

Rate of Energy Loss to Polar Modes

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(Received 18 October 1965)

The rates at which an electron is scattered by, and exchanges energy with, polar optical modes are calculated for the case of weak interaction.

It is well known that for polar optical-mode scattering a relaxation time does not exist for electron energies of the order of the optical-phonon energy.¹ It does not appear to be known, however, that even in this case the collision rate and rate of energy loss of an electron to polar modes can be calculated accurately and simply. In the present note we calculate these rates for the case of weak interaction with the polar modes, as is found in the III-V compounds, for example.

Since the interaction is weak, the calculations may be done using time-dependent perturbation theory. We have then for the collision frequency $1/\tau$ of an electron having wave vector \mathbf{k} initially:

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} \sum_{\mathbf{q}} [|\mathbf{k}+\mathbf{q}, N_{\mathbf{q}}-1| H' | \mathbf{k}, N_{\mathbf{q}} |]^2 \times \delta(\mathcal{E}_{\mathbf{k}+\mathbf{q}, N_{\mathbf{q}}-1} - \mathcal{E}_{\mathbf{k}, N_{\mathbf{q}}}) + | \mathbf{k}-\mathbf{q}, N_{\mathbf{q}}+1 | H' | \mathbf{k}, N_{\mathbf{q}} |]^2 \times \delta(\mathcal{E}_{\mathbf{k}-\mathbf{q}, N_{\mathbf{q}}+1} - \mathcal{E}_{\mathbf{k}, N_{\mathbf{q}}}), \quad (1)$$

where \mathbf{q} is the phonon wave vector, $N_{\mathbf{q}}$ the steady-state number of phonons with wave vector \mathbf{q} , and $\mathcal{E}_{\mathbf{k}, N_{\mathbf{q}}}$ the energy of the system when the electron has wave vector \mathbf{k} and there are $N_{\mathbf{q}}$ phonons with wave vector \mathbf{q} . The first term of (1) represents the transition probability due to phonon absorption, the second due to emission. No limitation on transitions due to the Pauli principle has been included since we shall consider only non-degenerate materials. The square of the matrix element for carriers having wave functions of s symmetry, as in the conduction band of GaAs, may be written²⁻⁴

$$| \langle \mathbf{k} \pm \mathbf{q} | H' | \mathbf{k} \rangle |^2 = (2\pi\hbar^2 e E_0 / V m q^2) \{ N_{\mathbf{q}} + \frac{1}{2} + \frac{1}{2} \delta N_{\mathbf{q}} \}, \quad (2)$$

where V is the volume of the crystal, m the effective mass, $\delta N_{\mathbf{q}} = +1$ for emission and -1 for absorption, and E_0 is an effective field given by

$$e E_0 = (m e^2 \hbar \omega_l / \hbar^2) (1/\kappa_{\infty} - 1/\kappa_0), \quad (3)$$

ω_l being the longitudinal optical frequency (we neglect dispersion) and κ_{∞} and κ_0 the dielectric constants for infinite and zero frequencies, respectively. For materials with high carrier concentrations (2) must be modified to take into account screening,⁵ but we shall not consider such high concentrations here.

¹ See, for example, D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London), **A219**, 53 (1953). Note, however, that a relaxation time does exist for $\mathcal{E} \gg \hbar \omega_l$.

² H. Frohlich, Proc. Roy. Soc. **A160**, 230 (1937); H. Frohlich, H. Pelzer, and S. Zienau, Phil. Mag. **41**, 221 (1950).

³ H. Callen, Phys. Rev. **76**, 1394 (1949).

⁴ H. Ehrenreich, J. Phys. Chem. Solids **2**, 131 (1957).

⁵ H. Ehrenreich, J. Phys. Chem. Solids **8**, 130 (1959).

It is convenient to transform the summation over \mathbf{q} to an integration over spherical coordinates q , θ , and φ with the \mathbf{k} direction taken as the z axis. For this purpose it is usually considered that the \mathbf{q} 's occupy a sphere in \mathbf{q} space with radius q_0 so chosen that the sphere contains the correct number of normal modes. It will be seen directly that the assumption made about the boundaries of the region occupied by the q 's is quite unimportant. Since the matrix element depends on the magnitude of \mathbf{q} only, integration over θ involves only the δ function. For the case of spherical constant-energy surfaces the integral over θ in the first term of (1) is, except for a constant factor,

$$I(\mathbf{k}+\mathbf{q}) = \int_{\theta=0}^{\pi} \delta\left(-kq \cos\theta + \frac{\hbar^2 q^2}{2m} - \hbar\omega_l\right) \sin\theta d\theta. \quad (4)$$

Applying the condition that the integral will vanish unless the region of integration includes the point at which the argument of the δ function vanishes, we find

$$I(\mathbf{k}+\mathbf{q}) = m/\hbar^2 k q \quad \text{for} \quad k[1 + \hbar\omega_l/\mathcal{E}]^{1/2} - 1 < q < k[1 + \hbar\omega_l/\mathcal{E}]^{1/2} + 1. \quad (5)$$

Outside the limits specified the integral vanishes. By a similar procedure we find for the corresponding integral over θ in the second term of (1):

$$I(\mathbf{k}-\mathbf{q}) = m/\hbar^2 k q \quad \text{for} \quad k[1 - (1 - \hbar\omega_l/\mathcal{E})^{1/2}] < q < k[1 + (1 - \hbar\omega_l/\mathcal{E})^{1/2}]. \quad (6)$$

An additional condition for this integral, which occurs in the emission term, to be nonvanishing is that \mathcal{E} must be greater than $\hbar\omega_l$. It is easily verified that the restrictions on q stipulated in (5) and (6) ensure conservation of energy in the transitions.

