k^2 p e^{-E_i/kT}}{\pi^2 N_v |(dE_i/dk) - (dE_j/dk)|} \quad (72)$$

$$N_v = 2(kT/2\pi\hbar^2)^{3/2}(\overline{m}_1{}^{3/2} + \overline{m}_2{}^{3/2}) \quad (73)$$

where E_i and E_j are the energies in the bands i and j between which transitions are made. The concentration of holes is p; $\overline{m}_1$, $\overline{m}_2$ are the average masses of the two upper valence bands. A density of states factor of two for spin is included for band i but not for band j in eq. (72) since the latter factor of two has already been accounted for in computing W_{ij} by summing over the two Kramers degenerate bands of the final state.

The equation for the absorption constant is then

$$\alpha_{ij} = \frac{2e^2 k^3 p W_{ij}(e^{-E_i/kT} - e^{-E_j/kT})}{c\hbar n N_v(E_i - E_j)[(dE_i/dk^2) - (dE_j/dk^2)]}. \quad (74)$$

Induced emission and absorption are both included. The above formula applies only to the case of spherical energy bands and Boltzmann statistics.

Band 1 to Band 3 Transitions

The free-carrier absorption has been calculated for the (100), (111), (110), and (Ψ) directions separately as if one had spherical bands. A crude numerical integration is then effected by weighting the directions appropriately. The weighting was made by considering the surface of a sphere in k space and assigning a small element of area to whichever of the four computed directions it was closest. The weightings were then made proportional to the area and were normalized. The following approximate weights were determined: (100), 0·09: (111), 0·16: (110), 0·22: (Y), 0·53.

The computations for the (100), (111), and (110) directions include explicit evaluation of all quantities given in eq. (74). For the (Y) direction, however, only the Boltzmann factor and the energy appropriate to (Y) were used. The matrix elements and values of $dE/d(k^2)$ were taken to be the same as
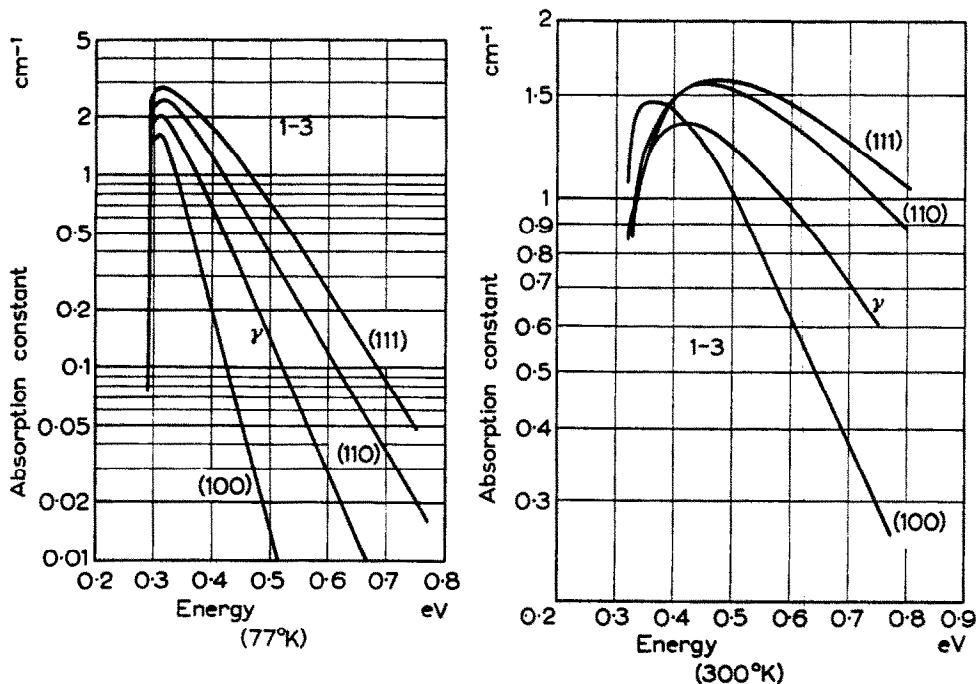
FIG. 7. Theoretical free-carrier absorption in *p*-germanium with 6×10^{15} holes.

for the (110) direction. The computations of absorption constant for the four directions are given in Fig. 7 for 77°K and 300°K. The weighted averages are compared with the experimental data of R. NEWMAN[10] in Fig. 8.

