

High-Temperature Measurements of the Electron Hall Mobility in the Alkali Halides*

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Using a modification of the Redfield technique, the electronic Hall mobility has been measured over the temperature range from 150 to 400 K in nine alkali halides made photoconducting by either x irradiation or electrolytic coloration. The measurements indicate that in all cases the Hall mobility decreases much more sharply with increasing temperature than wide-band optical-phonon scattering theories would predict. Preliminary consideration of the effects of polaron-band narrowing yield results which agree well with the temperature dependence of the data.

I. INTRODUCTION

The electron-lattice interaction in the alkali halides has long been recognized to be strong enough to require one to view the motion of excess charge in the lattice in terms of polaron theories. Generally, the theoretical work that is applied to the motion of the polarons in these materials invokes the continuum approximation¹; that is, the Hamiltonian which has been the subject of these studies is that for a particle in a dielectric continuum, rather than that appropriate to a charge carrier in a discrete lattice. Such a procedure is expected to be valid when the spatial extent of the polaron is sufficiently large compared to a length typical of the lattice atomicity, such as the lattice constant. In the alkali halides, typical estimates of the polaron radius in the continuum model have been of the order of twice the lattice constant.^{1,2} In view of these estimates, it is not at all clear that the continuum model is strictly applicable in this case. Further questions arise when it is noted that not all properties of polarons are equally sensitive to the continuum approximation.³ The ideal way of ascertaining the validity of this model would be to compare its predictions with that of a calculation which considers the discreteness of the lattice explicitly. To date, polaron theories which treat the discreteness of the lattice have concerned themselves with the small-polaron regime, in which the physical parameters are such that the polaron may be viewed as spread over only one lattice site.^{3,4} It is possible that although the polaron associated with motion of excess carriers in the alkali halides is not strictly believed to be a small polaron, its size may not be sufficiently large to rule out any effects of the discreteness of the lattice on its transport properties.

Within the framework of the continuum model, the strength of the electron-lattice coupling is characterized by the Fröhlich coupling constant

$\alpha = (me/2\omega\hbar^3)^{1/2} (\epsilon_\infty^{-1} - \epsilon_0^{-1})$. There is evidence to believe that for wide-band materials in the weak-coupling regime ($\alpha < 1$), it is justifiable to treat the electron as having a polaron mass $m^* = m(1 + \frac{1}{6}\alpha)$ in the calculation of transport properties.² Using this mass, the polar scattering theory of Howarth and Sondheimer,⁵ with later refinements,^{6,7} becomes applicable in the calculation of electron mobility.

In the intermediate-coupling regime ($10 < \alpha < 1$), however, it is clear that the Howarth-Sondheimer calculation, which basically treats the polaron as a "heavy" electron moving in a band whose width is $\gg kT$, may not be applicable. Several authors⁸⁻¹⁰ have calculated the mobility of the polaron in this intermediate-coupling regime while still retaining the wide-band approximation. All of these calculations, with one exception, are valid only at temperatures considerably lower than θ_{LO} , the LO phonon temperature, and are of little help in evaluating the results of the present experiments where θ_{LO}/T ranges from $\sim \frac{1}{3}$ to 2. The variational calculation of Feynman *et al.*⁹ has not as of yet been evaluated in this intermediate region of temperature. It is interesting that the treatment of Howarth and Sondheimer in the weak-coupling approximation and the theories developed for the intermediate-coupling regime all appear to predict the same temperature dependence of the electron mobility at low temperatures ($\theta_{LO}/T \gg 1$).

Small-polaron theories which specifically treat the carrier as moving in a discrete lattice possess a feature which has an important bearing on polaron transport properties. The bandlike polaron motion is strongly affected by the fact that the polaron bandwidth is a decreasing function of temperature. In other words, the small-polaron effective mass is an increasing function of temperature, increasing most sharply with temperature for $\theta_{LO}/T \lesssim 1$. Thus, the temperature dependence of the small-polaron bandlike mobility arises from the tempera-

ture dependence of the effective mass as well as from considerations of the scattering of polarons. Furthermore, above a temperature which is characterized by the energy uncertainty associated with the finite lifetime of the polaron-band states being comparable to the polaron bandwidth, it is appropriate to view the polaron as hopping between neighboring sites in the lattice rather than as moving in a band. While in the narrow-band limit of the small-polaron (electronic bandwidth $\leq \hbar\omega_{LO}$) the transition from bandlike to hopping behavior is estimated³ to occur at a temperature somewhat less than θ_{LO} , it is reasonable to assume that a comparable transition for a polaron in a much wider band will be characterized by a considerably higher temperature.

Hence, one is motivated to determine experimentally the temperature dependence of the Hall mobility at high temperatures ($\theta_{LO}/T \lesssim 1$) for intermediate-size polarons, such as those believed to exist in the alkali halides.

One of the important advantages of Hall-mobility measurements is that the Hall mobility is truly the "microscopic" mobility, whereas, the drift mobility may often be trap controlled when the sample contains enough shallow trapping centers. Thus, only the careful control of the presence of shallow traps in the sample, quite difficult in most cases, allows the experimentalist to be sure of what he has measured in drift mobility experiments. The difference in the role of traps in these two cases arises because the Lorentz force acts on the carrier only when it is in the untrapped state. The effect of traps on the Hall mobility is confined to their acting as actual scattering centers for the carrier. In materials with mobilities less than $\sim 10^3$ cm²/V sec., carrier mean free paths are generally so low as to rule out any significant scattering effects of traps unless their number is known to be unreasonably high ($> 10^{19}$ /cm³).

The second advantage of Hall-mobility measurements unique to the case of high-impedance samples is the availability of the Redfield¹¹ technique and its various refinements.^{12,13} This method allows measurements to be made with blocking electrodes, thus avoiding the problems associated with establishment of Ohmic contacts on wide-band-gap high-resistance crystals. The normal four-probe Hall technique becomes quite suspect when applied to a high-impedance sample due to magnetogalvanic effects as well as numerous other difficulties.

