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## The mean free path of electrons in polar crystals

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### 1. INTRODUCTION

Polar crystals of stoichiometric composition at low temperatures are insulators of electricity. If, however, electrons are raised into the normally empty conduction band of energy levels, either through the absorption of light or the thermal energy of surrounding atoms, the crystal can conduct. The purpose of this note is to calculate the mean free path of such electrons, and hence their mobility (velocity of drift in unit field). The results obtained will be compared with experimental material obtained from semi-conductors and from substances which show photoconductivity.

In both classes of substance, it is a fairly safe assumption that the electrons in the conduction band have a Maxwell distribution of energies;\*

\* Cf. for photoconductors, Mott (1939).

thus at room temperatures they have kinetic energies of the order 0.04 eV, in marked contrast to the conduction electrons in metals, which have energies of the order of 5 eV. In metals the mean free path,  $l$ , is of the order 100–1000 Å at room temperature. Fröhlich (1937) has given a theoretical formula for the mean free path in polar crystals of “stray” electrons having energies of several electron volts, and finds it to be of the same order of magnitude as for metals. As, however, the energy decreases, the mean free path,  $l$ , decreases, and according to Fröhlich’s formula, reaches for energies of the order  $k\Theta_D$  ( $\Theta_D \sim 300^\circ \text{K}$ ) values comparable with the lattice constant. For such energies the approximation used in deriving the formula breaks down.

For electrons in thermal equilibrium at temperatures below  $\Theta$ , however,  $l$  increases again, and for these energies the approximation used should again be valid. It is with these low energies that we deal in this paper. We do not know of any method of obtaining the mean free path at room temperature, except by a rough extrapolation of these formulae.

## 2. THE LATTICE VIBRATIONS

According to Fröhlich, the mean free path depends on longitudinal polarization waves in the crystal. For slow electrons it will depend on longitudinal waves of long wave-length. It does not seem to have been pointed out in the literature that the characteristic frequency for longitudinal waves of long wave-length is higher than that of transverse waves (the characteristic vibrations which are excited optically).\* The proof is as follows:

Let  $\nu_t, \nu_l$  be the characteristic frequencies of transverse and longitudinal waves, of wave length  $\lambda$  long compared with the interatomic distance but small compared with the dimensions of the crystal.† In a transverse wave the polarization is of the form, with  $k = 1/\lambda$ ,

$$P_y = \text{const.} \sin 2\pi(kx - \nu_t t).$$

Hence  $\text{div } P$  vanishes. Since there are no free charges in the crystal,  $\text{div } D = 0$ , and hence  $\text{div } E$  vanishes also. In a free vibration of the crystal we shall also

\* [Note added in proof. Professor Born has kindly informed us of unpublished calculations by Dr Kellermann, which confirm our result exactly. Also we overlooked a paper by Lyddane & Herzfeld (*Phys. Rev.* 54, 846, 1938) who obtain similar but not exactly equivalent results.]

† If this condition is not fulfilled, the distinction between transverse and longitudinal waves is lost.

have  $E = 0$  in the crystal; an electric field only exists in the crystal when an electromagnetic wave coming from outside is passing through it.

For longitudinal waves, the polarization is of the form

$$P_x = \text{const.} \sin 2\pi(kx - \nu_l t)$$

and  $\text{div } P \neq 0$ . Since as before  $\text{div } D$  vanishes, it follows that

$$\text{div } E = -4\pi \text{div } P.$$

As regards the periodic part of  $E$ , we have therefore

$$E = -4\pi P. \quad (1)$$

Suppose now that a positive and negative ion are displaced respectively by distances  $u^+$ ,  $u^-$ , and that

$$u = u^+ + u^-,$$

so that the polarization is given by

$$P = eu/\Omega,$$

where  $\Omega$  is the volume of the unit cell. Then the restoring force on either ion in a transverse wave is, if  $M = M_1 M_2 / (M_1 + M_2)$  is the reduced mass of the ions,

$$-4\pi^2 M \nu_l^2 u,$$

but in a longitudinal wave it is

$$-4\pi^2 M \nu_l^2 u + Ee, \quad (2)$$

which may be written  $-(4\pi^2 M \nu_l^2 + 4\pi e^2 / \Omega) u$ .

