

Steady-State Distribution Function in Dilute Electron Gases

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(Received April 15, 1960)

It is usually assumed that optically created carriers in a photoconductor rapidly thermalize to a Boltzmann distribution, regardless of the generation and recombination mechanisms. However, it can be shown that this distribution which is characteristic of thermodynamic equilibrium is incompatible with the requirements of steady state. A variational principle is introduced to find the steady-state distribution, which is found to approach the Maxwell-Boltzmann function in the limit of strong thermal scattering. Interband scattering is found to be potentially a strong thermalizing influence, in addition to the intraband scattering usually considered. For a simple model semiconductor, significant deviations from the Boltzmann distribution are found to be possible at temperatures below a few degrees Kelvin. This result is then discussed in connection with certain experiments on germanium.

I. INTRODUCTION

ELECTRONS in donor traps or in the valence band of semiconductors can be liberated into the conduction band by the absorption of a sufficiently energetic photon. This is the mechanism of photoconductivity, a phenomenon which is of itself important, and which, moreover, has been useful in providing carriers for experiments on semiconductors at low temperatures. The purpose of this investigation is to find the effects determining the distribution function of the liberated carriers and to establish the equation by which it may be calculated. This is done supposing the absence of electric or magnetic fields.

In the theoretical analysis of electronic properties under the conditions of low temperature and steady-state illumination, it is usual to assume that the carriers are in the Boltzmann distribution so that $n(\epsilon)$, the density of carriers per unit energy range, is given by

$$n(\epsilon) = A \exp(-\epsilon/kT), \quad (1)$$

where A is an appropriate function of the illumination and of the density of states. Indeed, some definite function must be chosen in order that the conductivity, the lifetime, and other electronic parameters be calculable, and the Boltzmann distribution is a natural choice because it is known that electron-phonon collisions exert a strong and rapidly thermalizing influence. However, general arguments indicate that in any case (1) is only an approximation to the correct distribution function for steady state, and a rather poor one under certain extreme conditions. The reasoning is transparent: the Boltzmann distribution (1) is a multiple of the equilibrium function describing carriers in the presence of the lattice, which is considered to be a heat bath because of the relatively large lattice specific heat. Therefore, the dilute electron gas describable by (1) cannot on the average either transmit heat to the lattice or absorb it from the latter. But the energy which the electrons absorb from the light source is independent of, and in general different from that dissipated in the recombination process, and unless heat flows between the conduction particles and the phonons, the former

will either gain or lose energy indefinitely, and will not be in steady state. Therefore, the steady-state distribution will not in general be a simple multiple of the Boltzmann distribution.

The correct function may be obtained as the solution of a rate equation which expresses the fact that in steady state the net rate of change of the population of each cell in phase space must vanish. But because of the complicated electron-phonon interaction this equation is intractable except by numerical techniques. However, a variational procedure similar to Kohler's¹ is found to remove some of the difficulty and to ensure rapid numerical convergence. What is more, by the use of a simple trial function one can then variationally determine the range of accuracy of the Boltzmann approximation (1) by analytical means, as in the example of Sec. III. When the experimental situation is such that (1) is no longer a valid approximation, unexpected results may occur such as in two interesting experiments discussed in Sec. IV, for which our calculations may be applicable.

II. THE VARIATIONAL PRINCIPLE

If we neglect the exclusion principle for a dilute gas, the electrons are scattered by phonons and impurities according to the equation

$$\left. \frac{\partial f(\mathbf{p})}{\partial t} \right|_{\text{scatt.}} = \sum_{\mathbf{p}'} S(\mathbf{p}, \mathbf{p}') [e^{\epsilon'/kT} f(\mathbf{p}') - e^{\epsilon/kT} f(\mathbf{p})], \quad (2)$$

where the energies ϵ and ϵ' are related to the momenta \mathbf{p} and \mathbf{p}' , and where $f(\mathbf{p})$ is the distribution in phase-space and $S(\mathbf{p}, \mathbf{p}')$ a symmetric kernel. The assumption is that the phonons are in thermal equilibrium. It is seen that the scattering rate vanishes when the electrons are themselves in thermal equilibrium, and also that for any $f(\mathbf{p})$, particles are conserved, i.e.,

$$\sum_{\mathbf{p}} \left. \frac{\partial f(\mathbf{p})}{\partial t} \right|_{\text{scatt.}} \equiv 0. \quad (3)$$

¹ See A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, New York, 1954), Chap. X.

