

## Electron Hall Mobility in the Alkali Halides\*†

R. K. AHRENKIEL‡ AND FREDERICK C. BROWN

*Department of Physics, University of Illinois, Urbana, Illinois*

(Received 4 May 1964)

New results will be presented on the mobility of electrons in alkali-halide crystals down to the temperature of liquid helium. An improved technique was used to observe the transient Hall effect for electrons released from color centers by light. Optical-mode scattering with mobility dependent upon  $\exp(\Theta/T)$  was generally observed above 40°K. The Debye temperature  $\Theta$  can be compared with the optical-mode frequency of the material, whereas the magnitude of the scattering can be used to estimate band and polaron mass parameters. Mobilities as high as 15 000 cm<sup>2</sup>/V-sec, depending upon *F*-center density, were observed for lightly colored crystals of KBr at 7°K. Similar high mobilities were found for KI and a sample of zone-refined KCl, but the largest mobility observed in NaCl was 1200 cm<sup>2</sup>/V-sec. The low-temperature mobility in KBr could be reduced an order of magnitude by optically converting *F* centers (neutral defects) to *F'* and  $\alpha$  centers (charged defects). The original mobility could then be restored by illumination in the *F'* band at low temperature.

### I. INTRODUCTION

THE mobility of electrons in the alkali halides is of current theoretical and experimental interest. These materials are the most strongly polar substances found in nature and serve as an ideal medium to test the various theories of the polaron and of scattering by the optical modes of lattice vibration. Also, a knowledge of electron mobility in these crystals is of value in the interpretation of experiments involving color centers.

The conventional techniques cannot be employed to measure mobility in the alkali halides mainly because of very high impedance and electrode difficulties even when the crystals are illuminated with intense light. Direct transit-time measurements<sup>1</sup> are impractical because the lifetime of a free electron before trapping is usually very short. On the other hand, Hall mobility is independent of trapping effects since deflection by the magnetic field arises only when the electron is free between trapping events. However, a steady Hall voltage is difficult to observe and to interpret for the alkali halides. The internal field is affected by electron trapping and the formation of space-charge polarization.<sup>2</sup> In order to overcome the difficulties, characteristic of high-impedance photoconductors, special alternating-current techniques have been developed<sup>3-5</sup> as well as transient-pulse techniques.<sup>6-10</sup> The transient method introduced by Redfield<sup>6</sup> allows the direct ob-

servation of Hall angle for electrons excited into the conduction band by single pulses of light. The Hall angle is determined prior to the onset of polarization and also before the formation of an internal Hall field. A flat sandwich-like geometry was originally used in which one electrode was an equipotential surface, the other a transparent resistance film along which a voltage gradient existed. The applied electric fields were non-uniform although the average field was determined analytically by solving a boundary-value problem.

An improved transient technique employing uniform electric field was developed for the present experiments. The Hall mobility of electrons released from *F* centers was observed for KBr, KCl, KI, and NaCl in the little-explored temperature range 7–100°K. Mobilities as high as 15 000 cm<sup>2</sup>/V-sec were obtained at low temperature in lightly colored samples of KBr. Optical-mode lattice scattering was generally observed above 40°K. Electrons appear to be scattered by *F* centers at very low temperatures and also by charged point defects such as *F'* and  $\alpha$  centers when these are present.

### II. EXPERIMENTAL METHODS

Figure 1 shows the method in a schematic fashion. The alkali-halide crystal is placed between two semi-conducting electrodes along which identical voltage gradients are established in the *x* direction. Due to the symmetry of the electrode geometry and neglecting edge effects, it is possible to establish a uniform electric field in the volume of the crystal,  $E_x = V/l$ , where *V* is the applied voltage and *l* is the length of the uniform film electrode. Electrons are released from *F* or *F'* centers by illuminating with a pulse of light through one of the transparent films. When a magnetic field is applied in the *z* direction the photoelectrons acquire a *y* component of drift velocity. This charge flow induces<sup>11</sup> a transient voltage pulse on the upper electrode (the electrodes are blocking) which is amplified by a pre-amplifier and displayed on an oscilloscope. The electric field in the crystal can be rotated about the *z* axis by

\* Supported in part by the U. S. Air Force Office of Scientific Research, Grant No. AF 62-215.

† This work is based on a thesis by one of the authors (RKA) submitted in partial fulfillment of the requirements for the Ph.D. degree.

‡ Present address: Research Laboratories, Eastman Kodak Company.

<sup>1</sup> R. S. Van Heyningen, Phys. Rev. **128**, 2142 (1962).

<sup>2</sup> J. Evans, Phys. Rev. **57**, 47 (1939).

<sup>3</sup> J. Ross MacDonald and J. E. Robinson, Phys. Rev. **95**, 44 (1954).

<sup>4</sup> D. Kahn and A. J. Glass, Phys. Chem. Solids **17**, 210 (1960).

<sup>5</sup> M. Onuki, J. Phys. Soc. Japan **16**, 981 (1961).

<sup>6</sup> A. G. Redfield, Phys. Rev. **94**, 526 (1954).

<sup>7</sup> A. G. Redfield, Phys. Rev. **94**, 537 (1954).

<sup>8</sup> K. Kobayashi and F. C. Brown, Phys. Rev. **113**, 507 (1959).

<sup>9</sup> D. C. Burnham, F. C. Brown, and R. S. Knox, Phys. Rev. **119**, 1560 (1960).

<sup>10</sup> F. C. Brown and N. Inchauspé, Phys. Rev. **121**, 1303 (1961).

<sup>11</sup> W. Shockley, J. Appl. Phys. **9**, 635 (1938).

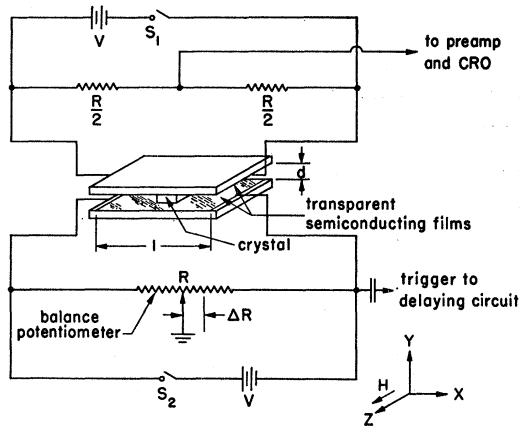


FIG. 1. Schematic diagram of double electrode configuration. The electric field is applied in the  $x$  direction by application of the voltage  $V$  across the resistance films of length  $l$ . The magnetic field  $\mathbf{H}$  is in the  $z$  direction.

varying the ground point of the lower electrode as indicated in Fig. 1. This allows one to search for a null in the photoresponse. The Hall angle can be ascertained simply by determining the amount the electric field has to be rotated for a null in the presence of a magnetic field.

