

## Variational Treatment of Warm Electrons in Nonpolar Crystals\*

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Deviations from Ohm's law in nonpolar crystals are treated for weak fields by the variational method. A simple band structure is assumed. Scattering by both acoustical and optical phonons, and ionized impurities is included. It is shown that the influence of optical phonons on the field dependent mobility ( $E^2$  term where  $E$  is the electrostatic field) is maximum for a temperature which corresponds approximately to the optical phonon energy. The field dependent mobility is highly sensitive to ionized impurity scattering as in the case of acoustical phonons alone. Finally, the convergence of the variational method is established in limiting cases using as a representation a set of polynomials which are orthonormal with respect to the collision operator. Extensive calculations are given for electrons in germanium and comparison with experiment is discussed.

### 1. INTRODUCTION

IN an earlier paper,<sup>1</sup> hereafter referred to as I, the application of the variational method to the problem of nonlinear conduction in solids has been discussed. In this paper we are concerned with an actual calculation of the second order term in the electrical conductivity of a nonpolar crystal such as germanium. This problem, the so-called warm electrons problem, has been discussed experimentally and theoretically by several authors.<sup>2-6</sup> Yamashita<sup>3</sup> has approximated the transport equation by a differential equation for which he gave a particular solution which actually violates the boundary condition at infinity. The passage to the differential equation is justified at high temperatures for nearly all energies and at all temperatures for high enough energies. Thus, in determining the high-temperature solution and the asymptotic trend, the differential equation is valuable, but only when the correct boundary condition is incorporated. Morgan<sup>2</sup> has emphasized the importance of optical phonons and published results based on a numerical solution of the transport equation.

Our treatment here is entirely different from those of Morgan and Yamashita and is based on the variational method. The first aim of this paper is to demonstrate the usefulness of the variational method in discussing this class of problems. It will become evident later that if one can calculate the zero field mobility (Ohm's law) analytically, then the higher order terms in the mobility can likewise be given analytically but in the form of a series. The second aim is to present an adequate overall picture of deviations from Ohm's law by studying the temperature

dependence of these deviations and their sensitivity to ionized impurity scattering. It will be shown that the relative importance of optical to acoustical phonon scattering is maximum at a temperature corresponding approximately to the optical phonon energy. The high- and low-temperature limits are determined mainly by acoustical phonons. We shall touch upon the question of electron-electron collision and see how Frohlich's<sup>7</sup> argument follows from a simple consideration of the thermalization problem.

In Appendix A the correct solution of the differential equation discussed by Yamashita is given. In Appendix B the convergence of the variational method is established in limiting cases.

### 2. TRANSPORT EQUATION

The model we shall discuss is formally covered in Sec. 3b of I. For brevity we shall use the formulation and notation of I. Additional notation will be introduced as needed. The central problem is to solve Eq. (18) of I for  $a_{01}$  and then use the result in Eq. (17) to calculate the mobility. For this purpose we have to define the relaxation time  $\tau$  and the collision operator  $\Lambda_0$ .

Consider a highly dilute classical electron gas in a nonpolar crystal interacting with the acoustical and optical branches of the lattice vibrations in the presence of a weak and uniform electrostatic field  $E$ . Let the electronic effective mass be the scalar  $m$ , and assume that the scattering probability of an electron by a single phonon be as given by equations (27) and (45a) of Seitz.<sup>8,9</sup> It follows then that the relaxation times  $\tau_a$  and  $\tau_{op}$  for acoustical and optical phonon scattering, respectively, are given by<sup>10</sup>

\* The results of this paper were presented at the meetings of the American Physical Society at Cambridge, 1959 and Detroit, 1960. See I. Adawi, *Bull. Am. Phys. Soc.* **4**, 129 (1959); **5**, 193 (1960).

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<sup>1</sup> I. Adawi, *Phys. Rev.* **115**, 1152 (1959).

<sup>2</sup> T. N. Morgan, *J. Phys. Chem. Solids* **8**, 245 (1959).

<sup>3</sup> J. Yamashita, *Phys. Rev.* **111**, 1529 (1958).

<sup>4</sup> J. B. Gunn, *Progress in Semiconductors*, edited by A. F. Gibson *et al.* (Heywood and Company, London, 1957), Vol. II, p. 216.

<sup>5</sup> J. B. Gunn, *J. Phys. Chem. Solids* **8**, 239 (1959).

<sup>6</sup> K. Seeger, *Phys. Rev.* **114**, 476 (1959).

<sup>7</sup> H. Frohlich and B. V. Paranjape, *Proc. Phys. Soc. (London)* **B69**, 21 (1956), see also, R. Stratton, *Proc. Roy. Soc. (London)* **A242**, 355 (1957).

<sup>8</sup> F. Seitz, *Phys. Rev.* **73**, 549 (1948).

<sup>9</sup> See also, W. A. Harrison, *Phys. Rev.* **104**, 1281 (1956). The important fact is that the optical phonon matrix element does not depend on the phonon wave vector which leads rigorously to a relaxation time.

<sup>10</sup> In defining  $\tau_a$  equipartition has been assumed. If we define the average energy of an electron distribution to be  $\frac{3}{2}kT_e$ , then

$$1/\tau_a = Wx^{\frac{1}{2}}, \quad (1)$$

$$1/\tau_{op} = Wbx_0[n(x+x_0)^{\frac{1}{2}} + (n+1)(x-x_0)^{\frac{1}{2}}], \quad (2)$$

where,

$$W = 4\sqrt{2}C^2(mKT)^{\frac{1}{2}}/\rho c^2\hbar^4, \quad (3)$$

$$b = 9D^2c^2K'^2/8C^2\omega_0^2. \quad (4)$$

In these equations  $x$  and  $x_0$  are the electron energy and the optical phonon energy  $\hbar\omega_0$ , respectively, scaled in units of the thermal energy  $KT$ .  $C$  and  $D$  are coupling constants defined by Seitz,<sup>8</sup>  $\rho$  is the mass of the crystal per unit volume,  $c$  is the speed of sound,  $K'$  is a reciprocal lattice wave vector,  $n$  is the equilibrium distribution of optical phonons, namely  $1/(e^x-1)$ , and the square root refers always to the positive real part.

The acoustical phonon collision operator  $\Lambda_0^a$  is defined, according to Eq. (7) of I, by

$$\Lambda_0^a\phi_0 = \frac{W}{4x_a\sqrt{x}} \left\{ \int_a^\infty nz^2 dz [\phi_0 - \phi_0(x+z)] + \int_0^{2(xx_a)^{\frac{1}{2}} - x_a} (n+1)z^2 dz [\phi_0 - \phi_0(x-z)] \right\}, \quad (5)$$

where  $x_a = 2mc^2/KT$ ,  $n$  is the equilibrium number of acoustical phonons, namely,  $1/(e^z-1)$  where  $z = \hbar\omega/KT$ . The first integral in (5) refers to absorbing phonons. The upper limit is  $2(xx_a)^{\frac{1}{2}} + x_a$ , and the lower limit is  $x_a - 2(xx_a)^{\frac{1}{2}}$  for  $x < x_a/4$  and zero otherwise. Equation (5) can be simplified by assuming equipartition and expanding<sup>1</sup> the integrand in a Taylor series to second order in  $z$  and thus arrive at the Lorentzian gas equation,<sup>11</sup>

$$\Lambda_0^a\phi_0 = -\frac{Wx_a}{\sqrt{x}} \frac{d}{dx} \left( e^{-x} x^2 \frac{d\phi_0}{dx} \right). \quad (6)$$

The optical phonon collision operator  $\Lambda_0^{op}$  is given by

$$\Lambda_0^{op}\phi_0 = Wbx_0 e^{-x} \{ n(x+x_0)^{\frac{1}{2}} [\phi_0 - \phi_0(x+x_0)] + (n+1)(x-x_0)^{\frac{1}{2}} [\phi_0 - \phi_0(x-x_0)] \}. \quad (7)$$

In Eq. (18) I, let

$$a_{01}E^2 = \psi y. \quad (8)$$

The field dimensionless constant<sup>11</sup>  $y$  is defined by

$$y = E^2 q^2 / 3m^2 c^2 W^2 = 3\pi\mu_a^2 E^2 / 16c^2, \quad (9)$$

where  $\mu_a = 4q/3mW\pi^{\frac{1}{2}}$  is the zero field mobility of acoustical phonons alone. With these definitions the basic equation we have to solve is

an average electron with this energy and momentum  $p = (3mKT_e)^{\frac{1}{2}}$  will interact on the average with an acoustical phonon of energy  $pc$ . Equipartition is then valid for  $pc \ll KT$  or  $T_e \ll T(KT/3mc^2)$ . Since  $3mc^2$  is of order  $1^\circ\text{K}$  and the distributions we discuss do not depart significantly from thermal equilibrium  $T_e \sim T$ , we see that the equipartition assumption is good down to a few degrees Kelvin.