Since this is equal to  $-4\pi^2 M \nu_l^2 u$ , we have

$$\nu_l^2 = \nu_l^2 + \frac{e^2}{\pi M \Omega}. \quad (3)$$

For crystals of sodium chloride type  $\Omega = 2a^3$ , where  $a$  is the interionic distance.

It is worth noting that  $\nu_l$  is also the frequency of vibrations of particles having dimensions small compared with the wave length, since in this case there will necessarily be a field within the particle given by (1). It would be of interest to investigate the scattering of infra-red rays by small particles of a polar salt dispersed in a non-polar medium (e.g. a fine grain emulsion of AgBr). If the dimensions of the particles were small, but the distances apart large, both compared with  $\lambda$ , the scattering should show a maximum at a frequency  $\nu_l$  quite different from the normal characteristic frequency of the

material, as determined from the absorption coefficient of thin films, as, for instance, in Barnes' experiments (1932), or from the frequency of the residual rays.

Equation (3) may be expressed in a different form. Born (cf. Born and Göppert-Mayer 1933) has given a formula connecting the characteristic frequency  $\nu_t$  of the transverse vibrations with the dielectric constant. The formula is

$$\epsilon - \epsilon_0 = \frac{e^2}{2\pi a^3 M \nu_t^2}, \tag{4}$$

where  $\epsilon$  is the dielectric constant for static fields, and  $\epsilon_0$  the contribution to the dielectric constant for the polarizability of the ions, so that  $\sqrt{\epsilon_0}$  is the refractive index in the near infra-red. From (3) and (4) we have

$$\nu_t^2 = (\epsilon - \epsilon_0 + 1) \nu_l^2. \tag{5}$$

For alkali halides the factor  $\epsilon - \epsilon_0 + 1$  is of the order 3.

Both formulae (3) and (4) are derived subject to the assumption that the force on an ion due to an electric field  $E$  is  $Ee$ , and not  $\left(E + \frac{4\pi}{3}P\right)e$ . This assumption appears to give results in agreement with experiment for alkali halides (cf. Mott and Littleton 1938).

It should also be noted that eqn. (5) is only correct for *long* longitudinal waves ( $\lambda \gg a$ ). The force  $eE$  in eqn. (2) acting on an ion has only in this case, i.e. if  $E$  is nearly constant within a unit cell, a unique value. It is possible to show that for short longitudinal waves  $\lambda \sim a$  the term corresponding to  $eE$  becomes very small so that their frequency is approximately  $\nu_t$  as for transverse waves.

### 3. CALCULATION OF THE MEAN FREE PATH

A calculation of the mean free path  $l$  or the time of relaxation  $\tau = l/v$  ( $v$  = velocity of the electron) has been carried out previously for electrons with an energy  $W$  of several electron-volts (Fröhlich 1937). For very slow thermal electrons, the calculation follows similar lines. Certain modifications have, however, to be made, since  $W \sim h\nu$ .

$\tau$  is defined in the following way:

$$\frac{1}{\tau} = - \sum_w \left(\frac{\Delta k}{k}\right)_x \phi_w,$$

where  $\phi_w$  is the probability per unit time that an electron makes a collision with a lattice wave of wave number  $w$ , and  $\Delta k$  is the average change of the

$x$ -component of the wave number  $k_x$  of the electron on each collision.  $\Delta k_x$  is, according to the conservation of momentum, equal to the  $x$ -component of  $w$ . We have to average over all directions of  $w$ , and obtain (cf. Fröhlich 1936, § 13, eqn. (38), since  $\hbar cw = \hbar v$ )

$$-\left(\frac{\Delta k}{k}\right)_x = -\frac{w^2}{2k^2} + \frac{m\hbar v}{\hbar^2 k^2} = \frac{w^2 - k_v^2}{2k^2}, \quad (6)$$