For both 77°K and 300°K the peak theoretical values of absorption constant are about a factor of 1·2 high. Since the theory contains no adjustable parameters this agreement is quite good. However the high-energy slopes show a significant discrepancy between theory and experiment for both 300°K and 77°K. The source of the disagreement is thought to be the neglected higher-order terms in the perturbation expansion which will have the effect of bringing band 3 closer to bands 1 and 2. The effect of higher-order terms on band 3 will be much larger than the effect on bands 1 and 2. The experimental curve can be used to obtain a rough estimate of the correction which should be made to band 3. The theoretical curve is first divided by a factor of 1·2 so that both curves have the same peak absorption. Then the horizontal energy displacement which is needed to make the two curves superpose is taken to be the vertical

energy displacement which should be added to band 3. A given absorption constant defines two values of $E_1 - E_3$, a value A for the experimental curve and a value B for the theoretical curve. The correction $A - B$ to band 3 is to be made at the point in k space where the band separation $E_1 - E_3$ is equal to B. This procedure assumes that the correction to band 3 is isotropic; it also assumes that the correction to band 3 will not alter the absorption computed for a given point in k space. The latter assumption is reasonable at 77°K but not too good at 300°K.

The correction to band 3 is made for both 77°K and 300°K and is plotted in Fig. 1 for the (Y) direction. Ideally, of course, the two corrections should coincide but actually there is a large discrepancy. A number of reasons which may contribute to the discrepancy can be cited.

The theoretical curve at nitrogen temperature is very sensitive to the cyclotron resonance constants because of the Boltzmann factor in band 1. The magnitude of the uncertainty in the absorption constant appears to be about a factor of 2 at 0·6 eV according to the limits of error quoted by

DKK. The slope at nitrogen temperatures may be influenced by phonon induced indirect transitions. The electron-phonon interaction will mix a small amount of large k vector wave function into the small k states. The probability of making a high-energy transition due to this admixture of k vector is proportional to H^2 (electron-phonon)$/E_1{}^2$ where E_1 is the large k energy in the upper valence band. For large E_1 this indirect transition probability will eventually exceed the direct transition probability which is multiplied by a Boltzmann factor $e^{-E_1/kT}$. A rough estimate of this effect indicates that it may not be negligible. However, it would appear that such an effect should cause a change in slope of absorption vs. energy for large energies which is not observed experimentally. This effect would be in a direction to increase the indicated correction to band 3 at nitrogen temperature.

The theoretical absorption at room temperature varies by less than a factor of 2 from 0·4 eV to 0·7 eV. This fact makes the computed correction to band 3 very sensitive to the value of the optical matrix element as a function of k. The computed matrix elements are influenced by the neglected higher-order terms just as are the band shapes. The direction of this effect is to reduce the indicated correction to band 3 at room temperature.

The room-temperature correction to band 3 would be changed somewhat by taking into account self-consistently the effect on the absorption of the correction itself. The direction of this effect is to increase the indicated correction.

A temperature dependence of the band E_3 is indicated by the fact that the band gap at $k = 0$ is significantly temperature dependent between 77°K and 300°K as shown by the optical absorption studies of DASH and NEWMAN[12]. This effect would decrease the effective mass of band 3 by about 10 per cent in going from nitrogen to room temperature and is in the opposite direction to the apparent change inferred from the present method of correcting the E_3 band.

In summary, no accurate method of determining the band E_3 has been found. The required alterations to theory are of the order of magnitude ($\sim$ 30 per cent) to be expected from estimates of higher-order terms. Although 300°K and 77°K corrections do not agree, they appear to be reconcilable in view of the uncertainties mentioned above. The correction to E_3 deduced from 77°K

data should be most accurate, particularly if the accuracy of the cyclotron resonance constants increases.

