gives

$$\Delta V_T \int\int\int ne\mu_{DT}(\partial \mathbf{E}/\partial V_T)^2 d^3\mathbf{x} = 2/c \int\int\int ne\mu_D\mu_{HT}(\mathbf{E}\times\mathbf{H})\cdot\partial\mathbf{E}/\partial V_T d^3\mathbf{x}. \qquad (11)$$

This equation is exact to second order in $\mathbf{H}$. The second-order (magnetoresistance) terms drop out because the measurement is made by reversing the magnetic field, not simply turning it on and off.

Equation (11) clearly applies to the arrangements of Figs. 1, 3, or 4. In these cases we can assume that $\partial\mathbf{E}/\partial V_T$ is a vector in the y direction of magnitude $1/D$, because Laplace's equation and the boundary conditions will then be satisfied. We can also assume that μ_D and μ_H are constant, and that $\mathbf{H}$ is uniform in the z direction. Under these assumptions Eq. (2) follows immediately.

PHYSICAL REVIEW VOLUME 94, NUMBER 3 MAY 1, 1954

Electronic Hall Effect in the Alkali Halides*

ALFRED G. REDFIELD†‡
Physics Department, University of Illinois, Urbana, Illinois

(Received January 19, 1954)

The Hall mobility of electrons in colored NaCl, KCl, KBr, and KI has been measured using an unconventional technique previously described by the author. Measurements on additively and x-ray colored NaCl yield an electronic mobility of 250±50 cm^2/volt sec at 84°K, decreasing to about 25±25 at 200°K. In additively colored KCl the mobility is 100±50 at 90°K; in additively colored KBr it is about 110 at 84°K. In additively colored KI the mobility is 155±30 at 84°K, decreasing to 30±15 at 200°K. In every case the sign of the Hall effect is electronic. These observations are consistent with the mobility theory of Low and Pines assuming effective mass ratios between 0.35 and 0.6 for the unpolarizable crystal, or polaron effective mass ratios between 0.5 and 0.9. These mobility data combined with photoconductive yield data give values of the capture cross section of *F* centers for electrons (to form *F'* centers) between 0.7 and 5 times 10^{-15} cm^2 at about 200°K.

A. INTRODUCTION

THIS paper reports some measurements of the electronic Hall mobility in colored NaCl, KBr, and KI using techniques described in the immediately preceding paper[1] (henceforth referred to as EHED). Previous investigations[2–4] in these crystals failed to give quantitative values of the mobility, although Evans[4] established an upper limit of 20 cm^2/volt sec at 300°K for the mobility in several colored alkali halides. While the present work was in progress, MacDonald and Robinson[5] succeeded in measuring the electronic mobility in KBr, obtaining a value of 12.4 cm^2/volt sec at 300°K.

This work was undertaken mainly to test the theory of electronic mobility in polar substances.[6–8] Theory predicts that the mobility will vary with temperature as $\exp(\Theta/T)$, where Θ is the Debye temperature corresponding to the longitudinal optical modes of vibration of the lattice, and provided $T \ll \Theta$. Θ can be deduced[9] from the infrared absorbtion peak[10] of the crystal and its low- and high-frequency dielectric constants.[11] The values of Θ for the crystals investigated in this research are NaCl, 370°K; KCl, 300°K; KBr, 236°K; KI, 190°K. Thus the theory applies to those alkali halides only considerably below room temperature.

The electrons in this experiment are obtained by ionizing *F* centers with light of the proper wavelength. The *F* centers act only as sources of electrons, and in view of their small concentration they should not affect the experimental measurements.

---

* Partially supported by U. S. Office of Naval Research. Part of a dissertation submitted to the University of Illinois for the Ph.D. degree.

† U. S. Atomic Energy Commission predoctoral fellow.

‡ Present address: Division of Applied Science, Harvard University, Cambridge, Massachusetts.

[1] A. Redfield, preceding paper, Phys. Rev. **94**, 526 (1954).

[2] P. Lukirski, *Reports of the Physical-Technical Roentgenological Institute and the Leningrad Physical-Technical Laboratory 1918–26* (Leningrad, 1926), p. 185.

[3] P. Tartakowski, Z. Physik **66**, 830 (1930).

[4] J. Evans, Phys. Rev. **57**, 47 (1940).