For weakly coupled materials where the polaron can be treated simply as an electron with mass $= m(1 + \frac{1}{6}\alpha)$ moving in a band whose width is $\gg kT$, the relationship between the Hall and "microscopic" drift mobility is straightforward. The ratio μ_H/μ_d can be shown¹⁴ for weak H fields ($\omega_c\tau < 1$, where ω_c

is the cyclotron frequency) to be a constant which depends only on the carrier scattering mechanism. For LO-phonon scattering, which appears to be dominant in the alkali halides, this ratio is unity. However, in the small-polaron regime in which a carrier can be described as moving in a small polaron band or "hopping," the Hall and drift mobilities may depend on temperature in quite different ways¹⁵⁻¹⁷ depending on lattice geometry and other factors. In the intermediate-coupling case, investigators generally have assumed that the two mobilities are equal, although no theoretical justification for this exists at present.

A number of measurements have been made of the low-temperature Hall mobility in several alkali halides made photoconducting by the introduction of color centers. Ahrenkiel and Brown¹⁸ measured μ_H in KBr, KCl, KI, and NaCl over the temperature range 7-100 K. In general, they found that at high temperatures the Hall mobility decreased as $e^{\theta/T}$, consistent with the expectations of wide-band optical-phonon scattering. At low temperatures, the mobility leveled off at values (in the region of 10^4 cm²/V sec) which depended inversely upon the number of defects introduced by coloration. In general, due to the experimental error limits and the narrow temperature range over which intrinsic lattice scattering could be observed, a precise determination of the temperature variation of μ_H due to LO-phonon scattering was not possible. The results were generally consistent with the weak- and intermediate-coupling predictions.

Only scattered measurements of μ_H on a few alkali halides above 100 K have been made to date. The only values reported over a wide range of temperature are those of Onuki¹⁹ in KBr. Since his value for μ_H at 300 K is a factor of 3 larger than the values reported by Kahn and Glass²⁰ and MacDonald and Robinson²¹ at this temperature, further clarification of this problem in the form of additional measurements is obviously needed.

Thus, it was the purpose of the present investigation to measure the Hall mobility of a variety of alkali halides in the temperature region above 100 K to elucidate the nature of polaron transport in the region around $\theta_{LO}/T \sim 1$. Accurate measurements of these mobilities were made possible by a further refinement of the Redfield technique¹³ utilizing signal-averaging techniques to improve the signal-to-noise ratio.

II. EXPERIMENTAL

A. Apparatus

Since a complete description of the Hall mobility apparatus has been published elsewhere,¹³ only a review of the essentials of its operation will be covered here. Figure 1 shows an exploded view of the sam-

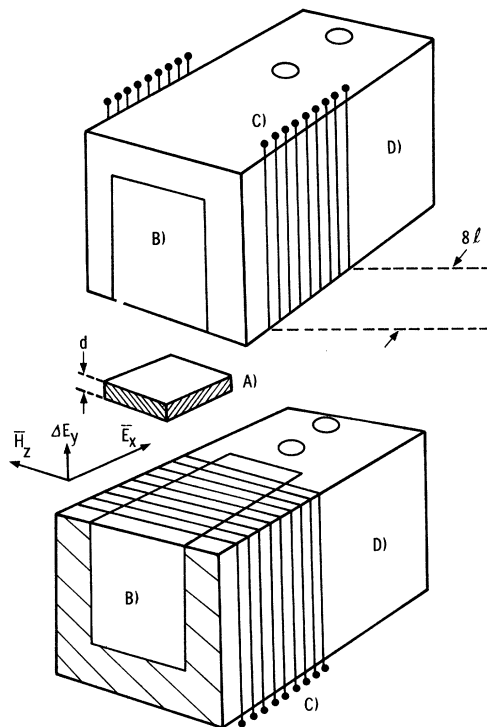


FIG. 1. Hall-effect sample holder.

ple holder used. Two sets of grid wires (C) are connected to an ac-coupled potential-divider network seen in detail in Fig. 2. Batteries are used to impress 225 V across the points A-A, and the resistances R_1 - R_{20} are sufficiently high ($10^8 \Omega$) to ensure that negligible current is drawn by the network. In actual operation, the two halves of the sample holder are fastened together, so that the distance between the grid wire sets is approximately the same as the

sample thickness ($D \approx 1$ mm). In this configuration, a reasonably uniform E field is maintained in the x direction throughout the sample as long as its dimensions in the x direction do not exceed $8l$ (5 mm). By changing the ganged resistors R_{25} and R_{26} ($10^8 \Omega$) by an amount ΔR , the E field is rotated in the plus or minus y direction, so that

$$\Delta E_y / E_x = 16 \Delta R l / R d, \quad (1)$$

where

$$R = \frac{1}{2}(R_{21} + R_{22}) + \sum_{i=1}^{10} R_i.$$

The photoexcitation pulses from a xenon flash lamp enter the 45° quartz prisms (B) in the x direction and are reflected to pass through both sides of the sample in the y direction. The grids present minimal obstruction to the light beams, and the sample is generally uniformly illuminated. In this orientation of E and H fields, the Lorentz force on the carriers is in the y direction, and the resulting charge pulse is measured by means of a charge-sensitive preamplifier connected across points B-B in Fig. 2. Since the grid wires are covered with a layer of insulating varnish and the sample is normally put in a small polyethylene packet (with thickness ≈ 0.003 cm) to ensure against photoemission, the electrode arrangement is completely blocking.

