

Mobility of Electrons and Holes in the Polar Crystal, PbS

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From measurements of the Hall effect and resistivity on single crystals of PbS, the mobility of electrons and holes has been found over the temperature range 77–600°K. The crystals had donor or acceptor concentrations in the range 10^{16} – 10^{19} /cm³. These data are used to critically examine theoretical work on the mobility in polar crystals and to obtain estimates of the effective masses of electrons and holes. The perturbation theory of Fröhlich and Mott (F-M), and Howarth and Sondheimer (H-S) for the scattering of electrons by the polar (optical) modes of the lattice vibration is first considered. The expansion parameter of the perturbation theory is evaluated as 0.28 (m_e^*/m_e)^{1/2} from published data on PbS; m_e is the free and m_e^* is the effective electron mass. The polaron theory of Low and Pines, which has been developed to replace the perturbation theory when the expansion parameter approaches or exceeds unity, is then discussed. m_e^*/m_e is the only unknown parameter in the two theories. The mobility data is first compared with the F-M, H-S theory from which $m_e^*/m_e=0.33$, $m_h^*/m_e=0.36$. These effective masses, when substituted in the Hall equation, provide for reasonable agreement with the Hall data. However, at high and low temperatures, dis-

crepancy exists between the theoretical and experimental mobility curves. Comparison of the mobility data with the polaron theory shows that the polaron theory is nearly identical with the F-M, H-S theory at low temperatures. The polaron theory has not been completed for the high temperature region.

Since the data does not indicate the presence of impurity scattering, an analysis is made combining polar (F-M, H-S theory) and acoustical scattering, which yields $m_e^*/m_e=0.22$ and $m_h^*/m_e=0.10$. These effective masses give theoretical Hall curves in reasonably good agreement with the data. While the theoretical and experimental mobility curves now agree at low and intermediate temperatures, discrepancy still exists at high temperatures. Possible reasons for the discrepancy are discussed. It is concluded that the most likely source of error lies in perturbation theory expressions for the scattering cross sections for electron energies greater than that corresponding to the frequency of the polar vibration. Comparison of the high-temperature data with the polaron theory awaits further development of the theory and should provide a sensitive test of the general polaron theory, as well as being of interest in the theory of mobility in polar crystals.

I. INTRODUCTION

MEASUREMENTS of the mobility of electrons and holes in crystals provide a means of studying basic scattering mechanisms in solids. When the mobility dependence is the same in crystals with different concentrations of donor and acceptor centers, the scattering can be attributed primarily to an interaction between electrons and lattice. Mobility studies then provide a basic method for investigating this fundamental aspect of solids.

Considerable study has been made of the mobility in nonpolar crystals such as germanium and silicon, and generally good agreement exists between theory and experiment. The classical polar crystals, the alkali halides, have low-electron conductivity with the result that mobility measurements¹ and their interpretation are complicated by ionic conductivity, polarization effects, and noise. Because of these difficulties, the simple dc Hall effect-resistivity method of measuring mobility has not been used.

Lead sulfide is a semiconducting polar crystal with high-electron conductivity at room temperature. Conventional Hall-resistivity methods for measuring mobility can be used with accuracy similar to that obtained on germanium. PbS therefore provides a useful material on which to study mobility in polar crystals.

Previous experiments² on PbS and other lead compounds indicate that the mobility can be represented

by an equation of the form $\mu=\mu_0T^{-5/2}$, over the temperature range 100°K–700°K. No theoretical basis for such a variation has been given.

A recent advance³ in the method of preparation of crystals of PbS has provided homogeneous single crystals of *n* and *p* types over a wide range of impurity concentrations, including high purity material. In this paper, we use the Hall-resistivity data³ obtained on these crystals to calculate mobility curves. This mobility data, in addition to providing basic experimental information concerning the motion of electrons and holes in PbS, is used as a basis for discussing, and in a sense evaluating, theoretical work on mobility in polar crystals.

Mobility studies have further interest as a method of measuring the effective mass of electrons and holes since the effective mass is the only unknown parameter in the polar mobility equation. In contrast, the acoustical scattering theory has the wave function and the effective mass in the mobility equation.

II. DISCUSSION OF THEORETICAL STUDIES OF THE MOBILITY IN POLAR CRYSTALS

In a crystal, conduction electrons are scattered at low temperatures by lattice defects and impurity atoms. At higher temperatures scattering due to thermal vibrations of the ions becomes significant. In ionic crystals these vibrations may be resolved into two general types. In one, called the acoustical mode, the positive and negative ions move in the same direction so that there is very little polarization effect. In the other, called the polar or optical mode, positive and

¹ A. J. Redfield, Phys. Rev. 94, 537 (1954); F. C. Brown, Phys. Rev. 92, 502 (1953); J. R. Haynes and W. Shockley, Phys. Rev. 82, 935 (1951).