Band-1 to Band-2 Transitions

The theoretical calculation of the free-carrier absorption at 300°K for transitions from band 1 to band 2 is given in Fig. 8 for the (110) direction. The decrease in slope of E vs. k^2 in band 2 for large k^2 brings the absorption down sharply before 0·23 eV where the experimental curve shows a minimum. The effect is even more marked for the (100) and (111) directions. In these directions, bands 1 and 2 become parallel asymptotically in the approximation of our calculations. The minimum separation of bands 1 and 2 is $(2/3)\Delta$ or 0·19 eV for both the (100) and (111) directions. Hence the absorption goes to zero at this point. The absolute magnitude of the theoretically computed absorption agrees quite well with the experimental value.

Band-2 to Band-3 Transitions

The approximation of direct transitions breaks down in the analysis of transitions between bands 2 and 3. Since the slopes are equal at $k^2 = 4 \times 10^{-4}$ atomic units the density of states in the spherical approximation becomes infinite at this point. The absorption approaching the point at which the slopes are equal increases as $(E-E_0)^{-\frac{1}{2}}$. The integrated absorption $\int \alpha \, dE$ remains finite. Any scattering mechanism such as phonons or impurities which makes the k vector of an electron uncertain will broaden the infinite narrow spike associated with direct transitions and produce a finite peak.

A source of broadening apart from indirect transitions is the fact that the surface in k space for which the slopes in bands 2 and 3 are equal does not coincide with the surface of constant energy separation. The maximum broadening to be expected from this source is only $1·5 \times 10^{-4}$ eV which is far less than the experimental width of about 0·02 eV.

In the range of 10^{15} carriers/cc the free-carrier absorption is independent of impurity concentration[10] so that the broadening of the α_{23} band is not caused by impurity scattering. The most likely source of broadening appears to be lattice scattering.
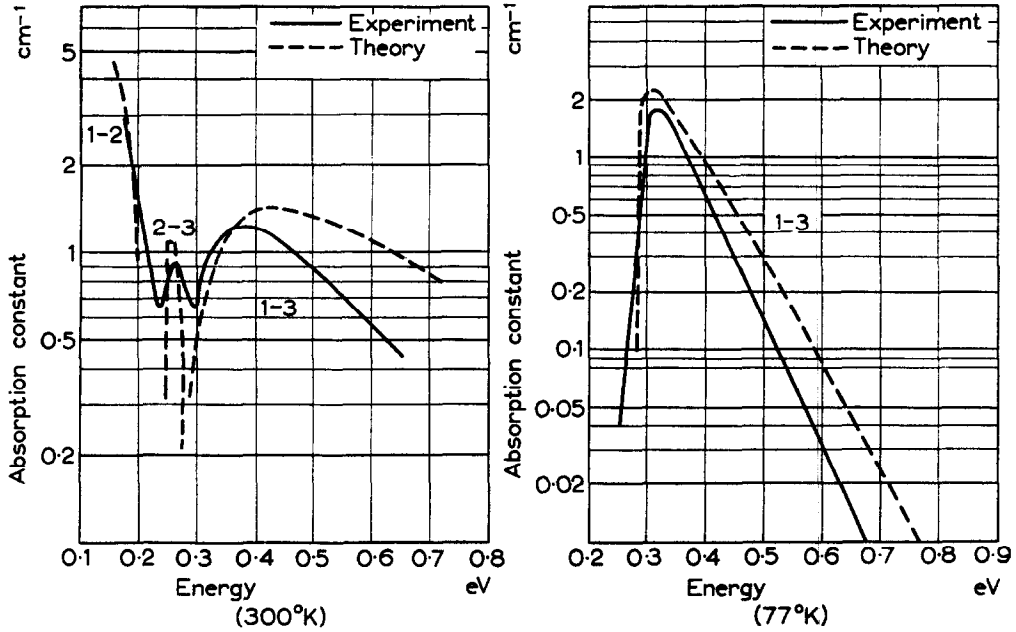
FIG. 8. Theoretical free-carrier absorption compared with experiment for 6×10^{15} holes.
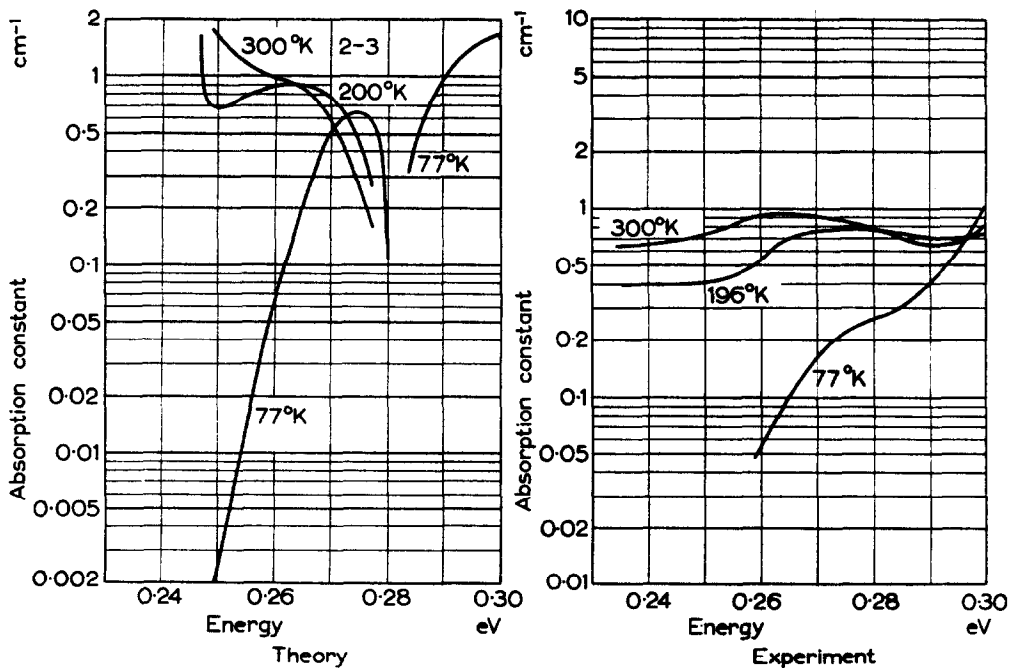