where

$$\hbar^2 k_v^2 / 2m = \hbar v. \quad (7)$$

In the former calculation, it was possible to neglect the term containing  $k_v^2$ . Furthermore, it was assumed that the frequency  $\nu$  of the polarization waves was equal to  $\nu_l$ . This was correct since the fast electrons are scattered mainly by short longitudinal waves, which have, as we mentioned above, a frequency of the order  $\nu_l$ . In our present case, however, the electrons are scattered mainly by long longitudinal waves, for it follows immediately from the energy and momentum laws that polarization waves can only contribute to the scattering if their wave number lies within the limits  $w_1, w_2$ , where

$$w_1, w_2 = \mp k + \sqrt{(k^2 + k_v^2)}. \quad (8)$$

$k$  is the wave number of the electronic wave of an electron with energy  $W$ , so that

$$W = \hbar^2 k^2 / 2m.$$

Now in the case  $W \sim \hbar v$  both  $w_1$  and  $w_2$  are approximately equal to  $k_v$ . Since  $\nu$  is an infra-red frequency,  $k_v \ll 1/a$ , i.e.  $2\pi/w_1$  and  $2\pi/w_2$  are long wavelengths. We have, therefore, to use now  $\nu_l$  as the frequency  $\nu$ .

Furthermore, if we assume that  $W < \hbar v_l$ , the electron can no longer give up energy  $\hbar v$  to the lattice vibrations, but only absorb it. The dependence of  $\tau$  on temperature is in consequence given by

$$\tau = \tau_0 (e^{\hbar v / kT} - 1) \quad (9)$$

instead of by eqn. (15) of Fröhlich (1937). For  $\tau_0$ , the previous calculation yielded (Fröhlich 1937), eqn. (16)

$$\frac{1}{\tau_0} = \frac{2^{\frac{1}{2}} \pi^2}{8 \sqrt{2} m^{\frac{1}{2}} M a^5 \nu E^{\frac{1}{2}}} = \frac{e^4 \hbar}{4 M a^3 \hbar \nu v} \frac{w_0^2}{k^2} \quad W > \frac{\hbar^2 w_0^2}{8m},$$

where

$$w_0 = 2^{\frac{1}{2}} \pi / a.$$

This equation was obtained by an integration over  $w$ , namely

$$\int_0^{w_0} w dw = \frac{1}{2} w_0^2.$$

According to our remarks above (cf. eqns. (6) and (8)) this integral has now to be replaced by

$$\int_{w_1}^{w_2} \frac{w^2 - k_\nu^2}{w} dw = 2k(k^2 + k_\nu^2)^{\frac{1}{2}} - k_\nu^2 \log \frac{\sqrt{(k^2 + k_\nu^2)} + k}{\sqrt{(k^2 + k_\nu^2)} - k} \approx \frac{4}{3} k^3 / k_\nu, \quad (W < h\nu),$$

and  $\nu$  is now given by  $\nu_l$ .

Thus in our case, we have

$$\frac{1}{\tau_0} = \frac{2e^4 k}{3Ma^3 \hbar \nu_l k_\nu}.$$

If we make use of eqn. (4), we obtain

$$\tau_0 = \frac{3}{4\pi} \frac{\hbar \nu}{e^2 (\epsilon - \epsilon_0)} \frac{\nu_l k_\nu}{\nu_l^2 k},$$

or finally for the mean free path, using eqns. (9), (7) and (5),

$$l = \tau v = \frac{3(\epsilon - \epsilon_0 + 1) a_0}{\epsilon - \epsilon_0} \left( \frac{W}{\hbar \nu_l} \right)^{\frac{1}{2}} (e^{h\nu_l/kT} - 1), \quad W < h\nu_l, \quad (10)$$

where 
$$a_0 = \frac{\hbar^2}{me^2} \sim 0.54 \times 10^{-8} \text{ cm.}$$

is the Bohr radius.\*

If we are dealing with electrons having a Maxwell distribution, we have to average (10) over all energies; we obtain

$$\bar{l} = \frac{6a_0}{\sqrt{\pi}} \frac{\epsilon - \epsilon_0 + 1}{\epsilon - \epsilon_0} \left( \frac{T}{\Theta} \right)^{\frac{1}{2}} (e^{\Theta/T} - 1), \quad (11)$$

where (cf. eqn. (5))

$$k\Theta = h\nu_l = h\nu_l(\epsilon - \epsilon_0 + 1)^{\frac{1}{2}}. \quad (12)$$

The formula is valid only for  $T < \Theta$ .