² An excellent review of the work on PbS and other lead compounds up to 1953 is given by R. A. Smith, *Advances in Physics* 2, 321 (1953).

³ R. F. Brebrick and W. W. Scanlon, Phys. Rev. 96, 598 (1954).

negative ions move in opposite directions and create polarization fields. When the polar modes are excited, they are expected to be more effective in scattering electrons than the acoustical or impurity mechanisms.

The first studies of the scattering of electrons by the polar modes were made by Fröhlich and Mott⁴ and by Davydov and Shmushkevitch⁵ from a quantum mechanical point of view, and by Seeger and Teller⁶ by a classical method. The results at absolute zero were essentially the same; Seeger and Teller did not discuss the temperature dependence. Fröhlich and Mott used the perturbation method for treating the scattering of electrons by polar modes.

The perturbation theory is based on a power series expansion in terms of the parameter, α , which is defined in Eq. (1) below. α is a measure of the strength of the interaction of the electrons with the polar modes^{7,8} and should be less than unity for the perturbation theory to be applicable. It should be much less than unity for rapid convergence of the theory.

The polaron theory of mobility has recently been developed⁸ to replace the perturbation theory when α approaches or exceeds unity.

To see if the perturbation theory is applicable in PbS we calculate α :

$$\alpha = \frac{e^2}{\hbar} \left(\frac{m_e}{2\hbar\omega_l} \right)^{\frac{1}{2}} \left(\frac{\epsilon - \epsilon_0}{\epsilon_0\epsilon} \right) \left(\frac{m_e^*}{m_e} \right)^{\frac{1}{2}} \quad (1)$$

ϵ is the static dielectric constant, ϵ_0 is the high-frequency or electronic-dielectric constant, ω_l is the angular frequency of the longitudinal polar modes, e is the electronic charge, m_e is the free electron mass, m_e^* is the effective electron mass, $\hbar = h/2\pi$, and h is Planck's constant. For PbS we have:

$$\begin{aligned} \epsilon &= 17.9, & \epsilon_0 &= 15.3,^9 \\ \omega_l &= (\epsilon/\epsilon_0)^{\frac{1}{2}}\omega_l,^{10} \\ \omega_l &= \text{infrared reststrahlung angular} \\ & \text{frequency} = 2\pi c/\lambda_l \\ \lambda_l &= 80 \text{ microns.}^{11} \end{aligned} \quad (2)$$

Substituting these into Eq. (1) we find $\alpha = 0.28 (m_e^*/m_e)^{\frac{1}{2}}$. For nominal values of (m_e^*/m_e) , α is only slightly less than unity. Thus we will compare the data with both the perturbation and the polaron theory, the former at present being further developed than the latter.

⁴ H. Fröhlich, Proc. Roy. Soc. (London) **A160**, 280 (1937); H. Fröhlich and N. F. Mott, Proc. Roy. Soc. (London) **A171**, 496 (1939).

⁵ B. Davydov and I. Shmushkevitch, J. Phys. U.S.S.R. **3**, 359 (1940).

⁶ R. J. Seeger and E. Teller, Phys. Rev. **54**, 515 (1938); **56**, 352 (1939).

⁷ H. Fröhlich, Pelzer, and Zienau, Phil. Mag. **41**, 221 (1950).

⁸ F. Low and D. Pines, Phys. Rev. **91**, 193 (1953).

⁹ International Critical Tables.

¹⁰ Lyddane, Sachs, and Teller, Phys. Rev. **59**, 673 (1941).

¹¹ J. Strong, Phys. Rev. **38**, 1818 (1931).

It is of interest to note that in PbS α is considerably less than in the alkali halides, where α is of the order 3-6. The main reason for this is that the high electronic dielectric constant in PbS weakens the electron-lattice interaction and reduces α . This is better shown by combining Eq. (1) with $\epsilon \cong \epsilon_0 + \epsilon_i$, where ϵ_i is the contribution to the dielectric constant from the ion motion:

$$\alpha \propto \epsilon_i / [\epsilon_0(\epsilon_0 + \epsilon_i)] \cong \epsilon_i / \epsilon_0^2. \quad (3)$$

Equation (3) shows that ϵ_0 reduces the electron-lattice interaction essentially as $1/\epsilon_0^2$, which agrees with the notion that the electronic polarization is rapid enough to follow the motion of conduction electrons. By a similar argument we show below that the mobility is proportional to ϵ_0^2 . Thus it is to be expected that in polar crystals of different values of ϵ_0 , the mobility will be roughly proportional to ϵ_0^2 . Thus high electronic dielectric constants characterize crystals with low intrinsic energy gaps¹² and high mobilities.