[5] J. Ross MacDonald and John E. Robinson, Phys. Rev. (to be published).

[6] H. Frohlich and N. F. Mott, Proc. Roy. Soc. (London) **A62**, 446 (1949).

[7] Frohlich, Pelzer, and Zienau, Phil. Mag. **41**, 221 (1950).

[8] F. Low and D. Pines, Phys. Rev. **91**, 193 (1953). The expression for the parameter α given by Low and Pines is too small by a factor 2π.

[9] Lyddane, Sachs, and Teller, Phys. Rev. **59**, 673 (1941); H. B. Callen, Phys. Rev. **76**, 1394 (1949).

[10] R. B. Barnes, Z. Physik **75**, 723 (1923).

[11] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), p. 12.

B. EXPERIMENTAL RESULTS

Because of bleaching or, what is equivalent, conversion to F' and other centers, it was desirable to make ΔV_T as large as possible compared to V_L; therefore, the method of Fig. 4, EHED, was used for almost all the measurements. The upper nonphotoconducting spacer was an uncolored piece of the same crystal. The thickness D varied between 0.5 and 1.5 centimeters in different crystals; the parameter a (defined in EHED) varied between 0.3 and 0.8, and b, the ratio of the colored thickness to the total thickness, varied from 0.1 to 0.5. The z dimension of the samples (Fig. 3, EHED) was usually about 1.5 centimeters.

The samples were single crystals purchased from the Harshaw Chemical Company. 50-kev x-rays from a molybdenum target were used for x-ray coloration. In some cases a thin NaCl crystal was placed between the x-ray tube and the sample to be colored to filter out soft x-rays and achieve more uniform coloration. X-irradiation was done at room temperature, and the samples were usually x-rayed on both sides.

To color samples additively they were heated with a fraction of a cubic centimeter of sodium in a copper bomb for up to three hours at 675°C or below. Shorter times and lower temperatures were used for KBr, KCl, and KI. The copper bomb was simply a short length of 1-inch i.d. copper tubing with two wrought copper solder fitting caps slid onto each end without soldering. These caps fit the tubing snugly enough to retard the escape of the sodium vapor for several hours.

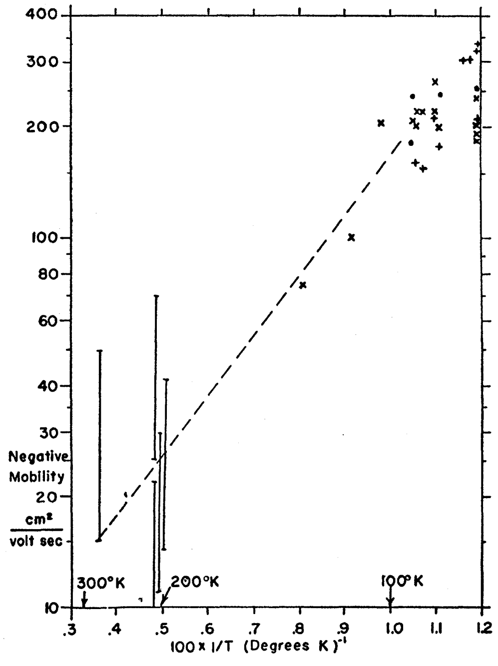

FIG. 1. Summary of mobility data on NaCl. Dots denote 10 percent probable accuracy in the mobility measurement, +'s denote 15 percent, and ×'s denote 20 percent.

After cooling slowly in the oven for several hours the bomb was forced open and the crystal was removed. The outer surfaces of the crystal were then cleaved off. KCl, KBr, and KI crystals produced in this way were deeply colored and ready for use, but in NaCl all the excess sodium was found to coagulate during cooling, imparting to the crystal a blue color for transmitted light and red for scattered light. By reheating the sample to above 500°C, where the F centers reformed, and dropping the crystal while hot into liquid air, it was possible to avoid the formation of these colloidal particles. The crystal then had the straw yellow color characteristic of F centers. Usually such a crystal contained several cracks due to thermal strains in cooling.