Transparent semiconducting electrodes were achieved by the use of 2000 to 4000  $\Omega$  per square tin oxide coating<sup>12</sup> on quartz. It has been found that a higher resistance coating has a large temperature coefficient of resistance and too high a resistance at low temperature. Several hundred volts could be applied to the electrodes, but it was necessary to use pulses to avoid Joule heating. The pulses applied to upper and to lower electrodes were synchronized. Furthermore, the upper electrode pulsing system had to be at high impedance and low capacitance with respect to ground and well shielded against noise pickup. This isolation was achieved by connecting two magnetically actuated mercury wetted contact switches<sup>13</sup> in series (one normally open, the other normally closed). The appropriate batteries and switches were isolated from ground in a shielded box. The switches were activated in synchronism from outside the box by permanent magnets mounted on a rotating wheel. By mounting the switches on micrometer heads, it was possible to stagger their positions relative to the rotating magnets such that a pulse of about 200  $\mu\text{sec}$  could be obtained.

The application of several hundred volts across the sensitive upper electrode disabled the preamplifier for several seconds. To prevent this blocking phenomenon, the input of the preamplifier was shorted by means of the contacts of a low noise, fast acting relay.<sup>14</sup> Then by

<sup>12</sup> NESA coating, Pittsburgh Plate Glass Company, or a similar product made by Corning Glass Company. See also D. N. Lyon and T. H. Geballe, *Rev. Sci. Instr.* **21**, 769 (1950).

<sup>13</sup> C. P. Clare Co. mercury wetted contact switch; Model HGX-1003.

<sup>14</sup> Elliot Brothers Ltd., synchroverter relay, Model No. C 1410.

means of a delay circuit, the relay was opened permitting the preamplifier to function. Cascade connected 6BQ7 triodes were used in the preamplifier for low tube noise and freedom from the Miller effect. The bandwidth and average noise signal was such that microsecond pulses corresponding to  $10^{-15}$  C of induced charge could be observed at the input of the preamplifier connected to the crystal and leads.

Microsecond pulses of light were provided by the discharge of a capacitor through a short arc xenon discharge tube.<sup>15</sup> Light of the desired wavelength was obtained by means of filters. The discharge was triggered by a delay circuit adjusted so that the preamplifier was sensitive following opening of the disabling switch. The sequence of operations repeated at very low repetition rate was as follows: application of synchronized voltage pulses to upper and lower electrodes, opening of preamplifier shorting switch, followed by discharge of the light and oscilloscope sweep.

The cryostat was similar to that described in Ref. 8. Temperature control was achieved by means of exchange in an inner glass tube which kept the liquid helium and the crystal separate. At temperatures above 30°K, thermal equilibrium was maintained by a small amount of exchange gas in the inner tube balanced by power to a heater on the chamber containing the crystal. A standardized platinum resistance thermometer in contact with the crystal chamber was used to measure temperature. The sample chamber itself was filled with helium gas to assure temperature equilibrium between crystal and thermometer. Magnetic fields up to about 6 kG were supplied by a 4-in. electromagnet.

Analysis of the measurement proceeds as follows. It may be shown that the Boltzmann equation in a cubic medium containing both electric and magnetic fields yields the following expression for the current density:

$$\mathbf{J} = \sigma \mathbf{E} + \alpha \mathbf{E} \times \mathbf{H} + \beta H^2 \mathbf{E} + \gamma \mathbf{H}(\mathbf{E} \cdot \mathbf{H}) + \dots, \quad (1)$$

where the coefficients are as given by Seitz<sup>16</sup> for the isotropic case. In the present measurements, the magnetic field is in the  $z$  direction, the electric field rotates in the  $xy$  plane and charge flow is measured in the  $y$  direction. The charge flow which is observed by the measuring apparatus is then:

$$J_y = \sigma E_y + \alpha E_x H + \beta H^2 E_x. \quad (2)$$

If a null is achieved by adjusting the balancing potentiometer first for  $H_z = H_z^0$  and then for  $H_z = -H$ , one may write the following two equations:

$$\sigma E_y + \alpha E_x H + \beta H^2 E_x = 0, \quad (3)$$

$$\sigma E_y' - \alpha E_x H + \beta H^2 E_x = 0. \quad (4)$$

We now subtract Eq. (3) from Eq. (4) with the result

$$\sigma(E_y' - E_y) = 2\alpha E_x H. \quad (5)$$

See also N. E. Spear, H. P. D. Lanyon, and J. Mort, *J. Sci. Instr.* **39**, 81 (1962).

<sup>15</sup> Edgerton, Germeshausen and Grier, Inc., Model FX-11.

<sup>16</sup> F. Seitz, *Phys. Rev.* **79**, 372 (1950).

Here  $E_y' - E_y = \Delta E_y$  which is simply  $\Delta V/d$  where  $\Delta V$  is related to the change in the balancing potentiometer for  $\pm H$  and  $d$  is the thickness of the crystal. Now a reasonable definition of low-field Hall mobility  $\mu_H$  is had by setting  $\mu_H H/c = \alpha H/\sigma$ .<sup>8</sup> This ratio may be found from Eq. (5) and  $\Delta E_y = \Delta V/d$  as follows:

$$\frac{\mu_H H}{c} = \frac{1}{2} \frac{\Delta V}{V} \frac{l}{d} = \frac{1}{2} \frac{l \Delta R}{d R}, \quad (6)$$

where  $R$  is the total resistance of the potentiometer (see Fig. 1). Thus, the Hall mobility is simply related to easily measured quantities.

To measure a small Hall angle or Hall mobility, one must observe a photoresponse above the noise and then adjust for a null. The accuracy to which we find this null point will increase with the number of carriers released until space-charge conditions begin to destroy the applied field. The onset of space-charge polarization during a single light pulse is the most serious limitation on the accuracy of a measurement and on the minimum measurable mobility.<sup>17</sup> The buildup of polarization after a series of light pulses is less serious and can be minimized by using a background depolarizing light of low intensity. For mobilities of 1000 cm<sup>2</sup>/V-sec or more, the intensity of the xenon discharge was reduced by means of attenuators to avoid polarization effects. However, when the mobility was less than 100 cm<sup>2</sup>/V-sec, intense illumination was required with the result that a significant amount of polarization sometimes occurred during a single light pulse. This had the effect of obscuring the null and reducing the accuracy of balance. In most of the materials studied, the minimum resolvable mobility was about 30–50 cm<sup>2</sup>/V-sec. The method, as applied with blocking electrodes, is limited in application to materials which are highly insulating in the dark. The alkali halides meet this requirement at low temperature.

