

Distribution Functions for Hot Electrons in Many-Valley Semiconductors

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The Boltzmann equation for electrons in many-valley semiconductors, with scattering by acoustical and optical lattice vibrations, is solved for high electric fields in the following two cases: (1) Intervalley-scattering is completely negligible. Then, in each particular valley, the distribution of the electrons over the energy is Maxwellian for energies of the electrons larger than the energy of an optical phonon. The corresponding electron temperature varies approximately with the square of the electric field strength and depends on the angle between the electric field and the longitudinal axis of the particular valley under consideration. The electron temperatures are therefore in general different in different valleys. The deviations of the electron distribution from the

Maxwellian one for energies of the electrons smaller than the energy of an optical phonon are small. (2) If allowance is made for a transfer of electrons between different valleys a finite difference in the populations is set up even for infinitesimally small intervalley scattering rate. In addition to this, for finite intervalley rate, the electron distribution deviates from the original Maxwellian one. The deviation increases with increasing intervalley rate constant, increasing lattice temperature, and increasing difference of the average electron energies in the different valleys. Both of these effects of intervalley scattering are important for the explanation of the field dependence of the Sasaki effect.

I. INTRODUCTION

EXPERIMENTAL determinations of the drift velocity of carriers in high electric fields were first carried out by Ryder and Shockley^{1,2} and have been extended by several authors.³⁻⁹ An explanation of the results was put forward by Shockley¹⁰ by considering the momentum and energy balance of carriers subject to the electric field and to scattering with acoustical and optical phonons.

Later theoretical work dealt with the quantitative aspects of the current vs voltage characteristics, either by considering the energy and momentum balance for displaced Maxwellian distributions in more detail and for the whole region of electric fields¹¹⁻¹⁷ or by solution of the Boltzmann equation in restricted regions of the electric field and under certain assumptions on the scattering mechanisms.¹⁸⁻²² All the theoretical work

hitherto mentioned was based on the simple parabolic model for the band structure.

After the discovery of the transverse and longitudinal anisotropy effects of hot electrons in *n*-Ge,²³⁻³⁰ it became obvious that the actual band structure plays a dominant role in these effects. Therefore, a theory of hot electron effects in *n*-Ge should be transport theory for a many-valley semiconductor at high electric fields. A first step in this direction was carried out by Shibuya.³¹ A more complete treatment has been given by Yamashita and Inoue³² by combination of a Boltzmann-type treatment for intravalley scattering, partly based on the actual band structure, with a balance-type treatment for intervalley processes. In this paper we start from the Boltzmann equation for electrons in many-valley semiconductors with intravalley and intervalley scattering. This equation, given in Sec. II, is based throughout on the modern form of the deformation potential theory.^{33,34} The Boltzmann equation is solved in Secs. III and IV for a case where intervalley scattering is assumed to be completely negligible. In Sec. V a solution of the Boltzmann equation is obtained for a case where intervalley scattering is small compared to intravalley scattering. The solution can be found by means of a perturbation treatment, where the solution for no intervalley scattering at all plays the role of the zeroth order approximation.

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- ² E. J. Ryder, *Phys. Rev.* **90**, 766 (1953).
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- ⁴ J. B. Arthur, A. F. Gibson, and J. W. Granville, *J. Electronics* **2**, 145 (1956).
- ⁵ K. S. Mendelson and R. Bray, *Proc. Phys. Soc. (London)* **A70**, 899 (1957).
- ⁶ T. N. Morgan, *J. Phys. Chem. Solids* **8**, 245 (1959).
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- ¹⁸ J. Yamashita and M. Watanabe, *Progr. Theoret. Phys. (Kyoto)* **12**, 443 (1954).
- ¹⁹ J. Yamashita, *Phys. Rev.* **111**, 1529 (1958).
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- ²² T. N. Morgan, *Bull. Am. Phys. Soc.* **3**, 13 (1958); **5**, 194 (1960).

- ²³ W. Sasaki and M. Shibuya, *J. Phys. Soc. Japan* **11**, 1202 (1956).
- ²⁴ W. Sasaki, M. Shibuya, and K. Mizuguchi, *J. Phys. Soc. Japan* **13**, 456 (1958).
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- ²⁶ M. I. Nathan, *Bull. Am. Phys. Soc.* **5**, 194 (1960).
- ²⁷ E. G. S. Paige, *Proc. Phys. Soc. (London)* **A72**, 921 (1958).
- ²⁸ S. H. Koenig, *Proc. Phys. Soc. (London)* **A73**, 959 (1959).
- ²⁹ E. G. S. Paige, *Proc. Phys. Soc. (London)* **A75**, 174 (1960).
- ³⁰ S. H. Koenig, M. I. Nathan, W. Paul, and A. C. Smith, *Phys. Rev.* **118**, 1217 (1960).
- ³¹ M. Shibuya, *Phys. Rev.* **99**, 1189 (1955).
- ³² J. Yamashita and K. Inoue, *J. Phys. Chem. Solids* **12**, 1 (1960); see also M. Shibuya and W. Sasaki, *J. Phys. Soc. Japan* **15**, 207 (1960).
- ³³ C. Herring and E. Vogt, *Phys. Rev.* **101**, 944 (1956).
- ³⁴ W. A. Harrison, *Phys. Rev.* **104**, 1281 (1956).

The results of this paper, unless stated otherwise, are applicable to any substance with a many-valley structure of the particular band under consideration, although special reference is given to *n*-Ge and all numerical estimates refer to this particular substance.