It was desired to anneal the samples used, because it was thought that dislocations and other imperfections in an unannealed crystal might decrease the mobility. As indicated in the last paragraph, however, colloidal particles will form if annealing is attempted. In KCl, KBr, and KI it was nevertheless possible to cool in a few hours without forming appreciable colloids. It was eventually found that this could also be done with NaCl, provided the F-center density was very small. The previously colored crystal was placed on a piece of platinum foil in an oven and kept for several hours above 600°C until almost all the coloration disappeared. The platinum made the amount of coloration visible when a flashlight was shone on the sample. The NaCl crystal was then cooled in a few hours and had a barely noticeable yellow tinge. It was found that such crystals apparently showed less tendency to form F' centers and more complex centers than NaCl crystals which were strongly colored and violently quenched.

It was not possible to make measurements on x-rayed KCl, KBr, and KI, because these crystals bleached too easily. The same was true of well-annealed x-rayed NaCl.

The data for a number of samples of NaCl is summarized in Fig. 1. To avoid confusion, the estimated maximum experimental error in mobility is indicated by the type of point used in the graph. The maximum temperature error is estimated at ±2° for most of the points. For some of the points near 100°K the error may be as large as ±4°. The data was taken with light from the tungsten lamp filtered with a blue filter to give high intensity mainly between 4000 and 5000A. The polarity of the Hall effect was electronic in every case. Since the light used contained little energy in the V bands, it is unlikely that holes contributed to the photoconductivity.

The maximum errors for these mobility measurements were estimated from the reproducibility of the setting of V_T. The percentage errors are relatively large compared to diamond because μ_H is smaller and because higher light intensity is required because of the relatively low photoconductive sensitivity of colored alkali halides. Whereas in diamond the spurious signal due to illumination mentioned in EHED was almost negligible, in the alkali halides it was probably the main source of error. This form of noise was more serious when the Nesa resistance plate was used, than in the lead glass plate, because of photoconductivity in the former. The spurious signal was apparently proportional to the incident light intensity, regardless of wavelength, and could be reduced relative to the desired signal by confining the light used more nearly to the center of the F band. Various procedures were used to try to separate the photoconductive signal from the spurious signals, with only partial success.

As can be seen from Fig. 1, the discrepancies between different points are in many cases larger than expected from the estimates of error based on reproducibility, even though these estimates were quite liberal. Probably the spurious signal due to light gave a larger error than was estimated, although some of the trouble might be in temperature control.

The Hall voltage was proportional to the magnetic field and the electric field, within error. This does not mean much because the error was so large. Usually the proper setting of V_T was determined for $H=0$ and $H=10\,000$ gauss. These three settings plotted as a function of H always fell on a straight line, within experimental error. The accuracy did not warrant making measurements for other values of H.

There appeared to be no clear-cut difference between the mobility in additively colored and x-rayed crystals. The mobility apparently did not depend on the degree of coloration. On the other hand, the mobility was reduced to about 150 cm²/volt sec at 84°K in two samples which had been violently quenched in liquid air as described above. However, a third crystal thus quenched showed no reduction in mobility. Apparently, slight differences in the fast quenching procedure could make a lot of difference in the mobility data. No difference in mobility was observed between crystals cooled in a few minutes and crystals cooled in a few hours, so it is assumed that further annealing would not have affected the measurement. The effect of impurities is unknown, because all the samples used came from the same source. It is unlikely that they are important, because the thermal scattering of the electrons is so strong.

$\bar{E}_x/E_0$ was determined from Eq. (5), EHED. No attempt was made to correct for the finite dimension of the sample. This is probably permissible as long as the z dimension is large compared to the thickness of the colored part of the crystal. No correction was made for the absorption of light by the sample. This correction would be only a few percent im most cases and cannot account for the scatter of the data.

Only a few measurements were made on the additively colored potassium halides. In KCl two measurements on one sample indicate a mobility of 100±50 cm²/volt sec at 90±10°K. In KBr three measurements on one sample indicate a mobility of 110±20 cm²/volt sec at 84±2°K. In KI, three measurements on two samples indicate a mobility of 155±30 cm²/volt sec at 84±2°K; a single measurement indicates a mobility of 30±15 at 200°K.

TABLE I. Effective mass ratios obtained from the mobility data using the theory of Low and Pines.[a] m is the free electron mass, m^* is the effective mass in an unpolarizable crystal, and m_p is the effective mass of the polaron (electron plus associated lattice polarization).

