Lifetime and Drift Mobility of Holes in AgBr

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(Received 17 June 1965; revised manuscript received 12 November 1965)

Holes with free lifetimes greater than 50 μsec have been found in silver bromide at temperatures above 200°K. The long hole lifetimes are observed only in strained pure crystals, apparently because of the precipitation on dislocations of point defects which are traps for holes. The drift mobility follows an approximately T^{-2} temperature dependence from 300 to 250°K before falling off because of multiple trapping of the holes by a low density ($\sim 10^9$ cm^{-3}) of large-cross-section ($\sim 10^{-10}$ cm^2) hole traps. The data suggest intermediate coupling of the hole to the lattice, and a hole polaron mass greater than that of the electron. The relevance of polaron theory to the present results is unclear because of possible high-temperature effects not included in the theory.

I. INTRODUCTION

INVESTIGATORS have found that electron photoconductivity is readily observable in the silver halides,[1–4] but attempts to observe photocurrents directly attributable to holes have not been successful.[2,3,5] The absence of observable hole photocurrents appears to be a consequence of the very short lifetime of holes in the samples that were used, of the order of 10^{-8} sec or less. The motion of photo-excited holes in AgBr has been clearly demonstrated, however, in experiments involving the bleaching of silver by holes displaced in strong electric fields.[6–8] These experiments showed that the holes could have an appreciable lifetime at room temperature, and that they have a drift mobility at room temperature of about 1 cm^2/V sec, in agreement with measurements of the Hall mobility of holes injected into AgBr by contact with halogen gas.[9]

In this work, techniques were found for increasing free-hole lifetimes to values of several hundred microseconds at temperatures above 220°K. Transit-time measurements were thus possible, from which the drift mobility of holes was determined in the temperature range 220 to 310°K.

II. EXPERIMENTAL

Samples

The crystals were grown from starting material of very high purity, which was zone-refined[10] in a bromine atmosphere prior to the final growth cycle. Eighty

zones were passed through the ingot at the rate of 0.6 in./h. A spectrochemical analysis indicated that the heavy-metal impurities, with the exception of iron, were undetectable except in regions near the end of the ingot and therefore that the concentration of these impurities was less than the detection limit of 0.01 ppm. Iron was detected in concentrations less than 0.07 ppm. Ionic-conductivity measurements further indicated that the concentration of charged impurities was very small.

Samples 2 mm thick were cut from the ingot with a high-speed saw, after which about 0.5 mm of material was taken from each surface by using successively finer mechanical abrasives. After thorough rinsing with distilled water, the crystal was etched down to a thickness of 0.2 to 0.5 mm with a KCN solution. This was followed by another rinse in distilled water and a quick etch in high-purity, concentrated HCl.

Apparatus

The measurements were carried out on an apparatus similar to that described previously for measuring the drift mobility of electrons.[11] A wide-band preamplifier in series with the crystal was used to measure the photocurrent, and a transient, produced by the application of a large voltage pulse, was bucked out by means of a difference amplifier arrangement. The pulsed electric field is required in order to avoid the relaxation of the internal electric field due to the collection of ions at blocked electrodes. An air spark of 0.1-μsec duration, filtered with a Corning 5860 ultraviolet filter, was delayed about 20 μsec from the beginning of the voltage pulse. This radiation is strongly absorbed at the incident surface, creating a sheet of free electrons and holes. Depending upon the polarity of the applied voltage, either electrons or holes are pulled into the volume, while the opposite carrier is held at the surface on which the light is incident. A discontinuity in the photocurrent marks the transit of a carrier to the other blocked electrode.

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III. RESULTS

Hole Lifetime

Crystals which were prepared in the manner previously described contain an appreciable density of dislocations due to the method of growth and sample preparation. Immediately after preparation, they usually showed little photoresponse with the applied field in the "hole polarity." However, if the crystals were allowed to remain in the dark at room temperature for several hundred hours, a large hole-photoresponse was observed. Hole lifetimes at room temperature in excess of 50 μsec were seen in almost all pure samples treated in this manner, as illustrated in Fig. 1(a). The fast electron response, measured with the electric field reversed, is shown in Fig. 1(b), to illustrate the strikingly different trapping properties of the crystal for the two carriers. A slight amount of cold work again reduces the hole response, but it gradually recovers after an extended period of time. Crystals which were severely deformed (10% compression), however, never again showed a measurable hole photoresponse.

