

Equations (A, 15), together with the relations

$$\begin{aligned} W_A(\varphi+2\pi) &= W_A(\varphi)+1, \\ W_A(0) &= 0, \\ W_A(\varphi) &= \text{monotonically nondecreasing in } \varphi, \end{aligned} \quad (\text{A, 16})$$

and the same relations for  $W_B$ , determine again the functions  $W_A$  and  $W_B$ . These functions, as well as the constants  $C_A(k)$  and  $C_B(k)$ , can be calculated from (A, 15) by iteration. Finally, for  $M(k)+\text{const}=(1/2\pi)\int \langle \varphi_{n+1}-\varphi_n \rangle_{Av}$ , which gives us the relative number of

eigenstates below  $k$ , we obtain

$$\begin{aligned} (1/2\pi)\langle \varphi_{n+1}-\varphi_n \rangle_{Av} &= p \int (\varphi_{n+1}-\varphi_n)_A w_A(\varphi_n) d\varphi_n \\ &+ q \int (\varphi_{n+1}-\varphi_n)_B w_B(\varphi_n) d\varphi_n. \end{aligned}$$

A short calculation using (A, 15) gives the result

$$M(k)+\text{const} = pC_A(k) + qC_B(k).$$

## Electron Self-Energy and Temperature-Dependent Effective Masses in Semiconductors: *n*-Type Ge and Si

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The electronic self-energy due to interaction with acoustic phonons is evaluated as a function of the electron propagation vector  $\mathbf{k}$ , and a relation is established connecting the Sommerfeld-Bethe interaction constant with the energy band separation and effective masses. For nondegenerate prolate ellipsoidal energy surfaces of revolution, the self-energy depends linearly on the temperature  $T$  at high temperatures and quadratically on  $T$  at low temperatures, this behavior being substantiated by the experimental results of Macfarlane and Roberts. The temperature dependence of the principal effective masses  $m_i(T)$  at high temperatures is given by ( $i=l$  or  $t$ )

$$m_i(0)/m_i(T) = 1 + (128\pi/9\rho h^3 s \Theta_D) m_i^2(0) \alpha_i(E) \langle C^2 \rangle_{Av} T$$

thus indicating a decrease in effective mass with rising temperatures. The result does not explain the deviation from the  $T^{-1}$  law for the lattice mobility as observed by Morin and Maita. The percentage decrease at room temperature for each of the electron effective masses amounts to less than 1%. These results do not account fully for the possible change determined by Lax and Mavroides.

### 1. INTRODUCTION

THE temperature variation of the electronic energy in crystals is usually attributed to radiation damping,<sup>1</sup> thermal expansion,<sup>2</sup> electron self-energy,<sup>3</sup> and mutual electrostatic interactions of charge carriers.<sup>4</sup>

In the present paper a study is made of the electron self-energy in homopolar semiconductors with specific reference to *n*-type Ge and Si. From the self-energy the temperature dependence of the principal effective masses is then deduced. At low temperatures the self-energy exhibits a quadratic behavior with temperature, thus substantiating the observations of Macfarlane and Roberts<sup>5</sup> on the temperature variation of the infrared

absorption edge. In addition, the percentage change in the principal effective masses from liquid helium temperatures to room temperature is computed and found to be much less than the possible change deduced by Lax and Mavroides.<sup>6</sup>

### 2. HAMILTONIAN AND THE LATTICE FIELD

The total Hamiltonian of the system, electron plus lattice, may be written as

$$H = H_r + V(\mathbf{R}, \mathbf{r}) + H_R, \quad (2.1)$$

where  $H_r$  is the Hamiltonian of a nonlocalized electron,  $V(\mathbf{R}, \mathbf{r})$  the electron lattice interaction and  $H_R$  the vibrational energy of the lattice. The latter two quantities are given by the relations

$$\begin{aligned} V(\mathbf{R}, \mathbf{r}) &= -\frac{1}{2(M\mathfrak{V})^{\frac{1}{2}} \sum_{i,\sigma} \xi_i(\sigma) \cdot \nabla V(\mathbf{r})} \\ &\times \{ \alpha_i(\sigma) e^{i\sigma \cdot \mathbf{r}} + \alpha_i^*(\sigma) e^{-i\sigma \cdot \mathbf{r}} \} \left( \frac{2\hbar}{\omega_i(\sigma)} \right)^{\frac{1}{2}} \end{aligned} \quad (2.2)$$

<sup>1</sup> A. Radkowsky, Phys. Rev. **73**, 749 (1948); Möglich, Riehl, and Rompe, Z. tech. Phys. **21**, 6, 128 (1940).

<sup>2</sup> R. Seiwert, Ann Physik **6**, 241 (1949); F. Möglich and R. Rompe, Z. tech. Phys. **119**, 472 (1942); J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950); W. Shockley and J. Bardeen, Phys. Rev. **77**, 407 (1950).