This sample holder is affixed to a copper block mounted at the base of the tailpiece of a standard liquid-nitrogen Dewar of stainless-steel construction manufactured by Sulfrin Cryogenics, Rahway, N. J. A $45\text{-}\Omega$ nichrome-wire heater was placed at the bottom of this copper block, and a $\frac{1}{16}$ -in.-thick piece of No. 304 stainless steel was mounted between the copper block and the Dewar tailpiece. Using up to 5 W of heater power and liquid N_2 as a cryogenic fluid, temperatures of up to 450 K could

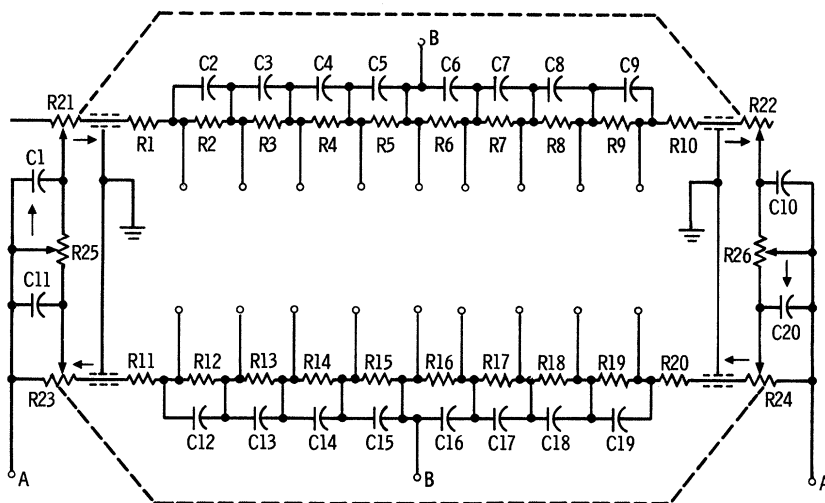


FIG. 2. Potential-divider network.

be maintained at the sample with most of the thermal gradient occurring across the stainless-steel intermediate piece. The temperature of the copper block was monitored by means of two calibrated chromel-*P*-constantan thermocouples mounted symmetrically about 5 mm above and below the sample. The thermocouple emf's were measured by means of a Leeds and Northrup potentiometric bridge and a dc null detector of the same make. The sample temperature was adjudged to be the mean of the two measurements with the error span equal to the difference in the two readings.

Both signal and *E* field leads were of shielded stainless-steel coax developed specifically for cryogenic applications. The Dewar was kept at a vacuum of at least 10^{-5} Torr by a Veeco vacuum station for all measurements of the Hall mobility. The photoexcitation light entered the Dewar through a single quartz window, and the entire Dewar was suspended between the pole faces of a Varian magnet capable of fields up to 19 kG. Figures 3 and 4, respectively, show a simplified schematic of the apparatus and the timing cycle of operation. Numerous timing, monitoring, and isolating circuits are not shown for reasons of clarity.

The basic cycle of operation is as follows: The *E* field is switched on for a period of ~ 100 msec. Near the end of the *E* field pulse, the xenon flash lamp pulse (~ 10 μ sec wide) generates 10^7 – 10^8 carriers in the colored alkali-halide sample. If a magnetic field is present in the *z* direction, the resulting Hall charge pulse across *B-B* is amplified, differentiated, and fed into two gated boxcar circuits, *A* and *B*. The gates are timed so that one channel receives the positive swing of the differentiated charge pulse and the other channel the negative swing. The next *E*-field pulse is applied with the opposite polarity, and the boxcar gates are reversed so that the channel that previously received the first half of the differentiated charge pulse now receives the second half. In this manner the boxcar "unlearns" any signal which does not reverse sign with

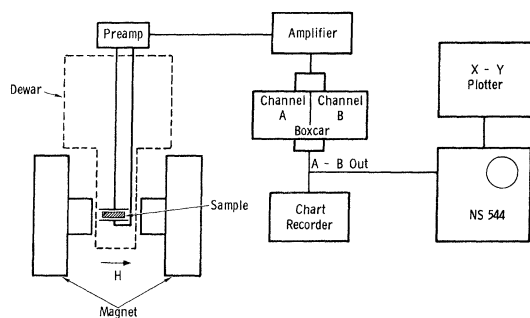


FIG. 3. Schematic of apparatus.

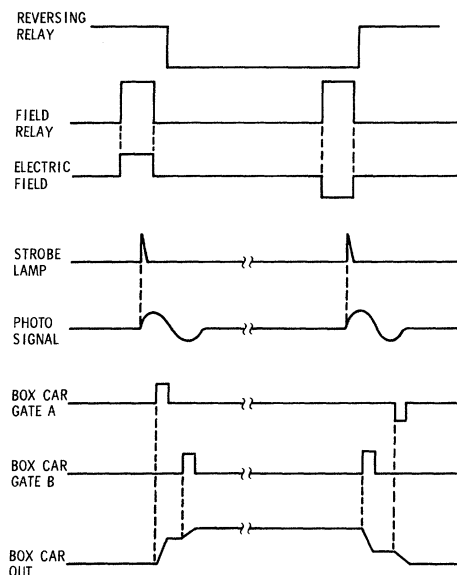


FIG. 4. Timing cycle.

the *E*-field reversal (as illustrated in Fig. 4). In this manner undesirable unipolar effects as well as any effects due to drift in the *E*-field balancing circuits are automatically removed. The *E* field is typically pulsed ~ 5 times per second. The difference between the boxcar outputs of channel *A* and channel *B* is thus a measure of the charge flow in the *y* (Hall) direction.

The actual measurement is performed as follows: After nulling the charge flow in the *y* direction with the coarse balancing resistors (R_{21} – R_{24}) to compensate for any grid wire misalignment, the magnetic field is increased linearly from 0 to 19 kG over a period of ~ 2.5 min while the *E* field and xenon lamp are pulsing according to the timing cycle just described. The output of the boxcar (*A*–*B*) is simultaneously fed to the input of Northern Scientific digital memory oscilloscope placed in the "add" mode of operation. This information is stored in synchronization with the magnetic field sweep so that the charge output in the Hall direction corresponding to a given magnitude of the magnetic field is stored in the same channel of the NS 544 every time the magnetic field sweep cycle is actuated. When the field has reached the maximum of 19 kG, the field drops to zero within the space of a few seconds. After a dead time of ~ 1 min, a magnetic field reversing relay closes, and the next sweep is accomplished with the *H* field sweeping in the opposite direction while the NS 544 receives the boxcar output in the "subtract" mode of operation. In this fashion, signals which do not reverse polarity with a change in magnetic field direction are disregarded. After a num-

ber of plus-minus magnetic field cycles the information from the NS 544 is fed to a xy -point plot recorder. The resultant plot of Hall charge versus magnetic field strength can be checked for linearity expected of a true Hall signal.