<sup>11</sup> See, e.g., I. Adawi, Phys. Rev. **112**, 1567 (1958).

$$\frac{1}{\sqrt{x}} \frac{d}{dx} \left( \frac{xe^{-x}}{1+h} \right) = -\frac{1}{\sqrt{x}} \frac{d}{dx} (e^{-x} x^2 \psi') + b(x_0/x_a) e^{-x} \times \{ n(x+x_0)^{\frac{1}{2}} [\psi - \psi(x+x_0)] + (n+1)(x-x_0)^{\frac{1}{2}} [\psi - \psi(x-x_0)] \}, \quad (10)$$

where,

$$h = bx_0 [n(1+x_0/x)^{\frac{1}{2}} + (n+1)(1-x_0/x)^{\frac{1}{2}}]. \quad (11)$$

The mobility  $\mu$  to second order<sup>12</sup> in  $E$  is expressed in terms of the zero field mobility  $\mu_0$  by

$$\mu = \mu_0(1+\beta\gamma), \quad (12)$$

where  $\beta$  is given from 17 I by

$$\beta = \left[ \int_0^\infty Fx dx \right]^{-1} \int_0^\infty Fx(\psi - \psi') dx, \quad (13)$$

$$F \equiv e^{-x}/(1+h).$$

### 3. SOLUTION

#### a. Matrix Elements

To solve Eq. (10), expand  $\psi$  in terms of a set of trial functions  $u_r$ :

$$\psi = \sum_{r=1}^N c_r u_r, \quad (14)$$

and it follows from I that<sup>13</sup> the  $c_r$ 's are determined by solving the  $N$  set of linear algebraic equations

$$b_r = \sum_s d_{rs} c_s,$$

where,<sup>14,15</sup>

$$b_r = \int_0^\infty Fx u_r' dx, \quad (15)$$

$$d_{rs} = \int_0^\infty e^{-x} x^2 u_r' u_s' dx + bn(x_0/x_a) \times \int_0^\infty e^{-x} [x(x+x_0)]^{\frac{1}{2}} [u_r(x+x_0) - u_r] \times [u_s(x+x_0) - u_s] dx.$$

<sup>12</sup> Rigorously, we should consider the coefficient  $a_{22}$  to obtain  $\mu$  correctly to order  $E^2$ . This refinement, however, will not be attempted here.

<sup>13</sup> The definitions of  $\beta$  and the matrix elements  $b_r$  and  $d_{rs}$  here differ from those of I by multiplicative constants but the structure is the same.

<sup>14</sup> In performing scalar products in Eq. (10) to obtain  $b_r$  and  $d_{rs}$ , we have the choice to keep the  $x^{-\frac{1}{2}}$  in both sides of the equation and treat the volume element as  $x^{\frac{1}{2}} dx$ , or lift it from both sides and consider the volume element as  $dx$ .

<sup>15</sup> The exact contribution to  $d_{rs}$  by acoustical phonons follows from the form (5) for  $\Lambda_0^a$ . It is

$$\frac{1}{4x_a^2} \int_0^{\theta/T} \frac{e^z}{e^z-1} z^2 dz \int_{(x_a+z)^2/4x_a}^\infty e^{-x} [u_r - u_r(x-z)] [u_s - u_s(x-z)] dx,$$

which can be approximated by

$$\frac{1}{4x_a^2} \int_{x_a/4}^\infty e^{-x} dx \int_0^{2(xx_a)^{\frac{1}{2}} - x_a} (e^z/(e^z-1)) z^2 dz [u_r - u_r(x-z)] \times [u_s - u_s(x-z)]$$

and which in turn leads to the first integral in (15) after obvious simplifications.  $\theta$  is the Debye temperature.

We shall basically use the representation of I, namely,

$$u_r = x^r - \frac{3}{2} \frac{5}{2} \cdots (2r+1)/2, \quad (16)$$

then,

$$b_r = r \int_0^\infty e^{-x} x^r dx / (1+h), \quad (17)$$

$$d_{rs} = rs(r+s)! + bn(x_0/x_a) \sum_{i=0}^{r-1} \sum_{j=0}^{s-1} \binom{r}{i} \binom{s}{j} x_0^{r+s-i-j} f_{i+j+\frac{1}{2}}. \quad (18)$$

The function  $f_m$  in (18) is defined<sup>16</sup> by

$$f_m(x_0) = \int_0^\infty e^{-x} x^m (x+x_0)^{\frac{1}{2}} dx \quad (19)$$

$$= m! e x_0^{1/2} x_0^{\frac{1}{2}m+\frac{1}{2}} W_{\frac{1}{2}-m/2, m/2+\frac{1}{2}},$$

and satisfies the recursion system,

$$f_{m+1} - (m - x_0 + \frac{3}{2}) f_m - m x_0 f_{m-1} = x_0^{\frac{3}{2}} \delta_{m0}, \quad (20)$$

deduced by one partial integration of (19). The function  $f_{\frac{1}{2}}$  and  $f_{\frac{3}{2}}$  are evaluated with the aid of Watson's formula.<sup>17</sup> The result is

$$f_{\frac{1}{2}} = (x_0/2) e^{x_0/2} K_1(x_0/2), \quad (21)$$

$$f_{\frac{3}{2}} = (x_0/2) e^{x_0/2} [(2-x_0/2) K_1(x_0/2) + (x_0/2) K_0(x_0/2)].$$

From (21) and (20) all  $f_m$ 's which occur in (18) can be generated and consequently all elements  $d_{rs}$  of the collision matrix  $\mathbf{D}$  can be evaluated analytically.

As for the matrix  $\mathbf{B}$ , (which could, for obvious reasons, be called the *source* or *drift matrix*), the elements  $b_r$  have to be calculated, in general by numerical methods. We recall that

$$\mu_0 = \mu_a b_1, \quad (22)$$

which means that the zero field mobility has to be calculated numerically because of the cumbersome function  $h$ . Since the evaluation of any  $b_r$  is similar to the evaluation of  $b_1$ , we conclude that if Ohm's law mobility can be calculated in terms of tabulated functions, the same will be true for the elements  $b_r$ .

Once the matrices  $\mathbf{B}$  and  $\mathbf{D}$  are computed the matrix equation of (15),  $\mathbf{B} = \mathbf{D}\mathbf{C}$ , is solved for the  $c_r$ 's and the result is used to calculate  $\beta$  or any other physical property desired. From (13),

$$\beta = \sum_{r=1}^N \frac{c_r}{b_1} \left( \frac{b_{r+1}}{r+1} - b_r - \frac{3}{2} \frac{5}{2} \cdots \frac{2r+1}{2} b_1 \right). \quad (23)$$

<sup>16</sup> The function  $W_{k,m}$  is the Whittaker function. See E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, New York, 1940), 4th ed., p. 340.

<sup>17</sup> G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, New York, 1922), p. 172 formula (4) and p. 79. Derivation of  $f_{\frac{1}{2}}$  is obvious. To derive  $f_{\frac{3}{2}}$  express  $2f_{\frac{1}{2}} + x_0 f_{\frac{1}{2}}$  in terms of  $K_2(x_0/2)$  by a partial integration.