<sup>3</sup> V. A. Johnson and H. Fan, Phys. Rev. **79**, 899 (1950); T. Muto and S. Oyama, Progr. Theoret. Phys. Japan **5**, 833 (1950); **6**, 61 (1951); H. Fan, Phys. Rev. **78**, 808 (1950); **82**, 900 (1951).

<sup>4</sup> F. J. Morin and J. P. Maita, Phys. Rev. **94**, 1525 (1954); **96**, 28 (1954).

<sup>5</sup> G. G. Macfarlane and V. Roberts, Phys. Rev. **97**, 1714 (1955); **98**, 1865 (1955).

<sup>6</sup> B. Lax and J. Mavroides, Phys. Rev. **100**, 1650 (1955).

and

$$H_R = \frac{1}{2} \sum_{\iota, \sigma} \hbar \omega_{\iota}(\sigma) \{ \alpha_{\iota}(\sigma) \alpha_{\iota}^*(\sigma) + \alpha_{\iota}^*(\sigma) \alpha_{\iota}(\sigma) \}, \quad (2.3)$$

where  $V(\mathbf{r})$  is the periodic potential occurring in  $H_r$  and  $\xi_{\iota}(\sigma)$  are the unit polarization vectors, one longitudinal and two transverse, corresponding to the phonon propagation vector  $\sigma$ . In addition,  $\alpha_{\iota}(\sigma)$  and  $\alpha_{\iota}^*(\sigma)$  are the familiar annihilation and creation operators satisfying the commutation relations

$$\begin{aligned} [\alpha_{\iota'}(\sigma'), \alpha_{\iota}^*(\sigma)] &= \pm \delta_{\sigma, \sigma'} \delta_{\iota, \iota'}, \\ [\alpha_{\iota'}(\sigma'), \alpha_{\iota}(\sigma)] &= 0, \end{aligned} \quad (2.4)$$

the + or - sign occurring according as  $\sigma$  is positive or negative.

We proceed to solve the Schrödinger equation

$$H\Psi_{n, \mathbf{k}, N} = E_{n, \mathbf{k}, N} \Psi_{n, \mathbf{k}, N}, \quad (2.5)$$

where  $\Psi_{n, \mathbf{k}, N}$  is the wave function for the complete system and  $E_{n, \mathbf{k}, N}$  the total energy. The quantum numbers ( $n, \mathbf{k}$ ) and  $N$  specify the electronic state and the state of excitation of the lattice respectively. Using the Born approximation for  $\Psi_{n, \mathbf{k}, N}$ , we write

$$\Psi_{n, \mathbf{k}, N} = \chi_{n, \mathbf{k}} \zeta_N, \quad (2.6)$$

where  $\zeta_N$  is the product of normalized single oscillator wave functions.

It has been usual in the literature to regard  $V(\mathbf{R}, \mathbf{r})$  in the total Hamiltonian  $H$ , as a perturbing term. However, we shall find it convenient for reasons which will become clear later, to write (2.5) in the form

$$\begin{aligned} [H_r + V(\mathbf{R}, \mathbf{r})] \chi_{n, \mathbf{k}} \zeta_N + \chi_{n, \mathbf{k}} H_R \zeta_N + H' \chi_{n, \mathbf{k}} \zeta_N \\ = E_{n, \mathbf{k}, N} \chi_{n, \mathbf{k}} \zeta_N, \end{aligned} \quad (2.7)$$

where  $H'$  is now the perturbing term given by

$$H' \chi_{n, \mathbf{k}} \zeta_N = H_R \chi_{n, \mathbf{k}} \zeta_N - \chi_{n, \mathbf{k}} H_R \zeta_N. \quad (2.8)$$

The wave function for an electron with propagation vector  $\mathbf{k}$ , may be written

$$\chi_{n, \mathbf{k}} = a \{ \psi_{n, \mathbf{k}} + \sum_{\iota', \sigma'} b_{n, \mathbf{k}}(\iota', n', \sigma') \alpha_{\iota'}(\sigma') \psi_{n', \mathbf{k} + \sigma'} \}, \quad (2.9)$$

where the  $\psi_{n, \mathbf{k}}$  are Bloch functions, the  $b_{n, \mathbf{k}}(\iota', n', \sigma')$  are adjustable parameters and  $a$  is a normalization constant. The  $\chi_{n, \mathbf{k}}$  we are using correspond approximately to the "superconducting" wave function of Bardeen<sup>7</sup>; functions of the same form have also been used by Takano.<sup>8</sup> With this wave function, the perturbing term becomes

$$\begin{aligned} H' \chi_{n, \mathbf{k}} = a \sum_{\iota', n', \sigma'} (\mp) b_{n, \mathbf{k}}(\iota', n', \sigma') \\ \times \hbar \omega_{\iota'}(\sigma') \alpha_{\iota'}(\sigma') \psi_{n', \mathbf{k} + \sigma'} \end{aligned} \quad (2.10)$$

the negative and positive signs occurring as  $\sigma$  is positive

or negative, respectively. We shall find on evaluating the total energy of the system that our perturbing term is negligible at ordinary temperatures, thus leading to a reformulation of electron-acoustic mobility theory, which forms the subject of a subsequent paper. Before proceeding to an evaluation of the total energy we shall consider briefly the Sommerfeld-Bethe interaction constant.