Calibration of the apparatus is accomplished as follows: With the magnetic field off the same cycle is followed, but this time a known electric field ΔE_y is impressed on the sample in a step-function manner for the 2.5-min duration by changing the resistors R_{25} and R_{26} . Usually, two cycles, one of positive ΔE_y and the other negative ΔE_y , are implemented to cancel any asymmetry of response. The point plot of this signal from the NS 544 when compared to the information received during the magnetic field cycling provides a direct calibration of the magnetic field response in terms of the known electric-field rotation.

In contrast to the original Redfield technique⁸ where the charge flow in the Hall direction with an impressed H field was nulled by simultaneously applying a known electric field rotation, this method suffers somewhat from the possibility of a change in the crystal photoresponse during the interval between the magnetic field cycle and the calibration cycle. To correct for this possibility the calibration procedure was carried out before and after the magnetic field cycling. Generally, the two calibration runs agreed to well within 10%. The data taken between two calibrations which did not agree were discarded, although this was an infrequent occurrence. Additional monitoring of the boxcar output ($A-B$) was accomplished with a strip-chart recorder. Unnatural fluctuations of output due to system malfunctions which would be masked in the NS 544 output (because of extensive averaging) could be detected by this procedure.

Clearly, the advantage of this technique is that unlike the original Redfield method, this procedure allows the use of intensive signal averaging, thus extending both the accuracy and sensitivity of Hall measurements.

B. Sample Preparation

Small blocks (typically 3 cm on a side) of NaCl, KCl, KBr, KI, RbBr, RbCl, and RbI were obtained from the Harshaw Chemical Co. The remaining samples, CsI and CsBr, were purchased from Semi-Elements Inc., Saxonburg, Pa. In order to induce photoconductivity in these materials two methods of coloration were employed: x irradiation and electrolytic coloration. Samples of NaCl, KCl, and KBr were cleaved with a cleaving hammer and razor blade to the working dimensions of $\sim 1 \times 3 \times 5$ mm and inserted into copper-foil envelopes. These specimens were then x irradiated at room temperature for 20 min on each side in a 45-kV tungsten

target x-ray machine operated at 35 mA. This procedure resulted in the production of 10^{16} – 10^{17} F centers per cm^3 . Blocks measuring $\sim 1 \times 1 \times 1$ cm of all the alkali halides used except NaCl were electrolytically colored by the standard technique.²²

These samples were heated in air in a resistance furnace to approximately 50°C below their melting points. An electric field of 50–250 V/cm was then applied to a combination of point and plane-surface electrodes until the coloration cloud had spread reasonably uniformly throughout the sample. Final F -center densities were generally on the order of $10^{17}/\text{cm}^3$. These specimens were then withdrawn from the furnace and rapidly quenched to 300 K by a cold air blast to prevent the formation of colloidal metal. Pieces measuring $1 \times 3 \times 5$ mm were then cleaved from these colored blocks in the case of all but the cesium halides. Due to the properties of CsBr and CsI, these materials had to be cut with a jeweler's saw and polished with moistened paper to the desired dimensions. All samples were kept at 300 K in the dark until use to prevent the formation of aggregate centers, although these were expected to have little effect on electron mobility. Measurements were carried out with the sample inserted in a small polyethylene packet as a precaution against photoemission effects.

C. Experimental Procedure

After the sample had been placed between the two halves of the sample holder, the Dewar was evacuated to $\sim 10^{-5}$ Torr. The normal procedure was then to lower the temperature of the Dewar and let it stabilize for a period of about 1 h. Then, a point consisting of two calibrations and several (up to 32) magnetic field sweeps was taken. The temperature of the Dewar rarely varied more than 0.1 K during the time required for obtaining the data. In general, experimental points were taken so that data obtained while raising the Dewar temperature interleaved that taken while the Dewar temperature was being lowered. This was done to reveal any long-term effects on the electron mobility which might arise from bleaching of the color centers or other long-term changes in the crystal properties. No effects of this kind were ever seen.

The standard definition of the Hall and drift mobilities is as follows:

$$\vec{v}_I = \mu_H (\vec{v}_D \times \vec{B}) \quad (\text{esu}), \quad (2)$$

$$\vec{v}_D = \mu_D \vec{E}, \quad (3)$$

where \vec{v}_I is the carrier velocity in the Lorentz direction, \vec{v}_D the carrier drift velocity in response to an applied \vec{E} field, and \vec{B} is the applied magnetic

field. Using the coordinate system of Fig. 1, where \vec{E} is in the x direction and \vec{B} in the z direction, Eq. (2) may be written in scalar form as

$$v_i = \mu_H(v_x B_z), \quad (4)$$

where v_i is now in the y direction. The definition of the Hall angle most often used in the theoretical discussions of the Hall effect is

$$\tan\theta = v_i/v_x \quad (5)$$

or

$$\theta = v_i/v_x, \quad (6)$$

if $\theta \ll 1$. Thus, Eq. (4) becomes

$$\mu_H = \theta/B \text{ for } \theta \ll 1. \quad (7)$$

In the case of experiments on anisotropic materials, care must be taken to specify not only the directions of the impressed \vec{B} and \vec{E} fields relative to the crystal axes, but also whether Hall fields or currents are being measured. In the case where the currents in the x and y directions are measured, we find

$$\mu_H = j_y/j_x B^{-1}, \quad (8)$$

since

$$v_i/v_x = j_y/j_x. \quad (9)$$

However, in the case where the Hall field E_y and the drift field E_x are measured, we have

$$\mu_H = \frac{E_y}{E_x} \frac{\mu_D^y}{\mu_D^x} \frac{1}{B}, \quad (10)$$

since

$$v_i = E_y \mu_D^y, \quad (11)$$

$$v_x = E_x \mu_D^x, \quad (12)$$

where μ_D^y and μ_D^x are the drift mobilities in the x and y directions. In application of the Redfield technique, or any technique involving the measurement of Hall fields rather than currents to anisotropic materials, cognizance should be taken of the fact that this ratio of drift mobilities must be known to permit calculation of the actual Hall mobility.