## b. Orthonormal Polynomials

In the interest of arriving at a simple set of linear equations in (15) we shall construct a set of polynomials which are orthonormal with respect to the collision operator. Multiply both sides of (10) by  $x^{\frac{1}{2}}$  and write the result in the abbreviated form:

$$g = \Lambda \psi, \quad (24)$$

then the polynomials  $p_r$  can be constructed from the  $u_r$ 's of (16) by the Schmidt process,

$$p_1 = u_1 / d_{11}^{\frac{1}{2}},$$

$$p_n = \left\{ u_n - \sum_{r=1}^{n-1} (u_n \Lambda p_r) p_r \right\} \left\{ d_{nn} - \sum_{r=1}^{n-1} (u_n \Lambda p_r)^2 \right\}^{-\frac{1}{2}}. \quad (25)$$

These polynomials satisfy the property

$$(p_r \Lambda p_s) = \delta_{rs}, \quad (26)$$

and the normalization condition of I

$$\int_0^\infty p_r e^{-x} x^{\frac{1}{2}} dx = 0. \quad (27)$$

If we write

$$\psi = \sum_{r=1}^N \alpha_r p_r, \quad (28)$$

we easily see that

$$\alpha_r = \int_0^\infty x p_r' F dx, \quad (29)$$

$$\beta = \sum_{r=1}^N \alpha_r \left( -\alpha_r + \int_0^\infty F p_r dx \right) / b_1, \quad (30)$$

and

$$(\psi \Lambda \psi) = \sum_{r=1}^N \alpha_r^2. \quad (31)$$

The use of orthonormal polynomials is valuable in discussing convergence questions. See Appendix B.

## c. General Remarks

Several helpful remarks about the nature of the problem can be made with little analysis.

(i) An energetic electron will lose energy to optical and acoustical phonons at the rates,<sup>18</sup>  $W b x_0 \hbar \omega_0 \sqrt{x}$  and  $2mc^2 W x^{\frac{3}{2}}$ , respectively. Therefore, for sufficiently large energy ( $2mc^2 x > b x_0 \hbar \omega_0$ ), the asymptotic solution of (10) is determined by acoustical phonons alone<sup>19</sup> and

<sup>18</sup> The energy transfer equation leads to the loss rates

$$W b x_0 \hbar \omega_0 [(n+1)(x-x_0)^{\frac{1}{2}} - n(x+x_0)^{\frac{1}{2}}]$$

and

$$2mc^2 W (x^{\frac{1}{2}} - 2x^{\frac{3}{2}}),$$

respectively, the former result is obvious, the latter was first derived by W. Shockley, Bell System Tech. J. **30**, 990 (1951).

<sup>19</sup> It is then obvious that (10) cannot have periodic solutions with periodicity  $x_0$  as claimed by T. N. Morgan in Bull. Am. Phys. Soc. **3**, 13 (1958).

$\psi \sim \ln x$ . This suggests that an improved asymptotic solution is obtained by expanding  $\psi(x \pm x_0)$  in a Taylor series. This solution is discussed at length in Appendix A in connection with Yamashita's work.

(ii) For *very low* temperatures such that  $b(x_0/x_a)n \ll 1$ , the optical phonon terms in (10) can be neglected and the answer<sup>11</sup> is

$$\psi = \ln x - \Psi\left(\frac{1}{2}\right), \quad (32)$$

$$\beta = -0.61.$$

(iii) For *low* temperatures such that  $bnx_0 \ll 1$ , optical phonons contribute very little to the mobility and the function  $h(x)$  can be ignored and  $b_r = rr!$  (as for acoustical phonons alone). But, optical phonon terms on the right of (10) must be retained.

(iv) For high temperatures  $x_0 \ll 1$ ,  $nx_0 \approx 1$ ,  $h \sim 2b$ , and the mobility  $\mu_0$  is reduced from its acoustical phonon value by the factor  $(1+2b)$ . From (17) and (15)

$$b_r = rr!/(1+2b), \quad (33)$$

$$\begin{aligned} d_{rs} &= \int_0^\infty \{x^2 + bn(x_0^3/x_a)[x(x+x_0)]^{\frac{1}{2}}\} e^{-x} u_r' u_s' dx \\ &\approx \int_0^\infty e^{-x} x(x + bx_0^2/x_a) u_r' u_s' dx. \end{aligned} \quad (34)$$

Indeed, the optical phonon collision operator can be reduced (in analogy with the form (6) for acoustical phonons) to

$$\Lambda_0 \text{op} \phi_0 = -Wbx_0^2 \frac{1}{\sqrt{x}} \frac{d}{dx} \left( e^{-x} x \frac{d\phi_0}{dx} \right), \quad (35)$$

and Eq. (10) reduces to

$$-\frac{d}{dx} \left( \frac{x e^{-x}}{1+2b} \right) = -\frac{d}{dx} [e^{-x} x(x + bx_0^2/x_a) \psi']. \quad (36)$$

The solution of (36) is

$$\begin{aligned} \psi &= (1+2b)^{-1} \left\{ \ln(x + bx_0^2/x_a) - 2\pi^{-\frac{1}{2}} \int_0^\infty e^{-x} x^{\frac{1}{2}} \right. \\ &\quad \left. \times \ln(x + bx_0^2/x_a) dx \right\}. \end{aligned} \quad (37)$$

From (37), (13), and (32) we obtain that

$$\beta(x_0=0) = -0.61/(1+2b). \quad (38)$$

The high-temperature limit of (38) is the same as the low-temperature limit of (32) except for the factor  $1+2b$ . In the former case the optical phonon operator in (36) or (10) approaches zero slowly as  $1/T$  (since  $x_0^2/x_a = (\hbar\omega_0)^2/2mc^2KT$ ), and in the latter case it

vanishes exponentially and rapidly like

$$\exp[-(\hbar\omega_0/KT)].$$

For some moderate temperature, therefore, the optical phonon operator should have a maximum influence on the solution and  $|\beta|$  should assume a minimum value when the thermal energy is of the order of the optical phonon energy.

#### 4. CALCULATIONS

In this section we present calculations of  $\beta$  for electrons in germanium.

##### a. Parameters

The parameter  $b$  relating the strength of scattering by optical to acoustical phonons is determined by fitting the temperature dependence of the mobility  $\mu_0$  to the experimental law<sup>20</sup>  $T^{-1.66}$ . Deviations from  $T^{-1.5}$  law are thus ascribed to optical phonons alone, although it is conceivable that a small change in the effective mass  $m$  with temperature might contribute.<sup>21</sup> There is some arbitrariness in determining  $b$  as can be seen from Figs. 1 and 2 and the graph of Herring.<sup>22</sup> We find  $b \sim 0.19$  if  $\log(\mu_0/\mu_a)$  versus  $\log T$  has the *average* slope  $-0.16$  for  $80^\circ < T < 300^\circ\text{K}$ . The accepted values  $c = 5.4 \times 10^5$  cm/sec, and  $\mu_0 = 3800$  cm<sup>2</sup>/volt sec at  $300^\circ\text{K}$  are used. The optical phonon energy is assumed to correspond<sup>23</sup> to  $400^\circ\text{K}$ . A scalar effective mass for germanium is clearly not defined. We shall take for  $m$  either the density of states effective mass<sup>24</sup> which is  $0.22 m_0$  or the conductivity effective mass which is  $0.12 m_0$ , where  $m_0$  is the electron rest mass. This leads to the two values of 475 and 870 for  $\hbar\omega_0/2mc^2$ . With

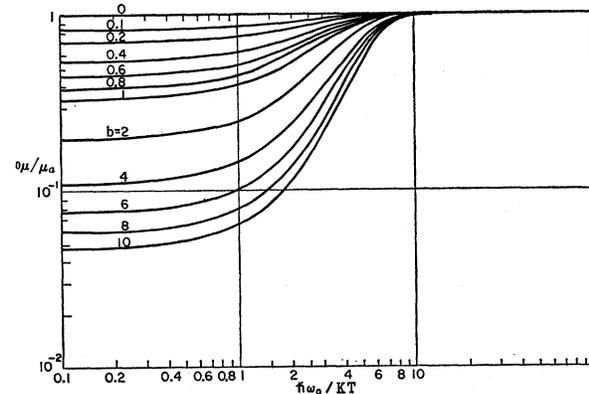


FIG. 1. Influence of optical phonon scattering on the temperature dependence of the reduced zero field mobility  $\mu_0/\mu_a$ , for various values of the optical phonon scattering parameter  $b$ .