A. Perturbation Theory of Fröhlich-Mott, Howarth-Sondheimer

The solution for the mobility as a function of temperature is normally made in two steps. The first is to find an expression for the scattering cross section for an electron of a fixed energy. The second is to make a statistical average over the thermal distribution of electron energies. The solution of the Boltzmann transport equation provides the most accurate method of performing the statistical average.

An approximate solution for the statistical part of the problem was obtained by Fröhlich and Mott⁴ by the use of a special definition of the relaxation time, without an attempt to solve the Boltzmann equation. Recently Howarth and Sondheimer¹³ have solved the Boltzmann equation and have obtained an expression for the mobility as a function of temperature. They used the scattering cross sections of Fröhlich-Mott in the Boltzmann equation. We therefore will call this the F-M, H-S theory.

The original Fröhlich-Mott result contained an error in the way the polarizability of the ions appears in the mobility equation. This has since been corrected^{7,10,14} but Howarth and Sondheimer's result does not include the correction. After briefly outlining their solution we will make this correction.

The solution of the Boltzmann equation for non-degenerate polar semiconductors is complicated because the energy exchanged in a collision is large relative to the electron energy. Thus, one cannot use the approximation of neglecting the energy exchanged in a collision to solve the Boltzmann equation. However, since the optical modes can, in good approximation, be con-

¹² T. S. Moss, *Photoconductivity in the Elements* (Academic Press, New York, 1952), p. 61.

¹³ D. Howarth and E. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).

¹⁴ H. Callen, Phys. Rev. **76**, 1394 (1949).

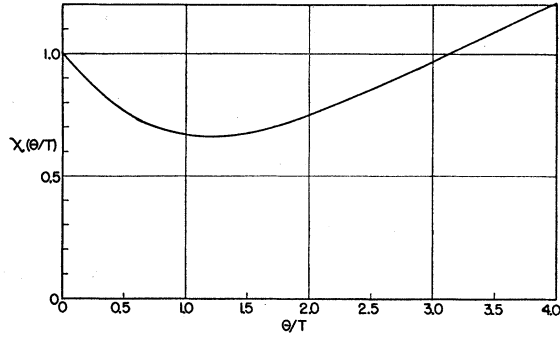


FIG. 1. Theoretical curve as given in reference 13, Curve 2 of Fig. 1.

sidered to be of a single frequency no integration over lattice frequencies is required. A finite difference equation results in place of the integral equation for metals.

H-S employ the variational method introduced by Kohler¹⁵ to obtain a solution for the whole range of temperature. The formula is expressed as ratios of infinite determinants and may be evaluated to any degree of accuracy by breaking off the determinants at a finite number of rows and columns. Closed form expressions are given for the limits, $T \rightarrow 0$ and $T \rightarrow \infty$.

The F-M, H-S expression¹³ for the conductivity σ is:

$$\sigma = \frac{16a^3 M \omega_i k^2 T^2 (e^z - 1) \chi(z) e^{E_f/kT}}{2\pi Q^2 3h^2}, \quad (4)$$

where $\chi(z)$ is shown in Fig. 1, which is Curve 2 of Fig. 1, reference 13; $z = \theta/T$, $\theta = \hbar\omega_i/k = 194^\circ\text{K}$, k is Boltzmann's constant, a is the lattice spacing between ions, M is the reduced mass of the ions, and E_f is the Fermi energy. Q is the ionic charge and is approximately $2e$, but is not known exactly without a knowledge of the amount of homopolar binding in the crystal.

Equation (4) is correct when the ions are not polarizable. When $\epsilon_0 > 1$ the necessary modification is to replace Q by Q/ϵ_0 . The physical basis of this is that the electronic polarization of the ions is rapid enough to follow the motion of the conduction electrons. Therefore the energy of interaction of an electron at a distance r from an ion is $eQ/\epsilon_0 r$ instead of eQ/r . Thus Q should be replaced by Q/ϵ_0 in Eq. (4). We have then:

$$\sigma = [(a^3 M \omega_i \epsilon_0^2 / (2\pi Q^2))] f(z), \quad (5)$$

where we have let $(16k^2 T^2 / 3h^2) (e^z - 1) \chi(z) e^{E_f/kT} = f(z)$. Equation (5) can be used in this form, but it is useful to eliminate Q since it is not precisely known. This can be done with the Born¹⁶ relation:

$$Q^2 = (\epsilon - \epsilon_0) a^3 M \omega_i^2 / 2\pi, \quad (6)$$

¹⁵ M. Kohler, *Z. Physik* **124**, 772 (1948); A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), second edition, Chap. 10.