In the case of materials with an isotropic-conductivity tensor such as the alkali halides, Eq. (10) reduces to

$$\mu_H = E_y/E_x B^{-1}. \quad (13)$$

Calculation of E_y/E_x in the present experiment is straightforward. If $\Delta E_y/E_x$ is the amount of field rotation impressed during the calibration procedure [calculated from Eq. (1), Sec. IIA], S_C , the magnitude of charge response in the y direction from the calibration procedure, and S_B , the magnitude

of charge response in the y direction with the impressed B field, then we obtain

$$E_y/E_x = (-S_B/S_C)(\Delta E_y/E_x). \quad (14)$$

This is most easily seen by noting that because of the linearity of charge response with the applied calibration field ΔE_y , a field $(-S_B/S_C)\Delta E_y$ applied with the magnetic field B_z present would result in zero charge flow in the y direction. Thus, $(-S_B/S_C)\Delta E_y$ is identical to the Hall field E_y .

III. RESULTS

Figures 5-10 show the measured Hall mobilities for the various alkali halides plotted versus reciprocal temperature. Consistent with previously reported data, the Hall effect had the sign of electrons in all cases. The vertical error bars were determined by calculating the possible maximum and minimum mobilities consistent with the noise spread of the magnetic field and calibration sweep outputs from the NS 544. Additional random errors associated with the measurements may spread the error brackets slightly, but these are estimated to be less than 5% of the plotted values. Except for the data taken in KCl, NaCl, and KBr, all points represent Hall mobilities obtained with electrolytically colored samples. No data were taken in KBr between 160 and 250 K because of polarization problems which occurred in several x-irradiated samples. No clear explanation for this phenomenon has been given, although the severity of the prob-

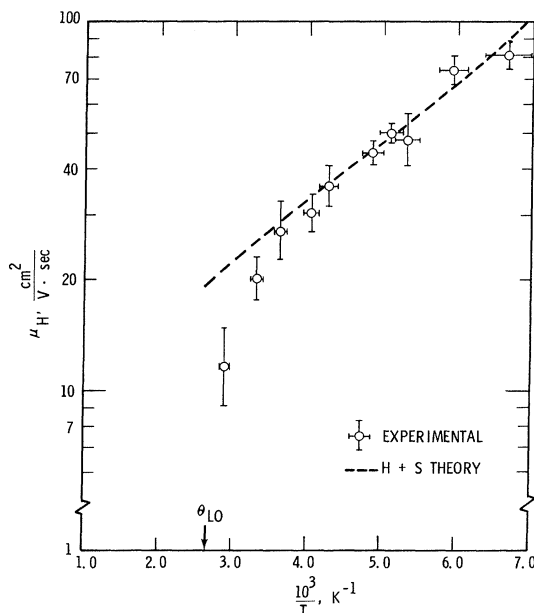


FIG. 5. Hall mobility in NaCl.

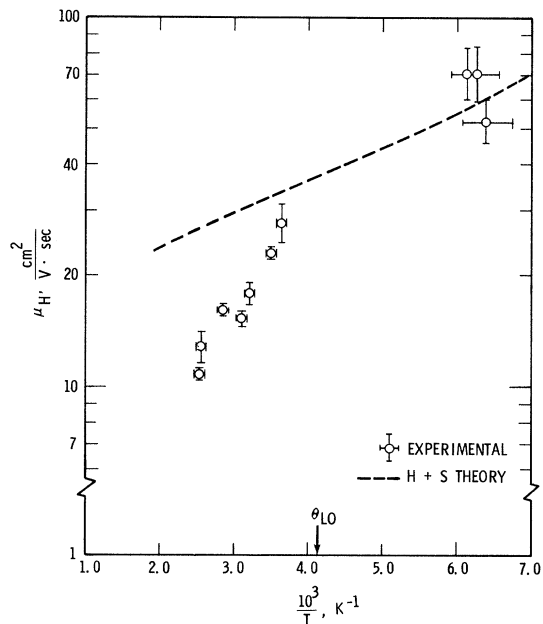


FIG. 6. Hall mobility in KBr.

lem was lessened considerably by using samples colored electrolytically. Samples from another source are presently being sought to enable measurements of the mobility to be made in this temperature region.

The agreement of the Hall data taken in x-irradi-

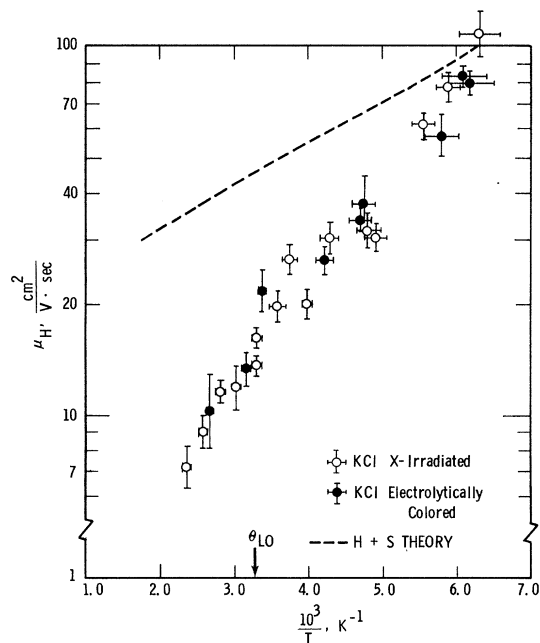


FIG. 7. Hall mobility in KCl.

