Studies of the Polaron Mobility in AgBr at High Temperatures

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The drift mobility of electronic polarons has been measured in AgBr from 50 to 300°K by a transit-time technique. Comparisons were made with the Langreth theory of polaron mobility at finite temperatures. Although the temperature dependence of the measured mobility agrees quite well with theory, there is a magnitude discrepancy between experiment and theory.

I. INTRODUCTION

RECENT work has dealt extensively with the mobility of polarons in ionic materials such as the alkali and silver halides. Both theoretical[1–6] and experimental[7–14] work has treated the general characteristics of polaron motion. For example, the polaron mass can be computed from the bare-electron mass m_b (or band mass) and the electron-lattice coupling constant α, where from Frohlich,[15]

$$\alpha=(e^2/\hbar)(1/2\hbar\omega_l)^{1/2}(1/\epsilon_\infty-1/\epsilon_s)(m_b)^{1/2}. \quad (1)$$

Computation of α upon inserting values of ϵ_∞ and ϵ_s appropriate to the alkali and silver halides produces values ranging from about 1 to 6.[16] As the polaron mass may be approximated by[17]

$$m_p\cong(1+\tfrac{1}{6}\alpha)m_b, \quad \alpha<6, \quad (2)$$

the polaron mass is significantly larger than the band mass.

The existence of polarons is ascertained by the temperature dependence of the carrier mobility. However, until recently, the polaron mobility theories were valid only for the temperature range[16] $T\ll\Theta$, where Θ corresponds to the Debye temperature of the longitudinal optical (LO) frequency. Unfortunately, in this temperature range, impurity scattering always dominates LO scattering, even in the purest materials studied.[13,14]

Recently, Langreth[6] has extended the Feynman model of the polaron[17] to finite temperatures $Z\gtrsim 2$ where $Z=\Theta/T$ and finite coupling α. Another significant development was the measurement of the polaron mass in the alkali, silver, and thallium halides by cyclotron resonance.[18] By using the mass parameters in the Langreth expression, the polaron mobility may be computed and compared with high-temperature mobility experiments in which LO scattering predominates.

II. EXPERIMENTAL STUDIES

Very precise measurements of the electronic-polaron drift mobility in AgCl have been reported by Van Heyningen[7] in the temperature range, $Z=1$ to $Z=4$. Drift mobility measurements in both AgCl and AgBr have been reported by Chollet and Rossel,[12] but the temperature range was limited from about $Z=1$ to $Z=2$ (for AgBr). Also the x-ray excitation of photoelectrons has been criticized.[19] Burnham *et al.*[9] measured the electronic Hall mobility in AgBr from 4 to 100°K. However, absolute measurements suffered from a systematic inaccuracy described elsewhere,[11] and little data were obtainable above 50°K ($Z=4$). The purpose then, of the present experiments was to get mobility data over a wider temperature range in which LO scattering is dominant.

In several crystals of AgBr in which the trap densities were especially low, mobility measurements were possible in the temperature range 50–300°K ($Z=4$ to $Z=0.6$). The electronic-polaron mobility in AgBr is compared with the Langreth theory and with earlier results in AgCl [7] and KBr.[11]

Drift mobility measurements were possible over a wide temperature range in selected samples from a zone-refined ingot. Several samples near the center of the ingot had exceptionally long electron lifetimes (20–30 μsec) even at 40°K. The pulsed field, pulsed light apparatus described by Van Heyningen[7] was used to obtain the data. A 3660-Å interference filter was placed in front of the pulsed light source to obtain nearly monochromatic (3.4 eV) radiation on the crystal surface. This radiation is very strongly absorbed

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($K=6\times10^3$ cm^{-1}) and the field direction is such as to move electrons away from the illuminated electrode. A discontinuity in the photocurrent marks the transit to the opposite (blocked) electrode.

III. DISCUSSION OF EXPERIMENTAL RESULTS

The data for two of the best AgBr crystals are shown in Fig. 1. There is considerably more scattering in the data than in the data of Ref. 7. However, repeated measurements indicate that the mobility is reproducible until the crystal has been extensively irradiated at low temperatures. Strong irradiation at low temperature produces a persistent (dark) conductivity, presumably due to shallow trapped or untrapped electrons which do not recombine. This effect has been noted in AgCl also,[13] and the dark current can be removed only by warming above 200°K.