¹⁶ M. Born and M. Göppert-Mayer, *Handbuch der Physik* **24**, 2, 646 (1933).

yielding

$$\sigma = \frac{\epsilon_0^2}{\omega_i (\epsilon - \epsilon_0)} \left(\frac{\omega_i}{\omega_i} \right) f(z). \quad (7)$$

Finally, it is convenient to substitute the Lyddane-Sachs-Teller relation,¹⁰ $(\omega_l/\omega_i)^2 = \epsilon/\epsilon_0$ [Eq. (2)] into Eq. (7):

$$\sigma = \left[\frac{\epsilon \epsilon_0}{\omega_l (\epsilon - \epsilon_0)} \right] f(z). \quad (8)$$

From Eq. (8) and $\epsilon \cong \epsilon_0 + \epsilon_i$, we conclude that

$$\sigma \propto \epsilon_0 (\epsilon_0 + \epsilon_i) / \epsilon_i \cong \epsilon_0^2 / \epsilon_i, \quad (9)$$

in agreement with our discussion above.

For comparison with experimental data it will be convenient to express Eq. (8) in terms of the mobility, μ . To do this it is first necessary to determine whether Fermi-Dirac or Boltzmann statistics are applicable. The degeneracy temperature is given by

$$\theta_D = (\hbar^2 / 2km_e) (3\pi^2 N_D)^{2/3} (m_e / m_e^*), \quad (10)$$

where N_D = density of donor atoms.

N_D is calculated from the Hall data in the exhaustion region and is listed in Fig. 2 for the samples studied. Unless m_e/m_e^* is abnormally large, these calculations show that θ_D is low enough that Boltzmann statistics can be employed for all but possibly one of the samples studied. Further comments on this will be made after evaluating m_e/m_e^* from the mobility data.

Assuming Boltzmann statistics, we have for the density of electrons in the conduction band:

$$n = 2(2\pi m_e kT / \hbar^2)^{3/2} e^{E_f/kT} (m_e^* / m_e)^{3/2}. \quad (11)$$

The zero of energy is at the bottom of the conduction band. Substituting Eq. (11) into Eq. (8) and using $\sigma = e\mu en$ we find:

$$\mu_e(\text{F-M, H-S}) = \frac{8a_0 e}{3} \frac{1}{(2\pi m_e k\theta)^{3/2}} \times \left(\frac{\epsilon \epsilon_0}{\epsilon - \epsilon_0} \right) \left(\frac{m_e}{m_e^*} \right)^{3/2} \frac{\chi(z) (e^z - 1)}{z^{3/2}}, \quad (12)$$

where $a_0 = \hbar^2 / m_e e^2$. Substituting the published data for PbS and converting to practical units, we have

$$\mu_e = 192 (m_e / m_e^*)^{3/2} \chi(z) (e^z - 1) / z^{3/2} \text{ cm}^2/\text{volt-sec.} \quad (13)$$

Closed-form expressions¹³ for $\chi(z)$ at low and high temperatures are

$$\begin{aligned} \chi(z) &= 1, & z \ll 1; \\ \chi(z) &= \frac{3}{8} (\pi z)^{1/2}, & z \gg 1. \end{aligned} \quad (14)$$

B. The Polaron Theory of Mobility

Whereas the perturbation theory of mobility uses the electron as the basic unit in a scattering process, the polaron theory uses the polaron as the basic unit.

