Ac Hall and Magnetostrictive Effects in Photoconducting Alkali Halides

J. Ross Macdonald* and John E. Robinson
Chemistry Division, Argonne National Laboratory, Lemont, Illinois

(Received November 16, 1953; revised version received March 15, 1954)

This paper reports the results of room-temperature measurements of the Hall and magnetoresistive effects for single-crystal potassium bromide containing a low concentration of F centers. Measurements were carried out with strong steady illumination in the F-absorption band by means of a new ac technique which avoids space-charge polarization effects. The current carriers were found to be negative in sign with a Hall mobility of 12.5 cm^2/volt-sec and are undoubtedly electrons photoexcited from F centers. Their maximum concentration was of the order of 10^{10} cm^{-3}. The mobility was found to be substantially independent of light intensity and signal frequency over the limited ranges investigated. Transverse magnetoresistive effects of both positive and negative sign were also observed. Finally, a phenomenological discussion of the experimental results is given.

I. INTRODUCTION

MEASUREMENT of the mobility of charge carriers in photoconductors by means of the Hall effect presents difficulties not encountered in similar measurements on metals and most semiconductors. These difficulties arise from the high impedance level of the photoconducting material and from the fact that it is not always possible to employ ohmic current electrodes with such materials. When the electrodes are not ohmic, space-charge effects within the photoconductor may so distort the electric field that most of the potential drop takes place near the electrodes. In the region between the Hall electrodes, halfway between the current electrodes, the electric field will then be very small and little Hall effect will be observed.

Using an electrometer, Lenz[1] has observed the Hall effect in photoconducting diamond and zinc sulfide. His measurements were greatly simplified by the fact that substantially ohmic electrodes could be employed. Evans[2] has attempted without success to measure the Hall effect in photoconducting alkali halide single crystals containing F centers. Using about 500 volts dc applied to crystals about 7 mm long and containing about $5\times10^{16}/cm^3$ F centers, and a magnetic field of 12 200 oersteds, he was unable to observe any appreciable effect with either a steady or a pulsed light source. Since few, if any, electrons can pass from metal electrodes into the conduction band in alkali halides at room temperature because of the potential hill between the conduction band levels and the Fermi energy in the metal,[3] large space-charge effects are observed when a dc voltage is applied to an illuminated crystal. By using 0.1-sec flashes of light, Evans hoped to measure the Hall effect before this space-charge distribution could be set up. However, as one of us has shown elsewhere,[4] with strong illumination the space-charge distribution can usually be established in less than 0.01 sec; thus, Evans' negative results are not surprising.

In the present work it was decided to make Hall and magnetorestistive measurements using a steady light source and ac rather than dc electric fields. Measurements of the photocapacitative effect on KBr single crystals[4] interpreted by means of a theory of space-charge polarization[5] had shown that space-charge effects were negligible in strongly illuminated crystals above 50 to 500 cps. The use of ac also largely eliminates undesired thermoelectric and galvanomagnetic effects present in a dc method of measurement.

The impedance level for illuminated crystals of convenient size was found to be between 10 and 100 megohms. A further decrease in impedance level by means of an increase in light intensity was not practical because of the appearance of heating and bleaching of the crystals with stronger light intensity. Therefore, in order to obtain meaningful measurements of the mobility in these crystals, an ac Hall voltage detector having an input impedance considerably greater than 100 megohms to above 10^3 cps was necessary. The principal limitation on input impedance is imposed at these frequencies by input capacitance between Hall leads. At 10^3 cps, one $\mu\mu$f has a reactance of only about 160 megohms, so that the input capacitance had to be reduced below even this value. The requirement of exceedingly low input capacitance together with variable frequency operation make the 24-cps Hall apparatus described by Pell and Sproull[6] unsuitable for the present application. We shall consider first the experimental techniques and results of the present investigation, then the theoretical interpretation and implications of these results.

II. SPECIMENS, APPARATUS, AND METHOD OF MEASUREMENT

Most of the crystals used in this work were KBr obtained from the Harshaw Chemical Company. They

* Then on leave to Argonne National Laboratory from Armour Research Foundation. Now at Texas Instruments, Inc., 6000 Lemmon Avenue, Dallas.

[1] H. Lenz, Ann. Physik **77**, 449 (1925); **82**, 775 (1927).

[2] J. Evans, Phys. Rev. **57**, 47 (1940). Further references to the older literature are given in this paper.