<sup>20</sup> F. J. Morin, Phys. Rev. **93**, 62 (1954).

<sup>21</sup> Intervalley scattering is ruled out by the symmetry argument of C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

<sup>22</sup> C. Herring, Bell System Tech. J. **34**, 237 (1955).

<sup>23</sup> I. Pelah *et al.*, Phys. Rev. **108**, 1091 (1957).

<sup>24</sup> G. Dresselhauss, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).

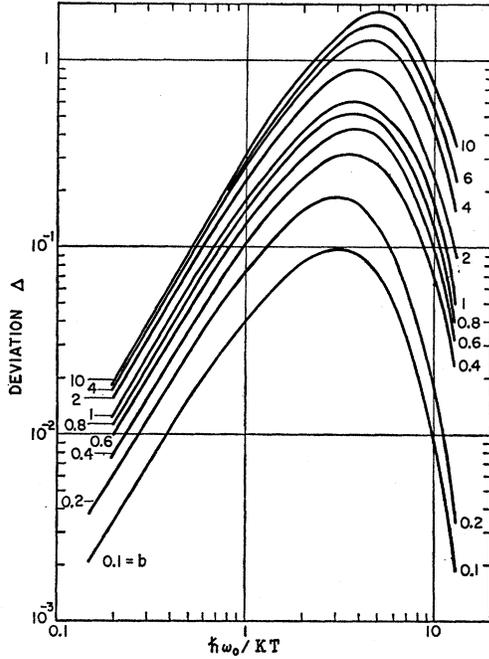


FIG. 2. Temperature dependence of deviations of the zero field mobility from the  $T^{-3}$  law, for various values of  $b$ . The ordinate scale shows the deviation  $\Delta$  where  $\mu_0 \propto T^{-(3+\Delta)}$ .  $\Delta$  is obtained by differentiating the curves of Fig. 1.

these values, the field parameter  $y$  can be written as

$$y = 1.92x_0^3 \times 10^{-5} E^2, \quad (39)$$

when  $E$  is expressed in volt/cm.

### b. Temperature Dependence of $\beta$

In these calculations the method of orthonormal polynomials was used as it proved to be more accurate, from a practical and not a fundamental point of view, than the power series method of (16). [This is particularly true if the system of linear equations (15) is illconditioned.] The convergence of  $\beta$  [and of course that of  $(\psi\Delta\psi)$ ] is monotonic. The last terms retained contributed no more than a few percent. In all no more than 10 terms were used. The variation of the  $E^2$  term in the mobility with temperature is shown in Figs. (3) and (4) where  $-\beta$  is plotted against  $\hbar\omega_0/KT = x_0$ . The first term in the series of Eq. (30) (which corresponds to a Maxwellian distribution) is also shown for comparison. It is seen that  $|\beta|$  assumes a minimum for  $\hbar\omega_0/KT \sim 0.8$ . For the Maxwellian this value is about  $4/3$ . No simple power law can describe the variation of  $\beta$  with temperature over a wide temperature range. For  $T < 80^\circ\text{K}$ ,  $\mu_0 \sim \mu_a$  and  $\hbar$  can be ignored. Below  $40^\circ\text{K}$ , optical phonons can be ignored altogether and we essentially have acoustical phonons alone.

### c. Ionized Impurities

It is customary to use for the potential of an ionized impurity center the screened Coulomb field,

$$V(r) = \pm q^2 e^{-r/a} / Dr, \quad (40)$$

where  $V$ ,  $q$ ,  $D$ ,  $r$ , and  $a$  are the potential energy, charge, dielectric constant, distance and screening radius, respectively. The  $+$  and  $-$  are for repulsive and attractive potentials, respectively. Conwell and Weisskopf (CW) omit the screening factor in (40) and introduce the cutoff by ignoring scattering for impact parameters greater than  $\frac{1}{2}N_I^{-1/3}$  where  $N_I$  is the number of ions per unit volume, while Brooks and Herring take  $a$  to be the Debye length.<sup>25</sup> The question of a rigorous potential with a natural cutoff is still open.<sup>26</sup>

For purposes of estimates  $a$  is of order  $N_I^{-1/3}$ . The validity of classical mechanics and the Born approximation for the calculation of a cross section and a relaxation time from (40) is excellently discussed by Bohr.<sup>27</sup> To summarize Bohr's results, the collision diameter  $b_c = 2q^2/Dmv^2$  and the de Broglie wavelength  $2\pi\lambda = \hbar/mv$  are introduced where  $v$  is the velocity of the

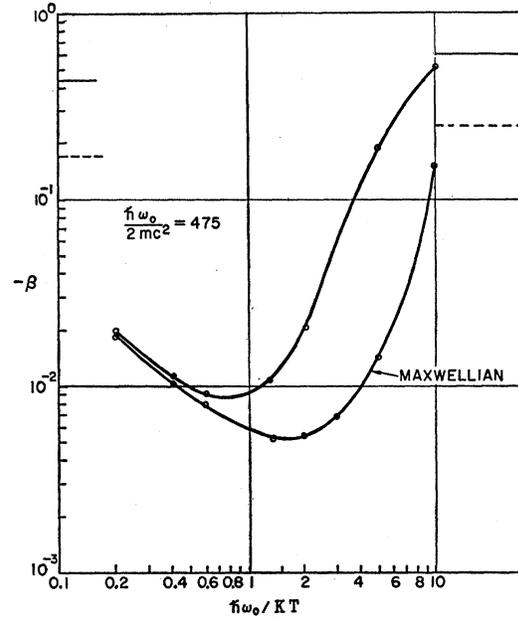


FIG. 3. Temperature dependence of  $-\beta$  for  $\hbar\omega_0/2mc^2 = 475$ .  $-\beta$  as given by a Maxwellian solution is shown for comparison. The straight line portions (dotted for the Maxwellian) are the high- and low-temperature limits.

<sup>25</sup> Both methods are discussed by P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954) and N. Sclar, Phys. Rev. **104**, 1548 (1956). See S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases*, (Cambridge University Press, New York, 1953), 2nd ed., Sec. 10-33.

<sup>26</sup> The question of a natural cutoff is discussed for a similar problem by O. Theimer and R. Gentry, Phys. Rev. **116**, 787 (1959) when the Debye Hückel theory is valid.

<sup>27</sup> N. Bohr, Kgl. Danske Videnskab. Selskab Mat.-fys. Medd. **18**, 8 (1948).

incident electron. Bohr defines the ratios,

$$\begin{aligned}\zeta &= b_c/a = 2q^2/Dmv^2a, \\ \kappa &= b_c/\lambda = 2q^2/D\hbar v,\end{aligned}\quad (41)$$

and the validity of various theories is defined in terms of regions in the  $\zeta\kappa$  plane. For minor screening  $\zeta \ll 1$ , classical physics is valid for  $\kappa > 1$  and the Born approximation holds for  $\kappa < 1$ . For excessive screening,  $\zeta > 1$ , the Born approximation applies when  $\kappa < \zeta^{1/2}$  and classical physics holds for  $\kappa \ll \zeta$  but only for angles greater than  $\lambda/a$ . Exact quantum methods must be used to fill in the gaps.

For our problem the constants  $D$ ,  $m$ , and  $a$  are given while  $v$  is variable, and hence the locus of  $(\zeta, \kappa)$  is the parabola,

$$\kappa^2 = (2q^2ma/D\hbar^2)\zeta. \quad (42)$$

From the above discussion it follows that if

$$a < D\hbar^2/2q^2m, \quad (43)$$

the Born approximation will hold for all velocities. Unfortunately, the quantity on the right of (43) is half the Bohr radius in a semiconductor and the inequality is satisfied only for high impurity densities leading to impurity conduction which does not concern us here. The case of interest corresponds to

$$a > D\hbar^2/2q^2m. \quad (44)$$

In this case, classical physics has partial validity (for angles  $\geq \lambda/a$ ) in the energy range,

$$\hbar^2/2ma^2 < \epsilon < q^2/Da, \quad (45)$$

and full validity for

$$q^2/Da \ll \epsilon < 2q^4m/D^2\hbar^2 = 4\epsilon_B, \quad (46)$$

where  $\epsilon$  is the energy  $\frac{1}{2}mv^2$ , and  $\epsilon_B$  is the binding energy of a hydrogen like impurity. The Born approximation applies for

$$\epsilon > 4\epsilon_B. \quad (47)$$

It can also be used for small angles to supplement the classical solution for energies given by (45), but the matching of the two solutions (classical and Born) still presents difficulties, as Lane and Everhart<sup>28</sup> have recently pointed out. Energies below  $\hbar^2/2ma^2$  (where  $\lambda > a$ ) definitely require rigorous quantum methods.