The onset of the persistent conductivity resulted in partial cancellation of the applied field, thus giving the appearance of a lower mobility. However, many measurements at low light intensity may be made before this condition occurs. Static polarization due to deep-trapped charge could be removed with a red light which was kept continuously on the crystal.

IV. SPACE-CHARGE-LIMITED-CURRENT EFFECTS

Measurements at high light levels resulted in the persistent current effects noted above. In Fig. 2, the mobility of a crystal at 100°K, which has been intensely illuminated, is shown as a function of electric field. At very low E fields, the observed mobility is about $\frac{1}{3}$ greater than that of Fig. 1. An oscillogram of the transient photocurrent in this region is shown in Fig. 3(A). An oscillogram at fields above 200 V/cm is shown in Fig. 3(B). We see in Fig. 3(A) that dI/dt is greater than zero; i.e., the current is increasing in time until transit occurs.

An acceleration of the charge sheet and the resulting current-time waveform has been described by Many and Rakavy[20] in terms of transient space-charge-limited current (SCLC). Such effects occur when the carrier charge in the crystal is greater than the charge on the electrodes and hence appear at low E fields and high light levels. In this case, the transit time is shorter than in the case of lower carrier concentrations. The "virtual cathode" accelerates in an increasingly high field as it is pulled away from the illuminated surface. According to the theory of Many,[20] the ratio of the mobility in the case of transient SCLC to the mobility at zero-space charge density μ_0 is given by $\mu_{SCLC}/\mu_0 = 1.27$. At 100°K, we get $\mu_0 \cong 340$ cm^2/V sec from Fig. 1 and $\mu_{SCLC}=450$ cm^2/V sec from Fig. 2. Hence $\mu_{SCLC}/\mu_0 = 1.32$, which is in good agreement with theory.

The step in the μ-versus-E curve at 330 V/cm occurs in crystals which have been subjected to intense prior illumination. This decrease in the mobility seems to be related to the onset of the dark conductivity and is probably due to build up of charge at the blocking layers. An explanation for this behavior is that the dark carriers originate from shallow donors which are field ionized at electric fields in excess of 300 V/cm. The situation then is similar to that of shallow donors in semiconductors.

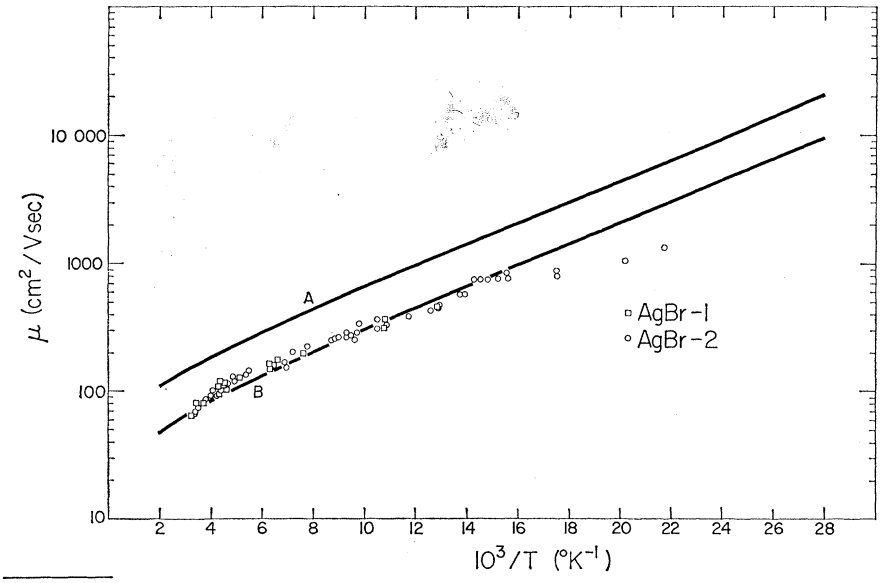

FIG. 1. Electron drift mobility of two crystals of AgBr. Curve A is the mobility predicted by using the measured polaron mass in the Langreth formula. Curve B is the least-squares fit to the data which is explained in the text.