[3] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1948), second edition, p. 169.

[4] J. R. Macdonald, Phys. Rev. **85**, 381 (1952); **90**, 364 (1953).

[5] J. R. Macdonald, Phys. Rev. **92**, 4 (1953).

[6] E. M. Pell and R. L. Sproull, Rev. Sci. Instr. **23**, 548 (1952).

were either additively colored with sodium or U centered,[7] then irradiated with Co^{60} gamma rays to produce a uniform distribution of F centers. In both cases, the concentration of F centers employed was not greater than $10^{16}/cm^3$. Most of the significant measurements were obtained on initially U centered crystals because, as discussed later, bleaching was much slower for such crystals than for additively-colored crystals and the impedance level for equal light intensity was about a factor of ten lower for the former. Current electrodes were formed by painting air-drying silver paint on the crystals. For Hall and magnetoresistance measurements, the crystals were supported on a polystyrene slab containing movable copper tabs which could be advanced to make firm pressure contact to the current electrodes. In order to reduce the Hall voltage impedance level as much as possible, knife edge rather than point Hall electrodes were employed. These line electrodes were parallel to the magnetic field and extended across the thickness[8] dimension of the crystals. Note than in an ac measurement, small errors in positioning the line Hall electrodes exactly perpendicular to the longitudinal electric field will cause no first-order effect on the measured Hall voltage. One of these electrodes was embedded in the polystyrene with only about 0.2 mm projecting above the surface. The other electrode was supported by means of a movable polystyrene framework exactly above and parallel to the bottom electrode. Both electrodes were of phosphor bronze. A crystal for measurement was positioned so that the Hall electrodes were midway between the current electrodes, then the top frame was screwed down tightly enough that the top and bottom knife edges left small scratches across the thickness of the crystal.

The magnetic field employed in these measurements was supplied by an electromagnet operated from storage batteries bridged across a selenium rectifier. Pole faces were 4 in. in diameter, separated by 2 in. The maximum field obtainable was about 10^4 oersteds. The field was calibrated *vs* magnet current to better than ± 1 percent using a fluxmeter. For the maximum field strength the field direction could be reversed in about 20 sec.

Light in the F-absorption band of the crystals was supplied by a 750-watt slide projector. The entire light output was focused on an area of about 14 cm^2 containing the crystal to be illuminated. A glass heat filter[9] was usually used in the measurements and the light intensity in the F band could be further reduced when desirable by means of accurately calibrated, perforated metal filters. When the projector was operated from the ac line, undesirable 120–cps modulation was found to be present which made Hall measurements difficult. Therefore, the projector was supplied from a 120-volt storage battery bank.

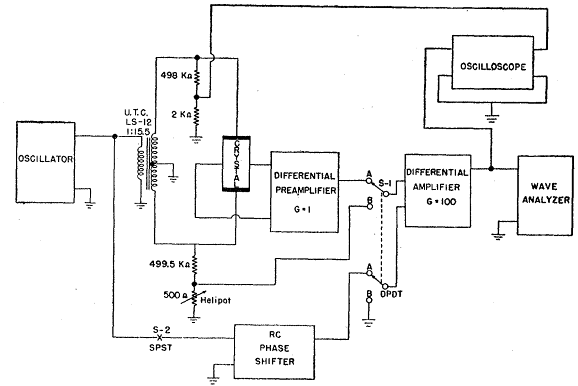

FIG. 1. Circuit diagram for Hall effect measurements.

Since it is, in general, impossible to position the Hall electrodes of a high impedance sample exactly on an equipotential line, some means is necessary for balancing out the resulting residual signal which is almost always greater than the desired Hall signal. The block diagram of the Hall apparatus with which such balancing was accomplished is shown in Fig. 1.[10] It was desired not to have to rely on the constancy of the gain of amplifiers in the circuit or of the calibration of the output meter in these measurements; therefore the circuit is arranged so that a quantity proportional to the Hall voltage ratio V_H/V_0 may be read directly on a helipot dial. Here V_H is the Hall voltage and V_0 the applied voltage across the current electrodes. The oscillator drives a step-up transformer whose output is applied push-pull to the crystal. The voltage at the Hall electrodes is applied to the very-high-input-impedance differential preamplifier. This preamplifier employs an input circuit which has already been described[11] and has a gain of unity heavily stabilized by negative feedback. Through the use of an active feedback path, it has an in-phase rejection ratio exceeding 10^3 over the frequency range of interest. The input leads of the preamplifier are double-shielded and the inner shields driven in phase with the input voltage as described previously.[11] The capacitance to ground at the input to either of the shielded leads is about 0.2 $\mu\mu$f to above 50 kcps, and the input resistance is above 4×10^9 ohms below 4700 cps. The shields of the Hall leads are extended to within 1 mm of the Hall electrodes to which the shielded center conductor is soldered.