II. BOLTZMANN EQUATION

In order to formulate the Boltzmann equation we have to discuss the structure of the particular band in that part of the Brillouin zone accessible to electrons for experimentally realizable electric field strengths and lattice temperatures and the scattering mechanisms for electrons in the part of the Brillouin zone under consideration. The band structure will be dealt with first. It is assumed to be of the nondegenerate many-valley type, eventually including higher, nonequivalent valleys with constant effective masses in the accessible range of energies. This restricts the \mathbf{k} vectors to values lying around the minima with distances Δk from the minimum smaller than 10^7 cm^{-1} , and obviously defines an upper limit for the field strength. The energy of an electron in the valley j is then given by

$$\epsilon^{(j)} = \Delta\epsilon^{(j)} + \frac{1}{2}\hbar^2 \left\{ \frac{[\Delta k_x^{(j)}]^2}{m_t} + \frac{[\Delta k_y^{(j)}]^2}{m_t} + \frac{[\Delta k_z^{(j)}]^2}{m_l} \right\}, \quad (1)$$

in the system of principal axes of the valley under consideration. Here $\Delta\epsilon^{(j)}$ is the energy of the j th minimum, relative to the band edge, $m_t^{(j)}$ and $m_l^{(j)}$ are the transverse and longitudinal masses.

In the following we restrict ourselves throughout to relatively pure samples, so that the influence of impurity scattering can be neglected everywhere. The interactions with the lattice vibrations give rise to intravalley and intervalley transitions of the electrons. To shorten the notation, the term intervalley phonon will be introduced for phonons involved in intervalley scattering. Under the restriction $\Delta k \leq 10^7 \text{ cm}^{-1}$ the frequencies of optical and intervalley phonons are independent of the wave number. The frequencies of the longitudinal and transverse acoustical phonons taking part in intravalley processes are given by the linear part of the dispersion law and are equipartitioned thermally for the lattice temperatures of experimental interest above 78°K .

With these assumptions, the formal Boltzmann equation for electrons in the valley j ,

$$\left[\frac{\partial f^{(j)}}{\partial t} \right]_{\text{field}} = \left[\frac{\partial f^{(j)}}{\partial t} \right]_{\text{coll}} = \left[\frac{\partial f^{(j)}}{\partial t} \right]_{\text{ac}} + \left[\frac{\partial f^{(j)}}{\partial t} \right]_{\text{opt}} + \left[\frac{\partial f^{(j)}}{\partial t} \right]_{\text{int}}, \quad (2)$$

can be worked out using the transition probabilities given by the deformation potential theory.^{33,34}

It is expedient to transform the surfaces of constant

energy to spheres in each particular valley. This is done by means of the transformation of Herring and Vogt,³³ by which effective wave vectors $\Delta\mathbf{k}^{*(j)}$ are introduced instead of $\Delta\mathbf{k}^{(j)}$ and effective fields $\mathbf{F}^{*(j)}$ instead of \mathbf{F} . The effective wave vectors and effective fields are defined by

$$\Delta\mathbf{k}^{*(j)} = [\tilde{\alpha}^{(j)}]^\frac{1}{2} \Delta\mathbf{k}^{(j)}, \quad (3)$$

$$\mathbf{F}^{*(j)} = [\tilde{\alpha}^{(j)}]^\frac{1}{2} \mathbf{F}, \quad (4)$$

where the tensor $\tilde{\alpha}^{(j)}$ is given by

$$\tilde{\alpha}^{(j)} = \begin{vmatrix} m_0/m_t^{(j)} & 0 & 0 \\ 0 & m_0/m_t^{(j)} & 0 \\ 0 & 0 & m_0/m_l^{(j)} \end{vmatrix}$$

in the system of principal axes of the valley under consideration. Here m_0 denotes the free electron mass. The transformation (3) is to be carried out simultaneously in the phonon q space for phonons interacting with electrons in the valley j .

A detailed analysis of the Boltzmann equation for the case of *n*-Ge has shown that the solution can be approximately expanded in terms of Legendre polynomials only:

$$f^{(j)}(\Delta\mathbf{k}^{*(j)}) = \sum_l f_l^{(j)}(\epsilon) P_l(\cos\Theta), \quad (5)$$

when Θ is the angle between the effective field and the effective wave vector in the valley under consideration. The φ dependence of the distribution function drops out approximately for this special choice of the coordinate system on account of the nearly isotropic effect of the combined transverse and longitudinal acoustical scattering.

It is obvious that the expansion (3) can be stopped after the P_1 term in the case of infinitesimal electric fields. The same appears to apply for high fields as well.³⁵ We therefore tentatively restrict ourselves to the first two terms. With this restriction, the insertion of (5) into (2) leads after regrouping to the following result:

$$P_0(\cos\Theta)[\eta_{\text{field}} - \eta_{\text{ac}} - \eta_{\text{opt}} - \eta_{\text{int}}] + P_1(\cos\Theta)[\zeta_{\text{field}} - \zeta_{\text{ac}} - \zeta_{\text{opt}} - \zeta_{\text{int}}] = 0. \quad (6)$$

The η and ζ are given by the following expressions, where the superscripts characterizing the particular valley have been dropped where possible:

$$\eta_{\text{field}} = -eF^* \frac{1}{3} \left(\frac{2}{m_0} \right)^\frac{1}{2} \epsilon^{-\frac{1}{2}} \frac{d}{d\epsilon} (\epsilon f_1), \quad (7)$$

$$\zeta_{\text{field}} = -eF^* \left(\frac{2}{m_0} \right)^\frac{1}{2} \epsilon^{-\frac{1}{2}} \frac{d}{d\epsilon} f_0. \quad (8)$$

The η_{ac} and ζ_{ac} have been obtained by the procedure of Herring and Vogt, using the transition probabilities

³⁵ A justification for this is contained in unpublished work of H. Risken and H. G. Reik.