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V. COMPARISON WITH POLARON THEORY

The earlier, low-temperature polaron theories[1–5] predict a temperature dependence of the polaron mobility of the form

$$\mu=\mu_0 e^{\Theta/T} \\ =\mu_0 e^{Z} \quad \text{for} \quad Z\to\infty . \tag{3}$$

However, experimental studies on KBr[11] and AgCl[7] indicate a somewhat weaker temperature dependence. An attempt to fit the data to Eq. (3) resulted in a value of Θ which was lower than the LO Debye temperature determined by other means. Noting this discrepancy, Langreth derived the following result, applicable to the *temperature region* $Z\gtrsim 2$:

$$\mu(Z)=(e/2m_p\omega_l\alpha)(1+1.53/Z)(e^Z-1). \tag{4}$$

This function reduces to the exponential form [Eq. (3)] of Osaka[1] at low temperature (high Z).

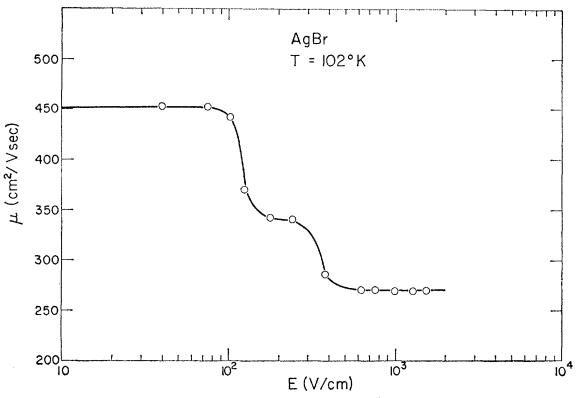

FIG. 2. Variation of electronic drift mobility with electric field for a crystal which has been exposed to intense uv light at low temperatures.

As noted by Van Heyningen,[7] the polaron mobility in AgCl does not vary as $e^{\Theta/T}$ in the range $Z=1$ to $Z=4$. The AgCl mobility could be best described by the function $\exp(225/T)$ for $Z=1$–4, whereas $\Theta=280$°K in AgCl. Thus, there is very little relationship between the actual Debye temperature of the material and the temperature dependence of the mobility in this temperature range.

The same observation was made in analyzing the present data. An attempt was made to fit the new data on AgBr given in Fig. 1 by a function of the form (4). As the parameters of the material such as the dielectric constants and Debye temperature are well known and m_p, the polaron mass, has been recently measured,[18] the only variable in Eq. (4) is α. Actually, one may compute α from Eq. (1) and the approximate expression of Langreth[6]:

$$m_p=m_b(1-0.008\alpha^2)/(1-\tfrac{1}{6}\alpha+0.0034\alpha^2). \tag{5}$$

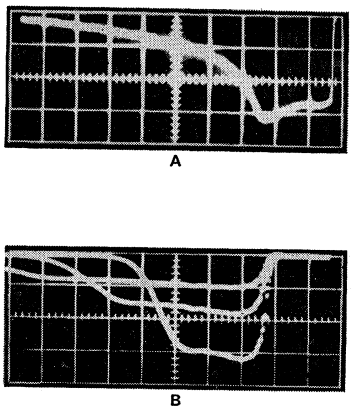

FIG. 3. Photocurrent-time oscillographs for data in Fig. 2. Positive time reads from right to left. (A) $E=100$ V/cm, time scale—5 μsec/cm; (B) $E=250$ V/cm (upper trace), $E=350$ V/cm (middle trace), $E=625$ V/cm (lower trace)—0.5 μsec/cm time scale.

Hence one could calculate the expected mobility directly as all of the parameters in Eq. (4) are known.

The expression (4) is actually more complicated than is apparent here as the parameters m_p, ω_l, α, and Θ are temperature-dependent. This temperature dependence was accounted for by machine fitting of the available data on these parameters, usually with a polynomial expression. For example, the restrahl data of Jones *et al.*[21] on AgBr are given fairly well by the following expression in units of 10^{12} sec^{-1}:

$$\omega_0(T)=1.74-0.72\times10^{-4}T-0.237\times10^{-5}T^2 \tag{6}$$

(T in °K). Likewise, the dielectric constant data of Lowndes[22] may be fitted by a quadratic polynomial. The LO frequency is then given by the Lyddane-Sachs-Teller (LST) relationship[23]:

$$\omega_l(T)=\omega_0(T)[\epsilon_s(T)/\epsilon_\infty]^{1/2}. \tag{7}$$

With this information, $\alpha(T)$ may be calculated from Eq. (1) and $m_p(T)$ from Eq. (5) knowing the polaron mass at 4°K from the resonance data.