If a sample with a long hole lifetime is annealed for several minutes at temperatures about 150°C, the hole response is greatly reduced. The lifetime drops to the order of microseconds, decreasing with increasing annealing temperature, indicating that a higher density of hole traps has been generated by the process. However, the initial photoresponse is again restored after the sample has remained at room temperature for more than 100 h. If a crystal is subjected to a high-temperature annealing (400°C) near the melting point, the hole response disappears and is never observed to recover.

Since a prolonged room-temperature annealing was effective in increasing the hole lifetime, attempts were made to hasten the process by annealing at tempera-
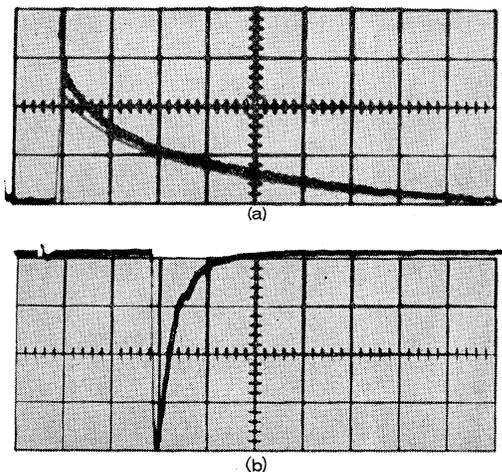
FIG. 1. (a) Hole photocurrents in AgBr at $T=295°$K, sweep 5 μsec/cm; (b) electron photocurrents at the same temperature, sweep 1 μsec/cm.
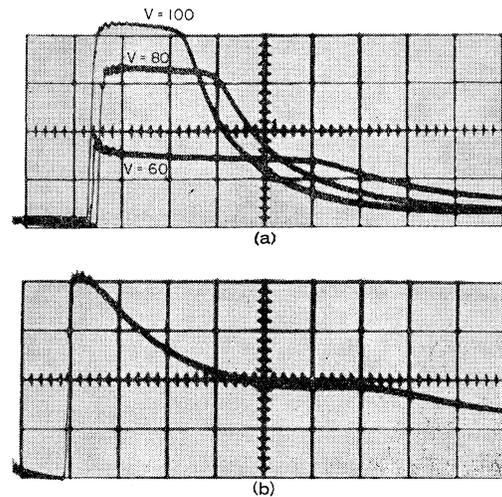
FIG. 2. (a) Transit of holes with various applied voltages at $T=267°$K, sweep 2 μsec/cm; (b) hole transit at $T=230.6°$K where multiple trapping is prevalent, sweep 5 μsec/cm.

tures above room temperature, but lower than 150°C, where the response was adversely affected. No significant increase in rate was observed.

Long hole lifetimes were found only in relatively pure crystals. Samples in which gold and copper had been added to concentrations in excess of several parts per million never exhibited a measurable hole photoresponse. Relatively pure material, which contained oxygen as a result of growth in air, did exhibit hole photoresponse, but generally there were indications of multiple trapping at room temperature. All reliable drift-mobility measurements were obtained with the zone-refined crystals.

It is known that dislocations act as electron traps in the silver halides[12] and that annealing near the melting point decreases the dislocation density and enhances the electron response.[2] In the strained samples used in this work, the electron lifetime was short, as found by other investigators (Fig. 2). Although the hole lifetime was greater than 50 μsec when holes alone were swept into the crystal, a different result occurred with volume illumination. Here the response appeared to be limited by a second-order recombination between electrons and holes released in the volume. The results are consistent with fast trapping of electrons at imperfections, followed by capture of the holes at the sites of the trapped electrons. In the case of strongly absorbed light, the holes were swept into the volume, while the electrons were held at the illuminated surface, so that appreciable recombination could not occur.