For the mobility  $w$  we have

$$w = \frac{e}{m} \frac{\bar{l}}{\sqrt{(3kT/m)}} = 2 \sqrt{\left\{ \frac{3}{\pi m k \Theta} \right\}} e a_0 (e^{\Theta/T} - 1) \frac{\epsilon - \epsilon_0 + 1}{\epsilon - \epsilon_0}. \quad (13)$$

\* In deriving eqn. (10) we have not considered any possible effect of a screening of the electronic charge. It was shown in a paper by Fröhlich (1939) that the effect of such a screening would be small for fast electrons. For very slow electrons, with energies  $W < h\nu_l$ , too, it should be correct to calculate  $l$  as above, i.e. with a screening occurring only in the second order of approximation. This is due to the fact that for such slow electrons, the de Broglie wave-length  $2\pi/k \geq 2\pi/k_\nu$ , is of the same order of magnitude as the wave-lengths of the lattice waves with which the electron interacts (cf. eqn. (8)). A screening could, however, occur only at distances from the electron which are great compared with  $2\pi/k$ , i.e. at distances which contribute only little to the interaction with the lattice waves.

## 4. COMPARISON WITH EXPERIMENT

## 4.1. Photoconduction

When an alkali halide crystal coloured by stoichiometric excess of alkali metal (i.e. by  $F$ -centres) is illuminated with light of wave-length lying in the  $F$ -band, it shows photoconductivity. The currents observed are interpreted in the following way: the electrons released by the light drift in the direction of the field a certain distance, and are then trapped in some way. The nature of the trapping centres has been discussed by Pohl (1937), but need not concern us here.

Let  $w$  be the mobility of an electron, and  $E$  the applied field, so that  $wE$  is the velocity of drift. Let  $t$  be the time that an electron released by the light remains free, before it is trapped. Then each electron released by the light drifts a distance

$$L = wEt.$$

If each quantum absorbed has a chance  $\eta$  of releasing an electron, the displacement of charge observed per quantum absorbed is

$$e\eta L = e\eta wEt.$$

This quantity may be observed experimentally; some results of Pohl (1937) for NaCl are shown in fig. 1, in arbitrary units, plotted as a function of the temperature.

The sudden drop at low temperatures has been discussed by Mott (1938) and is certainly due to a drop in  $\eta$ ; at higher temperatures, above about  $-100^\circ\text{C}$ , it is safe to assume that  $\eta = 1$ .

The time which an electron spends in the free state should be independent of the velocity of the electrons if its de Broglie wave-length is large compared with linear dimensions of the trapping centre† (i.e. for thermal electrons), for  $t$  must be proportional to the time which an electron spends within the range of a trapping centre. This time should be, in our case, independent of the electronic velocity.

We thus find that in the region where  $\eta \sim 1$  the temperature dependence of the magnitude  $\eta L$ , which is observable experimentally, is determined by  $w$  alone, so that

$$\eta L = \text{const.} (e^{\theta/T} - 1).$$

\* This leads to a cross-section, inversely proportional to the velocity (cf. the analogous law for the capture of slow neutrons by atomic nuclei). The conclusion is independent of the mechanism of trapping, i.e. whether it is due to radiation loss or to loss of energy as heat motion, provided only that the perturbing term in the wave equation may be treated as small.

In fig. 1 we have plotted this function against the temperature, fitting the curve to the experimental one at  $-75^{\circ}\text{C}$ . We have used two values of  $\Theta$ . According to Born and Göppert-Mayer (1933) for  $\text{NaCl}$   $c/\nu_l = 61.1 \times 10^{-4}\text{ cm.}$ , giving  $\Theta_l = h\nu_l/k = 232^{\circ}$ . According to the same authors  $\epsilon - \epsilon_0 + 1 = 3.94$ , so that  $\Theta_l = 460^{\circ}$ . We get a better fit for  $\Theta = \Theta_l$ , giving some evidence for our conclusion reached in § 2, that  $\Theta_l$  is larger than  $\Theta$ .