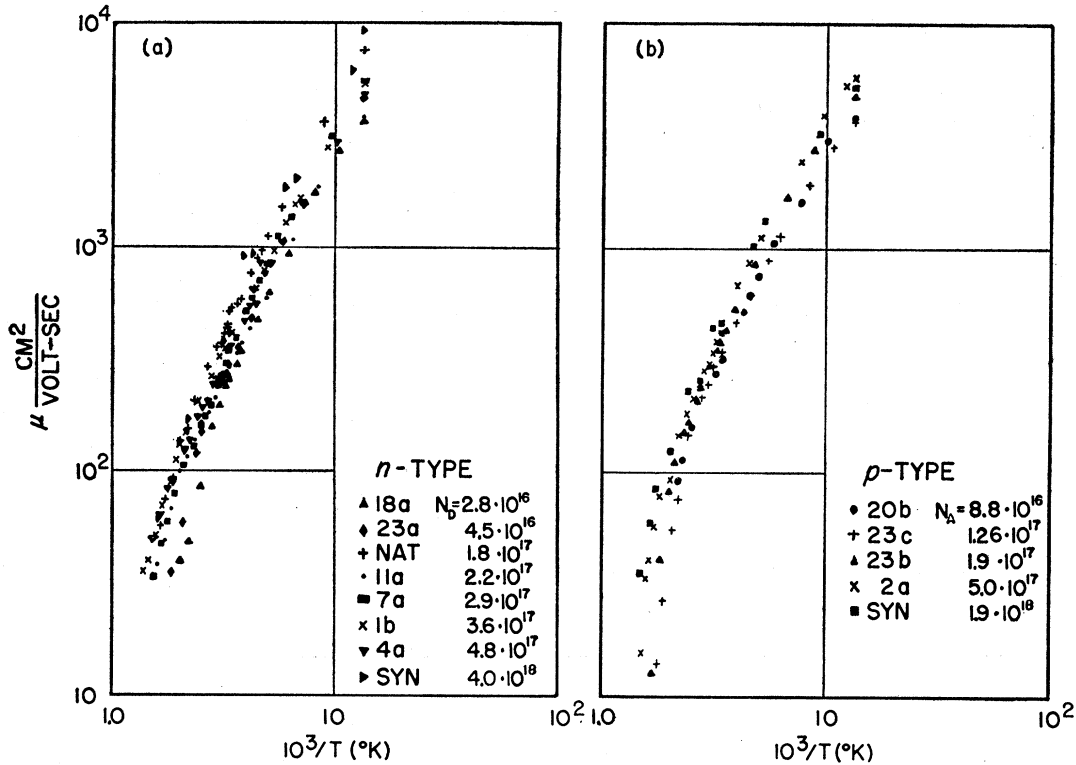


FIG. 2. Experimental data for mobility as calculated from Eq. (18).

A polaron^{7,8,17,18} is defined as an electron plus the polarization it induces in the lattice. A good approximation for the effective mass of the polaron, m_p , is¹⁸

$$m_p = m_e^* (1 + \alpha/6), \quad \text{when } \alpha < 6. \quad (15)$$

Low and Pines⁸ have used polaron wave functions in place of electron wave functions to calculate the mobility at low temperatures. Their result for $T < \theta$, with the 2π correction noted by Redfield¹ included, is

$$\mu_e(\text{L-P}) = \left(\frac{m_e^*}{m_p} \right)^2 f(\alpha) \frac{ea_0}{(2\hbar\omega_1 m_e)^{3/2}} \times \left(\frac{m_e}{m_e^*} \right)^{3/2} \left[\frac{\epsilon\epsilon_0}{\epsilon - \epsilon_0} \right] e^z, \quad (16)$$

where $f(\alpha)$ is a slowly varying function of α which may be taken to be $5/4$ for $3 < \alpha < 6$ and $f(\alpha) = 1$ in the limit $\alpha \rightarrow 0$.

For comparison with the F-M, H-S result at low temperatures we substitute Eq. (14) into Eq. (12) and compare with Eq. (16):

$$\mu_e(\text{L-P}) = (m_e^*/m_p)^2 f(\alpha) \mu_e(\text{F-M, H-S}), \quad T/\theta \ll 1. \quad (17)$$

¹⁷ S. Pekar, J. Phys. (U.S.S.R.) **10**, 341-347 (1946); J. Markham and F. Seitz, Phys. Rev. **74**, 1014 (1948); T. Landau and S. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) **18**, 419 (1948); S. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) **19**, 796 (1949).

¹⁸ Lee, Low, and Pines, Phys. Rev. **90**, 297 (1953).

If α is small there is little difference between these theories at low temperatures.

The high-temperature mobility formula for the polaron theory has not yet been worked out because of the complicated nature of the expressions⁸ for the scattering cross sections.

III. CALCULATION OF MOBILITY FROM THE HALL-RESISTIVITY DATA

We now describe the analysis of mobility data obtained on a group of p -type and n -type single crystals of PbS in which the impurity concentration covers the range from about $10^{16}/\text{cc}$ to $10^{19}/\text{cc}$.

From the analysis of a one-carrier semiconductor the mobility is given by the expression:

$$\mu = 8R/3\pi\rho \quad \text{cm}^2/\text{volt-sec}, \quad (18)$$

where R is the Hall coefficient and ρ is the resistivity. At low temperatures, where impurity conductivity predominates, this expression is satisfactory. Figure 2 shows the mobility as calculated from Eq. (18) with the Hall-resistivity data of reference 3. The mobility in the impurity range of conductivity is independent of the concentration of impurity centers and therefore appears to result from lattice scattering.