Drift Mobility

With such long hole lifetimes, one could very easily observe the transit of a sheet of holes across a thin

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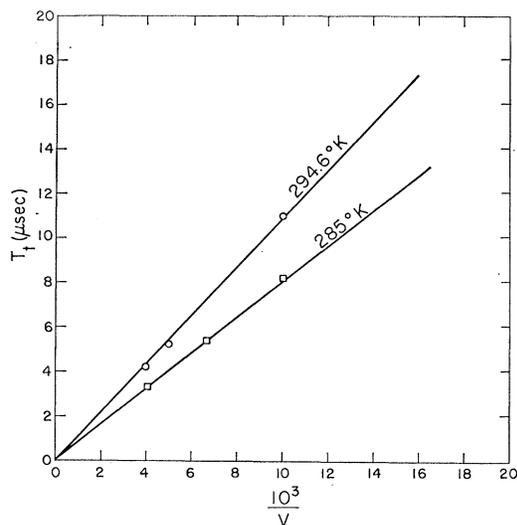
FIG. 3. Transit time of holes versus reciprocal voltage at two different temperatures.

crystal of silver bromide. In Fig. 2(a), the hole photocurrent versus time wave form, obtained with several values of applied voltage, is shown.

By using the relation

$$\mu_d = d^2/VT_t, \qquad (1)$$

where d is the crystal thickness, V is the applied voltage, and T_t is the transit time, the drift mobility may be calculated.

At a given temperature, the transit time was found to vary linearly with $1/V$. A typical plot of T_t versus $1/V$ is shown in Fig. 3. To increase the accuracy of the measurements, at least three values of applied voltage were used, and a plot of this type, the slope of which is proportional to μ_d^{-1}, was made for every mobility determination. Primarily because of the difficulty in defining the transit time, the uncertainty in the absolute values of the mobility is about 10%. The transit time was taken to be the time between the beginning of the current rise and the beginning of the current fall. The rise time of the current is just the duration of the spark excitation. However, a much longer current decay after transit was observed and was probably due to spreading of the charge sheet due to diffusion and space-charge effects. The same effect has been observed for electrons.[11]

At temperatures near 250°K, the character of the photoresponse was observed to change in most of these crystals. Evidence of multiple trapping became apparent as the transit became less distinct and very long "tails" were seen to develop on the wave forms. Also, the transit time began to increase, which is consistent with the carriers spending appreciable time in traps. A photocurrent versus time wave form in this temperature range is shown in Fig. 2(b).

Figure 4 shows a plot of drift mobility against reciprocal temperature for several different crystals from the zone-refined ingot. The reproducibility of the data at temperatures above 250°K was quite good and the values of mobility found in the different crystals were quite consistent. The mobility below 250°K was found to be trap limited.

All the measurements in Fig. 4 were made in the [111] crystallographic direction, as the crystals were cut from the ingot with faces perpendicular to the [111] direction. However, some later measurements made on crystals with other crystallographic orientations produced the same mobility values in the intrinsic-temperature region. Hence, the mobility was isotropic, at least within the limits of experimental error.

The upper temperature limit on the measurements was about 310°K. At higher temperatures, the transit times became comparable to the field relaxation time, owing to the rapidly increasing ionic conductivity. At temperatures below about 220°K, transit was very difficult to observe because of the very strong trapping effects.

IV. DISCUSSION OF RESULTS

Hole Lifetime

The results of annealing experiments indicate that dislocations do not necessarily degrade the hole photoresponse at room temperature but, in fact, appear to be related to large increases in the hole lifetime. A mechanism which might explain this behavior is the precipitation of hole traps on charged dislocations.

There has been considerable experimental[13–16] and theoretical[17,18] interest in the problem of charged dislocations in ionic crystals. The evidence indicates that charged dislocations exist in these materials and charge compensation occurs by means of a cloud of charged point defects which screen the dislocation. Very pronounced effects upon the mechanical properties of strained crystals are produced by the addition of divalent cations owing to changes in the charge distributions on and about the dislocations.