given in Table V of their paper. They are given by

$$\eta_{ac} = \frac{1}{\tau_{ac0}} \frac{d}{d\epsilon} \left[\epsilon^2 \left(\frac{f_0}{kT} + \frac{df_0}{d\epsilon} \right) \right], \quad (9)$$

$$\frac{1}{\tau_{ac0}} = \frac{\sqrt{2} 2^5 \pi^3 m_0^{\frac{3}{2}} m_i k T \Xi_0^2}{\rho h^4 [\det \tilde{\alpha}]^{\frac{1}{2}} \epsilon^{\frac{1}{2}}}, \quad (9a)$$

$$\Xi_0^2 = \Xi_d^2 \{ 1 + \frac{1}{3} [(\Xi_u/\Xi_d + 1)^2 m_i/m_t - 1] \}, \quad (9b)$$

$$\zeta_{ac} = -\tau_{ac0}^{-1} f_1, \quad (10)$$

$$\frac{1}{\tau_{ac1}} = \frac{\sqrt{2} 2^4 \pi^3 m_0^{\frac{3}{2}} k T \Xi_1^2 \epsilon^{\frac{1}{2}}}{\rho h^4 [\det \tilde{\alpha}]^{\frac{1}{2}} c_t^2}, \quad (10a)$$

$$\Xi_1^2 = \Xi_d^2 [1.31 + 1.61 \Xi_u/\Xi_d + 1.01 (\Xi_u/\Xi_d)^2]. \quad (10b)$$

Here $[\det \tilde{\alpha}]^{\frac{1}{2}} = m_0^{\frac{3}{2}} m_t^{-1} m_i^{-\frac{1}{2}}$, ρ is the density, c_t the longitudinal velocity of sound, Ξ_d and Ξ_u are the deformation potential constants for dilation and uniaxial shear. Equations (10), (10a), and (10b), describing essentially the momentum scattering, are already contained in Herring and Vogt's paper. In the derivation of (9), (9a), and (9b), which describe the energy scattering due to longitudinal and transverse acoustical phonons, the finite energy of the acoustical phonons has been taken into account and use has been made of the fact that the variation of $f_0(\epsilon)$ is small over the energy of an acoustical phonon.

The last statement is not true for optical and intervalley phonons. For these scattering mechanisms the following expressions for η and ζ are found, which all have the general form

$$\eta = \frac{1}{\tau} \sum_l \left\{ \left(\frac{\epsilon - \Delta\epsilon^{(l)} + \hbar\omega}{\epsilon} \right)^{\frac{1}{2}} \times [(n_q + 1) f_0^{(l)}(\epsilon + \hbar\omega) - n_q f_0^{(j)}(\epsilon)] + \left(\frac{\epsilon - \Delta\epsilon^{(l)} - \hbar\omega}{\epsilon} \right)^{\frac{1}{2}} \times [n_q f_0^{(l)}(\epsilon - \hbar\omega) - (n_q + 1) f_0^{(j)}(\epsilon)] \right\}, \quad (11)$$

$$\zeta = -\frac{1}{\tau} \sum_l \left\{ \left(\frac{\epsilon - \Delta\epsilon^{(l)} + \hbar\omega}{\epsilon} \right)^{\frac{1}{2}} n_q + \left(\frac{\epsilon - \Delta\epsilon^{(l)} - \hbar\omega}{\epsilon} \right)^{\frac{1}{2}} (n_q + 1) \right\} f_1^{(j)}(\epsilon), \quad (12)$$

$$\frac{1}{\tau} = \frac{\sqrt{2} 2^2 \pi^2 m_0^{\frac{3}{2}} D^2 \epsilon^{\frac{1}{2}}}{\rho h^3 \omega [\det \tilde{\alpha}^{(l)}]^{\frac{1}{2}}}. \quad (13)$$

The superscript j characterizes the initial, the superscript l the final valley, ω is the frequency of the phonon involved in the particular process, n_q the number of phonons present, D the deformation potential for the

process under consideration. $\Delta\epsilon^{(l)}$ is the energy of the minimum of the final valley, if the minimum of the initial valley is at the band edge. If $l \neq j$ and $\Delta\epsilon^{(j)} = 0$ we speak of equivalent intervalley scattering. In (11) and (12), use is to be made of the convention that $x^{\frac{1}{2}} = 0$ for $x \leq 0$. The expressions (7)–(13) are substantially the same as the corresponding ones in the paper of Yamashita and Inoue,³² apart from the fact that in (9)–(13) the true masses and the true deformation potential constants appear instead of some sort of averaged quantities. This difference is brought about by the fact that in their treatment the evaluation of the scattering terms is based on the simple parabolic model of the band structure and the Sommerfeld-Bethe-Seitz method^{36,37} is used instead of the method of Herring and Vogt.

III. SOLUTION OF THE BOLTZMANN EQUATION FOR INTRAVALLEY PROCESSES ONLY

The complete "Boltzmann equation" in the approximation where only the P_0 and P_1 terms in (5) are important consists of a set of $2N$ equations for $f_0^{(j)}(\epsilon)$ and $f_1^{(j)}(\epsilon)$ where N is the number of valleys under consideration. The two equations for a particular valley j are coupled to the other equations on account of intervalley processes.

A considerable simplification of the mathematical problem can be achieved if intervalley transitions of the electrons can be neglected in a first approximation. In the case of n -Ge this is possible for transitions to other equivalent valleys. The ratio $(D_i/D_0)^2$ where D_i is the deformation potential constant for equivalent intervalley scattering and D_0 the deformation potential constant for optical intravalley scattering is of the order of 10^{-3} .³⁸ Little is known about the corresponding ratio for nonequivalent intervalley scattering, but these transitions are certainly not important for average energies of the electrons smaller than the energy of the minimum of the nonequivalent valleys relative to the band edge. We therefore restrict ourselves in this and the following section to the solution of the Boltzmann equation for intravalley processes only. Under this simplification, the Boltzmann equation reads

$$\begin{aligned} & -E\tau_0^* \frac{d}{d\epsilon} (\epsilon f_1) \\ & = E_{ac} \frac{d}{d\epsilon} \left[\epsilon^2 \left(\frac{f_0}{kT} + \frac{df_0}{d\epsilon} \right) \right] \\ & \quad + (\epsilon + \hbar\omega_0)^{\frac{1}{2}} \epsilon^{\frac{1}{2}} [(n_q + 1) f_0(\epsilon + \hbar\omega_0) - n_q f_0(\epsilon)] \\ & \quad + (\epsilon - \hbar\omega_0)^{\frac{1}{2}} \epsilon^{\frac{1}{2}} [n_q f_0(\epsilon - \hbar\omega_0) - (n_q + 1) f_0(\epsilon)], \quad (14) \end{aligned}$$

³⁶ A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24.