The single-phase output of the preamplifier is applied to one of the inputs of a Textronix differential amplifier of gain 100. The other amplifier input is connected to the output of an RC phase shifter. This phase shifter has coarse and fine adjustment for both output amplitude and phase, and by a means of switched capacitances

[7] Reference 3, p. 147.

[8] By definition, the length, L, of the crystal is the separation between current electrodes, the width, W, the separation between Hall electrodes, and the thickness, T, the remaining dimension.

[9] Corning, number 3961 or 3962.

[10] All leads shown in this diagram were shielded; for greater clarity, such shielding is omitted from this diagram.

[11] J. R. Macdonald, Rev. Sci. Instr. **25**, 144 (1954).

can cover almost the entire 360° of output phase from 50 to 50 000 cps.

The crystal and crystal holder are positioned between the magnet poles so that the magnetic, Hall, and applied electric fields are all at right angles. The crystal was illuminated so that the incident light entered parallel to the width dimension of the crystal. With the light on and the magnetic field off, 50 to 100 volts rms was applied to the crystal. With switch S-1 in position A, the residual voltage across the Hall electrodes was then balanced out by adjustment of the phase and amplitude controls of the phase shifter. At 10^3 cps, this balancing could be carried out sufficiently well that less than a millivolt of the fundamental frequency signal could be measured at the amplifier output.

When the magnetic field was turned on, a voltage proportional to the Hall voltage could be read on the wave analyzer. In practice, several readings of this voltage were taken for each magnetic field direction and these readings averaged. Such averaging largely eliminates the effect of differences in Hall voltage for the two field directions arising from deviations of the Hall electrodes from an exact equipotential. Then S-1 was switched to position B. The voltage measured on the wave analyzer in this position was proportional to V_0, the voltage applied to the crystal. This voltage was varied by means of the helipot voltage divider until the wave analyzer output reading was equal to the averaged Hall readings. This adjustment made the helipot dial reading proportional to the desired Hall ratio V_H/V_0. Finally, the apparent mobility μ_a could be obtained from the measured value of V_H/V_0 by means of the formula

$$\mu_a=\frac{10^8(V_H/V_0)}{H(\chi W/L)}(\text{cm}^2/\text{volt-sec}). \tag{1}$$

H is the magnetic field strength in oersteds, W/L the ratio of width to length, and χ a geometrical factor to correct for possible shunting effects of the current electrodes.[12] The real Hall mobility, μ_H, of the current carriers is only equal to μ_a at frequencies where neither space-charge field effects nor capacitative loading of the Hall electrodes are important.

In order to determine the sign of the current carriers, the Hall output voltage was used, as shown in Fig. 1, to produce a Lissajou figure on the oscilloscope. The figure was a straight line of slope ± 1 or an ellipse of high axial ratio. The sign of the slope of the line or of the ellipse major axis always reversed on reversing the magnetic field. The sign of the current carriers was determined by comparing the slope of the Hall ellipse for known direction of magnetic field with the ellipse formed by connecting current electrodes individually to Hall electrodes and using a very small input voltage. Such sign determination always showed that the majority current carriers in these crystals were of negative sign.

No difficulty with 60-cps pickup was experienced with this apparatus in spite of the extremely high impedance levels encountered. The 60-cps signal measured at the amplifier output with the wave analyzer never exceeded 3 mv. On the other hand, considerable difficulty was experienced with low-frequency noise arising from the preamplifier input tubes. This noise depended on the input impedance level and roughly decreased with increasing frequency inversely proportional to frequency. With the preamplifier input leads shorted, the equivalent input noise level was essentially frequency independent and less than 10 μv. On the other hand, with the input leads connected to ground through resistances of 40 megohms, the equivalent 1000-cps input noise level was 20 μv, and the level measured with a wide-band vacuum-tube voltmeter was 300 μv. This low-frequency flicker noise was considerably greater than any internally generated crystal noise and limited the accuracy of the measurements at low frequencies. Above 100 cps, Hall measurements could be repeated to better than ± 2 percent for Hall voltages greater than 10 mv. It is estimated that the absolute accuracy of the measurements carried out with this apparatus is better than ± 5 percent.