Recent spin resonance experiments[19] on the Cu^{2+} center in AgCl have shown that the resonance signal disappears with a time constant of about 20 h after the crystal has been strained. The loss in resonance signal is accompanied by a major change in the optical absorption spectrum of the Cu^{2+} impurity. These effects are clearly a result of precipitation of Cu^{2+} ions

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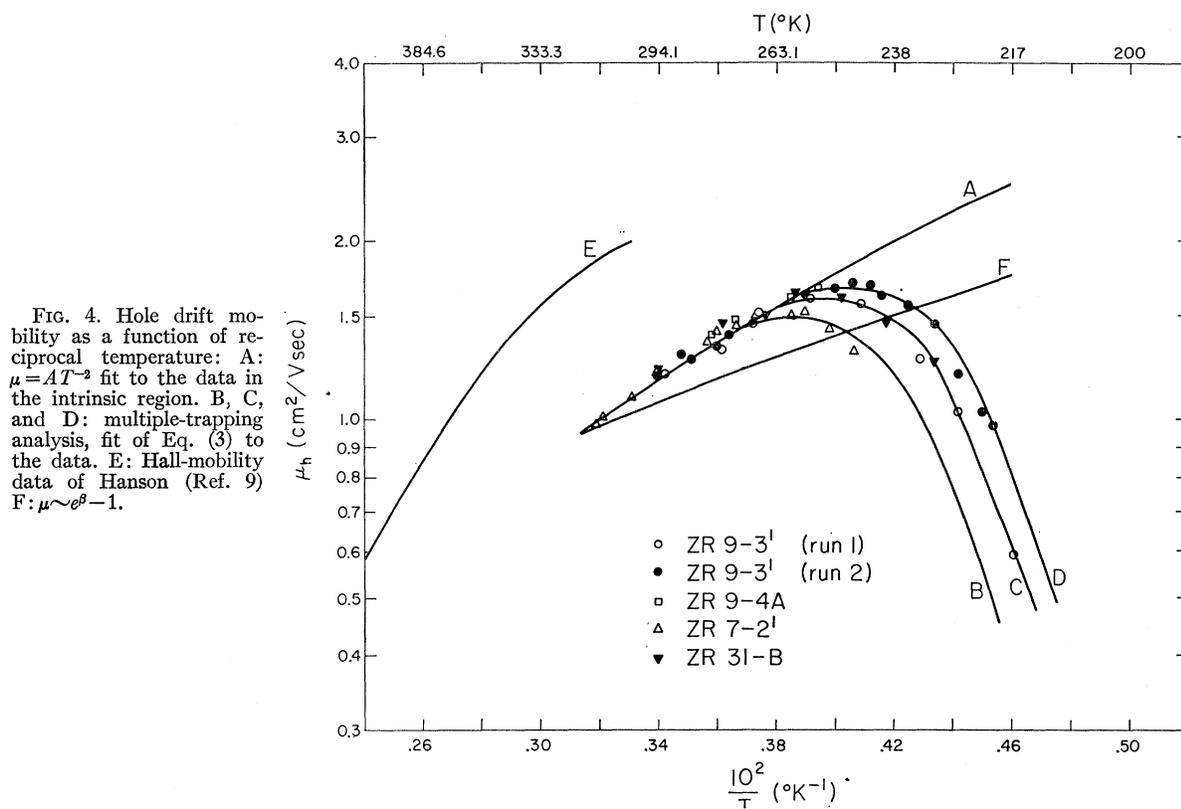
FIG. 4. Hole drift mobility as a function of reciprocal temperature: A: $\mu = AT^{-2}$ fit to the data in the intrinsic region. B, C, and D: multiple-trapping analysis, fit of Eq. (3) to the data. E: Hall-mobility data of Hanson (Ref. 9) F: $\mu \sim e^{\beta} - 1$.

caused by the strain. A pulse anneal above 130°C, such as that described above, temporarily restores the resonance signal produced by redispersal of the Cu^{2+} centers, but the signal decays again with a similar time constant. A stable signal may be achieved only after a careful high-temperature annealing which removes most of the strain. Similar statements hold for the optical absorption.

By comparison, the enhancement of the hole lifetime due to the presence of dislocations may be explained by the precipitation of point defects, which are hole traps, on the dislocations, or as charge clouds about them. These defects, which are effective hole traps when dispersed in the lattice, may become relatively ineffective as traps when localized and partly charge-compensated in the region of a dislocation. The pulse-annealing treatment may thermally excite point defects out of the configuration and temporarily disperse them in the lattice, with a corresponding temporary reduction in hole lifetime. A conventional, high-temperature annealing changes the dislocation networks and reduces the dislocation density to such an extent that permanent dispersal of the traps occurs and the hole response is permanently lost. Similarly, plastic deformation may break up charge cloud dislocation complexes, with a resulting dispersal of point defects. Gross deformation would conceivably create such a great disorder that it would itself be responsible for hole trapping.