### 3. SOMMERFELD-BETHE INTERACTION CONSTANTS

We shall require the matrix elements of  $V(\mathbf{R}, \mathbf{r})$  with respect to the Bloch functions  $\psi_{n, \mathbf{k}}$ . These are

$$\begin{aligned} M(n'', \mathbf{k}''; n', \mathbf{k}') = \sum_{\iota} \mathfrak{M}_{\iota}(n'', \mathbf{k}''; n', \mathbf{k}') \\ \times \{ \alpha_{\iota}(\sigma) \delta_{\mathbf{k}'', \mathbf{k}' + \sigma} + \alpha_{\iota}^*(\sigma) \delta_{\mathbf{k}'', \mathbf{k}' - \sigma} \}, \end{aligned} \quad (3.1)$$

where

$$\begin{aligned} \mathfrak{M}_{\iota}(n'', \mathbf{k}''; n', \mathbf{k}') = [\hbar/2M\mathfrak{M}\omega_{\iota}(\sigma)]^{\frac{1}{2}} I_{\iota} n'' n'(\mathbf{k}'', \mathbf{k}'), \\ I_{\iota} n'' n'(\mathbf{k}'', \mathbf{k}') = \xi_{\iota}(\sigma) \cdot \int_{\tau_0} u_{n'', \mathbf{k}''}^* u_{n', \mathbf{k}'} \nabla V(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (3.2)$$

and  $\tau_0$  indicates integration over the unit cell. The  $u_{n, \mathbf{k}}$  are the periodic part of  $\psi_{n, \mathbf{k}}$ . Making use of the eigenvalue equation satisfied by the  $u_{n, \mathbf{k}}$  we can easily show that for intraband transitions

$$I_{\iota} n'' n'(\mathbf{k}'', \mathbf{k}') = \pm (2/3) i C_{\iota} n'' n'(\mathbf{k}') \sigma, \quad (3.3)$$

with

$$C_{\iota} n'' n'(\mathbf{k}') = \left( \frac{3}{2m} \right) \sum_{i \neq n'} (\mathbf{s} \cdot \mathbf{p}_{n', i}) (\xi_{\iota} \cdot \mathbf{p}_{i, n'}), \quad (3.4)$$

where  $\mathbf{s}$  is a unit vector in the direction of propagation of the lattice wave  $\sigma$ , and

$$\mathbf{p}_{n'' n'} = \int_{\text{cryst.}} \psi_{n'', \mathbf{k}''}^* (-i\hbar \nabla) \psi_{n', \mathbf{k}'} d\mathbf{r}.$$

The above result is valid provided the kinetic energy of the electron in the initial state  $\mathbf{k}'$ , is small compared to the energy gap between the conduction band and filled band. The interaction constant given by (3.4) may be evaluated in terms of the energy gap and principal effective masses, by making use of the  $f$ -sum rule,

$$\frac{2}{m} \sum_{i \neq n'} \frac{p_{n' i}^{\alpha} p_{i n'}^{\beta}}{\epsilon_i(\mathbf{k}) - \epsilon_{n'}(\mathbf{k})} = \delta_{\alpha\beta} - \frac{m}{\hbar^2} \frac{\partial^2 \epsilon_{n'}(\mathbf{k})}{\partial k_{\alpha} \partial k_{\beta}}. \quad (3.5)$$

For an energy band  $\epsilon_{n'}(\mathbf{k})$  of the form,

$$\epsilon_{n'}(\mathbf{k}) = \frac{\hbar^2}{2} \left\{ \frac{(k_x - k_x^0)^2}{m_1} + \frac{k_y^2}{m_2} + \frac{k_z^2}{m_3} \right\}, \quad (3.6)$$

we find

$$C_{\iota} n'' n'(\mathbf{k}) \gtrsim \frac{3}{4} \{ \epsilon_{n''}(\mathbf{k}) - \epsilon_{n'}(\mathbf{k}) \} \sum_{\alpha} s_{\alpha} \xi_{\iota}^{\alpha} \left( 1 - \frac{m}{m_{\alpha}} \right). \quad (3.7)$$

<sup>7</sup> J. Bardeen, Phys. Rev. **80**, 567 (1950); Revs. Modern Phys. **23**, 261 (1951).

<sup>8</sup> F. Takano, J. Phys. Soc. Japan **9**, 430 (1954).