³⁷ F. Seitz, *Phys. Rev.* **73**, 549 (1948).

³⁸ G. Weinreich, T. M. Sanders, and H. G. White, *Phys. Rev.* **114**, 33 (1959).

and

$$E_{\langle\tau\rangle}^*(df_0/d\epsilon) = f_1. \quad (15)$$

Here

$$E_{\tau_0}^* = eF^*(\tau_0/3)(2\epsilon/m_0)^{1/2} \quad (16)$$

is the energy gain of an electron during the time $\tau_0/3$, where τ_0 is an optical relaxation time, defined by (13). As $\tau_0 \propto \epsilon^{-1/2}$ this quantity is independent of the energy. Similarly, $E_{\langle\tau\rangle}^*$ is also an energy gain:

$$E_{\langle\tau\rangle}^* = eF^*(\tau)(2\epsilon/m_0)^{1/2}. \quad (17)$$

Here $\langle\tau\rangle$ is a combination of the acoustical time of momentum relaxation τ_{ac} and the optical relaxation time τ_0 :

$$\frac{1}{\langle\tau\rangle} = \frac{1}{\tau_{ac}} + \frac{1}{\tau_0} \left[n_q \left(\frac{\epsilon + \hbar\omega_0}{\epsilon} \right)^{1/2} + (n_q + 1) \left(\frac{\epsilon - \hbar\omega_0}{\epsilon} \right)^{1/2} \right].$$

It is convenient to write this combined relaxation time in the form

$$\langle\tau\rangle = \tau_{ac} T/T_{eff}(\epsilon), \quad (18)$$

where

$$T_{eff}(\epsilon) = T + \frac{D_0^2 \hbar c^2}{2k\omega_0 \Xi_1^2} \times \left[n_q \left(\frac{\epsilon + \hbar\omega_0}{\epsilon} \right)^{1/2} + (n_q + 1) \left(\frac{\epsilon - \hbar\omega_0}{\epsilon} \right)^{1/2} \right] \quad (19)$$

is an effective temperature, characterizing the whole acoustical and optical excitation of the lattice, which affects the momentum relaxation. The quantity

$$E_{ac} = \epsilon\tau_0/\tau_{ac} \quad (20)$$

characterizes the ratio of the acoustical and the optical contribution to the energy relaxation of the electrons. E_{ac} is independent of the energy and can be seen to be of the order of $10^{-2}\hbar\omega_0$. For this estimate, the numerical values for n -Ge, $\Xi_0 \approx 30$ eV, $D_0 \approx 10^9$ eV/cm,³⁹⁻⁴¹ $\omega_0 \approx 5 \times 10^{13}$ sec⁻¹,⁴² are used.

Integration of (14) and elimination of f_1 by means of (15) gives

$$\begin{aligned} & -E_{\tau_0}^* E_{\langle\tau\rangle}^* \frac{df_0}{d\epsilon} \\ & = E_{ac} \epsilon \left[\frac{f_0}{kT} + \frac{df_0}{d\epsilon} \right] + \int_{\epsilon - \hbar\omega_0}^{\epsilon} \left(\frac{\xi + \hbar\omega_0}{\epsilon} \right)^{1/2} \left(\frac{\xi}{\epsilon} \right)^{1/2} \\ & \quad \times \left[(n_q + 1) f_0(\xi + \hbar\omega_0) - n_q f_0(\xi) \right] d\xi + \frac{C}{\epsilon}. \end{aligned} \quad (21)$$

³⁹ H. J. G. Meyer, Phys. Rev. **112**, 298 (1958).

⁴⁰ H. J. G. Meyer, J. Phys. Chem. Solids **8**, 264 (1959).

⁴¹ H. G. Reik, H. Risken, and G. Finger, Phys. Rev. Letters **5**, 423 (1960).

⁴² B. N. Brockhouse, J. Phys. Chem. Solids **8**, 400 (1959).

The lower limit of integration is to be replaced by zero for $\epsilon - \hbar\omega_0 \leq 0$. The constant of integration C must be zero on account of particle conservation.

The system of Eqs. (21) and (15) is similar to a system of equations given by Franz.^{43,44} He did not give a solution and the method of solution proposed by him is quite different from the way in which our solution is actually obtained. We shall come back to the method of Franz, after our solution is completed.

It is easy to get an approximate solution of (21) for arbitrary values of the electric field strength in two particular ranges of energy. The first, not very important one, is the range of very small energies, which is treated in the Appendix. The second range of energies is the range $2\hbar\omega_0 < \epsilon < \epsilon_m$ where ϵ_m is the energy above which the effective masses cease to be constants. In this energy range, we replace $\epsilon + \hbar\omega_0$ and $\epsilon - \hbar\omega_0$ by ϵ in the definition (19) of the effective temperature $T_{eff}(\epsilon)$. The effective temperature then becomes independent of the energy,

$$T_{eff} = T + \frac{D_0^2 \hbar c^2}{k\omega_0 \Xi_1^2} (n_q + \frac{1}{2}), \quad (22)$$

and so does $E_{\langle\tau\rangle}^*$. In the same approximation we replace the term $(\xi + \hbar\omega_0)^{1/2} \xi^{1/2} / \epsilon$ in the integrand of (21) by unity. Furthermore, we tentatively omit the E_{ac} terms in (21) on account of the smallness of E_{ac} . It will be shown in more detail in the next section that they are unimportant in the range of energy under consideration. Then a Maxwellian distribution

$$f_0(\epsilon) = \exp[-\epsilon/kT_e^*] \quad (23)$$

is a solution of the approximate equation

$$\begin{aligned} & -E_{\tau_0}^* E_{\langle\tau\rangle}^* \frac{df_0}{d\epsilon} \\ & = \int_{\epsilon - \hbar\omega_0}^{\epsilon} [(n_q + 1) f_0(\xi + \hbar\omega_0) - n_q f_0(\xi)] d\xi, \end{aligned} \quad (21a)$$

provided that kT_e^* is defined by

$$E_{\tau_0}^* E_{\langle\tau\rangle}^* = (kT_e^*)^2 [(2n_q + 1) - (n_q + 1) \exp(-\hbar\omega_0/kT_e^*) - n_q \exp(+\hbar\omega_0/kT_e^*)]. \quad (24)$$