No center has been identified as the trap responsible

for the prevalent hole-trapping effects in this material. It is reasonable to suspect an "intrinsic" defect such as a cation vacancy, or an impurity such as a doubly charged anion. However, it seems clear at this point that self-trapping such as occurs in the alkali halides (V_k center) does not occur in this material above 200°K.

Microscopic Mobility

In the temperature range above 250°K, the data in Fig. 4 show a mobility which decreases with increasing temperature and which is reproducible in different samples. This suggests an intrinsic phenomenon such as lattice scattering of the holes. Curve A is a best fit to the data in this temperature range, which shows on a log-log plot to be very nearly $\mu \propto T^{-2}$. For use in analyzing the effects of trapping at lower temperatures, curve A is extrapolated by assuming that this power law holds. Curve E shows the Hall-mobility data of Hanson.[9] The magnitude of the Hall mobility is seen to be about a factor of 2 larger in the narrow region of overlap with the drift-mobility data, but the slopes of curves A and E in this region are about the same.

In AgBr, one expects the holes to be fairly strongly coupled to the longitudinal optical (LO) modes of lattice vibration, as appears to be the case for electrons[11] which have a mobility more than an order of magnitude greater in this temperature range.[20] Assuming that the

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difference between the electron and hole mobility is largely a consequence of a mass difference, the hole mass must be the larger of the two. A larger mass implies a stronger coupling of the hole with the lattice, as may be seen from the Fröhlich coupling constant[21]

$$\alpha = \frac{e^2}{\hbar}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}\right)\left(\frac{m}{2\hbar\omega_l}\right)^{1/2}, \qquad (2)$$

where m is the band effective mass, ϵ_∞ and ϵ_s are the high-frequency and static dielectric constants, respectively, and ω_l is the LO mode frequency. The mass m^* of the polaron,[22] which is the carrier with which we must deal, is an increasing function of the coupling constant α, and thus depends on the nature of the energy bands and the coupling of the carrier to the polar lattice.

For purposes of comparison, the electron polaron mass in AgBr has been determined by cyclotron resonance[23] to be $m_n^* = 0.27m_e$, where m_e is the free-electron mass, and the coupling constant α_n to be about 2.0. Thus with even larger m_p^* and α_p for holes indicated by the present experiments, the hole problem appears to be well in the range of intermediate coupling, $2 < \alpha < 6$. The polaron mobility in this range of coupling has been investigated theoretically by a number of workers[22,24–29] who, with the exception of FHIP,[26] worked in the limit of very low temperatures ($T \ll \theta$, where θ is the LO mode temperature defined by $k\theta = \hbar\omega_l$). The mobility at finite temperatures has been calculated also for the weak-coupling case ($\alpha \ll 1$) by perturbation theory,[30] and a "hybrid" theory[31] has been formulated in the weak-coupling limit, with incorporation of strong-coupling effects by substitution of the Yokota polaron mass[32] for the band effective mass. [This latter work[31] includes the effects of magnetic fields. The Hall mobility was found to be as much as 25% greater than the microscopic mobility at certain temperatures because of dispersive (inelastic) scattering events.]

The present data fall into the theoretically difficult range of intermediate coupling and temperatures, for which the FHIP theory is formally the most appropriate. Unfortunately, under these conditions the FHIP mobility is not expressible in analytic form, and the actual dependence of μ on both T and α can be obtained only by laborious numerical calculations involving a variational fit of the Schultz-Feynman parameters[33] to the polaron free energy. The effort involved in attempting a detailed comparison with the FHIP theory does not appear to be warranted at the present time because of the limited temperature range of the available data. This is particularly true in view of possible other complications, not directly dependent upon polaron effects.