A considerable simplification is achieved in later calculations of the space average of the squares of (3.7) is determined at this point. The direction cosines of the unit polarization vectors are given by

$$\begin{aligned}\xi_1 &= \{\sin\phi, -\cos\phi, 0\}, \\ \xi_2 &= \{\cos\theta \cos\phi, \cos\theta \sin\phi, -\sin\theta\}, \\ \xi_3 &= \{\sin\theta \cos\phi, \sin\theta \sin\phi, \cos\theta\} = \mathbf{s},\end{aligned}\quad (3.8)$$

so that the mean interaction constant, which includes the effects of the longitudinal vibrational mode and the two transverse modes is given by

$$\begin{aligned}C^{n'n'}(\mathbf{k}) &= \left\{ \sum_t \langle [C_{t n' n'}(\mathbf{k})]^2 \rangle_{N_t} \right\}^{\frac{1}{2}} \\ &\gtrsim \frac{3}{4} \{ \epsilon_{n'}(\mathbf{k}) - \epsilon_{n''}(\mathbf{k}) \} \\ &\quad \times \left[ \left( \frac{m}{m_t} - 1 \right)^2 + \frac{1}{3} \left( \frac{m}{m_t} - \frac{m}{m_l} \right)^2 \right]^{\frac{1}{2}},\end{aligned}\quad (3.9)$$

the result being expressed for the case where the energy

$$b_{n, \mathbf{k}}(l', n', \sigma') = \frac{\mathfrak{N}_{l'}(n', \mathbf{k} \pm \sigma'; n, \mathbf{k})}{\{ \epsilon_n(\mathbf{k}) - \epsilon_{n'}(\mathbf{k} \pm \sigma') + \delta\epsilon_n(\mathbf{k}) \pm \hbar\omega_{l'}(\sigma') \}},\quad (4.1)$$

$$E_{n, \mathbf{k}, N} = \epsilon_n(\mathbf{k}) + \delta\epsilon_n(\mathbf{k}) + \sum_{t, \sigma} \hbar\omega_t(\sigma) (N_{t, \sigma} + \frac{1}{2}),\quad (4.2)$$

$$\begin{aligned}\delta\epsilon_n(\mathbf{k}) &= 2 \sum_{l', n', \sigma' > 0} \frac{|\mathfrak{N}_{l'}(n', \mathbf{k} + \sigma'; n, \mathbf{k})|^2 N_{l', \sigma'} \{1 - f(\mathbf{k} + \sigma')\}}{\epsilon_n(\mathbf{k}) - \epsilon_{n'}(\mathbf{k} + \sigma') + \hbar\omega_{l'}(\sigma') + \delta\epsilon_n(\mathbf{k})} \\ &\quad + 2 \sum_{l', n', \sigma' > 0} \frac{|\mathfrak{N}_{l'}(n', \mathbf{k} - \sigma'; n, \mathbf{k})|^2 (N_{l', \sigma'} + 1) \{1 - f(\mathbf{k} - \sigma')\}}{\epsilon_n(\mathbf{k}) - \epsilon_{n'}(\mathbf{k} - \sigma') - \hbar\omega_{l'}(\sigma') + \delta\epsilon_n(\mathbf{k})},\end{aligned}\quad (4.3)$$

where  $N_{l\sigma}$  is the phonon occupation number for the mode  $\sigma$ , of the  $l$ th vibrational branch. The above result (4.3) differs from that given by Frohlich<sup>9</sup> and Bardeen,<sup>7</sup> in that the self-energy  $\delta\epsilon_n(\mathbf{k})$  occurs in the denominator. If we omit the perturbing term  $H'$  from the total Hamiltonian and repeat the above analysis for the total energy  $E_{n, \mathbf{k}, N}$ , we obtain again the expressions (4.1), (4.2), and (4.3) with the difference, however, that the phonon energy  $\hbar\omega_t(\sigma)$  does not occur in the denominators of these expressions. In the following section we shall evaluate  $\delta\epsilon_n(\mathbf{k})$  approximately and show that at all temperatures above the liquid helium range the presence of the  $\hbar\omega_t(\sigma)$  term in the denominator has a negligible effect on the magnitude of the self-energy for the particular cases of Ge and Si.

### 5. ELECTRON SELF-ENERGY IN Ge AND Si

The conduction band of Si consists of six equivalent prolate ellipsoids of revolution oriented along the six equivalent  $\langle 1, 0, 0 \rangle$  directions in  $\mathbf{k}$  space. The conduction band of Ge consists of 8 (or 4 if centered at the zone boundary) equivalent ellipsoids of revolution oriented along the set of eight equivalent  $\langle 1, 1, 1 \rangle$  axes in  $\mathbf{k}$ -space.

<sup>9</sup> H. Frohlich, Phys. Rev. 79, 845 (1950).

surface is a prolate ellipsoid of revolution, having  $m_1 = m_l$ , and  $m_2 = m_3 = m_t$ . As expected, Eq. (3.7) or Eq. (3.9) indicate that for spherical energy surfaces, only the interaction with the longitudinal mode remains. In addition the interaction constant vanishes for free electrons. Since the energy difference in (3.9) is seldom known with accuracy, (3.9) may be used to determine the maximum vertical energy separation between the bottom of the conduction band and the top of the valence band, if  $C^{n'n'}(\mathbf{k})$  is determined from the acoustic lattice mobility expression.