In the high-temperature range, electron and hole mobilities can be found from the data by use of the two

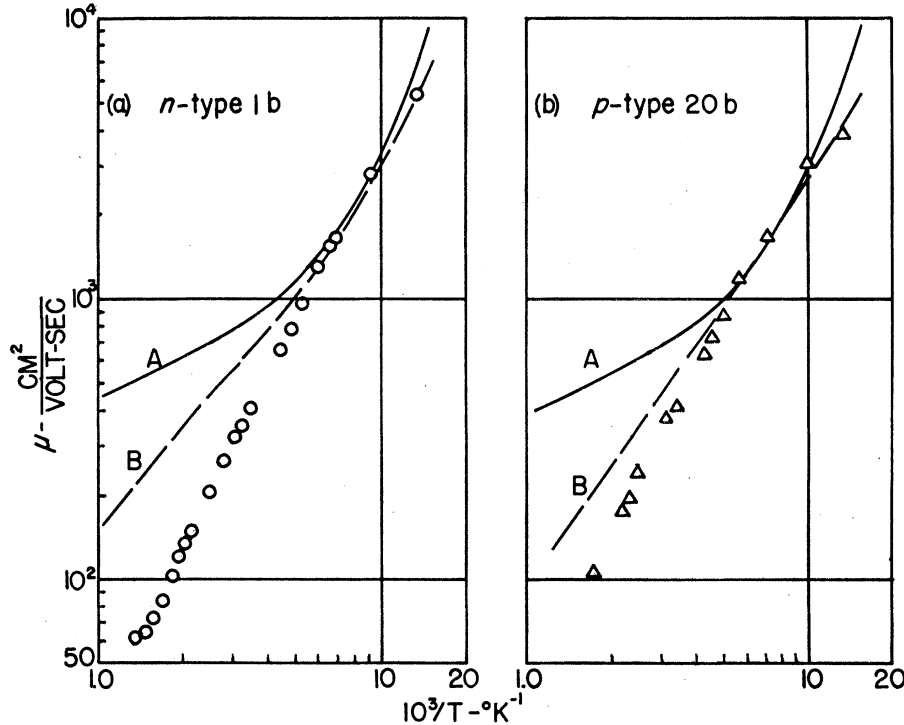


FIG. 3. Experimental data for single carrier mobilities as calculated from Eq. (20). Curve A is the theoretical polar mobility of F-M, H-S, Eq. (13). The polaron mobility, Eqs. (16) and (17), has the same shape as Curve A in the region $T < \theta$. No results have been published for the region $T \geq \theta$. Curve B is the combined theoretical polar (F-M, H-S theory) and acoustical mobility as given in Eq. (24).

carrier formulas for Hall and resistivity as follows:

$$R = -\frac{3\pi}{8e} \left[\frac{nc^2 - p}{(nc + p)^2} \right], \quad (19)$$

$$1/\rho = (e\mu_e/c)(nc + p),$$

$$n = p + N_D \text{ (n-type),}$$

where $c = \mu_e/\mu_h$, n = concentration of electrons, and p = concentration of holes. Solving for the electron mobility, one obtains

$$\mu_e = \frac{4R_I(c-1)}{3\pi\rho} \left[1 - \left(1 + \frac{4cR}{(c-1)^2 R_I} \right)^{\frac{1}{2}} \right], \quad (20)$$

where $R_I = -3\pi/8eN_D$ is the Hall coefficient in the exhaustion region.

The electron mobility data as calculated from Eq. (20) are shown in Fig. 3. The corresponding mean free path was calculated by using

$$l = (3\mu/4e)(2\pi mkT)^{\frac{1}{2}}, \quad (21)$$

and is shown in Fig. 4. Corresponding curves for holes are also shown in Figs. 3 and 4.

IV. COMPARISON OF THEORY AND EXPERIMENT

A. F-M, H-S Theory

Curve A on Fig. 3a is a plot of Eq. (13). Since θ is fixed the only unknown parameter of Eq. (13) is m_e^*/m_e^* .

By fitting the theoretical curve to the data for n -type material as shown in Fig. 3a we find $m_e^*/m_e = 0.33$. Similarly for holes the data is shown in Fig. 3b and we find $m_h^*/m_h = 0.36$. Substituting $m_e^*/m_e = 0.33$ into Eqs. (2) and (15) we find $\alpha = 0.16$ and $m_p/m_e^* = 1.03$. Substituting $m_e^*/m_e = 0.33$ into Eq. (10), we conclude that the use of Boltzmann statistics is permissible since $\theta_D = 62^\circ\text{K}$.