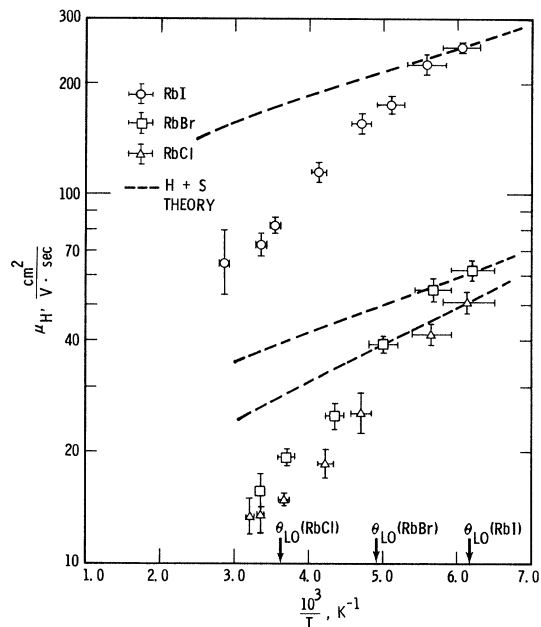


FIG. 8. Hall mobility in the rubidium halides.

ated KCl with that obtained in the electrolytically colored KCl sample is significant. This tends to confirm the notion that only intrinsic lattice scattering is important in limiting electronic mobility in the alkali halides at high temperatures where the electron mean free path is of the order of a few angstroms. Sample preparation is thus much less important in these measurements than it is in mea-

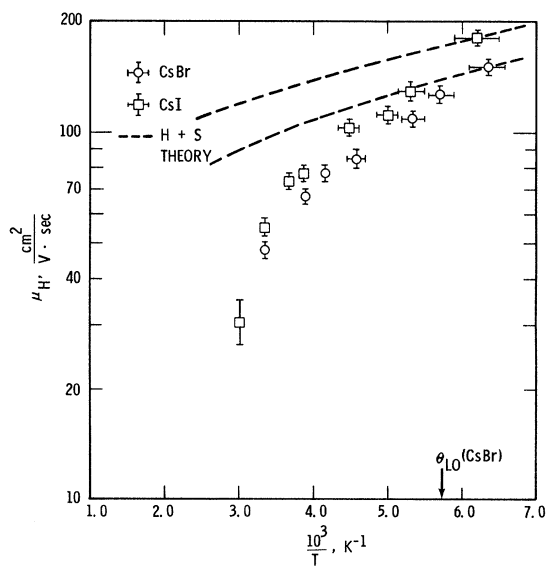


FIG. 9. Hall mobility in the cesium halides.

surements of drift mobilities in the alkali halides, where electron lifetimes and the presence of shallow traps are of major concern.

Agreement with previous Hall data is generally good. The Hall mobilities obtained at room temperature in KBr by Kahn and Glass²⁰ and MacDonald and Robinson²¹ both fall within the error bars of the present measurements. Similarly, the values obtained by Redfield²³ in NaCl at ~ 200 K agree well with the data presented here. The values of Onuki¹⁹ in KBr, however, appear to lie above both the present measurements and those obtained by Kahn and Glass and MacDonald and Robinson.

As has previously been emphasized, due to the strength of the electron-phonon interaction in the alkali halides, it is possible that the drift and Hall mobilities may differ both in magnitude and temperature dependence. It is thus of considerable interest to compare the present Hall-mobility results with previous measurements of the drift mobility. Unfortunately, due to the experimental difficulties inherent in measuring drift mobilities in highly insulating materials, few determinations of μ_D above $T = \theta_{LO}$ exist in these substances. The recent measurements of Hirth and Tödheide-Haupt²⁴ on KCl are of interest in this respect. By employing photoemission from gold electrodes to inject conduction-band electrons into their samples, they were able to use highly zone-refined KCl, and thus obtain electron lifetimes as long as 700 nsec. Above 300 K these lifetimes were long enough to permit observations of the transit of virtually the entire

injected charge pulse across the thickness of their crystals. Accordingly, although their curves of μ_D versus $10^3/T$ increased with temperature below 300 K, indicating that the drift mobility was trap controlled, above this temperature μ_D decreased with temperature, suggesting that the true "microscopic" drift mobility was indeed being measured. Since their values of μ_D between 300 and 400 K agree well with the present Hall-mobility measurements, it is likely that the present measurements of μ_H reflect the behavior of μ_D at least in the case of KCl.

The dashed lines in Figs. 5-10 are plots of the temperature dependence of μ_H calculated by Howarth and Sondheimer⁵ (HS). Due to the present lack of knowledge of the crystal-band mass in most of these materials, prediction of the magnitude of μ_H by this theory is uncertain. However, since θ_{LO} has been determined for all the alkali halides measured here, the variation of mobility with temperature is easily calculated for comparison with experiment. Accordingly, all plots of the HS theory are normalized to fit the values of μ_H measured at the lowest temperatures employed in the present experiments. It is clear that in all cases the measured mobilities decrease faster with increasing temperature than is predicted by the weak-coupling theory of Howarth and Sondheimer. Agreement with the theory seems particularly poor in the case of the cesium and rubidium halides. The only cases in which the theory is reasonably close to experiment are that of NaCl and, particularly, that of KI. As will be evident from the discussion of Sec. IV, it appears significant in this respect that NaCl has a rather large value of θ_{LO} and KI, a low value of the coupling constant α .

IV. DISCUSSION

We shall now proceed to speculate as to the origin of the rapid decline of μ_H with increasing temperature.

To begin, let us reemphasize that the polaron theories that have generally been applied in the case of the alkali halides have all been based on a model which assumes that (i) a conduction electron in a rigid periodic lattice may be viewed as an essentially free electron moving with an effective mass m^* which is a constant of the material, and (ii) the interaction of the electron with the vibrational motion of the lattice is that of an excess electron with a dielectric continuum. In the case of the alkali halides, such theories^{1,2} lead to estimates of the radius of the polaron which are typically somewhat larger than but of the order of a lattice spacing. In such a situation, the application of the continuum model becomes suspect. In fact, the conditions under which the continuum approximation is valid have not been thoroughly investigated; ideally,