### 4. ELECTRONIC SELF-ENERGY

In this section the energy  $E_{n, \mathbf{k}, N}$  is evaluated using a variation method following the scheme of Takano.<sup>8</sup> Multiplying the Schrödinger equation (3.7) on the left by  $\Psi_{n, \mathbf{k}, N}^*$  and integrating, we then minimize the total energy with respect to the parameters  $b_{n, \mathbf{k}}(l', n', \sigma')$ . The results are

Under a suitable orthogonal transformation each surface may be represented by an expression of the form (3.6) with  $m_1 = m_l$  and  $m_2 = m_3 = m_t$ . In the expression (4.3) the occupation number  $N_{l, \sigma}$  becomes small for large values of  $\sigma$ . Since virtual transitions between energy minima require  $\sigma$  of the order of magnitude of  $2\pi$  times the reciprocal lattice parameter, then intervally transitions should contribute very little to the self-energy. Furthermore, for the case where the states  $n$  and  $n'$  have large energy separations we may drop the summation over  $n'$  in (4.3) and put  $n = n'$ . For an approximate evaluation of  $\delta\epsilon_n(\mathbf{k})$  we drop the term  $\delta\epsilon_n(\mathbf{k})$  in the denominator of (4.3) and use classical statistics. Thus replacing the summation by integration over  $\sigma$  space, we find

$$\begin{aligned}\delta\epsilon_n(\mathbf{k}) &= - \sum_{l'} \frac{4}{9} \frac{m_l C_{l'}^2}{\rho \hbar s_{l'} (2\pi)^3} [J_+(\mathbf{k}) + J_-(\mathbf{k})] \\ &\quad - \sum_{l'} \frac{4}{9} \frac{m_l C_{l'}^2}{\rho \hbar s_{l'} (2\pi)^3} \int_0^{\sigma_m} \sigma^2 d\sigma \int_0^{2\pi} d\phi \\ &\quad \times \int_{-1}^{+1} dx [\sigma(1 - Ex^2) + 2\sigma_0 - B(x, \phi, \Theta)]^{-1},\end{aligned}\quad (5.1)$$

where

$$J_{\pm}(\mathbf{k}) = \int_0^{\sigma_m} N_{\nu, \sigma} d\sigma \int_0^{2\pi} d\phi \times \int_{-1}^{+1} dx [\sigma(1 - Ex^2) \mp 2\sigma_0 \pm B(x, \phi, \Theta)]^{-1}, \quad (5.2)$$

and

$$B(x, \phi, \Theta) = 2|\Delta\mathbf{k}| [(1-E)x \cos\Theta + (1-x^2)^{1/2} \cos\phi \sin\Theta]. \quad (5.3)$$

In the foregoing we have put  $\theta$  and  $\phi$  as the polar angles of  $\sigma$  and  $\Theta$  as the angle between  $\Delta\mathbf{k}$  (electron propagation vector measured from the energy minimum) and the longitudinal axis of the energy ellipsoid. The various quantities occurring in the above equation are defined as follows:  $\sigma_m$ , the maximum phonon wave number;  $s_t$ , the velocity of sound for the  $t$ th vibrational branch;  $\rho$ , the crystal density;  $\sigma_0 = m_t s_t / \hbar$ , the wave number of the electron traveling with the velocity of sound in the transverse direction, and  $E = (1-r)$ , where  $r = (m_t/m_i)$  is the effective mass ratio.

The mean phonon occupation number is given by

$$\bar{N}_{\nu, \sigma} = \{\exp(\hbar\omega_{\nu}(\sigma)/\kappa T) - 1\}^{-1} = \sum_{n=1}^{\infty} e^{-n\beta_{\nu}\sigma}, \quad (5.4)$$

where  $\beta_{\nu} = \hbar s_{\nu} / \kappa T$ . From (5.3) we obtain the result,

$$J_+(\mathbf{k}) + J_-(\mathbf{k}) = \int_0^{2\pi} d\phi \sum_{n=1}^{\infty} \frac{2}{n^2 \beta_{\nu}^2} \int_{-1}^{+1} \frac{dx}{(1 - Ex^2)} \times \left[ \int_0^{n\beta_{\nu}\sigma_m} \xi e^{-\xi} d\xi + n^2 \delta^2 \int_0^{n\beta_{\nu}\sigma_m} \frac{\xi e^{-\xi} d\xi}{\xi^2 - n^2 \delta^2} \right], \quad (5.5)$$

with

$$\delta = \beta_{\nu} (2\sigma_0 - B) / (1 - Ex^2).$$

At the energy band minimum located at  $\mathbf{k}^0$ , the quantity  $B=0$ , so that from (5.1) and (5.5)

$$\delta\epsilon_n(\mathbf{k}^0) = -\frac{1}{3} \frac{m_t \langle C^2 \rangle_n \alpha_1(E)}{\kappa M (10^3)} F(\Theta_D, T), \quad (5.6)$$

where

$$F(\Theta_D, T) = \frac{10^3}{\Theta_D} \left[ 1 + 4 \left\{ \left( \frac{T}{\Theta_D} \right)^2 \left( \frac{\pi^2}{6} - L_2(e^{-\Theta_D/T}) \right) + \left( \frac{T}{\Theta_D} \right) \ln(1 - e^{-\Theta_D/T}) \right\} \right], \quad (5.7)$$

where we have assumed equal phonon velocities and employed the relations

$$\sigma_m = \kappa \Theta_D / \hbar s_t = 2\pi (3/4\pi)^{1/2} \Omega^{-1/2}. \quad (5.8)$$