The poor agreement between theory and experiment (Fig. 3a) as a function of temperature raises the question as to the applicability of the perturbation theory to PbS and what significance should be placed on the values obtained for the effective masses. A check on this is provided by the high temperature Hall data. We have calculated Hall curves using Eqs. (11) and (19) and $c = 1.4$, (reference 3), $E_0 = 0.37$ eV, (reference 19), $m_e^*/m_e = 0.33$, and $m_h^*/m_e = 0.36$ and find that these curves fit the experimental Hall curves reasonably well. The spread in the mobility data over the samples studied is such that these values for effective masses have an accuracy not greater than ± 25 percent.

With $\alpha = 0.16$, the perturbation theory can be expected to have some validity in PbS. Improved agreement between theory and experiment may be expected by bringing into the analysis other scattering mechanisms. This is particularly the case at $T < \theta$ since the polar modes are being frozen out. We analyze this possibility in Sec. V.

¹⁹ W. W. Scanlon, Phys. Rev. 92, 1573 (1953).

B. Polaron Theory

Since the temperature dependence of the polaron theory for $T < \theta$ is the same as that of the perturbation theory [Eq. (17)], we can consider Curve A on Fig. 3a as representing the polaron theory for $T < \theta$. We obtain an equation for m_e^*/m_e directly from the polaron theory by combining Eqs. (1), (15), and (17) with Curve A of Fig. 3a:

$$\left(\frac{m_e^*}{m_e}\right)^{\frac{3}{2}} \frac{f(\alpha)}{[1 + (0.28/6)(m_e^*/m_e)^{\frac{3}{2}}]^2} = (0.33)^{\frac{3}{2}}. \quad (22)$$

Since α is a function of m_e^*/m_e , Eq. (22) can be solved for m_e^*/m_e . However, the functional form of $f(\alpha)$ has not been published so we consider its two extreme values. When $f(\alpha \rightarrow 0) = 1$ the solution of Eq. (22) is $m_e^*/m_e = 0.34$ and from Eq. (1) and (15) we find $\alpha = 0.16$ and $m_p/m_e^* = 1.03$.

Considering the other limit, $f(3 < \alpha < 6) = 5/4$, we find $m_e^*/m_e = 0.29$, $\alpha = 0.15$, and $m_p/m_e^* = 1.025$. From the close agreement of these two sets of results and those of the perturbation theory, we conclude that the perturbation and polaron theories are nearly identical in the low-temperature region.

V. ANALYSIS BASED ON POLAR AND ACOUSTICAL MODE SCATTERING

The mobility curves, Fig. 2, for the samples of PbS studied are very similar—there being no noticeable dependence on impurity concentration over the temperature range examined. We conclude that the mobility in the range of temperature is an intrinsic property of PbS. There are at least two intrinsic scattering mechanisms not yet considered in our analysis, acoustical vibrations of the lattice and those lattice defects inherent at thermal equilibrium. It is reasonable to expect that scattering in polar semiconductors, other than that arising from the polar vibrations of the lattice, will be similar to scattering in nonpolar semiconductors. Experiments on nonpolar semiconductors indicate that scattering by lattice defects is obscured at high temperatures by that from the acoustical modes. At low temperatures the density of intrinsic lattice defects in PbS can be expected to be small compared to the density of impurity atoms and/or defects arising from deviations from stoichiometry. Neither of these latter effects appear in our mobility data, Fig. 2. We therefore conclude that only the combined effects of polar and acoustical modes need be considered in the further analysis of the mobility data.

Since the perturbation and polaron theories are essentially the same at low temperatures in PbS, and since no results have been published for the polaron theory for $T \geq \theta$, we confine this analysis to combining the F-M, H-S polar theory with acoustical theory.

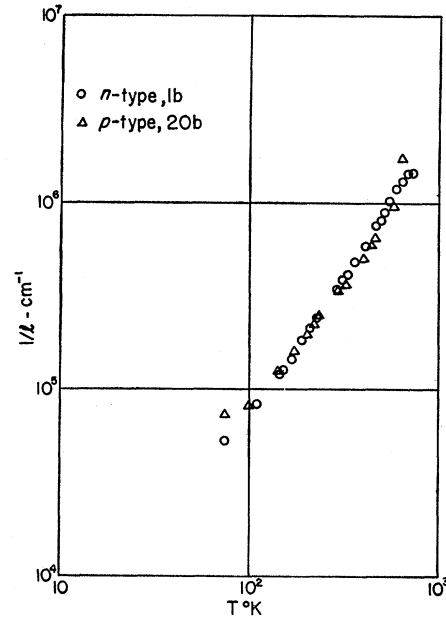


FIG. 4. Experimental reciprocal mean free path, Eq. (21).