Indeed, these three requirements are sufficient to determine the form (2) of the scattering operator.

Other processes which occur in the steady state are:

- (a) The generation of carriers (by optical absorption or any other means) at a rate

$$\left. \frac{\partial f(\mathbf{p})}{\partial t} \right|_{\text{o.a.}} = g(\mathbf{p}), \quad (4)$$

- (b) and their recombination, occurring at a rate

$$\left. \frac{\partial f(\mathbf{p})}{\partial t} \right|_{\text{rec.}} = -f(\mathbf{p})/\tau(\mathbf{p}). \quad (5)$$

The fundamental equation for steady state is, of course

$$\left. \frac{\partial f}{\partial t} \right|_{\text{scatt.}} + \left. \frac{\partial f}{\partial t} \right|_{\text{o.a.}} + \left. \frac{\partial f}{\partial t} \right|_{\text{rec.}} = 0, \quad (6)$$

and upon substitution of the relationships (2), (4), and (5) this becomes the rate equation which must be solved for $f(\mathbf{p})$.

When summed over states and combined with Eq. (3), this equation also provides us with a useful sum-rule;

$$\sum_{\mathbf{p}} g(\mathbf{p}) = \sum_{\mathbf{p}} f(\mathbf{p})/\tau(\mathbf{p}), \quad (7)$$

which may be used to check the accuracy of the solution $f(\mathbf{p})$, or alternately as a boundary condition.

The variational principle which relieves us from solving Eq. (6) is simplest formulated in terms of the function $x(\mathbf{p})$,

$$x(\mathbf{p}) = f(\mathbf{p}) e^{\epsilon/kT}, \quad (8)$$

for which the scattering term becomes a difference operator. Because of its simple relationship to $f(\mathbf{p})$, we shall need to concern ourselves only with this new function. For example, $x(\mathbf{p}) = \text{constant}$ corresponds to the Boltzmann distribution (1), and deviations from the latter will show up in the momentum dependence of the x function.

The rate equation is linear in the x function, so that by a simple quadrature one obtains a variational principle, whereby the x function which maximizes Φ is related to the solution $f(\mathbf{p})$ of the rate equation by Eq. (8), and thus determines it. We define,

$$\Phi = \sum_{\mathbf{p}} \left\{ g(\mathbf{p})x(\mathbf{p}) - \frac{x^2(\mathbf{p})e^{-\epsilon/kT}}{\tau(\mathbf{p})} - \frac{1}{4} \sum_{\mathbf{p}'} S(\mathbf{p}, \mathbf{p}') [x(\mathbf{p}) - x(\mathbf{p}')]^2 \right\}. \quad (9)$$

There is, of course, the possibility that carriers occupy two or more distinct bands, e.g., the valence bands of Ge. Our expressions are generalized to this case by substituting for \mathbf{p} wherever it occurs, the four-vector (\mathbf{p}, n) , where n is a band index. This does not in any way alter

the mathematical structure of the theory, and we shall, for the moment, continue to omit the band index.