In the above it can be easily shown by use of the Euler-Maclaurin summation formula that the second term in the square brackets of (5.5) is negligible down to liquid helium temperatures. The function  $L_2(x)$  is Euler's dilogarithmic integral defined by

$$L_2(x) = - \int_0^x \frac{1}{z} \ln(1-z) dz = \sum_{n=1}^{\infty} \frac{x^n}{n^2}.$$

In addition we have taken the principal values of the integral leading to

$$\alpha_1(E) = E^{-1/2} \ln \left| \frac{1+E^{1/2}}{1-E^{1/2}} \right|. \quad (5.9)$$

For spherical energy surfaces,  $r=1$ ,  $E=0$  and  $\alpha_1(0)=2$ . At high temperatures defined by  $(T/\Theta_D) \gg 1$ , expression (5.7) becomes

$$F(\Theta_D, T) = \frac{10^3}{\Theta_D} \left[ 1 + 4 \left( \frac{T}{\Theta_D} \right) \right], \quad (5.10)$$

and at low temperatures defined by  $(T/\Theta_D) \ll 1$ ,

$$F(\Theta_D, T) = \frac{10^3}{\Theta_D} \left[ 1 + \frac{2}{3} \pi^2 \left( \frac{T}{\Theta_D} \right)^2 \right]. \quad (5.11)$$

The result (5.6) is in agreement with that of Fan and Muto and Oyama, except for the introduction of the factor  $\alpha_1(E)$  and the function  $F(\Theta, T)$  which covers almost the entire temperature range of interest. For Ge and Si, the temperature rate of change of the self-energy is deduced from expression (5.7) rather than from (5.10), as Fan claims.

## 6. TEMPERATURE DEPENDENCE OF EFFECTIVE MASSES

Due to the electron lattice interaction the total electron energy  $\bar{\epsilon}_n(\mathbf{k})$  may be considered as

$$\bar{\epsilon}_n(\mathbf{k}) = \epsilon_n(\mathbf{k}) + \delta\epsilon_n(\mathbf{k}),$$

where  $\delta\epsilon_n(\mathbf{k})$  is the temperature-dependent term. The principal effective masses are then given by the solution of the secular determinant

$$\left| \frac{1}{\hbar^2} \frac{\partial^2 \bar{\epsilon}_n(\mathbf{k})}{\partial k_i \partial k_j} - \frac{1}{m_i(T)} \delta_{ij} \right| = 0, \quad (6.1)$$

if  $\bar{\epsilon}_n(\mathbf{k})$  is a quadratic function of the components of  $\mathbf{k}$ . Since  $\epsilon_n(\mathbf{k})$  is already in canonical form, it follows from expression (5.1) that the off-diagonal elements of the effective mass matrix are small in comparison with the diagonal elements. Thus diagonalization becomes unnecessary and the principal effective masses are given by

$$\frac{1}{m_i(T)} = \frac{1}{\hbar^2} \frac{\partial^2 \bar{\epsilon}_n(\mathbf{k})}{\partial k_i^2} \quad (6.2)$$

to a good approximation. At high temperatures we obtain from (5.2):

$$J_+(\mathbf{k}) + J_-(\mathbf{k}) = \left(\frac{\kappa T}{\hbar s_l}\right) \int_0^{2\pi} d\phi \int_{-1}^{+1} \frac{dx}{(1-Ex^2)} \left[ 2\sigma_m + \frac{(2\sigma_0 - B)}{(1-Ex^2)} \times \ln \left| \frac{\sigma_m(1-Ex^2) - (2\sigma_0 - B)}{\sigma_m(1-Ex^2) + (2\sigma_0 - B)} \right| \right]. \quad (6.3)$$

Since  $(B - 2\sigma_0)/\sigma_m(1 - Ex^2) < 1$  for electrons of average  $|\Delta\mathbf{k}|$  values, the logarithmic term may be expanded into a series, so that the principal effective masses are given by

$$m_i(0)/m_i(T) = 1 + (128\pi/9\rho\hbar^3)m_i^2(0)\alpha_i(E) \times \left(\sum_{\nu'} C_{\nu'}^2/s_{\nu'}\Theta_{D\nu'}\right)T, \quad (6.4)$$

where  $m_i(0)$  is the electron effective mass at absolute zero and includes the effect of the zero-point vibrations of the lattice. For the longitudinal direction

$$\alpha_l(E) = (1 - E)^3\alpha(E),$$

and for the transverse direction

$$\alpha_t(E) = \frac{1}{2}[\alpha_3(E) - \alpha(E)],$$

where the various  $\alpha$  functions are defined as

$$\alpha(E) = \frac{1}{4E} \left[ \frac{(1+E)}{(1-E)} - \frac{1}{2}\alpha_1(E) \right],$$

$$\alpha_3(E) = \frac{1}{2}(1-E)^{-2} + \frac{3}{4}(1-E)^{-1} + \frac{3}{8}\alpha_1(E).$$

For spherical energy surfaces,  $E=0$  and  $\alpha_i(0) = \frac{2}{3}$ .