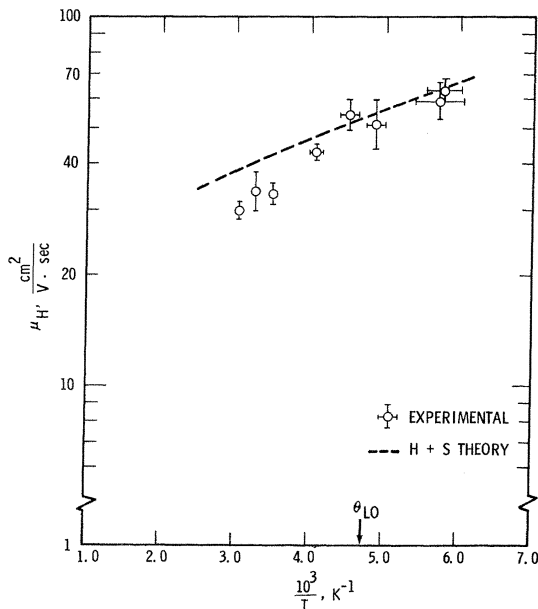


FIG. 10. Hall mobility in KI.

one should examine the results of a discrete model to ascertain when they approach the continuum results. At present, studies of a discrete model have been carried out only in the limit in which the polaron is taken to be localized at a single lattice site, this limiting situation being designated generally as the small-polaron regime.^{3, 15, 17}

The strong-coupling limit of the continuum theory developed by Fröhlich²⁵ and Allcock²⁶ may be employed to estimate the relevancy of these small-polaron theories to the case of the alkali halides. Specifically, the binding energy of a continuum polaron in the strong-coupling limit is given by $E_{cp} = 0.1 \alpha^2 \hbar \omega_0$, where α is the dimensionless Fröhlich coupling constant – typically about 5 or 6 for the alkali halides with the electronic effective mass taken to be its free-electron value. For the alkali halides E_{cp} is generally of the order 0.1 eV. As is apparent from Eqs. (18), (20), and (22) of Austin and Mott,²⁷ $E_{cp} \leq (E_{sp})^2 / W_{band}$, where E_{sp} is the binding energy associated with a small polaron, and W_{band} is an energy characterizing the rigid electronic band; this inequality arises from additional numerical factors which appear in Austin and Mott's formulas and from the fact, noted by Austin and Mott, that they probably underestimate E_{sp} by utilizing the continuum approximation near the center of the polaron. Taking W_{band} to be of the order of an electron volt,²⁸ E_{sp} is found to be at least a few tenths of an electron volt. Thus, the ratio of the radius of the continuum polaron to a lattice constant, given roughly by (W_{band} / E_{sp}) ,^{27, 29} may be sufficiently small for the alkali halides so that some physical effects associated with the discreteness of the lattice may be important. Thus, although the polaron formed in the alkali halides is not believed to be strictly a small polaron, it is felt that some features of small-polaron theory may be useful in understanding the present Hall-mobility results. In particular, we shall focus our attention on the temperature-dependent band-narrowing effect predicted by small-polaron theory.

In Holstein's tight-binding study of the small polaron,³ it is found that the band of polaron states is characterized by a transfer integral $J e^{-S}$ which is the product of an electronic transfer integral J between two neighboring lattice sites and a vibrational overlap integral e^{-S} . The vibrational overlap integral generally differs from unity because the shift of the excess electron from one lattice site to a neighboring site results in a change in the equilibrium positions of the ions in the crystal. In a rigid lattice no such effect occurs and the vibrational overlap integral is in fact unity. Furthermore, in the small-polaron problem, S is found to be an increasing function of temperature, being

proportional to $2N + 1$, where $N = (e^{\hbar \omega_0 / kT} - 1)^{-1}$ and ω_0 is the LO-phonon frequency. Thus, the polaron-band effective mass is an increasing function of temperature:

$$m^* \equiv \left(\frac{\hbar^{-2} \partial^2 \epsilon(k)}{\partial k^2} \right)^{-1} = m^*(0) \exp[\alpha_0 (2N + 1)], \quad (15)$$

which at high temperature varies as $\exp[\alpha_0 (2kT / \hbar \omega_0)]$.

In Holstein's theory, $\alpha_0 = E_{sp} / \hbar \omega_0$, the ratio of the small-polaron binding energy to the quantum of vibrational energy. However, this relationship is a consequence of the Holstein model, in which the electron-lattice interaction is taken to be a short-range interaction analogous to the usual deformation potential. For an arbitrary-range electron-lattice interaction which is taken to be linear in the lattice displacements, it is possible to show³⁰ that Holstein's α_0 constitutes an upper limit on α_0 . The actual reduction of α_0 from Holstein's value is dependent on the magnitude of various microscopic physical constants which are not easily estimated. However, for the "molecular-crystal polarization model"²⁹ (analogous to the continuum-polarization model but taking into account the discreteness of the lattice) α_0 is $\sim E_{sp} / 5 \hbar \omega_0$. Thus, even within small-polaron theory, the band-narrowing effect may be less dramatic than that suggested by Holstein's original study. Furthermore, it is suggested that the band-narrowing effect will become less pronounced as the polaron size is increased from that of a small polaron. It should be stressed that the band-narrowing factor arises from treating a particle in a discrete lattice rather than within the continuum approximation. In fact, in Toyozawa's variational calculation³¹ of the energy of an excess carrier interacting with a discrete lattice (analogous to the Lee, Low, and Pines approach¹), band narrowing appears for any finite electron-lattice coupling. Although the Toyozawa calculation is only carried out explicitly for the interactions of an excess carrier with acoustic phonons at $T = 0$, an analogous calculation appropriate for optical phonons at finite temperatures is easily performed. As is expected, the small-polaron results are obtained in the strong-coupling limit.