FIG. 9. Free-carrier absorption for band-2 to band-3 transitions.

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The theoretical calculations of free-carrier absorption for band-2 to band-3 transitions are shown in Fig. 9. The calculations were made for the (100) direction; the matrix element W_{23} was calculated for $k = 0$ only, since the variation with k is not very important. The assumption of direct transitions causes a rapid rise in absorption on the low-energy side of the curve. This rise is shown in the 200°K and 300°K curves. At 77°K the absorption falls to very low values before it rises again because of the infinite density of states. At 77°K the shape of the curve is not very sensitive to how the infinite, narrow peak is broadened. At 300°K the shape of the curve is entirely dependent on how the broadening is treated so that the direct transition approximation is of no value here.

The experimental α_{23} band is also shown at three temperatures in Fig. 9. The theoretical peak absorption at 200°K agrees roughly with the experimental values. At 77°K the α_{23} band has moved so close to the α_{13} band that the bands are not clearly resolved experimentally, presumably because of phonon broadening. It is difficult to compare theory and experiment for this case, although the absorption appears to be significantly lower than expected from theory.

For completeness the α_{23}-band calculations are included in Fig. 8. The absorption is arbitrarily clipped off at a peak value a factor of 1·2 above the experimental value.

A comparison of theory and experiment indicates that the spin-orbit splitting should have been taken as 0·29 eV. The α_{23} peak at 200°K, the α_{13} peak at 77°K, and the trough between the α_{13} and α_{23} peaks at 200°K all show this clearly. The most significant indication of the spin-orbit splitting is the trough between the α_{13} and α_{23} peaks at 200°K since the trough should occur quite accurately at the value Δ. The calculations have not been corrected for this revised estimate of the splitting.

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APPENDIX: DEGENERATE PERTURBATION THEORY

Two Perturbations of Different Order

If two perturbations are of different orders of magnitude they should clearly be assigned different powers of the expansion parameter λ in making a perturbation expansion. In the nondegenerate case, a different assignment of powers of λ merely results in a reordering of the terms of the perturbation series. In the case of degenerate perturbation theory, different powers of λ result in essentially different terms in the perturbation expansion.