Magnetoresistance measurements were made with much the same apparatus. No Hall electrodes were employed, and the driving voltage was applied to the crystals single phase. The low potential end of the crystal was connected to ground through a 3×10^4-ohm resistor. The voltage across this resistor, proportional to the current through the sample, was measured using the differential preamplifier with one input grounded. With the crystal illuminated and no magnetic field applied, the preamplifier output voltage was balanced by means of the phase shifter, with S-1 in position A. On turning on the magnetic field, the wave analyzer then read a quantity proportional to the change of current through the sample caused by the magnetic field. As soon as this reading was carried out, the magnetic field was turned off and the phase input removed with switch S-2. Since the resulting wave analyzer reading is proportional to the current, the ratio $\Delta I(H)/I(0)=\Delta\sigma(H)/\sigma(0)$ may be obtained from these two readings. Since the magnetic field was perpendicular to the current, the transverse magnetoresistive effect was investigated in this experiment.

III. EXPERIMENTAL RESULTS

As discussed above, space-charge effects may be expected to make the apparent mobility decrease at low frequencies and capacitative loading make it decrease at high frequencies. Before discussing the experimental results, it is of interest to consider the curve shapes to be expected from these processes. At sufficiently high frequencies, the impedance of the crystal between Hall electrodes will be purely resistive; when

[12] Isenberg, Russell, and Greene, Rev. Sci. Instr. 19, 685 (1948).

the capacitative reactance of any shunt capacity, C, present between these electrodes becomes comparable to the internal resistance, R, the measured Hall voltage will begin to decrease with frequency. The resulting decrease in apparent mobility is shown on a log-log plot in Fig. 2. The normalized frequency for the capacitative curve is $RCf/10$.

At low frequencies where space-charge effects become important, most of the potential drop across the crystal occurs near the current electrodes, and the electric field in the length direction at the Hall electrodes is very small. The Hall voltage is, to first order, directly proportional to this longitudinal field and hence will be abnormally small at low frequencies. The apparent mobility determined experimentally from Eq. (1) will therefore decrease at low frequencies in the same way as the longitudinal field at the center. This frequency dependence may be obtained, at least approximately, from the space-charge theory of one of the authors.[5] This theory shows that the absolute magnitude of the longitudinal field at the center (in the absence of a

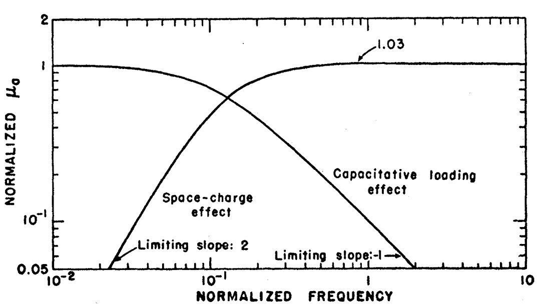

FIG. 2. Theoretical dependence of normalized apparent mobility on frequency arising from space-charge and capacitative-loading effects.

magnetic field) decreases proportionally to frequency at low frequencies, whereas the real part of the field decreases proportionally to the square of frequency. The field is complex because of the space-charge effects. It is not possible to decide definitely which of the above functions of the field will be most nearly effective in producing the Hall voltage without solving the pertinent two-dimensional boundary value problem with magnetic field present. This is an extremely complicated problem and its solution has not been obtained; instead, in Fig. 2, we have plotted the low-frequency dependence of μ_a, normalized to unity at high frequencies, which would arise from the real part of the longitudinal field since it is this result which agrees best with experiment. The normalized frequency for this curve is $2\pi f C_g/G_\infty$, where C_g is the ordinary geometric capacitance/cm^2 between current electrodes and G_∞ is the ordinary ohmic conductance/cm^2 between the electrodes in the absence of space charge.[5] Note that the field contribution in Fig. 2 overshoots its high-frequency value slightly. An experimental determination of μ_a should yield a frequency dependence made up of the two curves of Fig. 2,