The dependence of mobility on temperature for acoustical mode scattering²⁰ has been shown to be

$$\mu_A = BT^{-\frac{3}{2}} = Dz^{\frac{3}{2}}. \quad (23)$$

A rigorous method for combining the effect of two or more scattering mechanisms must recognize the velocity dependence of the mean free path of the electron for each scattering mechanism concerned. For the acoustical modes the mean free path is independent of velocity while for the optical modes it is proportional to the velocity. Because of this dependence on velocity it is not strictly correct to obtain a resultant mobility for the two scattering mechanisms by adding reciprocal mobilities. However, we will employ this approximation in our analysis for reasons of simplicity. This approximation has been used with good results in germanium to combine acoustical and impurity scattering. Combining reciprocal mobilities from Eqs. (13) and (23), we have

$$\frac{1}{\mu} = \frac{z^{\frac{3}{2}}}{192(m_e/m_e^*)^{\frac{3}{2}}(e^z - 1)\chi(z)} + \frac{1}{Dz^{\frac{3}{2}}}. \quad (24)$$

With θ fixed at 194°C the high-temperature region cannot be accurately fitted by this approximation. A reasonable fit at low and intermediate temperatures is shown by Curve B, Fig. 3a. From this we find $m_e^*/m_e = 0.22$ and $B = 5.7 \times 10^6$. A similar analysis for p-type material leads to $m_h^*/m_e = 0.1$ and $B = 3.1 \times 10^6$.

These values for m_e^*/m_e and m_h^*/m_e , when used in the calculation of the Hall curves, also provide reasonably good agreement with experiment. However, the

²⁰ C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), p. 277 for references to the original work.

additional parameter, B , is somewhat arbitrary because only a small part of the data extends into the $T^{-\frac{1}{2}}$ region. This reflects uncertainty in the value of m_e^*/m_e . Therefore, these values of effective masses are not significantly more accurate than those obtained in the polar mode analysis. Further data at temperatures below 77°K should improve the accuracy of these results.

As an additional check on the inclusion of the acoustical modes we compare our B 's with those of non-polar semiconductors.²¹ The values of B listed vary from 5×10^5 to 9×10^6 , which include our values.

VI. DISCUSSION

The combined theory has served to remove the discrepancy with experiment at $T < \theta$; the acoustical mode scattering provides an explanation of the approach to $T^{-\frac{1}{2}}$ behavior. Discrepancy still exists for $T > \theta$. A first consideration for sources of error is in the addition of reciprocal mobilities. This error is hardly significant since the data go as approximately $T^{-5/2}$ while the acoustical as $T^{-\frac{1}{2}}$ and the optical as $T^{-\frac{1}{2}}$. It is not likely that a more refined method of calculating the resultant mobility will bring it to a $T^{-5/2}$ dependence.

Since the $T^{-\frac{1}{2}}$ law for acoustical scattering has been experimentally verified in nonpolar semiconductors and metals we do not consider this further.

Considering next the statistical solution of H-S, they show that the variational solution of $\chi(z)$ at low and high temperatures agrees with the closed form solution [Eq. (14)]. The region of intermediate temperature is calculated to third order and appears to be rapidly converging. It therefore does not seem likely that the deviation between theory and experiment can be attributed to inadequacies in the solution of the Boltzmann equation.

Going back further one might question the use of a single frequency to represent the optical modes of the lattice since the reststrahlung data¹¹ does not indicate

a sharp frequency. However, the approximation that all modes are of the same frequency correctly counts the number of polar modes, and therefore should give the right order of magnitude of scattering when all modes are excited, as at high temperatures.

We thus conclude that the principal source of error in the perturbation theory of mobility is most likely to be in the expressions for the scattering cross section of the electron-polar mode interaction for electron energies greater than $k\theta$. In view of the closeness of α to unity it is not surprising that first order expressions for the scattering cross sections need revision.

VII. CONCLUSIONS

From the comparison of mobility data in PbS crystals with theory we conclude that the perturbation theory of mobility of Fröhlich-Mott, Howarth-Sondheimer, when combined with acoustical scattering, is valid in the temperature range 77°K to θ , and leads to effective masses for electrons and holes in the range of $0.1 m_e$ to $0.4 m_e$. In the region $T > \theta$ discrepancy exists between theory and experiment. It is concluded that the most likely source of error lies in the perturbation theory expressions for the scattering cross sections of the electron-polar mode interaction for electron energies greater than $k\theta$.

The polaron theory of mobility is nearly identical with the F-M, H-S theory at $T < \theta$ so the foregoing remarks concerning the low-temperature region also apply to it. Since the polaron theory is intended for use when $\alpha \cong 1$ it may, when completed, agree with experiment for $T > \theta$. A comparison with the PbS data at high temperatures should provide a sensitive test of the general polaron theory as well as being of interest in the theory of mobility in polar crystals.

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²¹ See reference 20, p. 277, Table 14.2.