One can readily show that not only is Φ an extremum when Eq. (6) is obeyed, but that this extremum is an absolute maximum. Let a trial function be x_i ,

$$x_i = f(\mathbf{p}) e^{\epsilon/kT} + \Delta(\mathbf{p}), \quad (10)$$

where Δ measures the error intrinsic in the trial function and $f(\mathbf{p})$ (although unknown) is supposed to be the solution of Eq. (6). We substitute (10) in Eq. (9), and use Eq. (6) to eliminate some terms in $f(\mathbf{p})$. There remains,

$$\Phi = \sum_{\mathbf{p}} \frac{1}{2} g(\mathbf{p}) f(\mathbf{p}) e^{\epsilon/kT} - \sum_{\mathbf{p}} \left\{ \frac{1}{2} [\Delta^2(\mathbf{p})/\tau(\mathbf{p})] e^{-\epsilon/kT} + \frac{1}{4} \sum_{\mathbf{p}'} S(\mathbf{p}, \mathbf{p}') [\Delta(\mathbf{p}) - \Delta(\mathbf{p}')]^2 \right\}, \quad (11)$$

and because of the linearity of Eq. (6) there are no higher order terms in Δ . This demonstrates that Φ is maximal, with a value

$$\Phi_{\text{max}} = \frac{1}{2} \sum g(\mathbf{p}) f(\mathbf{p}) e^{\epsilon/kT}, \quad (12)$$

if and only if $\Delta \equiv 0$, and the variational procedure of maximizing Φ results in minimizing the error in the trial function.

The variational principle makes it apparent that the Boltzmann distribution is generally correct in the limit of strong thermal scattering. For if in Eq. (9) we allow S to become infinite, then Φ is finite only for the Boltzmann distribution and equals $-\infty$ for any other. In this extreme case where the rate equation itself is indeterminate the variational procedure still provides the correct solution. We may also investigate the role of interband scattering in the same general way. For example, let us assume that interband scattering is weak, or absent. Then the equations decouple and a Φ for each band can be defined and separately maximized; the distributions in each band are then independent. At the opposite extreme, let us assume very strong but *elastic* interband scattering. That is,

$$S(\mathbf{p}, n; \mathbf{p}', n') \sim \delta(\epsilon_{\mathbf{p}', n} - \epsilon_{\mathbf{p}', n'}), \quad n \neq n'.$$

Then Φ will be maximal only if

$$x(\mathbf{p}, n) = x(\mathbf{p}', n') \quad \text{whenever} \quad \epsilon_{\mathbf{p}, n} = \epsilon_{\mathbf{p}', n'},$$

and only if the x 's are functions of the energy alone, i.e.,

$$x(\mathbf{p}, n) = t(\epsilon_{\mathbf{p}, n}).$$

The variational principle may then be solved for a single function $t(\epsilon)$, once interband scattering has been removed from the problem by this choice of constraints.

Finally, one notes that strong and *inelastic* interband scattering results in the Boltzmann distribution for all the bands, regardless of the relative strength of intra-band scattering. This suggests that interband scattering might also play an important role in semiconductor transport phenomena, where it has been largely ignored.

III. BOLTZMANN CRITERION FOR A MODEL SEMICONDUCTOR

As an illustration of this method we shall find a criterion for the applicability of the Boltzmann-function approximation to steady state for a model semiconductor. We shall assume for the carriers a constant effective mass m . Because it is convenient to consider only acoustical phonon scattering, the effect of optical modes will be approximated by cutting off the generation function $g(\mathbf{p})$ below the optical mode energy $\hbar\omega_0$. Moreover, because of the rapid scattering of particles along contours of constant energy, both $g(\mathbf{p})$ and $\tau(\mathbf{p})$ may be replaced by their averages along such contours, $g(\epsilon)$ and $\tau(\epsilon)$. The distribution will then be determined by the competition between the energy relaxation mechanism of acoustical phonons and the generation and recombination mechanisms, and elastic scattering is completely eliminated by the self-consistent choice of trial functions we shall make in Eq. (17).

For the generation function, we simply let

$$\begin{aligned} g(\epsilon) &= \text{constant} & \epsilon < \hbar\omega \\ g(\epsilon) &= 0 & \epsilon \geq \hbar\omega, \end{aligned} \quad (13)$$

where $\hbar\omega$ measures the injected electron "temperature," and must not under any circumstances exceed $\hbar\omega_0$, by our preceding arguments.