### III. RESULTS FOR POTASSIUM BROMIDE

#### A. Sample Preparation

Potassium bromide was studied most extensively since it yielded the highest values of mobility at low temperature. Results are shown in Figs. 2–4. The source of the crystals was the Harshaw Chemical Company, Cleveland, Ohio, except for the two samples marked ZrA-2 and Zr-1 which were zone refined at the University of Illinois.<sup>18</sup> Various methods of coloration were used. The samples labeled 1.2.1, 1.3.1, 1.4.1, 1.4.2A, and 1.5.1 were all additively colored in a fairly usual manner. They were cleaved from the same shipment of Harshaw material, but were selected for relatively low ultraviolet absorption due to OH. The

<sup>17</sup> R. K. Ahrenkiel, Ph.D. thesis, University of Illinois, 1964 (unpublished).

<sup>18</sup> T. N. Srinivasan, Technical Note No. 3 on U. S. Air Force Contract AF 49(638)-529, Department of Physics, University of Illinois, 1962 (unpublished).

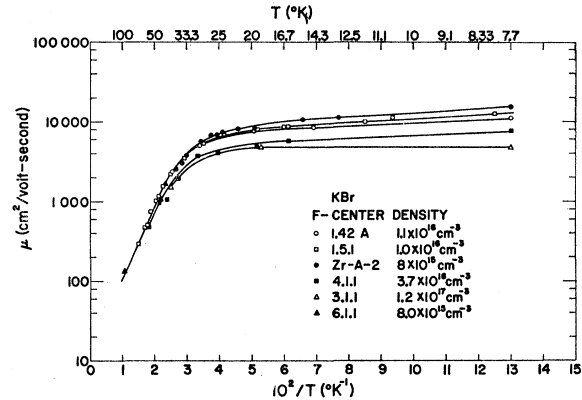


Fig. 2. Electronic Hall mobility in KBr as a function of reciprocal temperature for crystals of different  $F$ -center density.

coloration was carried out with triply distilled potassium in evacuated Pyrex tubing which had been cleaned with hot nitric acid. The crystals were contained in a sidearm during distillation to minimize contamination by impurities from the potassium.

Samples 4.1.1 and ZrA-2 were additively colored with extra care. The potassium was distilled several times in separate glassware and then sealed off under vacuum in a small capsule. This capsule was broken open within a larger tube in which dry nitrogen gas was flowing, and the large tube was then closed off. The system was pumped down and the potassium distilled two more times before being sealed off in a sidearm containing the crystals. Sample number 3.1.1 was colored in a stainless-steel tube according to the method of Van Doorn.<sup>19</sup>

All additively colored samples were cleaved and pulse annealed just prior to the mobility run. The cleaved samples were about 3 mm square by 1.5 mm thick. Each was placed on a platinum holder and heated in the dark for 60 sec at 400°C. The annealed sample was removed from the furnace, quenched on a copper block and immediately loaded in the cryostat. Optical measurements to determine the  $F$ -center density were usually made on a thicker piece of material cleaved from the same block. This permitted greater accuracy since there tended to be loss of  $F$  centers near the surface during pulse annealing. The optical absorption spectrum was obtained by means of a recording spectrophotometer, and the  $F$ -center density computed from Smakula's equation<sup>20</sup> using an oscillator strength of 0.81.<sup>21</sup>

The zone-refined sample labeled Zr-1 was not additively colored, but was irradiated with filtered 100-kV x rays at room temperature. It was then loaded into the cryostat and cooled in total darkness. Both this sample and the one additively colored, zone-refined

<sup>19</sup> C. Z. Van Doorn, Rev. Sci. Instr. **32**, 755 (1961).

<sup>20</sup> A. Smakula, Z. Physik **63**, 763 (1930).

<sup>21</sup> F. G. Kleinschrod, Ann. Physik **27**, 97 (1936).

crystal contained about 10 times lower concentration of divalent impurity as indicated by tests of ionic conductivity.<sup>18</sup>

### B. Intrinsic Temperature Range—Mobility due to Lattice Scattering

If the mobility is dominated by optical-mode phonon scattering, one would expect a temperature-dependent mobility of the form  $\exp(\theta/T)$  where  $\theta = \hbar\omega_l/k$ . Here  $\omega_l$  is the vibrational frequency corresponding to the longitudinal optical mode of lattice vibration. Experimental results are shown in Figs. 2 and 3 where the log of the observed Hall mobility is plotted versus  $1/T$  for the various samples studied. The straight line dependence at intermediate and high temperatures indicates the expected exponential variation with reciprocal temperature. The mobility is seen to depart from a straight line near 40°K and to increase more slowly with decreasing temperature to a final value which depends upon  $F$ -center concentration. The slope of the optical-mode region gives a Debye temperature of  $\theta = 233 \pm 15^\circ\text{K}$ . This observed value is in good agreement with recent inelastic neutron-scattering experiments<sup>22</sup> which indicate a Debye temperature of  $\theta = 244^\circ\text{K}$  at 4.2°K and  $\theta = 240^\circ\text{K}$  at 90°K. The observed Hall mobility in the optical-mode range can be represented by

$$\mu_{\text{op}} = 8.7 \exp(233/T) \text{ cm}^2/\text{V-sec.} \quad (7)$$

A great deal of attention has been given in recent years to the problem of an electron in an ionic crystal such as an alkali halide. The theoretical work is roughly divided between consideration of polaron effective mass or self-energy and the more difficult problem of polaron mobility. Most polaron theories treat the lattice as a continuum and use the coupling constant introduced by Frohlich<sup>23</sup>

$$\alpha = \frac{e^2}{\hbar} \left( \frac{m}{2\hbar\omega_l} \right)^{1/2} \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right), \quad (8)$$

where  $m$  is the crystal band mass,  $\omega_l$  is the longitudinal optical mode frequency,  $\epsilon_s$  the static, and  $\epsilon_\infty$  the high-frequency dielectric constant. This constant  $\alpha$  is a measure of the number of phonons which surround the electron since for a slow electron, it is found that the self-energy is of the order of  $E = \alpha\hbar\omega_l$ . The perturbation theory shows that an electron in an ionic crystal has an effective mass  $m^*$  which is larger than the band mass  $m$  and which is given by  $m^* = m(1 + \alpha/6)$ . Further discussion is to be found in a recent book.<sup>24</sup>

<sup>22</sup> A. D. B. Woods, B. H. Brockhouse, and R. A. Cowley, *Phys. Rev.* **131**, 1025 (1963).