Let us consider the particular case of two perturbations, P and Q, where P removes degeneracy in second order and Q removes degeneracy in first order. If $\sum_{K} P_{iK} P_{Kj} (E_i{}^0 - E_K{}^0)^{-1}$ is of the order of Q_{ij}, then clearly we should write $\lambda P + \lambda^2 Q$ in making a perturbation expansion. Then both perturbation matrices will be diagonalized together in determining the correct unperturbed function set. Convergence is never impaired by this procedure even when $\sum_{K} P_{iK} P_{Kj} (E_i{}^0 - E_K{}^0)^{-1}$ is actually much smaller than Q_{ij}.

We give the formulae for the energies up to fourth order for this case assuming $P_{ii} = 0$ so that the first-order energy vanishes.

$$E_i{}^{[1]} = 0 \tag{A1}$$

$$E_i{}^{[2]} = Q_{ii} + \sum_{K} \frac{P_{iK} P_{Ki}}{E_i{}^0 - E_K{}^0} \tag{A2}$$

$$E_i^{[3]} = 2Re \sum_K{}' \frac{Q_{iK}P_{Ki}}{E_i^0-E_K^0} + \qquad\qquad + \sum_{J,K,L}{}' \frac{P_{iL}P_{LK}P_{KJ}P_{Ji}}{(E_i^0-E_L^0)(E_i^0-E_K^0)(E_i^0-E_J^0)} +$$

$$+ \sum_{K,J}{}' \frac{P_{iJ}P_{JK}P_{Ki}}{(E_j^0-E_J^0)(E_i^0-E_K^0)} \qquad (A3) \qquad +2Re \sum_{K,L}{}' \frac{P_{iL}P_{LK}Q_{Ki}}{(E_i^0-E_L^0)(E_i^0-E_K^0)} +$$

$$E_i^{[4]} = \sum_K{}' \frac{Q_{iK}Q_{Ki}}{E_i^0-E_K^0} - E_i^{[2]}\sum_K{}' \frac{P_{iK}P_{Ki}}{(E_i^0-E_K^0)^2} + \qquad\qquad + \sum_{J,K}{}' \frac{P_{iK}Q_{KJ}P_{Ji}}{(E_i^0-E_K^0)(E_i^0-E_J^0)} +$$

$$+ \sum_{k,J,K,L,M}{}' \frac{P_{iL}P_{LM}P_{Mk}P_{kK}P_{KJ}P_{Ji}}{(E_i^0-E_L^0)(E_i^0-E_M^0)(E_i^0-E_K^0)(E_i^0-E_J^0)\,(E_i^{[2]}-E_k^{[2]})} +$$

$$+2Re \sum_{k,J,K,L}{}' \frac{Q_{iL}P_{LK}P_{kK}P_{KJ}P_{Ji}}{(E_i^0-E_L^0)(E_i^0-E_K^0)(E_i^0-E_J^0)(E_i^{[4]}-E_k^{[2]})} +$$

$$+2Re \sum_{k,J,K,L}{}' \frac{P_{iL}Q_{Lk}P_{kK}P_{KJ}P_{Ji}}{(E_i^0-E_L^0)(E_i^0-E_K^0)(E_i^0-E_J^0)(E_i^{[2]}-E_k^{[2]})} +$$

$$+2Re \sum_{k,K,L}{}' \frac{P_{iL}Q_{Lk}P_{kK}Q_{Ki}}{(E_i^0-E_L^0)(E_i^0-E_K^0)(E_i^{[2]}-E_k^{[2]})} +$$

$$+ \sum_{k,K,L}{}' \frac{Q_{iL}P_{Lk}P_{kK}Q_{Ki}}{(E_i^0-E_L^0)(E_i^0-E_K^0)(E_i^{[2]}-E_k^{[2]})} +$$

$$+ \sum_{k,K,L}{}' \frac{P_{iL}Q_{Lk}Q_{kK}P_{Ki}}{(E_i^0-E_L^0)(E_i^0-E_K^0)(E_i^{[2]}-E_k^{[2]})}. \qquad (A4)$$

Capital indices J, K, L index states not degenerate with the state i under consideration. Indices j, k, l refer to states which are degenerate with i in the unperturbed problem. Primes on the summation signs indicate that the term $i = j$ is omitted. The unperturbed function set has been determined by the requirement

$$\sum_K{}' \frac{P_{iK}P_{Kj}}{E_i^0-E_K^0} + Q_{ij} = 0 \quad i \neq j.$$

Similar formulae are discussed in CONDON and SHORTLEY[13].