For the lifetime, there is evidence^{2,3} that slow carriers are more efficiently trapped than fast ones. Indeed, the theory of Lax³ on giant traps indicates that carriers in the lowest levels of the conduction band are virtually captured by these traps; their lifetime is therefore zero, whereas the lifetime of energetic carriers may be millions of lattice collision times. Experiments by Koenig² suggest a lifetime dependence of the form (roughly),

$$\tau(\epsilon) = \epsilon^{\frac{1}{2}}/R(T). \quad (14)$$

In the capture process the binding energy must be dissipated, and this results in the temperature-dependence of the coefficient $R(T)$.

This describes the sort of situation where the Boltzmann distribution seemingly cannot apply, else the system of conducting particles would gain energy at a

rate of approximately $\frac{1}{2}g\hbar\omega$ ergs/sec. However, at reasonable temperatures, as we shall see, it takes only a minute modification of the equilibrium distribution to dissipate this heat to the lattice. Let us now consider the mechanism whereby this is accomplished.

The scattering of carriers by lattice vibrations in typical semiconductors has been considered by Bardeen and Shockley.⁴ From their work on the deformation potential, we find an expression for the scattering kernel,

$$\begin{aligned} S(\mathbf{p}, \mathbf{p}') &= \text{const} \times \sum_q \frac{\hbar\omega_q}{e^{\hbar\omega_q/kT} - 1} \\ &\times \begin{cases} \delta(\epsilon' - \epsilon - \hbar\omega_q) \delta_{\mathbf{p}', \mathbf{p} + \hbar\mathbf{q}} e^{-\epsilon/kT} & (\epsilon' > \epsilon) \\ \delta(\epsilon - \epsilon' - \hbar\omega_q) \delta_{\mathbf{p}, \mathbf{p}' + \hbar\mathbf{q}} e^{-\epsilon'/kT} & (\epsilon > \epsilon'). \end{cases} \end{aligned} \quad (15)$$

We shall assume that the phonon energy $\hbar\omega_q$ and momentum $\hbar\mathbf{q}$ are related by a constant speed of sound $s = \omega_q/q$. Next, we note that the variational principle (but not the rate equation) may be simplified for a kernel of this form by the use of the identity,

$$\begin{aligned} \sum_{\mathbf{p}} \sum_{\mathbf{p}'} S(\mathbf{p}, \mathbf{p}') [x(\mathbf{p}) - x(\mathbf{p}')]^2 \\ = 2 \sum_{\mathbf{p}} \sum_{\mathbf{p}', \epsilon' > \epsilon} S(\mathbf{p}, \mathbf{p}') [x(\mathbf{p}) - x(\mathbf{p}')]^2. \end{aligned} \quad (16)$$

By assumption, the x function must only depend on the kinetic energy of the carriers in the conduction band. We therefore let

$$x(\mathbf{p}) = a + b t(\epsilon), \quad (17)$$

requiring only that

$$t(0) = 0, \quad t(\epsilon) \neq 0. \quad (18)$$

The parameters a and b are to be determined variationally, and one notes that a measures the pure Boltzmann contribution to the optically created carrier density. From the conditions

$$\frac{\partial \Phi}{\partial a} = \frac{\partial \Phi}{\partial b} = 0, \quad (19)$$

we obtain the simultaneous equations

$$a = \frac{\sum g(\mathbf{p}) - b \sum [t(\epsilon)/\tau(\mathbf{p})] e^{-\epsilon/kT}}{\sum e^{-\epsilon/kT}/\tau(\mathbf{p})}, \quad (20)$$

$$b = \frac{\sum g(\mathbf{p}) t(\epsilon) - a \sum [t(\epsilon)/\tau(\mathbf{p})] e^{-\epsilon/kT}}{\sum \{t^2(\epsilon) e^{-\epsilon/kT}/\tau(\mathbf{p}) + 2 \sum_{\mathbf{p}', \epsilon' > \epsilon} S(\mathbf{p}, \mathbf{p}') [t(\epsilon') - t(\epsilon)]^2\}}. \quad (21)$$

² S. Koenig, J. Phys. Chem. Solids 8, 227 (1959).