<sup>23</sup> H. Frohlich, H. Pelzer, and S. Zienau, *Phil. Mag.* **41**, 221 (1950).

<sup>24</sup> *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Edinburgh, 1963).

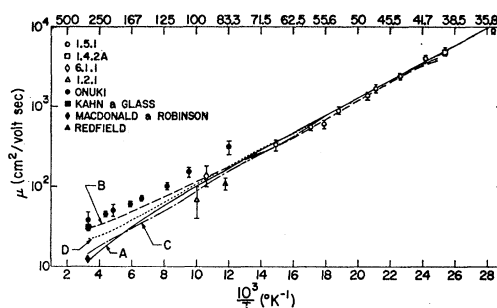


FIG. 3. Mobility of electrons in the intermediate and high-temperature range. Curve A,  $\mu = 8.7 \exp(244/T) - 1$ ; B, Low-Pines theory (Ref. 27) modified by Yokota polaron mass (Ref. 36); C, Howarth-Sondheimer theory (Ref. 26); D, Garcia-Moliner theory (Ref. 32).

Various polaron mobility theories<sup>25-30</sup> have been published including a recent theory which gives the mobility as a function of the frequency<sup>31</sup> of applied electric field. In general the direct-current mobility at low temperatures,  $T \ll \theta$ , is found to be of the form  $\mu = \mu_0 \exp(\theta/T)$  where the exponential factor comes simply from the density of optical phonons available for scattering. The strength of the scattering is incorporated into the constant  $\mu_0$  in a different way in the various theories. It is strongly dependent upon the band effective mass  $m$  as well as upon other constants of the material such as  $\epsilon_s$ ,  $\epsilon_\infty$ , and  $\omega_l$ .

The conduction band mass  $m$  is unknown for the various alkali halides. However, in a case such as KBr where  $\omega_l$  is accurately known from inelastic neutron scattering data,<sup>22</sup> one can choose  $m$  for the best fit between experiment and theory in the optical scattering range. The theoretical mobility formulas usually apply to microscopic mobility, the drift mobility in the absence of shallow trapping. Although the present experimental results are for Hall mobility the difference between these two quantities is not large at very low temperature.<sup>32</sup> The effective masses required to bring

TABLE I. Values of the mass parameters and electron-lattice coupling constant for KBr determined by normalizing the theoretical expressions of various workers to the experimental data. Here  $m$  is the band effective mass,  $m^*$  is the polaron mass, and  $m_e$  the mass of the free electron.

Theory	$m/m_e$	$m^*/m_e$	$\alpha$
Low-Pines	0.34	0.52	3.07
Osaka	0.43	0.87	3.45
Howarth-Sondheimer	0.62	...	...
Garcia-Moliner	0.43	0.68	3.53

<sup>25</sup> H. Frohlich, *Advan. Phys.* **3**, 325 (1954).

<sup>26</sup> D. S. Howarth and E. H. Sondheimer, *Proc. Roy. Soc. (London)* **A219**, 53 (1953).

<sup>27</sup> F. E. Low and D. Pines, *Phys. Rev.* **98**, 414 (1955).

<sup>28</sup> T. D. Schultz, *Phys. Rev.* **116**, 526 (1959).

<sup>29</sup> Y. Osaka, *Progr. Theoret. Phys. (Kyoto)* **25**, 517 (1961).

<sup>30</sup> L. P. Kadanoff, *Phys. Rev.* **130**, 1364 (1963).

<sup>31</sup> R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, *Phys. Rev.* **127**, 1004 (1962).

<sup>32</sup> F. Garcia-Moliner, *Phys. Rev.* **130**, 2290 (1963).

the various theories into agreement with the data of Fig. 2 for the lattice-scattering range are given in Table I along with coupling constants  $\alpha$ . A low-temperature value of static dielectric constant  $\epsilon_s = 4.52$  was used which is in agreement with recent measurements down to 77°K at the University of Illinois<sup>33</sup> and high-temperature measurements elsewhere.<sup>34</sup> The optical dielectric constant was taken to be<sup>35</sup>  $\epsilon_\infty = n^2 = 2.33$  and is not very temperature-dependent. Notice from Table II that the  $m$  used to fit the Howarth-Sondheimer theory<sup>26</sup> is about 50% larger than in the case of the other polaron theories. The polaron-mass correction is not taken into account in this treatment; consequently the discrepancy is understandable.

Figure 3 shows the observed mobility in the high-temperature range including  $T \sim \theta$ . The data of other workers<sup>3-7</sup> have been used to supplement our data above 77°K. Unfortunately, most of the polaron-mobility theories are not applicable throughout this entire temperature range. The Howarth-Sondheimer perturbation calculation is valid to high temperature, but is not expected to be useful for these high  $\alpha$  materials. Yokota<sup>36</sup> calculated the temperature dependence of the polaron mass within the framework of the Low-Pines intermediate coupling theory. We cannot use this temperature-dependent mass directly in the intermediate coupling-mobility formula, however, since this would not renormalize the scattering interaction at high temperature. The theory of Feynman *et al.*<sup>31</sup> should apply in principle, but they do not give results for low-frequency mobility at high temperature. On the other hand, Garcia-Moliner<sup>32</sup> has extended the perturbation technique of Howarth and Sondheimer by including the Yokota correction. This is a hybrid theory which may

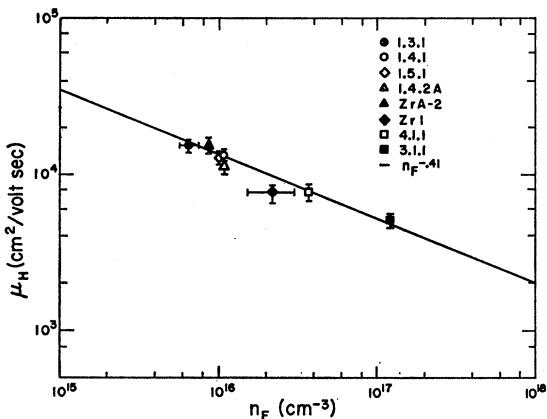


FIG. 4. The Hall mobility in KBr at  $T = 7.7^\circ\text{K}$  as a function of  $F$ -center concentration. The solid line is a plot of the function  $\mu_H n_F^{-0.41}$  where  $A$  is a constant.