For high fields (high electron temperatures) most of the electrons populate the energy range under consideration. In this case the following expression for the electron temperature is obtained from (24)⁴¹:

$$kT_e^* = E_{\tau_0}^* E_{\langle\tau\rangle}^* / \hbar\omega_0 + \hbar\omega_0 (n_q + \frac{1}{2}), \quad (25)$$

where

$$E_{\tau_0}^* E_{\langle\tau\rangle}^* = \frac{2}{3} (eF^*)^2 \tau_0 \langle\tau\rangle \epsilon / m_0. \quad (26)$$

⁴³ W. Franz, Z. Naturforschung **15a**, 366 (1960).

⁴⁴ W. Franz, Proceedings of the International Conference on Semiconductors Physics, Prague, 1960 [Czech. J. Phys. (to be published)].

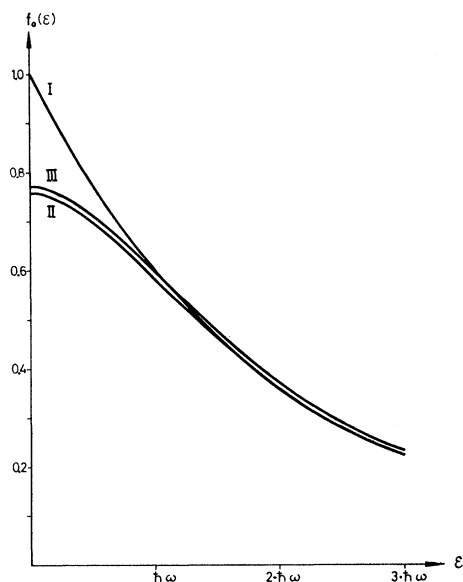


FIG. 1. $f_0(\epsilon)$ as function of the energy for $kT_e^* = 2\hbar\omega_0$. I—high-energy limit function $\exp(-\epsilon/kT_e^*)$; II—corrected function; III—corrected function with the same normalization integral as I.

The electron temperature of each particular valley varies approximately as the square of the electric field strength. On account of the dependence of the effective field on the direction of the electric field, the electron temperatures are in general different for different valleys.

The function $f_1(\epsilon)$, describing the nonuniformity of the electron distribution, is now easily found by means of (15), (23), and (25). This function,

$$f_1(\epsilon) = -(E_{\langle\tau\rangle}^*/kT_e^*)f_0(\epsilon), \quad (27)$$

decreases approximately as the inverse first power of the electric field. The smallness of f_1 at high fields makes it plausible that the omission of higher terms in the expansion (3) is not unjustified (see also reference 35).

The function $f_0(\epsilon)$, which for $\epsilon > 2\hbar\omega_0$ is given by (23) and (25), can be easily obtained for smaller energies by means of a numerical integration of (21), where—as a zeroth approximation—the function $f_0(\epsilon)$ in the integrand is to be replaced by (23). The result of such a numerical integration for the somewhat marginal case $kT_e^* = 2\hbar\omega_0$ is given in Fig. 1. Comparison of (23) and the corrected function shows that deviations from (23) only occur for energies $\epsilon < \hbar\omega_0$. The range of validity of (23) seems therefore to be larger than one might expect from its derivation. The deviations are due to a sweep-out effect of electrons with $\epsilon < \hbar\omega_0$ caused by the electric field, as for those electrons the influence of scattering on the distribution is gradually dying out with decreasing energy. We therefore conclude that for high electric fields $f_0(\epsilon)$ may be replaced by (23), and for the calculation of the drift velocity $f_1(\epsilon)$ may be replaced by

(27) in the entire region of energy, without introducing any serious error.

In concluding this section, let us digress for a moment to the case of small electric fields. Here from (27) the following expression for the electron temperature, which now only describes the very tail of the distribution, is obtained:

$$kT_e^* = kT + E_{\tau 0}^* E_{\langle\tau\rangle}^* / \hbar\omega_0. \quad (28)$$

Most of the electrons however are now in the energy range $0 < \epsilon < 2\hbar\omega_0$ where the solution is difficult to obtain. This explains the mathematical complications which are met in the theory of warm electrons.

IV. RELATIVE CONTRIBUTION OF ACOUSTICAL AND OPTICAL SCATTERING

In the preceding section the solution of the Boltzmann Eq. (21), (15) has been given for the case of mixed optical and acoustical scattering in the sense that in (15), which essentially describes the momentum scattering, the acoustical contributions have been taken into account, whereas they have been neglected in the scattering terms of (21). This means, as was already mentioned, that the contribution of the acoustical phonons to the energy loss of the electrons has been neglected. In the literature, considerable attention has been given to the question of the relative contribution of the acoustical phonons to the energy loss of the electrons. We therefore want to reconsider this problem in more detail and to give a justification for the procedure employed in the preceding section for the case of high fields by discussion of the solution of (21) when the E_{ac} terms are not neglected.