³ M. Lax, J. Phys. Chem. Solids 8, 66 (1959).

⁴ See W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), Chap. 17.

The sum-rule (7) is automatically satisfied by the solution to these equations. For our particular choice of $\tau(p)$ the denominator in Eq. (20) diverges, and the pure Boltzmann contribution, a , vanishes. When Eqs. (17) and (21) are combined with Eq. (9), the variational principle becomes the maximization of

$$\Phi = \frac{\left[\int_0^{\hbar\omega} d\epsilon \epsilon^{\frac{1}{2}} l(\epsilon) \right]^2}{\int_0^{\infty} d\epsilon \epsilon^{\frac{1}{2}} e^{-\epsilon/kT} \left\{ \frac{R(T) l^2(\epsilon)}{\epsilon^{\frac{3}{2}}} + \frac{B}{\epsilon^{\frac{1}{2}}} \int_{\delta_\epsilon}^{2+(8\epsilon/ms^2)^{\frac{1}{2}}} dx x^2 \frac{[l(\epsilon+xms^2)-l(\epsilon)]^2}{\exp(xms^2/kT)-1} \right\}}, \quad (22)$$

by means of the trial function $l(\epsilon)$. Here, integrals have replaced sums over states for the purposes of the calculation. B is a constant related to the strength of the scattering, and the ratio of scattering to recombination rates for a thermal electron is measured by the quantity

$$r = BkT/R(T). \quad (23)$$

In our approximate analysis, this ratio need only be known to within several orders of magnitude and therefore its temperature dependence is irrelevant. In the case of germanium, it is valid to assume $10^2 < r < 10^{10}$.

The lower limit δ_ϵ on the scattering integral in Eq. (22) (as well as the upper limit) reflects the conservation of momentum and energy in the scattering, and is given by

$$\begin{aligned} \delta_\epsilon &= 2 - (8\epsilon/ms^2)^{\frac{1}{2}} & \epsilon &\leq \frac{1}{2}ms^2 \\ \delta_\epsilon &= 0 & \epsilon &> \frac{1}{2}ms^2. \end{aligned} \quad (24)$$

We note that ms^2 is a very small unit of energy corresponding to a fraction of a degree Kelvin, so that for all temperatures of interest $2kT/ms^2 \gg 1$.

The simplest satisfactory trial function for this problem is the unit step,

$$\begin{aligned} l(\epsilon) &= l^2(\epsilon) = 0 & \epsilon < y \\ l(\epsilon) &= l^2(\epsilon) = 1 & \epsilon > y, \end{aligned} \quad (25)$$

where y is the parameter to be determined variationally. This represents a displaced Boltzmann distribution, and a criterion for the applicability of the approximation (1) to $f(p)$ can be taken as $y \ll kT$.

At relatively high temperatures ($kT \sim \hbar\omega$), we can expect this criterion to hold, and so we look for a maximum of Φ at small y . Indeed, the denominator in Eq. (22) does pass through a minimum at a point which we denote y_1 ,

$$y_1 = (8\sqrt{2}r)^{-\frac{2}{3}} ms^2. \quad (26)$$

The corresponding value of Φ is a maximum,

$$\Phi_1 \doteq \frac{(4/9)(\hbar\omega)^3}{R(T) \ln[(kT/1.78ms^2)(8\sqrt{2}r)^{\frac{2}{3}}]}. \quad (27)$$

As the lifetime is allowed to increase ($R \rightarrow 0$), Φ_1 will increase accordingly. Therefore, we see the trapping mechanism as the bottleneck in the diffusion of carriers through the states in the conduction band, and in this

temperature range a situation of quasi-thermal equilibrium can be readily achieved; that is, $y_1 \ll kT$.