<sup>33</sup> K. Kanazawa (private communication).

<sup>34</sup> G. C. Smith, M.S. thesis, Cornell University, 1962 (unpublished).

<sup>35</sup> K. Hojendahl, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. 16, No. 2 (1938).

<sup>36</sup> T. Yokota, *Busseiron Kenkyo* 69, 137 (1953).

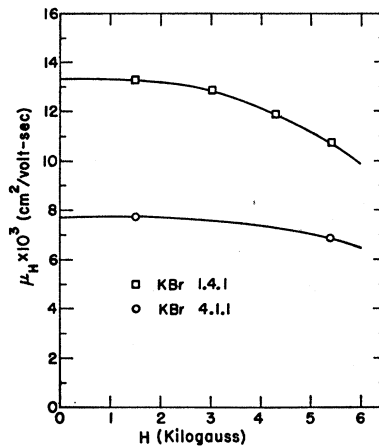


FIG. 5. Hall mobility versus magnetic field for samples KBr 1.4.1 and KBr 4.1.1 at 7.7°K.

be useful to fairly high values of  $\alpha$ . His theory gives mass values consistent with the strong coupling theory of Kadanoff and Osaka at low temperature and is perhaps the most reliable for KBr at high temperature. It is difficult to use experimental data as a test of the various theories at high temperature because of low mobility and scatter of the high-temperature data.

### C. Extrinsic Temperature Range—Residual Mobility

The mobility at low temperatures (less than 20°K) is apparently limited by scattering from  $F$  centers since the observed values decrease with increasing  $F$ -center concentration  $n_F$ . If  $F$  centers are the only scattering mechanism at low temperatures, the simplest considerations would predict that  $\mu$  varies as  $1/n_F$ . In Fig. 4 the mobility at about 7°K is plotted as a function of  $n_F$ , and over the range of concentrations given  $\mu$  varies as  $n_F^{-0.4}$ . The only significant deviation is found in the zone-refined sample (Zr-1) which was colored by x irradiation at room temperature and gave a slightly lower mobility than expected.

If defects other than  $F$  centers are significantly limiting the mobility, one would expect scatter due to the varying purity of these samples. For example, the concentration of divalent impurities in the zone-refined samples (ZrA-2 and Zr-1) is known<sup>18</sup> to be at least 10 times less than the other samples of similar  $F$ -center densities and yet the mobilities are consistent. Likewise, the x-rayed (Zr-1) sample would presumably have a lower dislocation density than the additively colored sample (ZrA-2) which was taken from the same zone-refined ingot but was quenched from 400°C.

If the  $F$  center is the dominant scatterer at low temperatures, it is about 10 times more effective than a neutral impurity in a semiconductor.<sup>37</sup> This was also found to be the case for KCl.<sup>10</sup> Because the  $F$  center is a neutral defect, the scattering in a simple model should be nondispersive and the Hall mobility independent of

<sup>37</sup> C. Erginsoy, *Phys. Rev.* 79, 1013 (1950).

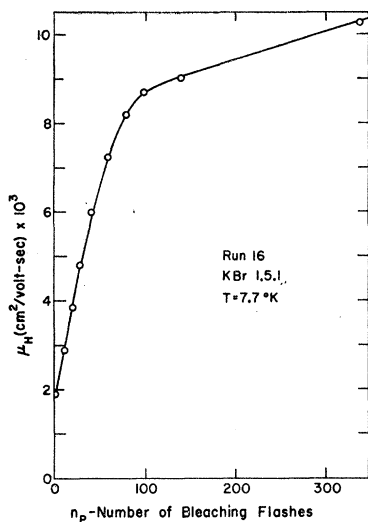


FIG. 6. The Hall mobility of sample KBr 1.5.1 at 7.7°K as a function of the number of bleaching flashes (Corning filter CS 2-58). The initial  $\alpha$ -center density was about  $4 \times 10^{16}$  per  $\text{cm}^3$ .

magnetic field.<sup>9</sup> In Fig. 5, the Hall mobility of two samples at 7°K is plotted as a function of magnetic field and a relatively strong dependence on  $H$  is noted. This would indicate the presence of a scattering mechanism for which the scattering time is dependent upon the energy of the electrons. A proper theoretical treatment of scattering due to  $F$  centers has not been given. It is of course, possible that the experimental results are complicated by a mixture of scattering defects including a small concentration of aggregate centers.

In order to explain the slow rise in mobility between 40 and 20°K where the optical modes are nearly frozen out, it was necessary to artificially introduce the idea of acoustical-mode phonon scattering. Impurity scattering should show a decreasing or possibly a constant mobility with decreasing temperature. However, the data in this intermediate region could be approximated quite well with a  $T^{-3/2}$  dependence of the form

$$\mu_{ac} = 1.85 \times 10^6 T^{-3/2} \text{ (cm}^2/\text{V-sec)}. \quad (9)$$

Polar acoustical scattering theory<sup>38</sup> predicts an interaction about an order of magnitude weaker than observed. If the result, Eq. (9), is inserted into the formula for deformation potential theory,<sup>39</sup> the quantity  $E_1$  is found to be 6.9 eV. There are no available calculations of the deformation potential in KBr, but Kawamura<sup>40</sup> has found  $E_1 = 5.4$  eV in KCl. Acoustical-mode scattering, however, cannot account for any significant background of scattering at liquid-helium temperatures as can be seen from an extrapolation of Eq. (9).

A variation of the observed low-temperature mobility with wavelength of the exciting light was looked for. However, no such effect was found. The measured mobility was the same when electrons were excited in the  $F$ ,  $F'$ , or  $L_1$  absorption-band regions. Also, no

variation in mobility with light intensity was found over at least two orders of magnitude.

Finally, the electric-field dependence of the photoconductivity at 7°K was investigated. Non-Ohmic behavior was observed for fields greater than about 80 V/cm. The Hall measurements were carried out in the low-field region.