Here, we shall apply the above criteria to a thermal electron of energy  $3KT/2$  and restrict ourselves to the case of "minor screening" where we can use the classical or the Born approximation. At 80°K,  $b_c \sim 10^{-6}$  cm for an electron in Ge and the condition for minor screening is well satisfied for  $N_I < 10^{17}$  cm<sup>-3</sup> and  $T > 80^\circ\text{K}$ . The equality  $4\epsilon_B = 3KT/2$  (or  $\kappa = 1$ ) holds for  $T \sim 145^\circ\text{K}$  if  $m \sim 0.1m_0$ . The relaxation time  $\tau_I$  for ionized impurity

<sup>28</sup> G. H. Lane and E. Everhart, Phys. Rev. **117**, 920 (1960).

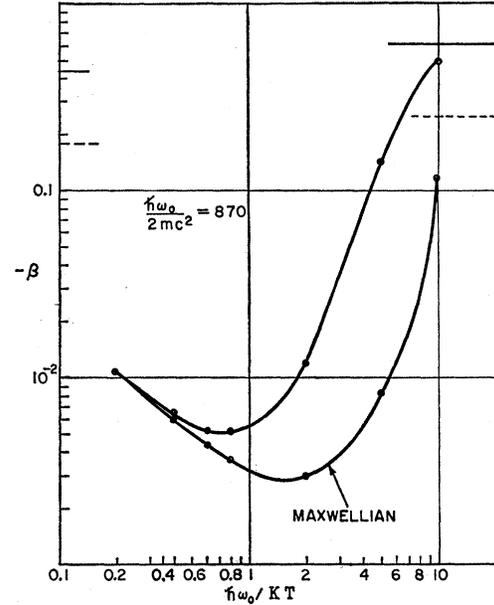


FIG. 4. Temperature dependence of  $-\beta$  for  $\hbar\omega_0/2mc^2=870$ .  $-\beta$  as given by a Maxwellian solution is shown for comparison. The straight line portions (dotted for the Maxwellian) are the high- and low-temperature limits.

scattering is given by<sup>25,29</sup>

$$\begin{aligned}1/\tau_I &= (2\pi q^4 N_I / D^2 m^2 v^3) L, \\ L &= \ln(1 + D^2 a^2 m^2 v^4 / q^4) \quad (\text{Rutherford}) \\ &= \ln[1 + (2a/\lambda)^2] - 4a^2 / (4a^2 + \lambda^2). \quad (\text{Born})\end{aligned}\quad (48)$$

For simplicity  $L$  is treated as a constant which is insignificant except for low energies, but then the whole theory is open to question and the form (48) has to be revised. In the manner of an earlier paper<sup>11</sup> the parameter  $\alpha$  is introduced and defined by

$$\alpha^2 = 6\mu_a/\mu_I, \quad (49)$$

where  $\mu_I$  is the zero field mobility for ionized impurities alone. Observe that  $\alpha$  for the same  $N_I$  is proportional roughly to  $T^{-3/2}$ . Calculations of  $\beta$  versus  $\alpha$  were carried out for  $T=80^\circ\text{K}$  and  $300^\circ\text{K}$  as discussed in Sec. 3, with the only modification,

$$F(x) = e^{-x} / (1 + h + \alpha^2 x^{-2}). \quad (50)$$

The advantage of treating the logarithmic term in (48) as a constant is that the matrix elements  $b_r$  (or  $\alpha_r$ ) can be evaluated analytically in terms of sine and cosine integrals for  $T \leq 80^\circ\text{K}$  when  $h$  can be ignored. It is important to notice that the collision matrix  $\mathbf{D}$  or the polynomials  $p_r$  are the same for all  $\alpha$ . The convergence of  $\beta$  for  $\alpha \geq 1$  at  $80^\circ\text{K}$  ( $x_0 = 5$ ) is not monotonic and some oscillations do occur. Results based on using 10 poly-

<sup>29</sup> Here the Rutherford formula is used for impact parameters less than  $a$ , and not an actual classical cross section for the potential (40) as Lane and Everhart do. The difference should not be significant for  $b_c \ll a$ .

nomials are presented in Figs. 5, 6, and 7. The values of  $\beta$  here are lower than the values based on acoustical phonons alone<sup>11,30</sup> by a factor 3 to 10 at 80°K, and a factor of 50 to 100 at 300°K.

We see that  $\beta$  as calculated here differs considerably from its value for a Maxwellian distribution, particularly at 80°K where the discrepancy could be a factor of 15. Deviations from Ohm's law (as measured by  $\beta$ ) are strongly sensitive to ionized impurity scattering. Ionized impurity densities which alter Ohm's law mobility  $\mu_0$  by only a few percent ( $\alpha \sim 0.1$ ) and are hardly detectable in  $\mu_0$  measurements can induce relative changes in the field dependent mobility  $\beta$  of order 30%. This conclusion, which was reached earlier by Adawi<sup>11</sup> for acoustical phonons alone, might be exploited in checking various theories of ionized impurity scattering by measuring  $\beta$ , rather than  $\mu_0$ , for various densities  $N_I$ .

#### d. Discussion

In Table I a comparison of theory and experiment is made assuming  $\hbar\omega_0/2mc^2 = 870$  (or  $m \sim 0.12m_0$ ). The measurements on high-purity samples at 300°K and 200°K are taken from Seeger's paper<sup>6</sup> and agree surprisingly well with theory. The measurements on impure samples where ionized impurities play a role were carried out at 78.5°K by Gunn<sup>5</sup> and are compared to our calculations for  $x_0 = 5$  or  $T = 80^\circ\text{K}$ , which is close enough. In computing  $\alpha$  we follow CW and take  $a = \frac{1}{2}N_I^{\frac{1}{3}}$  and set  $mv^2/2 = 3KT$  inside the logarithmic term.<sup>25</sup> If we recall that, in a random distribution of noninteracting particles, the average nearest neighbor distance<sup>31</sup> is  $0.55N_I^{-\frac{1}{3}}$  we see that the Conwell Weisskopf choice is reasonable. Theory gives  $\beta = 0$  for  $\alpha \sim 1.25$  while the experimental value is  $\alpha = 1.12$ . For  $\alpha$  below unity the theoretical values are about a factor of 2 higher than the measured values. For  $2 < \alpha < 4$  theory and experiment give a broad maxi-

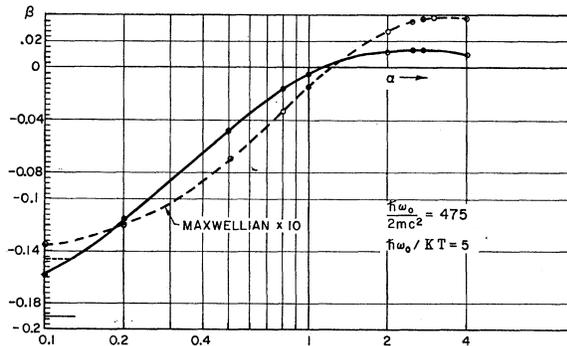


FIG. 5.  $\beta$  as a function of  $\alpha$  for  $\hbar\omega_0/2mc^2 = 475$  and  $x_0 = 5$ . The dotted curve is the Maxwellian result multiplied by 10. The straight line portion refers to the value of  $\beta$  when  $\alpha = 0$ .

<sup>30</sup> An arithmetical error has been detected in Table I of reference 11. For  $\alpha = 2, 8, 10$  and  $15$ ,  $\beta'$  should read  $0.069, 0.042, 0.032$ , and  $0.017$ , respectively, instead of the values given, thus bringing  $\beta'$  and  $\beta$  closer for  $\alpha > 1$ .