At very low temperatures, however, it is found that $y \sim \hbar\omega$ yields a greater value for Φ . Denoting this point y_2 , and setting

$$y_2 = \hbar\omega - z, \quad (28)$$

we see that this second maximum occurs at

$$\frac{d}{dz} \left(\frac{z^2}{e^{z/kT}} \right) = 0;$$

i.e., at

$$z = 2kT, \quad y_2 = \hbar\omega - 2kT. \quad (29)$$

The trapping term scarcely contributes to Φ_2 , for which the thermal scattering is now the limiting factor. By direct calculation one finds

$$\Phi_2 \doteq \frac{4\hbar\omega(kT)^2}{e^{2-\hbar\omega/kT} \left[\frac{1}{3} BkT (8\hbar\omega/ms^2)^{\frac{2}{3}} \right]}. \quad (30)$$

It is at very low temperatures (where the exponential factor in the above expression becomes large) that Φ_2 is expected to exceed Φ_1 and where $y_2 \gg kT$ will locate the peak in the distribution, rather than $y_1 \ll kT$. The temperature T_0 separating the two regimes is found by equating $\Phi_1(T_0)$ to $\Phi_2(T_0)$. That is,

$$\begin{aligned} 3.68 \left(\frac{kT_0}{\hbar\omega} \right)^2 e^{\hbar\omega/kT_0} \\ = \left(\frac{8\hbar\omega}{ms^2} \right)^{\frac{2}{3}} \frac{r}{\ln[(kT_0/1.78ms^2)(8\sqrt{2}r)^{\frac{2}{3}}]}. \end{aligned} \quad (31)$$

Above T_0 the Boltzmann approximation would appear to be excellent, according to the criterion $y \ll kT$. Below T_0 , however, the electrons are characterized by a distinctly "hot" distribution with a mean energy of order of $\hbar\omega$.

Other than these qualitative observations, the inherent inaccuracy of the one-parameter solution prevents one from drawing more detailed conclusions about the shape of the distribution. The temperature T_0 is to be interpreted as an order-of-magnitude estimate of the highest temperature at which a highly non-thermal carrier population may be established. We now turn to a more general trial function so that we may have some

information about the shape of the distribution to supplement our knowledge of where it peaks.

Let the new trial function be

$$\begin{aligned} l(\epsilon) &= 0 & \epsilon < y_1 \\ l(\epsilon) &= 1 & y_1 < \epsilon < y_2 \\ l(\epsilon) &= 1+d & y_2 < \epsilon \end{aligned} \quad (32)$$

where y_1 and y_2 have the values given in Eqs. (26) and (29), respectively, which turn out to be optimum parameters in the present case as well. If we restrict the analysis to low temperatures ($kT \ll \hbar\omega$) the ratio of the number n_2 of carriers with energy $\sim y_2$ to the number of carriers n_1 with energy $\sim kT$ will be

$$n_2/n_1 \sim (\hbar\omega/kT)^{1/2} d. \quad (33)$$

As we shall see, the temperature at which this ratio is unity lies very close to the solution T_0 of Eq. (31). But in contradistinction to the previous trial functions, the present one changes continuously at T_0 , and provides us with the means to estimate the ratio n_2/n_1 in a continuous manner. Clearly, the Boltzmann criterion is satisfied if this ratio is much less than unity, whereas when it exceeds unity the distribution is nonthermal.