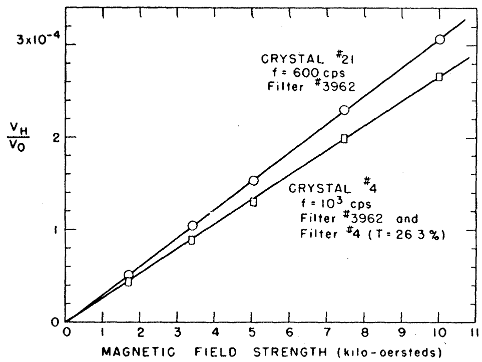

FIG. 3. Dependence of Hall voltage ratio, V_H/V_0, on magnetic field strength for fixed frequency and light intensity.

possibly separated by a flat plateau between. The value of μ_a at the plateau should be the true value of the Hall mobility. Note that if the curves of Fig. 2 overlap sufficiently, no true plateau will be observed and the correct Hall mobility will not be obtained.

Equation (1) indicates that the Hall ratio V_H/V_0 should depend linearly on magnetic field strength provided the Hall mobility is independent thereof. Figure 3 shows the dependence on field strength of this ratio for two different crystals at different frequencies and light intensities. The dependence was linear within experimental error for all crystals for which it was measured. For all crystals the carriers were found to be negatively charged, as one would expect for electrons near the bottom of the conduction band. Free holes should not be present in any of the crystals measured.

Typical frequency response curves for different light intensities are presented in Fig. 4 for crystal No. 4. The dimensions and the treatment of this and other crystals are summarized in Table I. As expected, the high-frequency decrease in μ_a is inversely proportional to frequency. Further, reducing the light intensity increases the source resistance of the Hall voltage and causes the high-frequency decrease to occur at lower frequencies the lower the light intensity. From the absence of a low-frequency decrease in μ_a for these curves, one can conclude that space-charge effects were practically negligible in the frequency range covered. In this range, possible space-charge effects at the Hall electrodes themselves will also be negligible. A rough

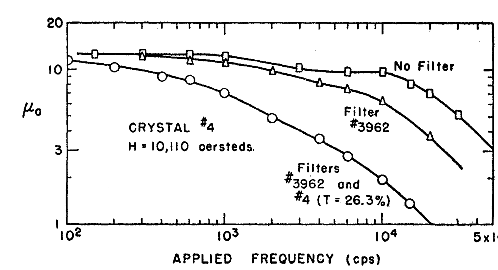

FIG. 4. Dependence of apparent mobility on Crystal No. 4 on frequency and light intensity.

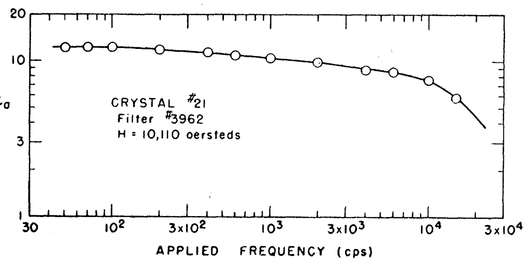

FIG. 5. Dependence of apparent mobility of Crystal No. 21 on frequency for fixed light intensity.

measurement of the impedance of this crystal showed in fact that with the highest light intensity, space-charge parallel capacitative susceptance was negligible above about 30 cps compared with the normal conductance of the crystal. The upper curve in Fig. 4 shows the presence of two plateaus. Such behavior, or a very slow rise in μ_a with decreasing frequency to a final limiting plateau was generally observed. The increase observed is too large to be accounted for by the small overshoot in the real part of the longitudinal field discussed in connection with Fig. 2. The theory from which this curve is taken is based on the assumption that the electrodes are blocking for all carriers, however. It is shown in another paper by one of the authors[13] that the acutal electrodes used in this work, silver paint directly on the crystal, are only rectifying for electrons. The dependence on frequency of the current within the crystals with rectifying electrodes is considerably different from that with blocking electrodes, and it is possible that such difference may lead to a sufficiently large overshoot in the actual longitudinal field to explain the results. Unfortunately, no Hall measurements have been made with blocking electrodes. These circumstances make the real value of the Hall mobility somewhat ambiguous. It seems likely, however, that the final low-frequency plateau value of μ_a is the Hall mobility, since practically all crystals measured yield the same value for this quantity.