Proceeding in this way, we calculate the theoretical mobility curve A which is plotted in Fig. 1. We see that the predicted mobility is about twice that which is measured here. However, the *temperature dependence* of the theory and experiment seem to agree fairly well.

The only way to appreciably change the magnitude of the mobility in Eq. (4) at any given temperature is to change the polaron mass. As there is definitely a discrepancy involving the experimental results, i.e., polaron mass and polaron mobility and the theory,[6] let us determine what polaron mass would be required to fit our data using the expression in (4).

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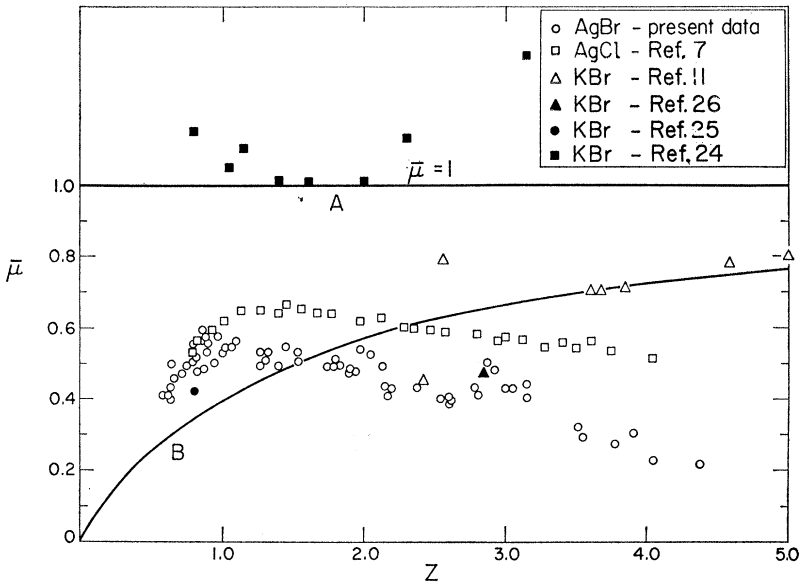

FIG. 4. $\bar{\mu}$ versus Z for AgBr, AgCl, and KBr.

Actually, knowledge of any one of the quantities m_b, m_p, and α, gives the other two through expressions (1) and (7) as has been discussed. In practice, it is easier to vary m_b, and then calculate $m_p(T)$, $\alpha(T)$, and $\mu(Z)$ through the expressions (7), (1), and (4), respectively. A computer program was written to vary m_b such that the sum of least squares was minimized. The resulting expression for the mobility is given by curve B. However as is shown in Table I, the theory gives an incorrect value of the polaron mass.

The *temperature dependence* of the measured mobility agrees quite well with the Langreth theory,[6] however, as is seen in Fig. 1. There are discrepancies at low temperatures ($T<55$°K), where other scattering mechanisms or multiple trapping may become effective. Also, at high temperatures ($T>250$°K, $Z<1$), there is a noticeable difference in the slope of the μ-versus-T data and the theoretical curve A but the theory is not expected to apply in this region. Thus, the principal discrepancy between experiment and theory is the magnitude of the mobility as evidenced by curves A and B of Fig. 1.

To amplify the comparison with theory, let us define a new dimensionless variable for comparison with the Langreth theory:

$$\bar{\mu}(Z)=\mu_{\text{expt}}(Z)/\mu_{\text{theoret}}(Z). \tag{8}$$

Here $\mu_{\text{theoret}}(Z)$ is given by Eq. (4) using the measured polaron mass of Ref. 18. In practice then, $\bar{\mu}$ is determined by computing $\mu_{\text{theoret}}(Z_1)$ for each experimental point (μ_1,Z_1) and dividing the latter by the former. As all of the parameters characteristic of the material have been removed, absolute comparisons can be made with other materials.

In Fig. 4, the present data, along with prior data on AgCl [7] and KBr,[11,24–26] have been plotted. In these two latter cases, polaron mass data[18] are also available so that absolute comparisons may be made. The magnitude and Z dependence of $\bar{\mu}$ for AgCl and AgBr are seen to be very similar. We may ignore $\mu(Z)$ for $Z<2$, as the theory is not expected to apply.

We find $\bar{\mu}(Z)$ to be fairly constant (about 0.5–0.6), at least over the range where the other mechanisms mentioned above do not influence the transport of polarons.