It is a straightforward matter to maximize Φ by means of the new trial function, for the integrals which occur have for the most part been evaluated in connection with the calculation of Φ_1 and Φ_2 . One finds for the optimum value of d , under the restriction $kT \ll \hbar\omega$,

$$d = \frac{1.23kT \ln[kT(8\sqrt{2}r)^{1/2}/1.78ms^2]}{\hbar\omega(8\hbar\omega/ms^2)^{1/2}} \exp \hbar\omega/kT. \quad (34)$$

Writing this as $d_0 \exp \hbar\omega/kT$ we may neglect the weak dependence of d_0 on temperature and just use the fact that it is an extremely small parameter. And if we define T_1 as the temperature at which the ratio (33) is unity, the n we readily find that

$$kT_1 = \hbar\omega / \ln \left[\frac{1}{d_0} \left(\frac{kT_1}{\hbar\omega} \right)^{1/2} \right] \sim kT_0. \quad (35)$$

In terms of this temperature, the ratio (33) may then be expressed as

$$\frac{n_2}{n_1} \sim \exp \left[\hbar\omega \left(\frac{1}{kT} - \frac{1}{kT_1} \right) \right]. \quad (36)$$

We see that for d_0 sufficiently small this ratio may change by several orders of magnitude near T_0 or T_1 , and if one is interested in temperatures even only a few degrees above T_1 , the distribution is quasi-thermal by any criterion.

So far, we have assumed that the distribution was a function of energy alone. Let us now assume, however, that because of some feature of the optical selection rules the excitation is anisotropic, say

$$g = g_0(1 + \mu\delta), \quad \delta \leq 1,$$

where g_0 is the excitation denoted g in Eq. (13), δ is a constant characteristic of the anisotropy, and μ a direction cosine. We may choose a suitable trial function, such as

$$x(\mathbf{p}) = (b + \mu c)l(\epsilon),$$

and determine c variationally. An upper limit on c is obtained by neglecting elastic (impurity) scattering, and by a simple extension of the foregoing analysis one finds

$$\begin{aligned} c/b &= \delta \times O(1/r) & T > T_0 \\ c/b &= \delta \times O(1) & T < T_0. \end{aligned} \quad (37)$$

The magnitude of T_0 depends in a negligible way on δ . One concludes that a substantially anisotropic distribution can exist only below T_0 , and that above this temperature phonon scattering is effectively in the strong limit discussed at the end of Sec. II.

IV. APPLICATIONS

The first of two problems in which the foregoing analysis finds an application concerns the giant electron traps in germanium. The theory of Lax³ is in excellent agreement with experiments by Koenig² for the temperature range above 5°K, where a (positive) power law is found to describe the temperature dependence of the average carrier lifetime. Below this temperature the lifetime saturates (experiment) whereas it is expected to continue to decrease according to essentially the same power law as at higher temperatures (theory). However, the theoretically predicted lifetime is based upon a Boltzmann average and should be modified below T_0 . This temperature may be readily calculated in this connection with Eq. (31), using Koenig's value of $\hbar\omega = k100^\circ\text{K}$. For r in the range 10^2 – 10^{10} , one finds T_0 in the range 2°K–8°K, in rough agreement with the experimental value. Below T_0 , the variational calculation has indicated that few carriers will be present in states of high trapping probability, so that the average lifetime will not be expected to further decrease with temperature, but rather to saturate as is observed. A direct experimental check of this proposed mechanism is possible because, to a good accuracy the present theory predicts that T_0 scales with $\hbar\omega$, provided $T_0 \ll \hbar\omega$. Thus if the temperature-dependence of the lifetime does saturate at T_0 as we have supposed, then this saturation temperature can experimentally be doubled—or halved, by doubling—or halving the “electron temperature” $\hbar\omega$.

The second direct application of the calculation in Sec. III is to the theory of negative-mass cyclotron resonance in p -type germanium. The experiments of Dousmanis *et al.*⁵ have shown an emissive spectrum associated with hole carriers of negative mass. The theory analyzing this phenomenon⁶ makes it clear, however, that even carriers of negative mass must absorb

⁵ G. C. Dousmanis *et al.*, Phys. Rev. Letters **1**, 404 (1958).