#### D. The Influence of $\alpha$ and $F'$ Centers at Low Temperature

Since the  $F$  center is a neutral defect and  $F'$  and  $\alpha$  centers are charged, one would expect a decrease in the low-temperature mobility upon making an  $F$  to  $F'$  conversion. Indeed, this is a material in which the number of charged and neutral defects can be varied by illumination in the appropriate regions of the spectrum.<sup>41</sup> The partial conversion of  $F$  centers to  $\alpha$  and  $F'$  centers can be carried out most efficiently in KBr by illuminating in the  $F$  band near 120°K.

It was not feasible to observe optical density in the Hall apparatus so as to determine the number of  $\alpha$  (or  $F'$ ) centers present at any time. However, one could estimate the initial  $F/\alpha$  ratios by making separate optical-absorption measurements in an optical Dewar system. The  $F/\alpha$  equilibrium concentration is a function of the spectral distribution of the exciting light and the temperature of the crystal. By using a narrow-band interference filter peaking in the  $F$  band, the same light spectrum could be obtained for the separate optical Dewar and also for the Hall Dewar system. A temperature calibration of  $F/\alpha$  for the given filter was made in the optical Dewar system by means of absorption measurements. This result was used then to obtain

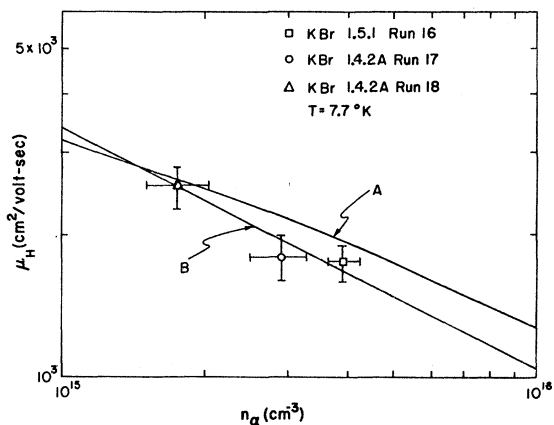


FIG. 7. Hall mobility in KBr at 7.7°K versus the number of  $\alpha$  centers per  $\text{cm}^3$ . Curve A, Conwell-Weisskopf mobility formula in which  $N_I$  is replaced by  $2n_\alpha$ ; Curve B,  $\mu = An_\alpha^{-0.52}$ . The  $\alpha$ -center concentrations were approximately known for the three experimental points shown.

<sup>38</sup> H. J. Meijer and D. Polder, *Physica* **19**, 255 (1958).

<sup>39</sup> J. Bardeen and W. Shockley, *Phys. Rev.* **80**, 72 (1950).

<sup>40</sup> H. Kawamura, *Phys. Chem. Solids* **5**, 256 (1958).

<sup>41</sup> F. Lüty, in *Halbleiterprobleme*, edited by W. Schottky (Frederich Vieweg und Sohn, Braunschweig, Germany, 1961), Vol. VI.

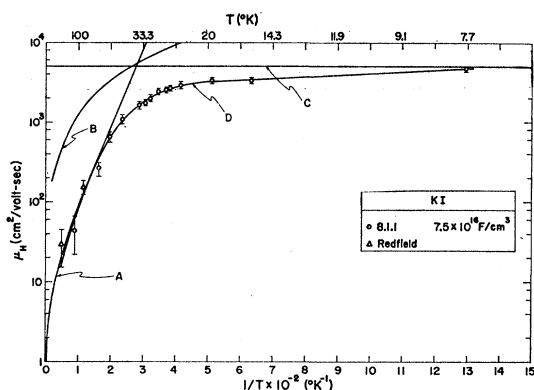


FIG. 8. Hall mobility in KI versus reciprocal temperature. Curve A,  $\mu_{op} = 10 \exp(222/T) - 1$ ; Curve B,  $\mu_{ac} = 1.15 \times 10^6 T^{-3/2}$ ; Curve C,  $\mu_e = 5000$  ( $\text{cm}^2/\text{V-sec}$ ); Curve D, approximate total mobility  $\mu_H$  where  $1/\mu_H = 1/\mu_{op} + 1/\mu_{ac} + 1/\mu_e$ .

known  $F/\alpha$  ratios by conversion in the Hall apparatus with carefully controlled temperature.

For sample 1.5.1, in which the mobility at  $7.7^\circ\text{K}$  was  $11\,000 \text{ cm}^2/\text{V-sec}$  before the conversion, a 40%  $F$  to  $F'$  conversion reduced the mobility to 1800. In Fig. 6, the mobility is seen to gradually increase to the original values upon bleaching by illumination in the  $F'$  band at  $7.7^\circ\text{K}$ . The fact that the original mobility was restored indicates that there are few traps in the crystal which compete effectively with the  $\alpha$  and  $F'$  centers even when they are reduced to relatively low concentration by bleaching at low temperature.

It is interesting to see if the Conwell-Weisskopf<sup>42</sup> formula for charged-defect scattering applies to this situation. Since each defect carries one electronic charge, one might expect both  $\alpha$  and  $F'$  centers to have about the same scattering cross section. If we replace  $N_I$  by  $2n_\alpha$  in the Conwell-Weisskopf formula and insert the static dielectric constant for KBr as well as an effective  $m^* = m_e$ , we obtain curve A in Fig. 7. Also plotted here are the experimental results of three different runs in which known amounts of  $F'$  and  $\alpha$  centers were introduced into the crystal by  $F$ -band irradiation at the appropriate intermediate temperature. Curve B is the experimental curve. The close agreement of the measurements with the Conwell-Weisskopf theory may be fortuitous but at least it indicates the importance of Coulomb interaction.

#### IV. RESULTS FOR POTASSIUM CHLORIDE, POTASSIUM IODIDE, AND SODIUM CHLORIDE

##### A. Potassium Chloride

Hall measurements were carried out on KCl, KI, and NaCl in order to determine the residual mobilities in these crystals and the general trend with temperature. The results on KCl will be presented first.

<sup>42</sup> E. Conwell and V. Weisskopf, Phys. Rev. **17**, 388 (1950).

TABLE II. Low-temperature Hall mobility in KCl.