Figures 5 and 6 show the dependence of μ_a on frequency and light intensity for another sample. The measurements presented in Fig. 5 could not be extended to sufficiently low frequencies to detect an appreciable drop in μ_a because of the increase of flicker noise level with decreasing frequency. Figure 6 shows that the apparent mobility at a fixed frequency decreases with a decrease in light intensity because of the resulting increase in impedance level which leads to greater capacitative loading. This curve does not show a clearly-defined saturation in the value of μ_a at high light intensities because at 600 cps a relative intensity slightly greater than 100 would have been required to reach saturation. At lower frequencies, similar curves for this and other crystals did show such saturation even for smaller light intensities. Thus, for sufficiently low frequencies and high light intensities, the apparent mobility is independent of light intensity.

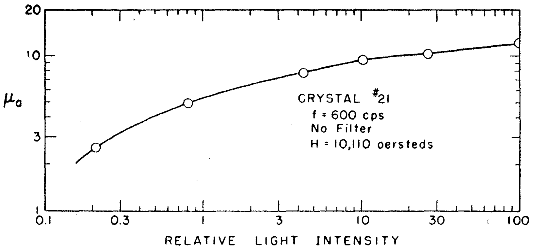

FIG. 6. Dependence of apparent mobility of Crystal No. 21 on light intensity for fixed frequency.

[13] J. R. Macdonald (submitted to J. Chem. Phys.).

Figure 7 shows the frequency dependence of μ_a for the one crystal found which did show a clearly-defined decrease in μ_a at low frequencies. This decrease is proportional to frequency squared. Since the apparent plateau of thic curve gives a value of μ_a considerably below that obtained for all other U-centered crystals, it seems likely that there was too much overlap between the low- and high-frequency curves shown in Fig. 2 to allow the true Hall mobility plateau to be reached for this crystal.

TABLE I. Summary of treatment, dimensions, and Hall mobility for KBr single crystals containing about 10^{16} F centers per cm^3.

Crystal	Treatment	Dimensions (cm) L	W	T	μ_H cm^2/volt-sec
2	U centered	1.240	0.463	1.020	12.4
3	U centered	1.685	0.495	1.098	12.5
4	U centered	1.278	0.476	1.017	12.5
7	U centered	1.422	0.196	1.020	12.3
8	Additively colored	1.556	0.363	1.050	>7.5
14	U centered	1.039	0.382	0.757	12.8
16	U centered	1.041	0.333	0.732	>7.5
21	U centered	1.696	0.479	1.040	12.3

Figure 8 shows the results of measurements on an additively-colored KBr crystal. Measurements on this crystal were difficult because even with maximum light intensity its impedance level was many times higher than that of similar U-centered crystals containing the same F-center concentration. Further, it was necessary to use considerably less than maximum light intensity to reduce its bleaching rate sufficiently that negligible change occurred during the course of a measurement. This necessity increased the impedance level even further. The result of the impedance level of several hundred megohms is shown by the loading apparent in the figure. It was impossible to carry out measurements to sufficiently low frequencies that a plateau could be reached. Even at the lowest frequencies for which accurate results could be obtained, capacitative loading was still dominant.

There is no reason to believe that the Hall mobility of electrons in additively-colored crystals should be appreciably different from that of electrons in U-centered crystals. The U-center concentration, about

$10^{18}/cm^3$, is so small relative to the normal ionic concentration that additional impurity scattering from U centers should be entirely negligible. Therefore, it is likely that the final plateau value of the curve of Fig. 8 is the same as that obtained for U-centered crystals. Certainly, it is not greatly less. Similar measurements were carried out for an additively-colored potassium iodide crystal, and, although a Hall effect could be detected, capacitative loading reduced μ_a even further for this crystal. Results for the Hall mobility of a number of crystals are summarized in Table I.

For a substance exhibiting electronic conduction, the relative change in conductivity due to a magnetic field, provided that electrons from only one energy band are appreciably involved, should follow[14] for low fields,

$$\frac{\sigma(0)-\sigma(H)}{\sigma(0)}=\frac{\Delta\sigma}{\sigma(0)}=BH^2. \quad (2)$$

This quantity is plotted *vs* H^2 in Fig. 9 and it is evident that such proportionality is fairly good. Note that a field of 10 kilo-oersteds causes a 7 percent decrease in