⁶ D. C. Mattis and M. J. Stevenson, Phys. Rev. Letters **3**, 18 (1959).

rather than emit resonant radiation, unless either (or both) of the following conditions are satisfied:

- (a) The distribution is not a function of energy alone,
- (b) The resonating states do not exist above a certain energy ϵ_e , and the distribution function satisfies the condition

$$\int_0^{\epsilon_e} d\epsilon \epsilon^{\frac{1}{2}} \frac{\partial f}{\partial \epsilon} > 0.$$

Neither condition can be satisfied above T_0 . Below this temperature, however, both are possibilities. The first can be satisfied if g and τ are not functions of energy alone; this is likely to be true to a limited extent. The second condition is met if $\epsilon_e < \hbar\omega$; however, the existence and the value of ϵ_e have not yet been established.

Self-Diffusion of the Chloride Ion in Sodium Chloride*†

NEAL LAURANCE†

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(Received May 18, 1960)

The diffusion coefficient of Cl^{36} in NaCl has been measured in the temperature range from 520° to 740°C. Diffusion was measured in pure Harshaw crystals and in crystals containing from 0.01 to 0.1 mole percent calcium. The diffusion coefficient in pure crystals is represented by the equation $D = 56 \exp(-2.12 \text{ ev}/kT)$ cm^2/sec . The diffusion coefficient in crystals containing calcium was smaller than that measured in pure crystals by a factor of from 5 to 10, and had an activation energy of 2.5 ev. Over the range of impurity concentration employed the diffusion coefficient was insensitive to differences in calcium concentration. The results are discussed in terms of motion of free negative ion vacancies and of vacancy pairs. Possible complicating effects of dislocation lines on the diffusion coefficient are also considered.

INTRODUCTION

THE ionic conduction process in alkali halides has been extensively studied, and the details of the ionic motion are quite well understood.¹ Schottky defects predominate, and the positive ion vacancy is responsible for the conductivity. The contribution of the negative ion to the conductivity is usually quite small, under 10% in most pure crystals, and essentially zero in the impurity controlled range of temperature. Kerkhoff² found that in highly purified KCl at high temperature the contribution of the negative ion to the total conductivity may be as large as 40%, but over the region of interest in most experiments it has been satisfactory to assume that the conductivity is due to the positive ion alone. For this reason early work in this field centered around the measurements of the conductivity and of the positive ion diffusion coefficient. Such studies have produced a detailed picture of the motion of a positive ion vacancy in a lattice. In contrast, although there have been several measurements of negative ion diffusion coefficients, no such detailed information on negative ion vacancies has resulted. It

has been generally assumed that the diffusion of negative ions proceeds by motion of negative ion vacancies, in analogy to the findings in the case of the positive ion, but the evidence for this is far from conclusive.

Chemla³ performed the first measurements of diffusion of Cl^{36} in NaCl over a limited temperature range as a part of a survey of diffusion properties of NaCl. Laurent and Bénard⁴ repeated these experiments, extending the range of temperature investigated. Schamp and Katz⁵ measured the negative ion self-diffusion coefficient in NaBr. All of these measurements were made by a sectioning technique involving the removal of thin layers of crystal and measuring the amount of radioactive isotope which had penetrated from the surface. Ewles and Jain⁶ have interpreted the time decay of conductivity in quenched samples of KCl as due to the motion of negative ion vacancies and have arrived at an expression for the diffusion coefficient of the negative ion. Recently Schamp has reported the results of diffusion measurements of the chloride ion in KCl.⁷

Within the last few years a group at Ottawa, Canada, under the direction of Morrison has developed a new technique for the measurement of the diffusion coefficient. They have applied this technique to the measure-

* This work was partially supported by the Office of Naval Research.

† Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

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¹ For a review of this work see A. B. Lidiard, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, pp. 246-349.

² F. Kerkhoff, *Z. Physik* **130**, 449 (1951).

³ M. Chemla, *Compt. rend.* **234**, 2601 (1952), also *Ann. phys.* **1**, 959 (1956).

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