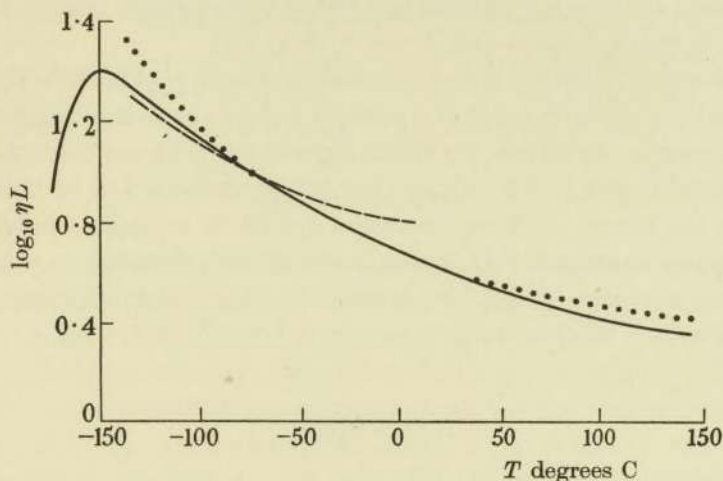


FIG. 1. Current per absorbed quantum in coloured rock salt. — observed (Pohl). ···· theoretical.  $\Theta = \Theta_l = 460^{\circ}$ . - - - theoretical.  $\Theta = \Theta_l = 232^{\circ}$ . The experimental and theoretical curves are fitted at  $-75^{\circ}\text{C}$ .

#### 4.2. Semi-conductors

Engelhard (1933) has measured the Hall constant  $R$  and specific conductivity  $\sigma$  of cuprous oxide. Since the conductivity is given by

$$\sigma = New$$

and  $R$  by

$$R = 3\pi c/8Ne,$$

where  $N$  is the number of electrons in the conduction band, we can deduce the mobility  $w$  from  $R$  and  $\sigma$

$$w = 8\sigma R/3\pi c.$$

Engelhard then deduces the mean free path  $l$  from the equations  $w = el/mv$ ,  $\frac{1}{2}mv^2 = \frac{3}{2}kT$ . He finds that  $l$  drops from a value  $25 \times 10^{-7}\text{ cm.}$  at  $80^{\circ}\text{K}$  to a roughly constant value of  $6 \times 10^{-7}\text{ cm.}$  at  $200^{\circ}\text{K}$  and higher temperatures.

Unfortunately we have no direct measurements of  $\Theta$ . A value of  $\Theta$  equal to  $280^{\circ}$  gives roughly the right temperature dependence of  $l$ , but gives absolute values about eight times too small.



However, in this connexion it should be noticed that in  $\text{Cu}_2\text{O}$  the electrons are carried by positive holes in a full band. The widths of the bands for oxides have been shown from the X-ray emission bands obtained by Skinner to be about 12 eV. There is some evidence (cf. Mott 1939) that in cuprous oxide the energy interval separating the full band from the first empty band is rather narrow (2 eV). If this is the case we expect the "effective mass" of a positive hole in a state near the top of the  $d$  band to be rather small, smaller than that of a free electron (cf. Mott and Jones 1936, p. 84).

The theoretical formula for  $w$  contains  $m$  to the power  $m^{-\frac{1}{2}}$ . Thus if we assume that the effective mass of a positive hole is about one-quarter of that of a free electron, we obtain results in agreement with experiment.

[*Note added in proof.* Dr Skinner has kindly informed us of preliminary results on the shape of X-ray emission bands in metallic oxides. These bands have a low intensity at the high energy end, showing an abnormally low density of states. Since the density of states is proportional of  $m^{\frac{1}{2}}$ , these results give additional evidence for a low effective mass.]

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