<sup>31</sup> S. Chandrasekhar, *Revs. Modern Phys.* **15**, 1 (1943).

imum value for  $\beta$ . However, the theoretical values on the right of column 3 in Table I are about a factor of 4 higher than measurements; while the theoretical values on the left of column 3 which are based on a Maxwellian distribution agree quite well with experimental values. This is suggestive, but not conclusive, that electron-electron collision (which we are ignoring here) for densities of order  $10^{16} \text{ cm}^{-3}$  at 80°K might become important enough to impose a Maxwellian distribution.

Some idea about electron-electron collision can be obtained from an elementary consideration of the thermalization problem. Consider an electron gas of density  $n$  at thermal equilibrium (Maxwellian) in a crystal. At time  $t = 0$  introduce into the crystal a group of electrons whose number is negligible compared to  $n$  and let their initial distribution be  $f(x, 0)$  which is isotropic. For future time, the injected group of electrons will tend to be thermalized through their interactions with the  $n$  host electrons and the lattice vibrations. If we write the time dependent distribution  $f(x, t) = e^{-x}\phi_0(x, t)$ , then  $\phi_0$  satisfies the equation:

$$e^{-x}\partial\phi_0/\partial t = -(\Lambda_0^a + \Lambda_0^{op} + \Lambda_0^e)\phi_0, \quad (51)$$

where the acoustical and optical phonon operators have been defined in (6) and (7). The electron-electron collision operator  $\Lambda_0^e$ , which is linear for our problem, has been derived by Rosenbluth, MacDonald, and Judd,<sup>32</sup> and Kranzer<sup>33</sup> and is defined by<sup>33a</sup>

$$\Lambda_0^e\phi_0 = -\frac{4\pi n q^4 \ln \gamma}{D^2 m^{\frac{1}{2}} (KT)^{\frac{3}{2}} \sqrt{x}} \frac{\partial}{\partial x} \left[ G[(2x)^{\frac{1}{2}}](x)^{\frac{1}{2}} e^{-x} \frac{\partial \phi_0}{\partial x} \right], \quad (52)$$

$$G(z) \equiv (2/\pi)^{\frac{1}{2}} \left[ \int_0^z \exp(-y^2/2) dy/z - \exp(-z^2/2) \right],$$

$$\gamma = 3(DKT)^{\frac{3}{2}} / 2\pi^{\frac{1}{2}} n^{\frac{1}{2}} q^3.$$

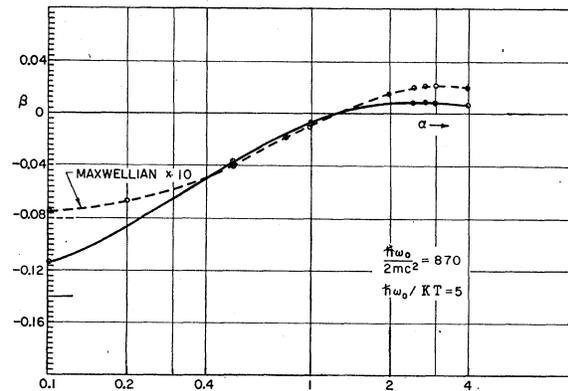


FIG. 6.  $\beta$  as a function of  $\alpha$  for  $\hbar\omega_0/2mc^2 = 870$  and  $x_0 = 5$ . The dotted curve is the Maxwellian result multiplied by 10. The straight line portion refers to the value of  $\beta$  when  $\alpha = 0$ .

<sup>32</sup> M. N. Rosenbluth, W. M. MacDonald, and D. L. Judd, *Phys. Rev.* **107**, 350 (1957).

<sup>33</sup> H. C. Kranzer, Atomic Energy Commission Report NYO-

TABLE I. Comparison of theory and experiment. The last two rows refer to values at 300° and 200°K and the remainder of the table applies to ionized impurity scattering at 78.5°K.

$N_I$ cm <sup>-3</sup>	$\alpha$	$(\mu - \mu_0)/\mu_0 E^2$ theory	$V^{-2}$ cm <sup>2</sup> experiment
$6.6 \times 10^{13}$	0.25	$-1.8 \times 10^{-4}$	$-1.1 \times 10^{-4}$
$1.45 \times 10^{14}$	0.36	$-1.3 \times 10^{-4}$	$-8 \times 10^{-5}$
$2.7 \times 10^{14}$	0.48	$-9.6 \times 10^{-5}$	$-5.5 \times 10^{-5}$
$4.9 \times 10^{14}$	0.63	$-6.2 \times 10^{-5}$	$-3 \times 10^{-5}$
$1.8 \times 10^{15}$	1.12	...	0
$7.8 \times 10^{15}$	2.14	$3.8 \times 10^{-6} + 1.9 \times 10^{-5}$	$4 \times 10^{-6}$
$1.25 \times 10^{16}$	2.6	$4.8 \times 10^{-6} + 1.9 \times 10^{-5}$	$5 \times 10^{-6}$
$2.95 \times 10^{16}$	3.75	$4.8 \times 10^{-6} + 1.7 \times 10^{-5}$	$4 \times 10^{-6}$
	0	300°K	$-3 \times 10^{-7}$
	0	200°K	$-2 \times 10^{-6}$

From (6) and (52) we see that the frequencies

$$\begin{aligned} V_a &= W x_a, \\ V_e &= 4\pi n q^4 \ln \gamma / D^2 m^{\frac{1}{2}} (KT)^{\frac{1}{2}}, \end{aligned} \quad (53)$$

can be looked upon as thermalization coupling constants to acoustical phonons and electrons, respectively. For  $x$  of order unity (or energies of order  $KT$ ) we anticipate that electron-electron collision will be important relative to acoustical phonons for electron densities given by

$$n > n_0 = W x_a D^2 m^{\frac{1}{2}} (KT)^{\frac{1}{2}} / 4\pi q^4 \ln \gamma. \quad (54)$$

The density  $n_0$  as given by (54) is the same as that of Fröhlich<sup>7</sup> (except for factors of order unity) when we replace  $E$  in Fröhlich's Eq. (1.4) by  $KT$ .  $W$  is of order  $q/m\mu_a$ , and  $n_0$  is about  $10^{14}$  cm<sup>-3</sup> and  $10^{13}$  cm<sup>-3</sup> at 300°K and 80°K, respectively. Since the calculations of this paper have shown that, due to optical phonons, deviations from Ohm's law are lower than their acoustical phonon values by a factor of order 100 and 10 at 300°K

2880, Institute of Mathematical Sciences, New York University, 1959 (unpublished).

<sup>33a</sup> Note added in proof.—To obtain a formal solution to Eq. (51) multiply both sides by  $\sqrt{x}$  and expand  $\phi_0$  in terms of the orthonormal Laguerre polynomials  $l_n^{\frac{1}{2}}(x)$ , where,  $l_n^{\frac{1}{2}} = l_n^{\frac{1}{2}} / [n!(n + \frac{1}{2})!]^{\frac{1}{2}}$ , (see Appendix B). Thus,

$$\phi_0(x, t) = \sum_{n=0}^{\infty} c_n(t) l_n^{\frac{1}{2}}(x).$$

Let  $\mathbf{C}$  be the column matrix whose elements are  $c_1, c_2, c_3, \dots$  and we have the two equations,

$$\begin{aligned} \dot{c}_0(t) &= c_0(0), \\ \dot{\mathbf{C}} &= -\mathbf{D}\mathbf{C}, \end{aligned}$$

where  $\mathbf{D}$  is the total collision matrix of Eq. (51) formed with respect to the polynomials  $l_n^{\frac{1}{2}}(x)$ . The first equation simply reflects the conservation of the number of particles. Since  $\mathbf{D}$  is symmetric and positive definite its eigenvalues,  $\lambda_1, \lambda_2, \dots$  are positive and its eigenvectors,  $\mathbf{X}_1, \mathbf{X}_2, \dots$  can be orthonormalized. Form the matrix  $\mathbf{X}$  whose  $X_{i,k}$  element is the  $i$ th component of the  $k$ th eigenvector where these vectors are orthonormal. After some matrix algebra we have

$$\mathbf{C}(t) = \mathbf{X}[\exp -t\mathbf{H}]\mathbf{X}^T \mathbf{C}(0),$$

where  $H_{ij} = \lambda_j \delta_{ij}$ . The solution written in full is

$$c_i(t) = \sum_{j,k} X_{i,k} X_{j,k} c_j(0) \exp - (t\lambda_k).$$

It is seen that the eigenvalues  $\lambda_k$  can be identified with reciprocals of relaxation times, the lowest  $\lambda_k$  leads to the longest relaxation time.