In the case of high fields, $f_0(\epsilon)$ is a slowly varying function of energy. In the range $\epsilon > \hbar\omega_0$, $f_0(\epsilon + \hbar\omega_0)$ and $(\epsilon + \hbar\omega_0)^{\frac{1}{2}}$ in the integrand of (21) can be expanded. One then gets instead of (21) the approximate equation

$$\frac{df_0}{d\epsilon} \left(kT_e^* + \frac{E_{ac}\epsilon}{\hbar\omega_0} \right) = - \left(1 + \frac{E_{ac}\epsilon}{kT\hbar\omega_0} \right) f_0, \quad (29)$$

with kT_e^* given by (24). For $(E_{ac}/\hbar\omega_0)(\epsilon/kT_e^*) \ll 1$, a condition which is not very restrictive, this equation has a Yamashita and Watanabe type of solution

$$f_0(\epsilon) \sim \exp \left\{ -\frac{\epsilon}{kT_e^*} \left[1 + \frac{E_{ac}\epsilon}{2\hbar\omega_0} \left(\frac{1}{kT} - \frac{1}{kT_e^*} \right) \right] \right\}. \quad (30)$$

According to the estimate $E_{ac} \approx 10^{-2}\hbar\omega_0$, the E_{ac} term, which varies quadratically with the energy, preponderates over the linear one only for energies $\epsilon > 30\hbar\omega_0$. Under the experimental conditions $78^\circ\text{K} \leq T \leq 300^\circ\text{K}$ and $10^3 \text{ v/cm} \leq F^* \leq 7 \times 10^3 \text{ v/cm}$, kT_e^* has values between $\hbar\omega_0$ and $10\hbar\omega_0$. Therefore the E_{ac} terms preponderate only in the unimportant tail of a Maxwellian distribution and can be omitted. This means physically that the energy loss of the electrons by interactions with

acoustical phonons can be neglected for those energies which actually are accessible to electrons under the experimental conditions under consideration. In the earlier work of Yamashita and Watanabe⁴⁸ only the quadratic term in the energy was retained in (27), and the conclusion was drawn⁴⁵ that even in the case of mixed acoustical and optical scattering, a Shockley type of behavior should result. This, in fact, corresponds to a complete neglect of the contribution of the optical phonons to the energy loss of the electrons. It is interesting in this context to discuss briefly a method of solution for Eq. (21) which has been proposed by Franz.^{43,44} Franz takes as a starting point for an iterative numerical solution a zeroth order approximation which is obtained from (21) if the optical scattering terms are neglected. For $\epsilon > 2\hbar\omega_0$ he consequently gets a Gaussian distribution, which for the case of high fields has a large half-width. This zeroth order approximation deviates greatly from the nearly correct Maxwellian distribution with the same normalization in the entire range of energies. It is therefore not a good starting point for an iterative solution in the case of high electric fields.

In concluding this discussion, two remarks must be added. In the foregoing it has been tacitly assumed that thermal equipartition holds for the acoustical phonons interacting with the electrons. It has been pointed out by Stratton¹² and by Conwell and Brown¹⁷ that for high average energies of the electrons, a considerable amount of interaction consists of the emission of acoustical phonons which are not excited thermally. This, of course, gives rise to a higher contribution of acoustical phonons to the energy loss of the electrons; the more, the lower the lattice temperature. In our case, in fact even for $kT_e^* = 10\hbar\omega_0$, most of the electrons are situated in k space with an average distance $\Delta k \approx 10^7 \text{ cm}^{-1}$, and therefore equipartition is still valid for the range of lattice temperatures indicated above.

For $kT_e^* > 10\hbar\omega_0$, where the emissive acoustical processes would become important, the whole theory as given in this paper is not applicable, because then the distribution of electrons extends appreciably to such values of the energy that the basic assumption of constant effective masses certainly breaks down.

V. INFLUENCE OF INTERVALLEY SCATTERING

In the absence of intervalley scattering, the electrons are distributed in a Maxwellian fashion around the different energy minima under consideration, with electron temperatures which, in general, are different for different valleys. We consider now the influence of scattering to other equivalent valleys on the distribution of electrons.

If equivalent intervalley scattering is taken into account, the function $f_0^{(j)}$ for a particular valley is a

solution of the equation

$$\begin{aligned}
 & -E_{\tau 0}^{*(j)} E_{\langle \tau \rangle}^{*(j)} \frac{df_0^{(j)}}{d\epsilon} \\
 & = \int_{\epsilon - \hbar\omega_0}^{\epsilon} \left(\frac{\xi + \hbar\omega_0}{\epsilon} \right)^{\frac{1}{2}} \left(\frac{\xi}{\epsilon} \right)^{\frac{1}{2}} \\
 & \quad \times [(n_q + 1)f_0^{(j)}(\xi + \hbar\omega_0) - n_q f_0^{(j)}(\xi)] d\xi \\
 & \quad + \gamma \frac{\omega_0}{\omega_i} \int_{\infty}^{\epsilon} \left\{ \left(\frac{\xi + \hbar\omega_i}{\epsilon} \right)^{\frac{1}{2}} \left(\frac{\xi}{\epsilon} \right)^{\frac{1}{2}} \right. \\
 & \quad \times \sum_{l \neq j} [(n_i + 1)f_0^{(l)}(\xi + \hbar\omega_i) - n_i f_0^{(l)}(\xi)] \\
 & \quad \left. + \left(\frac{\xi - \hbar\omega_i}{\epsilon} \right)^{\frac{1}{2}} \left(\frac{\xi}{\epsilon} \right)^{\frac{1}{2}} \right. \\
 & \quad \left. \times \sum_{l \neq j} [(n_i + 1)f_0^{(l)}(\xi - \hbar\omega_i) - n_i f_0^{(l)}(\xi)] \right\} d\xi, \quad (31)
 \end{aligned}$$

in which the unimportant contribution of the acoustical intravalley scattering on the energy relaxation of the electrons has already been omitted. Here $\gamma = (D_i/D_0)^2$, where D_i is the deformation potential constant for equivalent intervalley scattering, ω_i denotes the frequency of an intervalley phonon, and n_i is the number of intervalley phonons present. The sums in the intervalley scattering terms of (31) extend over all equivalent valleys with the exception of the particular valley j under consideration. The functions $f_1^{(j)}(\epsilon)$ and the energy gains $E_{\tau 0}^{*(j)}$ and $E_{\langle \tau \rangle}^{*(j)}$ are, as in Sec. III, given by Eqs. (15)–(18) where the effective temperature is now defined as