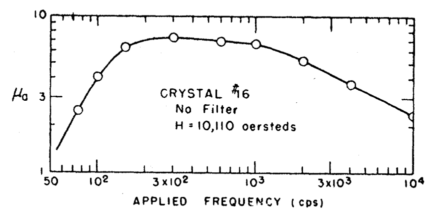

FIG. 7. Dependence of apparent mobility of Crystal No. 16 on frequency for fixed light intensity.

current. Two other crystals gave similar results and a check of frequency response at this field strength indicated no appreciable dependence between 10^2 and 10^3 cps. Measurements of this nature must be carried out within a frequency range where the current is almost entirely conductive, or spurious results will be obtained. At low frequencies a large part of the current will arise from parallel space-charge capacitance whereas at high frequencies where such capacitance may be negligible the geometrical capacitance of the crystal will begin to account for a large share of the observed current. Rough impedance measurements were carried out preparatory to making magnetoresistance measurements to establish that the current at the operating frequency was, in fact, largely conductive. While it was true that three crystals were found that gave results similar to those presented in Fig. 9, all other crystals which were measured gave very anomalous magnetoresistive results. With 10 kilo-oersteds applied, the maximum change in conductance observed for these crystals was not greater than 1 percent and apparently corresponded to an increase in conductance, rather

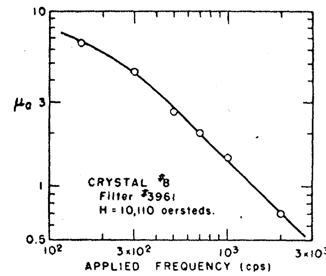

FIG. 8. Dependence of apparent mobility of additively-colored Crystal No. 8 on frequency for fixed light intensity.

than a decrease with magnetic field strength. No difference between the Hall mobilities of the crystals which gave high or low magnetoresistance values could be detected. The reason for the magnetoresistive discrepancy could not be determined in the limited time available for this work.

IV. DISCUSSION

Interpretation of the experimental results is complicated not only by the limitations on the data imposed by the time available but also by the well-known shortcomings of the theory of electronic transport properties in polar crystals. Accordingly, a complete discussion is not possible at present.

For discussion purposes, the electric and magnetic fields are assumed homogeneous over that part of the crystal in which are to be found the electrons with whose properties we are concerned. Any conceivable relaxation time for electrons is negligibly small compared to the period of the applied fields; thus, it is permissible to treat the fields as time-independent.

Because of the low density of centers from which electrons are excited, it seems reasonable to expect the electrons in the conduction band to have approximately thermal velocities and a Maxwellian distribution. So far as the authors are aware, no satisfactory theoretical treatment has been given which can be applied to the present case in discussing either the energy states of the conduction electrons or their scattering by the longitudinal optical lattice vibrations. The field theoretic approximational procedures of Frohlich,

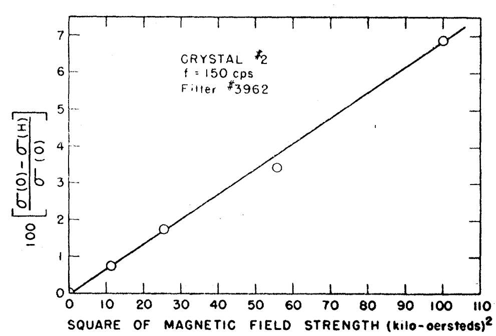

FIG. 9. Dependence of percentage relative change in conductance of Crystal No. 2 on the square of magnetic field strength; fixed frequency, fixed light intensity.

[14] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 184.

Pelzer, and Zienau,[15] of Lee, Low, and Pines,[16] and of Low and Pines[17] break down for electrons of kinetic energy comparable to $h\nu$, where ν is the frequency of the logitudinal optical modes of greatest wavelength; and for KBr, $(kT/h\nu)\approx(T/250)$ is of order unity at room temperature. As discussed by several authors,[15–17] the coupling between the electrons and the longitudinal optical modes is too strong to be treated properly as a small perturbation.