Thus, one may ask what the effects of band narrowing would be on the Hall mobility in the alkali halides. Although little theoretical justification exists at present for applying the results of small-polaron theory to the alkali halides, it is interesting to consider the temperature dependence of μ_H that arises from the Howarth-Sondheimer theory, which describes the effects of optical scattering on an excess carrier in a band much wider than kT , if we now take the carrier mass to have

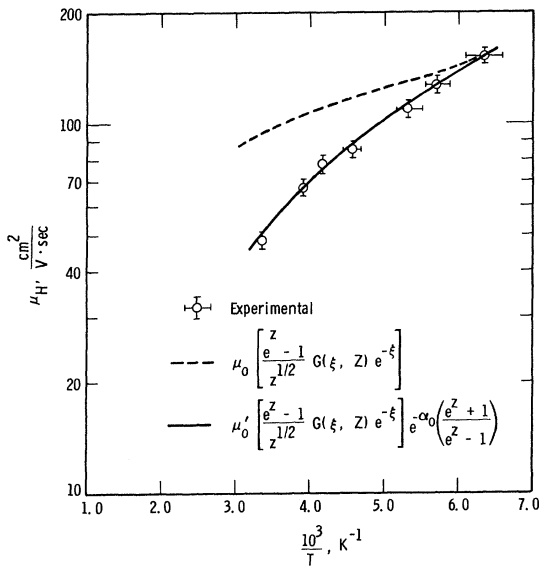


FIG. 11. Hall mobility in CsBr.

the temperature dependence found from small-polaron theory.

Thus, we consider

$$\mu_H = \mu_{H+s} \exp\left(-\alpha_0 \frac{e^Z + 1}{e^Z - 1}\right), \quad (16)$$

where

$$Z \equiv \theta_{LO} / T.$$

Figure 11 shows the Hall mobility of CsBr fitted with both Eq. (16) and the HS theory. It is readily seen that the addition of the band-narrowing term greatly improves the agreement between experiment and theory. Similar fits of μ_H for the other alkali halides were made with good agreement between experiment and the predictions of Eq. (16) using values of α_0 between 0.2 and 0.9. While these values of α_0 are much smaller than expected for small-polaron motion, as has been stressed previously, they may not be unreasonable for a somewhat larger polaron. It should be emphasized that these arguments are to be regarded as no more than plausible in the absence of an accurate theoretical treatment of the problem. If band narrowing

is important, however, it is clear that extension of the wide-band theories of Feynman and Langreth to temperatures $\approx \theta_{LO}$ is unlikely to lead to the proper predictions for polaron transport properties in these materials. Certainly before more definitive conclusions can be drawn concerning the temperature dependence of the Hall mobility in the alkali halides, continuum theories (such as FHIP) would have to be extended to the high-temperature regime ($Z < 1$). Furthermore, a treatment of a larger than small polaron in a discrete lattice would be useful in developing accurate criteria for the applicability of continuum theories.

V. CONCLUSIONS

Using a modification of the Redfield technique, the electronic Hall mobility has been measured over the temperature range from 150 to 400 K in nine alkali halides made photoconducting by either x irradiation or electrolytic coloration. The measurements indicate that in all cases the Hall mobility decreases much more sharply with increasing temperature than wide-band optical-phonon scattering theories would predict. Preliminary consideration of the effects of polaron band narrowing yields results which agree well with the temperature dependence of the data. It is evident that full treatment of the problem of polaron transport in the intermediate-coupling regime is needed for an understanding of the present measurements.

Note added in proof. Feynman and Thornber [Phys. Rev. B 1, 4099 (1970)] have recently quoted an expression [Eq. (24)] for the FHIP polaron mobility which is valid for all Z . We have numerically evaluated this expression and find that the predicted temperature dependence of the mobility is, as in the case of the HS theory, much weaker than that displayed by the present experimental data.

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¹J. Appel, Solid State Phys. 21, 193 (1968).

²*Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Plenum, New York, 1963).

³T. Holstein, Ann. Phys. (N. Y.) 8, 343 (1959).

⁴L. Friedman, Phys. Rev. 135, 233 (1964).

⁵D. Howarth and E. Sondheimer, Proc. Roy. Soc.

(London) A219, 53 (1953).

⁶R. L. Petritz and W. W. Scanlon, Phys. Rev. 97, 1620 (1955).

⁷F. Garcia-Moliner, Phys. Rev. 130, 2290 (1963).

⁸F. E. Low and D. Pines, Phys. Rev. 98, 414 (1955).

⁹R. P. Feynman, R. W. Hellwarth, C. K. Addings, and P. M. Platzman, Phys. Rev. 127, 1004 (1962).

¹⁰D. C. Langreth, Phys. Rev. 159, 717 (1967).

- ¹¹A. G. Redfield, Phys. Rev. 94, 526 (1954).
¹²F. C. Brown and N. Inchauspé, Phys. Rev. 121, 1303 (1961).
¹³G. C. Smith, Rev. Sci. Instr. 40, 1454 (1969).
¹⁴F. Seitz, Phys. Rev. 79, 372 (1950).
¹⁵D. Emin and T. Holstein, Ann. Phys. (N. Y.) 53, 439 (1969).
¹⁶L. Friedman, Phys. Rev. 131, 2445 (1963).
¹⁷L. Friedman and T. Holstein, Ann. Phys. (N. Y.) 21, 494 (1963).
¹⁸R. K. Ahrenkiel and F. C. Brown, Phys. Rev. 136, A223 (1964).
¹⁹M. Onuki, J. Phys. Soc. Japan 16, 981 (1961).
²⁰D. Kahn and A. J. Glass, Phys. Chem. Solids 17, 210 (1960).
²¹J. R. MacDonald and J. E. Robinson, Phys. Rev. 95, 44 (1954).
²²*Color Centers in Solids*, edited by J. Schulman and W. Compton (Pergamon, New York, 1962), p. 38.
²³A. G. Redfield, Phys. Rev. 94, 537 (1954).
²⁴H. Hirth and U. Tödheide-Haupt, Phys. Status Solidi 31, 455 (1969).
²⁵H. Fröhlich, Advan. Phys. 3, 325 (1954).
²⁶G. R. Allcock, Advan. Phys. 5, 412 (1956).
²⁷J. G. Austin and N. F. Mott, Advan. Phys. 71, 41 (1969).
²⁸J. C. Phillips, Phys. Rev. 136, A1705 (1964).
²⁹T. Holstein, Ann. Phys. (N. Y.) 8, 325 (1959).
³⁰D. Emin (unpublished).
³¹Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) 26, 29 (1961).