$$\begin{aligned}
 T_{\text{eff}}(\epsilon) = T + \frac{D_0^2 \hbar c \tau^2}{\Xi_1^2 2k\omega_0} & \left\{ n_q \left(\frac{\epsilon + \hbar\omega_0}{\epsilon} \right)^{\frac{1}{2}} \right. \\
 & \left. + (n_q + 1) \left(\frac{\epsilon - \hbar\omega_0}{\epsilon} \right)^{\frac{1}{2}} + (N - 1) \gamma \frac{\omega_0}{\omega_i} \right. \\
 & \left. \times \left[n_i \left(\frac{\epsilon + \hbar\omega_i}{\epsilon} \right)^{\frac{1}{2}} + (n_i + 1) \left(\frac{\epsilon - \hbar\omega_i}{\epsilon} \right)^{\frac{1}{2}} \right] \right\}. \quad (32)
 \end{aligned}$$

Here N is the number of equivalent valleys in the band under consideration. Equation (31) can be solved for high electric fields, if intervalley scattering is small as compared to intravalley scattering. This is the case for $n\text{-Ge}$,³⁸ because intervalley transitions of the electrons in which transverse acoustical phonons are involved are forbidden.⁴⁶

In this case of high fields the energy range $\epsilon > 2\hbar\omega_0$ is, just as in Sec. III, the most important one. In this range, the effective temperature and the energy gain

⁴⁵ S. H. Koenig, J. Phys. Chem. Solids 8, 227 (1959).

⁴⁶ R. J. Elliot and R. Loudon, J. Phys. Chem. Solids, 15, 146 (1960).

$L_{(r)}^{*(j)}$ become independent of the energy because $(\epsilon + \hbar\omega)$ and $(\epsilon - \hbar\omega)$ in (32) can be replaced by ϵ . In the same approximation, the expression $(\xi + \hbar\omega_0)\xi$ in the optical scattering term of (31) can be replaced by ϵ^2 . If furthermore, in contradistinction to the procedure followed in Sec. III, the function $f_0^{(j)}(\xi + \hbar\omega_0)$ is also expanded, the equation

$$\begin{aligned} & -\frac{d}{d\epsilon} [f_0^{(j)} \exp(\beta_j \epsilon)] \\ &= \gamma \frac{\beta_j}{\omega_i \hbar\omega_0} \exp(\beta_j \epsilon) \int_{\infty}^{\epsilon} \left\{ \left(\frac{\xi + \hbar\omega_i}{\epsilon} \right)^{\frac{1}{2}} \left(\frac{\xi}{\epsilon} \right)^{\frac{1}{2}} \right. \\ & \quad \times \sum_{l \neq j} [(n_i + 1) f_0^{(l)}(\xi + \hbar\omega_i) - n_i f_0^{(j)}(\xi)] \\ & \quad + \left(\frac{\xi - \hbar\omega_i}{\epsilon} \right)^{\frac{1}{2}} \left(\frac{\xi}{\epsilon} \right)^{\frac{1}{2}} \\ & \quad \times \sum_{l \neq j} [n_i f_0^{(l)}(\xi - \hbar\omega_i) - (n_i + 1) f_0^{(j)}(\xi)] \Big\} d\xi \quad (33) \end{aligned}$$

is obtained instead of (31). Here $\beta_j = 1/kT_e^{*(j)}$ and $kT_e^{*(j)}$ is given by (25).

If γ is so small that the influence of intervalley scattering on the energy relaxation can be neglected, while it is still large enough to establish a stationary state distribution between the valleys, the Maxwellian distribution

$$f_0^{(j)}(\epsilon) = C_j \exp(-\beta_j \epsilon) \quad (34)$$

is a solution of (33). The constants C_j , however, are no longer independent, but are determined by the principle of detailed balance:

$$\int_0^{\infty} \epsilon^{\frac{1}{2}} (\epsilon + \hbar\omega_i)^{\frac{1}{2}} \times [(n_i + 1) f_0^{(j)}(\epsilon + \hbar\omega_i) + n_i f_0^{(i)}(\epsilon)] d\epsilon = K, \quad (35)$$

which can be easily obtained from (33). Insertion of (34) in (35) leads to the following proportionality:

$$C_j \sim \frac{\beta_j}{[(n_i + 1) \exp(-\beta_j \hbar\omega_i/2) + n_i \exp(\beta_j \hbar\omega_i/2)] K_1(\beta_j \hbar\omega_i/2)}, \quad (36)$$

where K_1 is a modified Hankel function. In the case of high fields, the argument of K_1 and the exponential functions is small and the functions can be expanded. Then the following result is obtained:

$$C_j = C \beta_j^2 \left[1 - \frac{\hbar\omega_i \beta_j}{2(2n_i + 1)} \right]^{-1}. \quad (37)$$

It follows from the normalization condition for $f_0^{(j)}(\epsilon)$ that the number n_j of electrons in the valley j is proportional to $C_j \beta_j^{-3}$. Therefore the population ratio n_j/n is given by

$$\frac{n_j}{n} = \frac{\beta_j^3 [1 - \hbar\omega_i \beta_j / 2(2n_i + 1)]^{-1}}{\sum_l \beta_l^3 [1 - \hbar\omega_i \beta_l / 2(2n_i + 1)]^{-1}}. \quad (38)$$

If furthermore in (37) and (38) the small terms $\beta_j \hbar\omega_i / 2(2n_i + 1)$ are neglected, one gets

$$C_j = C \beta_j^2 \quad (37a)$$

and

$$n_j/n = \beta_j^3 / \sum_l \beta_l^3, \quad (38a)$$

where (38a) is now exactly the ratio of number densities for Knudsen gases in N containers with different temperatures. This result is plausible because in going from (38) to (38a) the energy of the intervalley phonon is considered negligible as compared to the average energy of the electrons.