On the same plot, an exponential expression (e^Z-1) is plotted for comparison. The Z dependence of μ for both AgCl and AgBr is in radical disagreement with low-temperature theory and is certainly more consistent with Eq. (4). However, there is a magnitude discrepancy [$\mu(Z)$ should equal unity for all materials] which is not understood.

There is a great deal of scatter in the KBr data. The data of Refs. 11, 25, and 26 are in quantitative agreement and again would indicate mobilities lower than

TABLE I. Mass parameters characteristic of AgBr.

	m_p	m_b	α
Mobility fit	0.577 (low temp.)	0.382	2.13 (low temp.)
Other data	0.33[a]	0.241[b]	1.69[b]

[a] Measured by cyclotron resonance in Ref. 18.
[b] Calculated from Eqs. (1) and (5) using the data of Ref. 18.

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those predicted by theory. The data of Ref. 24 are in fair agreement with $\bar{\mu}=1$, but the experimental method precludes certainty in absolute values to within about a factor of two.[27]

VI. DISCUSSION OF RESULTS

The high-temperature mobility theory[6] describes the temperature dependence of the electronic polaron in AgBr fairly successfully (for $Z>1$) but the predicated magnitude is too high by a factor of two. Comparison of theory with the data of Van Heyningen[7] indicates a very similar result. In both of these cases, the mobility is measured by a drift technique. The Hall mobility may be as much as 25% higher than the drift mobility for optical-mode scattering in the range $Z=2$ to 3.[28] As the carrier lifetime in the alkali halides is extremely short, all of the data on KBr were obtained by the Hall effect. Hence, the KBr normalized mobility $\bar{\mu}$ is expected to be somewhat larger than the silver-halide drift data.

Other characteristics of the materials might affect the measurements of either mass or mobility. For example, in the alkali-halide measurements, the electrons are released from F centers and therefore holes are not present in the crystals. On the other hand, electron-hole pairs were created by band-gap irradiation in all the measurements on the silver halides. However, it is doubtful that holes influenced the transport measurements. Recent measurements[14] of hole transport in AgBr indicate that the hole polaron is considerably heavier than the electronic polaron and therefore would not be likely to influence the cyclotron resonance spectrum.

Space charge effects and trapping always add uncertainty to transport data in these materials as the trap densities are very high. However, the new drift data on AgBr and the previous AgCl measurements show no indication of trap-limited transport at the higher temperatures ($Z<2$). Partial cancellation of the internal field, due to the unknown build up of dark conductivity, may account for a systematic error in the drift measurements. However, if the description used to discuss Fig. 2 is accurate, such effects do not occur except at high fields. The close agreement of $\bar{\mu}(Z)$ for the three cases discussed (AgBr, AgCl, KBr) indicates that the theory may seriously underestimate the strength of the interaction although improving somewhat the formulation of the temperature dependence.

The weak-temperature dependence of $\bar{\mu}(Z)$ for AgCl and AgBr is easily accounted for. The theory[6] is an approximation and higher-order terms in Z are neglected. Also, the material parameters are subject to some uncertainty. Reflectance measurements[29] at 290°K on AgBr and AgCl in which ω_l is directly measured indicate a discrepancy of about 5% in the LST[23] relationship. The approximation of a single lattice frequency may also cause significant error, as pointed out in Ref. 13. According to Bottger and Geddes,[29] the half-width of the LO absorption in AgCl and AgBr is about 40 cm^{-1}.

VII. CONCLUSION

The Langreth mobility theory is quite successful in predicting the temperature dependence of the polaron mobility at high temperatures $1<Z<4$. However, the magnitude of the predicted mobility seems to be about two times larger than indicated by data on AgCl and AgBr. Data presented on the mobility in AgBr are in excellent agreement with published AgCl data when presented in normalized form.

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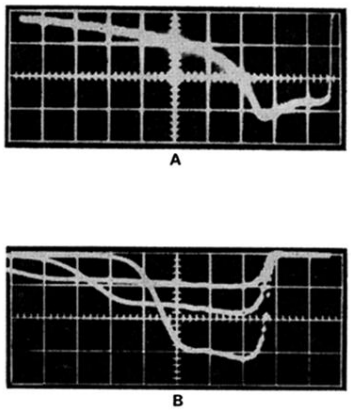

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