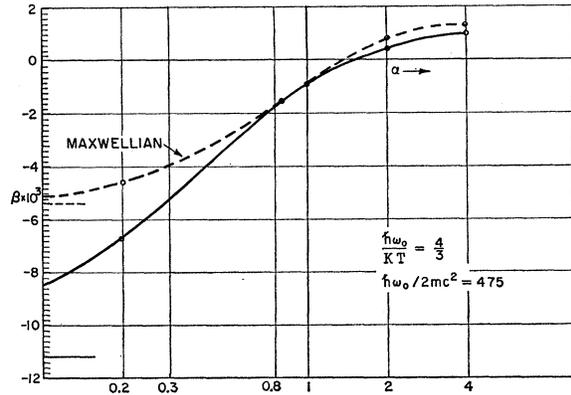


FIG. 7.  $\beta$  as a function of  $\alpha$  for  $\hbar\omega_0/2mc^2=475$  and  $x_0=4/3$ . The dotted curve is the Maxwellian result shown for comparison. The straight line portion refers to the value of  $\beta$  when  $\alpha=0$ .

and 80°K, respectively, we anticipate that electron-electron collision will become important for densities of order  $10^{16}$  cm<sup>-3</sup> at room temperature and  $10^{14}$  cm<sup>-3</sup> at liquid nitrogen, when all the three interactions are present. This does not mean, however, that for these densities electron-electron collision will impose a Maxwellian distribution. The question can only be answered by a rigorous treatment. In passing we remark that if we were interested in the influence of electron-electron collision on the zero field mobility we might compare  $W$  to  $V_e$ .  $W$  is of the order of the frequency of momentum randomization by acoustical phonons.  $V_e$  is  $3.6/t_c$  where  $t_c$  is the Spitzer<sup>34</sup> self collision time which is the time necessary for an average electron to be deflected by  $\pi/2$  by collisions with other electrons. This suggests that electron densities of order  $(KT/2mc^2)n_0$  are necessary to influence the zero field mobility which are about a factor  $T$  higher than  $n_0$ . Electron-electron collision, however, has no influence on  $\mu_0$  if  $\tau$  is independent of energy.

#### ACKNOWLEDGMENTS

I am deeply indebted to Dr. R. W. Klopfenstein, Mr. N. L. Gordon, and Mr. F. W. Schneider for carrying out the numerical calculations on an IBM 650 computer.

#### APPENDIX A

In this appendix we shall give the correct solution to Yamashita's basic equation. We shall therefore use the notation of Yamashita (Y). In his notation,  $J, s, B/A, x$ , and  $p\xi$  correspond to our symbols  $b, x_0, bnx_0^2/x_a, x/x_0$ , and  $\psi$ , respectively. On solving<sup>35</sup> Eq. Y (16) for  $\zeta$  in terms of  $\chi$ , Yamashita has ignored the optical phonon terms in the coefficient of  $\zeta$ . Consequently, the contribution of optical phonons to the inhomogeneous term of Eq. Y (22) has been omitted. The correct equation

<sup>34</sup> L. Spitzer, Jr., *Physics of Fully Ionized Gases* (Interscience Publishers, Inc., New York, 1955), p. 76.

<sup>35</sup> Reference to an equation in Yamashita's paper is made by inserting Y before the number of that equation.

should read:

$$R(x)\frac{d^2\xi}{dx^2}+S(x)\frac{d\xi}{dx}+T(x)=0, \quad (\text{A.1})$$

where,

$$\begin{aligned} R(x) &= x^2 + \frac{1}{2}(B/A)\{[x(x+1)]^{\frac{1}{2}} + e^s \epsilon(x)[x(x-1)]^{\frac{1}{2}}\}, \\ S(x) &= -sx^2 + 2x \\ &\quad + (B/A)\{[x(x+1)]^{\frac{1}{2}} - \epsilon(x)e^s[x(x-1)]^{\frac{1}{2}}\}, \\ T(x) &= [xs/(1+h)] - (d/dx)[x/(1+h)], \\ h &= Js(e^s - 1)^{-1}[(1-1/x)^{\frac{1}{2}} + \epsilon(x)e^s(1-1/x)^{\frac{1}{2}}]. \end{aligned}$$

Equation Y (22) corresponds to  $h(x)=0$ . Define

$$\begin{aligned} q(x) &\equiv S(x)/R(x), \\ t(x) &= -T(x)/R(x), \end{aligned} \quad (\text{A.2})$$

then Eq. (A.1) reads:

$$\xi'' + q(x)\xi' = t(x). \quad (\text{A.3})$$

The boundary condition is such that as  $x \rightarrow \infty$ ,  $e^{-sx}\xi x^n \rightarrow 0$  for  $n > 0$ . This is necessary for the moments of the distribution, such as  $\langle \text{energy} \rangle_{\text{av}}$  for example, to be finite. The behavior at the origin must allow the distribution to be normalized. Now the homogeneous solutions of (A.3) are  $\xi_1$ , which is a constant and  $\xi_2$  which behaves like  $e^{sx}$  as  $x \rightarrow \infty$ , since  $q(x) \sim -s$  for  $x \gg 1$ .  $\xi_2$  violates the boundary condition at  $\infty$  and must therefore be excluded from the particular solution of (A.3). This together with the normalization condition makes the solution unique. For  $x \gg 1$ ,  $q(x) \sim -s$ ,  $t(x) \sim -s/x$ ,  $\xi \sim \ln x$  (which satisfies the boundary condition at  $\infty$ ) and  $\xi' = 0$  for  $x = \infty$ . This physically means that the acoustical phonons determine the distribution for sufficiently large values of  $x$ . This can also be seen from energy losses consideration. Consequently,

$$\xi'(x) = \int_{\infty}^x \exp\left[\int_x^v q(u)du\right] t(v)dv, \quad (\text{A.4})$$

and

$$\xi'(0) = \int_{\infty}^0 dv t(v) \exp\int_0^v q(u)du. \quad (\text{A.5})$$

Thus, in general,  $\xi'(0)$  is finite and not zero as Yamashita seems to have taken it. Equation Y (25) implies that for  $x \ll 1$ ,  $\xi(x) \propto x^{\frac{3}{2}}$ . If we take  $h(x)=0$ , as Y does, we should get in addition to the  $x^{\frac{3}{2}}$  term the term  $\xi'(0)x$  which is the dominant term [assuming that we assign  $\xi(0)$  the value zero before we normalize]. If we take  $h(x) \neq 0$ , as we should in general, then near the origin  $T(x) \propto \sqrt{x}$  and so are both  $R$  and  $S$ . Consequently Yamashita's  $x^{\frac{3}{2}}$  term becomes a term in  $x^2$  and here again  $\xi'(0)x$  dominates.

The solution of Y can be written as

$$\xi'(x) = \int_0^x dv t(v) \exp\int_x^v q(u)du, \quad (\text{A.6})$$

and this can be shown to diverge like  $e^{sx}$  for

$x > x_1 \gg (B/2A)(e^s + 1)$ . The proof simply uses the fact that for  $v > x_1$ ,  $t(v) \sim -s/v$  and  $q(u) \sim -s$ , and does not depend on whether  $h(x)$  is zero or not. Therefore Yamashita's solution for  $\xi(x)$  will also diverge like  $e^{sx}$ . Only the value  $\xi'(0)$  as given by (5) can lead to a well-behaved solution at  $\infty$  which is the solution to the problem, namely,

$$\xi(x) = \text{const} + \int_0^x dz \left\{ \int_{\infty}^z t(v)dv \exp\int_z^v q(u)du \right\}. \quad (\text{A.7})$$

In conclusion, the solution (A.7) is valid, in general for  $x \gg 1$  (asymptotic solution), and is expected to become a good solution for all  $x$  in the high-temperature limit,  $s \ll 1$ , where the optical phonon energy is below the thermal energy. Yamashita's approximation,  $h(x)=0$ , can be justified only for low temperatures corresponding to, say,  $s \geq 5$ . As for the assumption  $\xi'(0)=0$ , it is not valid and leads to a divergent solution. We have, in fact, evaluated  $\xi'(0)$  from (A.5) using the same parameters as Y (and set  $h=0$ ) and found that  $\xi'(0)$  is 0.04 and 0.56 for 320°K and 90°K, respectively.