With (5) and (6) and the matrix element (2) the integrations over q and φ are elementary, and the result for τ is quickly found to be

$$\frac{1}{\tau} = \frac{2eE_0}{(2m\mathcal{E})^{1/2}} \left[N_{\mathbf{q}} \sinh^{-1}\left(\frac{\mathcal{E}}{\hbar\omega_l}\right)^{1/2} + (N_{\mathbf{q}}+1) \sinh^{-1}\left(\frac{\mathcal{E}-\hbar\omega_l}{\hbar\omega_l}\right)^{1/2} \right]. \quad (7)$$

The first term of (7) represents the rate at which electrons are scattered out of \mathbf{k} with absorption, the second the rate at which they are scattered out with emission. It is interesting to note that even where a relaxation time does exist, i.e., for $\mathcal{E} \gg \hbar\omega_l$, the τ of (7) differs from that time in the form of the dependence on energy.

The rate of change of carrier energy due to polar

optical scattering is simply $\hbar\omega_l$ times the difference between the probability per unit time for absorption and that for emission. To obtain this difference we need only change the plus sign in the angular bracket of (7) to a minus. The resulting rate of change of carrier energy is

$$\frac{d\mathcal{E}}{dt} = \frac{2eE_0\hbar\omega_l}{(2m\mathcal{E})^{1/2}} \left[N_a \sinh^{-1} \left(\frac{\mathcal{E}}{\hbar\omega_l} \right)^{1/2} - (N_a + 1) \sinh^{-1} \left(\frac{\mathcal{E} - \hbar\omega_l}{\hbar\omega_l} \right)^{1/2} \right]. \quad (8)$$

For $\mathcal{E} \gg \hbar\omega_l$ the rate of energy loss, according to (8), is given actually by the spontaneous emission since absorption and stimulated emission essentially cancel in this limit. Because the dependence of the angular bracket on energy is essentially logarithmic for $\mathcal{E} \gg \hbar\omega_l$ it is seen that the rate of energy loss decreases approximately as $\mathcal{E}^{-1/2}$ in the limit of large \mathcal{E} . This is also true of the collision frequency. Since the rate of energy input from the field is, roughly, inversely proportional to the collision frequency, it is clear that the combination of these two changes could result in an instability if only this scattering mechanism were operative. Of course, the appearance of breakdown in ionic crystals (to which this calculation is not applicable since perturbation theory is not valid there) has been connected with just this mechanism. In the III-V compounds it seems clear, if only on the evidence that breakdown does not occur,

that other mechanisms take over when the polar optical scattering gets less effective.

To obtain from (8) the average rate of energy loss of all the electrons in a given sample under a given set of external conditions, it is, of course, necessary to average over the correct electron distribution for the given conditions. What this distribution is depends on the size of the electric field, all of the scattering processes operative, the band structure, etc. The fact that a relaxation time does not exist for the polar optical scattering for $\mathcal{E} \sim \hbar\omega_l$ makes the determination of the distribution function quite difficult, of course. In the absence of knowledge about this function it has frequently been assumed that it is a Maxwell-Boltzmann distribution with temperature T_e greater than the lattice temperature T . When (8) is averaged over such a distribution the result is

$$\left\langle \frac{d\mathcal{E}}{dt} \right\rangle = - \left(\frac{2k_0\Theta_D}{\pi m} \right)^{1/2} \frac{eE_0}{e^{x_0} - 1} \frac{e^{x_0 - x_e} - 1}{x_e^{1/2} e^{x_e/2} K_0(x_e/2)}, \quad (9)$$

where Θ_D is the Debye temperature, x_0 and x_e represent $\hbar\omega_l/k_0T$ and $\hbar\omega_l/k_0T_e$, respectively, and K_0 is a Bessel function. This result was obtained earlier in somewhat less direct fashion by taking the average of \mathcal{E} times the collision operator for polar optical scattering over the Maxwell-Boltzmann distribution.⁶

⁶ B. V. Paranjape, Rep. Brit. Elec. Ind. Res. Ass. L/T 285, 1953 (unpublished). See also, R. Stratton, Proc. Roy. Soc. (London) A246, 406 (1958).

Theory of Diffusion in Ionic Crystals

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(Received 30 August 1965)

A theory of the Schottky defect is given, and an explicit formula is derived for the formation energy in terms of the elastic and dielectric constants. The Einstein model of an ionic solid is the basis for the theory, with ion correlations treated as a perturbation. Also, semiempirical equations are derived for the energy of motion of positive- and negative-ion vacancies, for both self-diffusion and monovalent-impurity diffusion. The theory is applied to several cases, and the agreement with experiment is excellent.

SINCE the pioneering work of Jost¹ a number of papers have appeared which are related to the problem of forming and moving Schottky defects in solids. The most noted of these efforts is that due to Mott and Littleton² which has served as a pattern for most of the other calculations.³⁻⁸

* Work supported in part by the Advanced Research Projects Agency.

¹ W. Jost, J. Chem. Phys. **1**, 466 (1933).

² N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

³ P. Brauer, Z. Naturforsch. **7a**, 372 (1952).

Before discussing the present calculation it is desirable to review earlier theoretical work on the subject. The Jost theory has never been very useful because no

⁴ F. G. Fumi and M. P. Tosi, Discussions Faraday Soc. **23**, 92 (1957).

⁵ R. Guccione, M. P. Tosi, and M. Asdente, J. Phys. Chem. Solids **10**, 162 (1958).

⁶ T. Kurosawa, J. Phys. Soc. Japan **13**, 153 (1958).

⁷ G. Arai and J. G. Mullen, Bull. Am. Phys. Soc. **9**, 657 (1964); M. P. Tosi, M. Doyama, and J. G. Mullen, *ibid.* **10**, 77 (1965).

⁸ For a review see A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.