## 7. ADIABATIC APPROXIMATION

The variational method employed in Sec. 4 for the derivation of the interaction energy  $\delta\epsilon_n(\mathbf{k})$  suffers one disadvantage in that the evaluation of the interaction energy requires, as a first approximation, the omission of the  $\delta\epsilon_n(\mathbf{k})$  term in the denominators of expression (4.3). However, one advantage arises in establishing immediately a criterion for the validity of the adiabatic approximation, which is of importance in scattering problems. Seitz<sup>10</sup> has shown that if the electronic wave function is practically independent of the normal lattice coordinates, then the term  $H'$  in the total Hamiltonian is negligible. This is evident from the definition of  $H'$ . Since our trial wave function  $\chi_{n,\mathbf{k}}$  involves the normal lattice coordinates and their canonically conjugate momenta, it is important to determine the effect of omitting the  $H'$  term from the Hamiltonian. As mentioned at the end of Sec. 4, the change in the electronic energy takes the form of expression (4.3) in which,

<sup>10</sup> F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 470.

however, the  $\hbar\omega_l(\sigma)$  term is absent from the denominators. Thus a criterion for the validity of the adiabatic approximation may be written as

$$\hbar\omega_l(\sigma) \ll |\delta\epsilon_n(\mathbf{k}) + \epsilon_n(\mathbf{k}) - \epsilon_{n'}(\mathbf{k} \pm \boldsymbol{\sigma})|,$$

which must hold for all values of  $\sigma$  up to  $\sigma_m$ . The relationship is satisfied where the bands  $n$  and  $n'$  are well separated. For the case  $n=n'$ , the criterion may be expressed as

$$\hbar\omega_l(\sigma) \ll |\delta\epsilon_n(\mathbf{k})|,$$

which is satisfied for Ge and Si for sufficiently long waves. Since it is precisely the small  $\sigma$ , which contribute most to the interaction energy, we may conclude that the adiabatic approximation is valid.<sup>11</sup>

## 8. DISCUSSION

The temperature variation of the energy gap in semiconductors is generally accounted for, by determining the electron and hole self-energies at the band edges, and the effect of lattice expansion with increasing temperature. The high temperature variation for semiconductors having spherical energy surfaces has already been considered.<sup>3</sup> An adequate analysis of the effect of lattice expansion at both high and low temperatures for semiconductors with ellipsoidal or degenerate spherical energy surfaces has yet to be developed. The quadratic behavior with temperature, for the self-energy, as predicted by Eq. (5.11) is substantiated by the work of Macfarlane and Roberts<sup>5</sup> who have observed a quadratic temperature dependence of the energy gap at low temperatures, in both Si and Ge. However, an actual comparison of (5.11) with their experimental data must await a similar calculation for holes.

With regard to the temperature dependence of the electron effective masses, Eq. (6.4) indicates that there is a decrease in effective mass with increasing temperature. Lax and Mavroides,<sup>6</sup> assuming an eight- and six-valley model for Ge and Si, respectively, have analyzed the data of Macfarlane and Roberts and have concluded that there is a possible 30% decrease in the density of states mass  $m_n = m_t^{\frac{1}{2}}m_l^{\frac{1}{2}}$  for electrons in Ge at 300°K. For Si, however, they deduce a slight increase in the combined density of states mass  $(m_n m_p)^{\frac{1}{2}}$ , which appears to be in contradiction with the theoretical result (6.4), since hole effective masses are also expected to decrease with increasing temperature. The observed result in Si, may be due therefore to the greater influence of lattice expansion on the curvature of the energy surfaces, as well as to the increase with temperature of

<sup>11</sup> K. Huang, Proc. Phys. Soc. (London) **A64**, 867 (1951). In his discussion of Wentzels' lattice instability, Huang dropped the  $\hbar\omega_l(\sigma)$  term in the denominators of (4.3) (which did not contain the  $\delta\epsilon_n(\mathbf{k})$  term), and had, as he remarked, used the adiabatic approximation, which he considered as valid for long waves. This conclusion is particularly evident from our expressions (5.2) and (5.5), where  $\sigma_0$  [which arises from the  $\hbar\omega_l(\sigma)$  term] occurs only in the term which is negligible at temperatures above approximately 4°K.

the statistically derived hole density of states effective mass.<sup>12</sup> The later possibility is definitely operative since the spin-orbit splitting  $\Delta = (0.035 \text{ eV})$  in Si is small.