Sample	Material	Mobility ( $7.7^\circ\text{K}$ )
KCl 1.1.1	Harshaw	$3200 \text{ cm}^2/\text{V-sec}$
KCl Zr-1	Zone-refined	$8000 \text{ cm}^2/\text{V-sec}$

Experiments on the Hall effect in KCl at low temperatures were carried out by Brown and Inchauspé.<sup>10</sup> They found a steep mobility increase with decreasing temperature down to about  $30^\circ\text{K}$  after which the mobility leveled off at values near  $4000 \text{ cm}^2/\text{V-sec}$ . The more lightly colored crystals had mobilities of about 5000 near liquid-helium temperatures, but the mobility did not seem to decrease smoothly with  $F$ -center density was found here with KBr. The work reported here allows a comparison of the low-temperature mobility of Harshaw crystals with crystals which were purified by zone refining. It is known that the concentration of electrically active impurities was about 100 times less in the zone-refined samples than in the best Harshaw material.<sup>18</sup> One would expect that the purer zone-refined crystals have higher mobilities at low temperature and low  $F$ -center concentration.

The KCl samples were prepared by irradiating at room temperature with 100-kV x rays in order to obtain uniform coloration. Also, to aid in this respect, the soft x rays were screened out by a thin copper sheet and a block of KCl about 2 cm thick. Another crystal about 2 mm thick was placed between the sample and the screens which served to calibrate the  $F$ -center density in the sample without exposing it to light. The optical density of this calibration crystal was measured in the spectrophotometer several hours after irradiation to avoid the effects of thermal bleaching. It was found that the coloration became relatively stable after several hours in the dark.

The results of measurements on two crystals at  $7.7^\circ\text{K}$  are indicated in Table II. The zone-refined sample has a higher mobility, presumably due to a lower density of impurities. However, one cannot give the concentration or say what impurities are controlling the mobility from these limited data. The concentration of some metallic impurities in KCl has been found to be of the order of  $10^{16}$ – $10^{17} \text{ cm}^{-3}$ .<sup>43</sup> It would appear that these impurities are relatively ineffective as scattering centers in comparison with  $\alpha$  or  $F'$  centers. This might

TABLE III. The mass parameters and coupling constant in KI when the experimental data are compared with the Osaka theory. The band effective mass is  $m$ , the polaron mass  $m^*$ , and the free-electron mass is  $m_e$ .

	$m/m_e$	$m^*/m_e$	$\alpha$
Osaka	0.47	0.88	3.16

<sup>43</sup> S. Anderson, J. S. Wiley and L. J. Hendricks, J. Chem. Phys. **32**, 949 (1960).

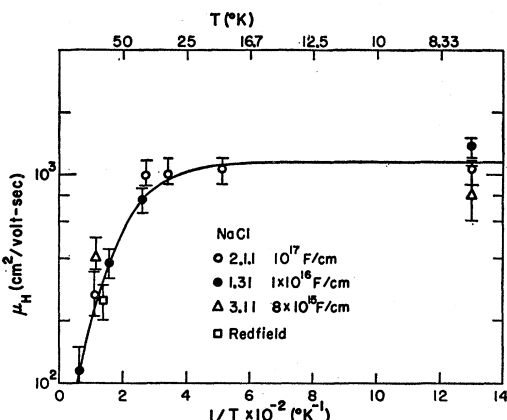


Fig. 9. Hall mobility in NaCl versus reciprocal temperature for crystals with various  $F$ -center concentrations.

be because divalent impurities and positive ion vacancies, for example, are associated so as to scatter like dipoles rather than isolated point charges. A dipole of atomic dimensions is a great deal less effective as a scattering center than an isolated point charge.<sup>44</sup>

### B. Potassium Iodide

An additively colored sample of KI was studied over the temperature range of 7–110°K. The temperature dependence of the mobility, which is plotted in Fig. 8, is quite similar to that found in KBr. A linear variation of the mobility at temperatures above 40°K is again indicative of optical-mode phonon scattering, and the slope corresponds to a Debye temperature of 222°K  $\pm$  20°K. Although no inelastic neutron scattering data are available on this material, one may calculate  $\omega_l$  from the Reststrahl data<sup>45</sup> and the dielectric constants<sup>46</sup> by means of the relation<sup>47</sup>  $\omega_l = (\epsilon_s/\epsilon_\infty)^{1/2}\omega_t$ . The result is  $\theta = 212^\circ\text{K}$ .

The observed mobility in the region of optical-mode scattering for KI can be approximated by the expression

$$\mu_{\text{op}} = 10[\exp(222/T) - 1] \text{ (cm}^2/\text{V-sec)}. \quad (10)$$

Comparing this experimental result with theory,<sup>29,30</sup> one deduces the mass parameters and coupling constant which are given in Table III. Again to explain the temperature dependence of the mobility between 20 and 40°K, it is necessary to introduce acoustical-mode scattering which is given by curve B of Fig. 8. The equation of this curve is found to be

$$\mu_{\text{ac}} = 1.15 \times 10^6 T^{-3/2} \text{ (cm}^2/\text{V-sec)}. \quad (11)$$

By fitting the deformation potential-scattering theory<sup>39</sup>

<sup>44</sup> J. Appel and W. B. Teutsch, Phys. Chem. Solids **23**, 1521 (1962).

<sup>45</sup> G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London) **A261**, 10 (1961).

<sup>46</sup> A. Etichen and E. Büchner, Z. Physik Chem. **27**, 321 (1934).

<sup>47</sup> R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).

to this result, a deformation potential of 8.8 eV is obtained for KI. The residual mobility is about the same as that in KBr of the same  $F$ -center density.

### C. Sodium Chloride

Crystals of NaCl were both additively colored (samples 2.1.1 and 1.3.1) and irradiated with kilovolt x rays (sample 3.1.1) at room temperature. The samples were generally cleaved from Harshaw stock although sample 3.1.1 had been annealed in chlorine to remove the oxygen. The data from the Hall measurements are plotted in Fig. 9.

The data are in agreement with a possible exponential dependence above 50°K, but the mobility does not rise much above 1000 cm<sup>2</sup>/V-sec in any of the samples tested. The high-temperature mobility is in reasonable agreement with the measurement of Redfield<sup>7</sup> at 84°K. The relatively low mobility found below 50°K is presumably due to the presence of large amounts of impurity not present in the other alkali halides studied. One might suspect oxygen in NaCl, but the chlorination of a sample did not give rise to higher mobilities although it is known to reduce the OH band.

### V. CONCLUSIONS

The mobility above 40°K in the various alkali halides studied was controlled by optical-mode phonon scattering. In general the exponential slope of the mobility versus  $1/T$  curves agrees with other measurements of the Debye temperature corresponding to longitudinal optical-mode phonons. A comparison of the observed mobility with polaron mobility theory<sup>29,30</sup> gives polaron masses of 0.87  $m_e$  and 0.88  $m_e$  for KBr and KI, respectively. Roughly similar results are found for the other alkali halides tested so it would seem that polaron masses in these materials are of the order of a free-electron mass or lighter. There is an indication that a reasonable amount of acoustical-mode scattering may occur in the range 20–40°K for KBr and KI.