#### APPENDIX B: CONVERGENCE

The acoustical phonon problem can be written in general as

$$g = \Lambda\psi \equiv - (d/dx)(e^{-sx^2}\psi'). \quad (\text{B.1})$$

The polynomials which are orthonormal with respect to this collision operator are easily identified. Laguerre polynomials  $L_n^\alpha(x)$  are defined by the generating function<sup>36,37</sup>

$$e^{-xt/(1-t)}/(1-t)^{1+\alpha} = \sum_{n=0}^{\infty} (-1)^n t^n L_n^\alpha(x)/n!, \quad (\text{B.2})$$

from which follow the properties

$$L_n^\alpha = (-1)^n e^{sx} x^{-\alpha} (d^n/dx^n)(e^{-sx} x^{n+\alpha}), \quad (\text{B.3})$$

$$L_n^{\alpha'} = n L_{n-1}^{\alpha+1}, \quad (\text{B.4})$$

$$\int_0^{\infty} e^{-sx} x^\alpha L_m^\alpha L_n^\alpha dx = n!(n+\alpha)! \delta_{nm}. \quad (\text{B.5})$$

From these properties we see that

$$- (d/dx)(e^{-sx} x^2 L_n^{1'}) = n e^{-sx} x L_n^1, \quad (\text{B.6})$$

which shows that  $L_n^1$  are not only orthogonal with respect to  $\Lambda$  of (B.1), but are also eigenfunctions with the positive integers  $n$  as eigenvalues. The orthonormal polynomials are then given by

$$p_n = L_n^1 / [nn!(n+1)!]^{\frac{1}{2}}, \quad (\text{B.7})$$

and the variational method reduces to expanding  $\psi$  in terms of the complete set  $L_n^1(x)$ . Such an expansion is

<sup>36</sup> D. Jackson, *Fourier Series and Orthogonal Polynomials* (Mathematical Association of America, Oberlin, Ohio, 1941).

<sup>37</sup> G. Sansone, *Orthogonal Functions* (Interscience Publishers, Inc., New York, 1959), translated by A. H. Diamond.

known to converge, not only in the mean, but point by point, (at points of continuity) from Uspensky's theorem.<sup>37</sup> We shall demonstrate this in the simple case when  $g = -(d/dx)e^{-x}x$  to which the answer is well known (Eq. 32). We easily find that from (29)

$$\psi = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n(n+1)!} \left( L_n^1(x) + (-1)^{n-1} \frac{1}{2} \frac{3}{2} \dots \frac{2n-1}{2} \right), \quad (\text{B.8})$$

where  $\psi$  is normalized to zero. Let

$$S = \sum_{n=1}^{\infty} \frac{(-1)^{n-1} L_n^1(x)}{n(n+1)!} = - \sum_{n=1}^{\infty} \left( \frac{1}{n} - \frac{1}{n+1} \right) (-1)^n \frac{L_n^1}{n!}.$$

Using (B.2), we see that

$$S = \int_0^1 \left( 1 - \frac{e^{-xt/(1-t)}}{(1-t)^2} \right) \left( \frac{1}{t} - 1 \right) dt.$$

substitute  $z = t/(1-t)$  and

$$S = \left( \int_0^1 + \int_1^{\infty} \right) \left( \frac{1}{z(z+1)^2} - \frac{e^{-xz}}{z} \right) dz,$$

which reduces to

$$S = \int_0^1 (1 - e^{-xz}) \frac{dz}{z} - 1 + \int_0^{\infty} e^{-t} \frac{dt}{t}. \quad (\text{B.9})$$

The first integral in (B.9) is expressed as a power series, and the second integral (which is the exponential integral) is simply  $\ln x + C$ —the same power series.  $C$  is Euler's constant 0.577. The result is

$$S = C + \ln x - 1. \quad (\text{B.10})$$

The constant term in (B.8) which has not been considered is given by

$$R = \sum_{n=1}^{\infty} \left( \frac{1}{n} - \frac{1}{n+1} \right) \prod_{r=1}^n \frac{2r-1}{2r}. \quad (\text{B.11})$$

By the binomial theorem

$$R = \int_0^1 [(1-x)^{-\frac{1}{2}} - 1] dx/x - \int_0^1 [(1-x)^{-\frac{1}{2}} - 1] dx \\ = 2 \ln 2 - 1. \quad (\text{B.12})$$

Therefore, from (B.10), (B.12), and (B.8)

$$\psi = \ln x + C + 2(\ln 2 - 1) = \ln x - \psi(\frac{1}{2}), \quad (\text{B.13})$$

and the pointwise convergence of  $\psi$  is established. The convergence, however, is very slow in this case. If we take only the first  $N$  terms in (B.8) and denote that sum by  $\psi_N$  we see that

$$(\psi_N \Delta \psi_N) = N/(N+1), \quad (\text{B.14})$$

which approaches the limit 1 rather slowly.

One can also see that  $\beta$  as computed from (B.8) and Eq. (13) (with  $h=0$ ) is given by

$$\beta = - \sum_{n=1}^{\infty} \left( \frac{1}{n} - \frac{1}{n+1} \right) + R \\ = 2(\ln 2 - 1), \quad (\text{B.15})$$

which is exact. However, if we consider only the first ten polynomials, then we obtain  $\beta = -0.53$  which is about 13% higher than the limit value of (B.15).

It is of interest to observe that if we attempted to solve the acoustical phonon problem by the power series representation of Eq. (16) we would have been led to the system of equations

$$r r! = \sum_{s=1}^N r s (r+s)! c_s. \quad (\text{B.16})$$

The solution of this system follows from comparing the coefficients of  $x^r$  in  $\sum c_r x^r$  with those of the first  $N$  terms of (B.8). We find after some algebra that

$$c_r = (-1)^{r+1} \binom{N}{r} / r(r+1)!. \quad (\text{B.17})$$

The problem of acoustical phonons and ionized impurities which we solved<sup>11</sup> earlier, using numerical integration, can now be solved, by these methods, analytically, and  $\beta$  is evaluated from a series involving the sine and cosine integrals.

Now we mention briefly the high-temperature limit for acoustical and optical phonons. As in Sec. 3, with  $\psi = \sum \alpha_r p_r$  and  $g = \Delta \psi$ , we see that

$$\psi' = \sum_r \alpha_r p_r' = \sum_r (p_r, g) p_r'. \quad (\text{B.18})$$

Now in (B.18) we substitute  $\Delta \psi$  for  $g$  and

$$\psi' = \sum (p_r \Delta \psi) p_r', \quad (\text{B.19})$$

which, from (34), can be written as

$$\psi' = \sum_r p_r' \int_0^{\infty} \rho p_r' \psi' dx,$$

where,

$$\rho = e^{-x} \{ x^2 + b n (x_0^3/x_a) [x(x+x_0)]^{\frac{1}{2}} \}. \quad (\text{B.20})$$

The orthonormality of the polynomials  $p_r$  with respect to  $\Delta$  implies the orthonormality of their derivatives  $p_r'$  with respect to the weight function  $\rho$  given in (B.20). Thus, in essence, the variational method reduces to expanding  $\psi'$  in terms of a set of polynomials ( $p_r'$ ) which are orthonormal with respect to  $\rho$ . One anticipates that the convergence for these polynomials is similar to the convergence for Laguerre polynomials.

Finally, the eigenfunctions of the reduced optical phonon operator given in Eq. (35) (after lifting  $\sqrt{x}$  and  $W b x_0^2$ ) are the Laguerre polynomials  $L_n^0$  with  $n$  as eigenvalues.