An approximate evaluation of the percentage change in the principal effective masses in Ge and Si at 300°K may be made, by assuming that the phonon velocities are isotropic. Expression (6.4) may be written as

$$\frac{m_i(0)}{m_i(T)} = 1 + (128\pi/9\rho h^3 s \Theta_D) m_i^2(0) \alpha_i(E) \langle C^2 \rangle_{Av} T, \quad (8.1)$$

where  $\langle C^2 \rangle_{Av}$  is the mean square Sommerfeld-Bethe interaction constant, defined by

$$\langle C^2 \rangle_{Av} = \sum_{i'} \langle C_{i'}^2 \rangle_{Av},$$

and determined from the standard expression for acoustic lattice mobility

$$\langle C^2 \rangle_{Av} = - \frac{9}{4} \left\{ \frac{3.2 \times 10^{-5} c_{ii}}{\mu T^{\frac{3}{2}}} \right\} \left( \frac{m}{m^*} \right)^{5/2} \text{ ev}. \quad (8.2)$$

Here  $m^*$  is the mobility effective mass given by<sup>13</sup>

$$m^* = (m_n^3 m_\sigma^2)^{1/5}, \quad (8.3)$$

with

$$m_n = (m_i^2 m_l)^{\frac{1}{3}},$$

$$\frac{1}{m_\sigma} = \frac{1}{3} \left( \frac{1}{m_l} + \frac{2}{m_t} \right).$$

It may be remarked here that Morin and Maita<sup>14</sup> have observed experimentally a deviation from the  $T^{-\frac{1}{2}}$  law for the lattice mobility as given by (8.2). One possible explanation of the deviation, as put forward by Benedek, Paul, and Brooks<sup>15</sup> is that the effective mass  $m^*$  in (8.2)

<sup>12</sup> In Ge and Si, the valence band is doubly degenerate at  $\mathbf{k}=0$  and characterized by effective masses  $m_1$  and  $m_2$ , while a third band separated by spin-orbit interaction  $\Delta$  is characterized by  $m_3$ . In this case

$$m_p = [m_1^{\frac{1}{3}} + m_2^{\frac{1}{3}} + m_3^{\frac{1}{3}} \exp(-\Delta/\kappa T)]^{\frac{3}{2}}.$$

<sup>13</sup> B. Abeles and S. Meiboom, Phys. Rev. **95**, 31 (1954); M. Shibuya, Phys. Rev. **95**, 1385 (1954).

<sup>14</sup> F. J. Morin, Phys. Rev. **93**, 62 (1954); F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

<sup>15</sup> Benedek, Paul, and Brooks, Phys. Rev. **100**, 1129 (1955).

be temperature dependent. If this be the case, then the temperature dependence of  $m^*$  must arise solely from lattice expansion, and is not given by expression (8.1). This is most clearly seen by examining the different roles played by the electron-lattice interaction term  $V(\mathbf{R}, \mathbf{r})$  in the mobility theory leading to (8.2) and in the self energy calculation leading to (8.1). It thus appears possible to reformulate mobility theory on the latter basis, using  $H'$  as the perturbing term for transition probabilities, since, as we have seen, the adiabatic approximation is valid. From the above observations we conclude, that it is not an entirely consistent procedure to use expression (8.2) in conjunction with (8.1). In spite of the inconsistency it is hoped that the mobility expression (8.2) will give an approximately correct value for  $\langle C^2 \rangle_{Av}$  to be used in determining the temperature variation of the effective mass. With the further approximation of using the low temperature effective masses  $m_t(0)$  and  $m_l(0)$ , as determined by cyclotron resonance experiments,<sup>16</sup> in (8.2), we find that for Ge,  $m_\sigma = 0.12m$ ,  $m_n = 0.22m$ , and  $m^* = 0.17m$ . For Si the same quantities are  $m_\sigma = 0.26m$ ,  $m_n = 0.33m$ , and  $m^* = 0.30m$ . The Morin-Maita electron mobilities<sup>14</sup> at 300°K are  $\mu(\text{Ge}) = 3800 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$  and  $\mu(\text{Si}) = 1400 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ . From (8.2) we then obtain  $(\langle C^2 \rangle_{Av})^{\frac{1}{2}} = 22 \text{ ev}$  for Ge and  $(\langle C^2 \rangle_{Av})^{\frac{1}{2}} = 20 \text{ ev}$  for Si. Substituting for the known values of the parameters in (8.1), we find that for Ge at 300°K, the longitudinal effective mass has decreased by 0.26%, and the transverse effective mass by 0.14%. The respective changes for Si are 0.23% and 0.12%. From these results the decrease in the electron density of states mass amounts to 1.0% for Ge and 0.8% for Si. In the case of Ge the decrease is considerably less than the 30% decrease estimated by Lax and Mavroides. The value of 22 ev for the interaction constant in Ge does not appear unreasonably high since the same value in expression (3.9) leads to a maximum vertical energy separation of 2.2 ev between the bottom of the conduction band and the valence band. We conclude that a large part of the effective-mass decrease must be due to lattice expansion.

<sup>16</sup> Lax, Zeiger, and Dexter, Physica **20**, 818 (1954); C. Kittel, Physica **20**, 829 (1954); F. Herman, Proc. Inst. Radio Engrs. **43**, 1703 (1955).