In KBr the conversion of  $F$  centers to  $F'$  and  $\alpha$  centers produces a large decrease in the low-temperature mobility. The  $F'$  and  $\alpha$  centers scatter very effectively and essentially control the low-temperature mobility when present in detectable concentrations. The  $F$  center in KBr when present in concentrations of  $10^{16}$ – $10^{17}$  cm<sup>-3</sup> is partially effective in controlling the mobility. However, there is an anomalous concentration dependence and the situation both theoretical and experimental is not clear. In general the effect of purification on the residual mobility was smaller than expected, although only a few zone-refined samples of KBr and KCl were tested.

### ACKNOWLEDGMENTS

The authors would like to express their appreciation for discussions with various colleagues, especially



Professor F. Garcia-Moliner, Professor L. Kadanoff, Professor R. J. Maurer, and Professor W. D. Compton. Dr. R. Candall helped on numerous occasions especially in connection with sample preparation and  $F$  to  $F'$  conversion. Dr. K. Kanazawa, Dr. R. Swank, and Dr. F. Lüty contributed to various aspects of the experiment and its interpretation. Dr. R. Tucker of Corning

Glass Corporation kindly supplied some samples of electrically conducting glass. Thanks are also due to Dr. T. M. Srinivasan and Professor M. V. Klein for supplying certain crystals. One of the authors (RKA) was the recipient of fellowships from the National Science Foundation and the General Atomics Corporation. These are gratefully acknowledged.

PHYSICAL REVIEW

VOLUME 136, NUMBER 1A

5 OCTOBER 1964

## Paramagnetic Resonance of $\text{Fe}^{3+}$ and $\text{Gd}^{3+}$ in Yttrium Orthoaluminate\*

R. L. WHITE

*Stanford Electronics Laboratories, Stanford University, Stanford, California*

G. F. HERRMANN

*Lockheed Research Laboratories, Palo Alto, California*

J. W. CARSON

*Aerospace Group, Hughes Aircraft Company, Culver City, California*

AND

M. MANDEL

*Genetics Department, School of Medicine, Stanford University, Stanford, California*

(Received 30 March 1964; revised manuscript received 4 June 1964)

The paramagnetic-resonance spectra of  $\text{Fe}^{3+}$  and  $\text{Gd}^{3+}$  in yttrium orthoaluminate were measured as part of an effort directed at understanding the isomorphous orthoferrites. The low symmetry of the ion sites and the complicated nature of the spectra necessitated the development of a special method of analysis for obtaining the relevant spin Hamiltonians. The method consisted of constructing directly from the angular dependence of the data "anisotropy surfaces," classical counterparts of the spin Hamiltonian, from which the spin Hamiltonian itself could be extracted by the method of operator equivalents. The predominant term in both  $\text{Fe}^{3+}$  and  $\text{Gd}^{3+}$  Hamiltonians was quadratic in the spin components. The fourth-order term of the  $\text{Fe}^{3+}$  Hamiltonian manifested very nearly cubic symmetry with the biquadratic coefficient  $a$  negative, contrary to general expectations. The  $\text{Gd}^{3+}$  spin Hamiltonian displayed no visible cubicity in the fourth-order terms. The "preferred" spin directions as determined in the orthoaluminate were compared with the observed spin configurations in the orthoferrites, and with the predictions of crystal-field calculations based on the ion position parameters of  $\text{GdFeO}_3$ . Correlation was very poor in both instances. No conclusive explanation of the discrepancies is at present available; the most likely explanation involved differences in the local crystal distortions between the orthoaluminate and the orthoferrite.

### I. INTRODUCTION

IN recent years a great deal of progress has been made in understanding the magnetic properties of several classes of magnetic insulators on an atomic basis. Among experimental tools, paramagnetic resonance has been the chief instrument for investigating the individual magnetic ions (as opposed to the collective behavior observed in macroscopic studies), such studies being made, as a rule, in dilutely doped isomorphous nonmagnetic crystals, where the single-ion interactions can be observed separately from exchange.

Yttrium orthoaluminate, a nonmagnetic crystal, is of particular interest as a host for paramagnetic ions because of its crystallographic similarity to the important

and relatively poorly understood class of magnetic materials—the orthoferrites. These are a family of mixed oxides of composition  $ABO_3$  which crystallize in a slightly distorted perovskite form.<sup>1-8</sup>  $A$  is typically a trivalent rare earth and  $B$  a trivalent transition metal, though variations (involving, say, Ca or Ba substitutes) have been studied.<sup>9-13</sup> The magnetic sites in the ortho-

<sup>1</sup> S. Geller and E. A. Wood, *Acta Cryst.* **9**, 563 (1956).

<sup>2</sup> S. Geller and V. B. Bala, *Acta Cryst.* **9**, 1019 (1956).

<sup>3</sup> M. A. Gilleo, *Acta Cryst.* **10**, 161 (1957).

<sup>4</sup> S. Geller, *Acta Cryst.* **10**, 243 (1957).

<sup>5</sup> S. Geller, *Acta Cryst.* **10**, 248 (1957).

<sup>6</sup> S. Geller, *J. Chem. Phys.* **24**, 1236 (1956).

<sup>7</sup> S. Geller, *Acta Cryst.* **9**, 885 (1956).

<sup>8</sup> F. Bertaut and F. Forrat, *J. Phys. Radium* **17**, 129 (1956).

<sup>9</sup> E. O. Wollan and W. C. Koehler, *Phys. Rev.* **100**, 545 (1955).

<sup>10</sup> J. B. Goodenough, *Phys. Rev.* **100**, 564 (1955).

<sup>11</sup> U. H. Bents, *Phys. Rev.* **106**, 225 (1957).

<sup>12</sup> W. C. Koehler and E. O. Wollan, *Chem. Phys. Solids* **2**, 100 (1957).

<sup>13</sup> W. C. Koehler, E. O. Wollan, and M. K. Wilkinson, *Phys. Rev.* **118**, 58 (1960).

\* The investigation reported here was performed for the greatest part at the Palo Alto Laboratories of the General Telephone and Electronics Corporation and was sponsored in part by the U. S. Air Force Cambridge Research Laboratories, Office of Aerospace Research, under contract No. AF 19(628)-387.