Let us now turn to the case of such values of γ that intervalley scattering not only results in a particle transfer between different valleys, but also does affect the

energy relaxation of electrons in a particular valley. The function $f_0^{(j)}(\epsilon)$ then deviates from the original Maxwellian distribution (34). The influence of intervalley scattering on $f_0^{(j)}(\epsilon)$ can be obtained to first order if in the intervalley scattering terms of (33) the zeroth approximation (34) is inserted. This perturbation procedure can only be easily done if in the intervalley terms the energy of the intervalley phonon is neglected, which implies that in a consequent form of the approximation C_j from (37a) should be inserted.

If this is done, we get the first approximation as solution of the equation

$$\begin{aligned} & -\frac{d}{d\epsilon} [f_0^{(j)}(\epsilon) \exp(\beta_j \epsilon)] \\ &= \bar{\gamma} \exp(\beta_j \epsilon) \frac{C \beta_j}{\epsilon} \\ & \quad \times \int_{\infty}^{\epsilon} \xi \sum_{l \neq j} [\beta_l^2 \exp(-\beta_l \xi) - \beta_j^2 \exp(-\beta_j \xi)] d\xi, \quad (39) \end{aligned}$$

where

$$\bar{\gamma} = \gamma(2n_i + 1)/\hbar\omega_i. \quad (40)$$

Before explicitly writing down the solution, we shall discuss its general structure, which is of the form

$$f_0^{(j)}(\epsilon) = C_j \exp(-\beta_j \epsilon) + \bar{\gamma} \sum_l A_l(\epsilon) \exp(-\beta_l \epsilon),$$

where l extends over all valleys, including j . This solution is composed of the original zeroth order solution plus a small admixture of the Maxwellian distributions

from all valleys including j with energy-dependent coefficients, the variation of which with the energy however is small as compared to the variation of the exponential function. The admixture of "foreign" Maxwellian distributions can be understood from the fact that electrons passing from the valley l to the valley j after the interaction still have the average energy of the valley l . They need a certain time until they lose the memory of their origin by participating in intravalley processes. Furthermore, the energy dependence of the coefficients A_l and A_j is a consequence of the energy-dependent scattering probability for intervalley and intravalley processes. That the deviation from the original Maxwellian distribution increases with increasing intervalley rate constant and increasing excitation ($2n_i+1$) of the intervalley phonon is obvious.

After this general discussion, the explicit form of the solution of (39),

$$f_0^{(j)}(\epsilon) = \left\{ K_j - \bar{\gamma}\beta_j C \left[(N-1)\beta_j\epsilon + \sum_{l \neq j} \left(\frac{\beta_l}{\beta_j - \beta_l} - \int_0^\epsilon \frac{\exp[(\beta_j - \beta_l)\xi] - 1}{\xi} d\xi \right) \right] \right\} \\ \times \exp(-\beta_j\epsilon) + \bar{\gamma}\beta_j C \sum_{l \neq j} \frac{\beta_l}{\beta_j - \beta_l} \exp(-\beta_l\epsilon), \quad (41)$$

can be given. As is seen from (41), the deviations from the original Maxwellian distribution also depend on the differences of the electron temperatures. Application of the principle of detailed balance to (41) finally leads to the following expression for the constant K_j :

$$K_j = C \left\{ \beta_j^2 \left[1 - \frac{\beta_j \hbar \omega_i}{2(2n_i+1)} \right]^{-1} - 2\bar{\gamma}\beta_j^2 \sum_l [1/\beta_l - 1/\beta_j] - \bar{\gamma}\beta_j \sum_l \ln(\beta_j/\beta_l) \right\}. \quad (42)$$

In a subsequent paper, a theory of current and anisotropy of hot electrons, based on the distribution functions of this paper, will be given. It will be shown that a quantitative description of hot electron phe-

nomena can be achieved by using the distribution function (41) and (42). This opens the possibility of a new determination of the intervalley rate constant by an analysis of hot-electron experiments.

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APPENDIX

A solution of Eq. (21) without the acoustical term can also be obtained for small energies as long as

$$(n_q+1)f_0(\epsilon + \hbar\omega_0) - n_q f_0(\epsilon) \approx (n_q+1)f_0(\hbar\omega_0) - n_q f_0(0). \quad (43)$$

The analytical behavior of the solution in this energy range is determined by the energy dependence of $E_{\langle\tau\rangle}^*$. Here two cases have to be distinguished. For energies $\epsilon < \epsilon_0 = 10^{-3}\hbar\omega_0$, $E_{\langle\tau\rangle}^*$ is approximately given by

$$E_{\langle\tau\rangle}^* = E_{\tau_0}^* (\epsilon/\hbar\omega_0)^{1/2} n_q.$$

The solution of Eq. (21) in this energy range consequently reads

$$f_0(\epsilon) = f_0(0) - 2 \frac{n_q \hbar \omega_0}{[E_{\tau_0}^*]^2} [(n_q+1)f_0(\hbar\omega_0) - n_q f_0(0)].$$

For energies $\epsilon_0 = 10^{-3}\hbar\omega_0 < \epsilon < \hbar\omega_0$, $E_{\langle\tau\rangle}^*$ is nearly independent of the energy:

$$E_{\langle\tau\rangle}^* \approx E_{ac} = eF^* r_{ac} (2\epsilon/m_0)^{1/2}.$$

The solution for small energies in this energy range (as long as (43) still holds) is then

$$f_0(\epsilon) = f_0(0) - \frac{4(\hbar\omega_0)^{1/2}}{3E_{\tau_0}^* E_{ac}} \times [(n_q+1)f_0(\hbar\omega_0) - n_q f_0(0)] (\epsilon^3 - \epsilon_0^3).$$

The omission of the acoustical terms in (21) is possible if $f_0(\hbar\omega_0)$ is not too small compared to $f_0(0)$. This is always the case for hot electrons.