Failing the apparatus for a detailed calculation, it is of interest to see if the present data can be brought in any simple way within a familiar phenomenological structure by making an educated guess at the energy spectrum of the conduction electrons and at the energy dependence of their relaxation time. It seems reasonable to assume in the present instance that an electron excited to the conduction band has a constant effective mass and a kinetic energy of thermal magnitude which is an isotropic function of crystal momentum. With regard to the relaxation time, it cannot be supposed that the theoretical results derived by low temperature approximations could nevertheless be usefully applied here if the polarization waves were the only important scatterers. Both perturbation theory[18] and field theory[15,17] methods give a relaxation time independent of electron (or polaron) kinetic energy; and for a constant relaxation time, there is no change of resistance in a magnetic field as long as the energy surfaces are spherically symmetric. For scattering by the optical modes at high temperatures we adopt

$$\tau(\epsilon)=(\pi^{\frac{1}{2}}/2)(\epsilon/kT)^{\frac{1}{2}}\tau_0, \tag{3}$$

where ϵ is the kinetic energy and τ_0 the average of this $\tau(\epsilon)$ over the occupied energy states. Such an energy dependence is indicated by the Boltzmann transport equation for the case of weak electron-phonon coupling at elevated temperatures, and corresponds to a $(1/v)$ scattering cross section. For scattering by the acoustic modes, we take as valid the constant mean free path found, e.g., by the method of deformation potentials and write

$$\tau(\epsilon)=(\pi^{\frac{1}{2}}/2)(kT/\epsilon)^{\frac{1}{2}}\tau_a, \tag{4}$$

where τ_a is the average of (4) over the filled states.

The formal theoretical expressions appropriate under the above assumptions may all be obtained directly from Wilson's treatise.[19] The magnetic fields employed in the measurements were always sufficiently small that only the leading terms of expansions in powers of H^2 need be retained. We have, for the Hall angle,

$$\theta(H)=(K_2/K_1)\omega, \tag{5}$$

and for the relative change of resistance,

$$\frac{\rho(H)}{\rho(0)}-1\doteq\left[\frac{K_3K_1}{K_2^2}-1\right]\theta^2(H), \tag{6}$$

where $\omega=(eH/mc)$, m = effective electronic mass, e is the absolute value of the electronic charge, and

$$K_r\equiv\frac{4ne^2}{3\pi^{\frac{1}{2}}m}\int_0^\infty \tau^r(xkT)x^{\frac{3}{2}}e^{-x}dx,$$

with n the number of conduction electrons per cm^3. The coefficient of $\theta^2(H)$ in Eq. (6) would be 0.085, if only the optical phonons were significant and would be 0.27 for purely acoustical scattering. In either case, the change of resistance computed by using the observed Hall angles is too small by a factor of 10^6. No conceivable single-term power-law expression for the relaxation time can reduce the discrepancy much. With so few electrons in the conduction band, it is hard to believe that re-entrant energy surfaces can be invoked as for semiconductors to account for the magnitude of the effect of Fig. 9. Clearly something more drastic than adjustment of an empirical effective mass and of a single relaxation time will be required to correlate the Hall and magnetoresistance effects in KBr.

V. NUMERICAL RESULTS

From the measured resistivities and Hall angles we can estimate the number of electrons excited to the conduction band under strong illumination. It is of the order of 10^{10} cm^{-3} or less for all U-centered crystals herein reported. As discussed elsewhere by one of the authors,[13] not only negative ion vacancies but also other traps for electrons are important in determining the conduction band population, and the situation is sufficiently complex to preclude estimates of recombination times without further data.

If we ignore any difference between Hall and microscopic mobilities and assume the effective mass to be equal to the free electron mass, we find that a Hall mobility of 12.5 cm^2/volt-sec gives a mean relaxation time of 6×10^{-15} sec. Allowing for an effective mass of between one and four electron masses, we can conclude that the mean relaxation time lies between 10^{-14} and 10^{-15} sec. Assuming thermal velocities for the electrons, one then finds mean free paths which to order of magnitude are greater than 10^{-8} cm and less than 10^{-7} cm. These values are in conformity with what one would expect from other evidence.[20]

ACKNOWLEDGMENTS

The authors wish to thank Elson Hutchinson for aid in making the measurements. One of us (J.R.M.) is greatly indebted to the Argonne National Laboratory for a visiting appointment.

[15] Frohlich, Pelzer, and Zienau, Phil. Mag. **41**, 221 (1950).
[16] Lee, Low, and Pines, Phys. Rev. **90**, 297 (1953).
[17] F. E. Low and D. Pines, Phys. Rev. **91**, 193 (1953).
[18] H. Frohlich and N. F. Mott, Proc. Roy. Soc. (London) **A171**, 496 (1939).
[19] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), second edition, Secs. 8.51 and 8.64.
[20] Reference 3, p. 104; reference 14, p. 558.