The FHIP theory indicates an increasingly stronger functional dependence of μ on α as α increases, e.g., in the low-temperature limit $\mu \sim \alpha^{-1}$ for $\alpha \ll 1$, and $\mu \sim \alpha^{-7}e^{\alpha^2}$ for $\alpha \gg 1$. Thus, if this general behavior persists to higher temperatures, the mobility could be quite sensitive to changes in α with temperature. A variation of α with temperature does occur[11] because of temperature-dependent changes in ϵ_s[34] and ω_l[35,36] and in addition the band mass m may be temperature-dependent. Again, the temperature dependence of the mobility, particularly at higher temperatures, could be affected by "inter-hill" scattering (the analog of inter-valley scattering[37]) in the complicated multi-hilled valence band of AgBr.[38] The scattering would then be more complicated than the optical mode scattering considered in the theory, and would result in a stronger dependence of the mobility on the temperature than is that theoretically predicted. Such effects have recently been seen in germanium.[39]

In the low-temperature limit, the polaron mobility should vary inversely as the density of LO phonons, i.e., $\mu \sim e^\beta - 1$, where $\beta = \hbar\omega_l/kT$. At higher temperatures, as the carrier decouples from the lattice one would expect an over-all temperature dependence that is weaker than this. Although the $e^\beta - 1$ dependence does not apply in the temperature range of the data, it is plotted as curve F in Fig. 4 for purposes of comparison. It is seen that the experimentally observed temperature dependence is appreciably stronger than $e^\beta - 1$ for both the present drift-mobility data and the Hall-mobility data at higher temperatures. This may be taken as support for the conjecture that the real situation is more complicated than the one considered in the theory. However, without explicit evaluation of the FHIP expression, it is not possible to assess the actual importance of nonpolar scattering. It is thought

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that the data should be extended over a broader tem-
perature range with samples in which trapping is under
better control before such an analysis is attempted.

The large discrepancy in magnitude between the
Hall- and the drift-mobility data is not completely
understood. However, the error limits in the Hall
mobility were fairly large. For example, the Hall
mobility at 300°K is given as 2.0 ± 0.5 cm²/V sec,
whereas the drift measurements give 1.20 ± 0.10 cm²/V
sec. The uncertainties do not quite overlap, but the
Hall mobility is predicted to be larger in this tempera-
ture region.[31]

Multiple Trapping

In Fig. 4 (curves B, C, and D), a drop in the mobility,
which occurs at different temperatures for different
crystals, is seen to occur at low temperatures. In the
same temperature region, the hole photocurrent-time
response changes, as seen in Fig. 2(b), to a response
quite indicative of multiple trapping.

The drift mobility in the presence of multiple
trapping at a single trapping level is given by[40]

$$\mu_d = \frac{\mu_c}{1+(g_1/g_0)(N_t/N_c)\exp E/kT}. \qquad (3)$$

Here μ_c is the miscroscopic mobility; N_t is the trap
density; E is the trap depth; N_c is the effective density
of states in the valence band; and g_1 and g_0 are the
statistical weights of full and empty traps, respectively.

By using curve A of Fig. 4 for μ_c, the low-temperature
mobility for several crystals may be fit by this ex-
pression by choosing a trap depth of 0.44 eV and

different trap densities N_t, as indicated by curves B,
C, and D. The factor g_1/g_0 was taken to be 2, and in
calculating N_c, m_h^* was taken to be one electron mass.
For crystal ZR 7-2', $N_t=3.04\times10^9$/cm³ (curve B), but
for ZR 31-B and ZR 9-3', N_t was chosen to be 1.54×10^9/
cm³ (curve C). A second measurement of crystal
ZR 9-3', obtained several weeks after the first measure-
ment, indicated a lower trap density than found previ-
ously. The low-temperature mobility had shifted from
curve E to curve D, and N_t found for curve D was
1.05×10^9/cm³. This result is consistent with a model
of hole traps precipitating on dislocations which was
discussed in the last section.

Thus, the drift mobility at lower temperatures is
controlled by a relatively small trap concentration
(10^9/cm³) and the trapping cross section would be
expected to be quite large. By using the expression

$$\sigma = 1/N_t\tau_t v, \qquad (4)$$

where τ_t is the trapping lifetime and v is the hole
thermal velocity, one may calculate the trap cross
section σ. Using $N_t=10^9$/cm³, $v=5\times10^6$ cm/sec, and
$\tau_t=1$ μsec, we find $\sigma=2\times10^{-10}$ cm². Such large cross
sections have been found recently for α centers in the
alkali halides[41] and may be representative of traps in
these very polar lattices. The identity of the centers
responsible for this trapping is unknown but one would
expect it to be a charge defect.

ACKNOWLEDGMENTS

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