	NaCl	KCl	KBr	KI
μ cm²/volt sec	250	100	110	155
T°K	84	90	84	84
m^*/m	0.55	0.6	0.35	0.35
m_p/m	0.8	0.9	0.71	0.5

[a] See reference 8.

C. DISCUSSION

In view of the large scatter in these data, extreme caution should be used in their interpretation. Little can be said about the temperature dependence of the mobility, except that it behaves qualitatively as expected. The NaCl data are barely consistent with an $\exp(\Theta/T)$ dependence with $\Theta=370$°K, the value deduced from optical absorption in the infrared (dotted line in Fig. 1). The data fit a lower Debye temperature better. The two measurements on KI are consistent with $\Theta=187$°K as predicted, and the one measurement on KBr combined with the room temperature measurement of MacDonald and Robinson ($\mu=12.4$) is consistent with a Debye temperature of 230°K as predicted. This agreement is probably fortuitous and should *not* be regarded as a confirmation of theory; the data are not good enough.

If we assume that the Debye temperature decuced from optical and dielectric constant measurements are correct, these values of mobility can be combined with the theory of Low and Pines[8] to give values of the polaron effective mass and the electron effective mass in the absence of polarization. The results of this calculation for the crystals studied are summarized in Table I, together with the assumed mobilities.

The values of the effective masses obtained in this way are reasonable, but unfortunately there are no independent experimental or theroetical values of these quantities for comparison.

The mobility data can be used to determine approximately the probability and cross section for the capture of electrons by F centers to form F' centers. To do this we use the data of Glaser and Lehfeldt,[12] who measured the charge released for a given amount of light absorbed in a colored crystal of known F-center concentration. Doing this gives the product $\eta\mu\tau$, where η is the probability that an electron excited by a light quantum to an upper level of an F center will be excited thermally to the conduction band, and τ is the mean lifetime of the

---

[12] G. Glaser and W. Lehfeldt, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. (N.F.) Phys. **2**, 91 (1936); see, however, H. Rogener, Nachr. Akad. Wiss. Göttingen **3**, 219 (1941).

Table II. Mean free time and capture probability for an electron by an F center, deduced from the mobility data and the quantum yield data of Glaser and Lehfeldt.[a]

	NaCl	KCl	KBr
T°K	200	200	150
μ cm^2/volt sec	25	15	15
$\eta\mu\tau$ cm^2/volt	5×10^{-8}	10^{-8}	7×10^{-8}
N cm^{-3}	10^{16}	2×10^{17}	1.6×10^{16}
τ sec	2×10^{-9}	7×10^{-10}	5×10^{-9}
$(N\tau)^{-1}$	5×10^{-8}	7×10^{-9}	1×10^{-8}
σ cm^2	5×10^{-15}	7×10^{-16}	10^{-15}

[a] See reference 12.

electrons against trapping by an F center. In a certain temperature range, η is almost certainly unity, and the electrons are captured almost entirely by F centers to form F' centers. Then the capture probability in cm^3/F-center sec is given by $1/N\tau \cong \mu/N(\eta\mu\tau)$, where N is the number of F centers per cubic centimeter. The capture cross section σ, as usually defined, is the capture probability divided by the thermal velocity of the electrons.

Values of $1/N\tau$ and σ determined in this way are given in Table II. The mobilities assumed are given in the table and are interpolated or extrapolated to a suitable temperature. The thermal velocity is assumed to be $(3kT/m_p)^{\frac{1}{2}}$, the root-mean-square classical value. Not much can be said about variation of the cross section with temperature, although it does not seem to vary strongly, because $\mu\tau$ apparently varies with temperature about the same way μ does. The capture cross section is nearly the same as the area of an F center, as might be expected.

It should be possible to obtain more accurate mobility measurements on the alkali halides by using either the present method or that of MacDonald and Robinson. Measurements at lower temperatures should be interesting, although more difficult because of decreasing photoconductive sensitivity.

The author wishes to thank Professor F. Seitz, Professor D. Pines, and Dr. W. Heller for their encouragement and discussions, and Mr. B. Houston for experimental assistance.

PHYSICAL REVIEW VOLUME 94, NUMBER 3 MAY 1, 1954

Latent Heat of Transition of Superconducting Lead

R. L. Dolecek
Naval Research Laboratory, Washington, D. C.

(Received November 16, 1953)

Utilizing magnetic heating, calorimetric measurements of the latent heat of transition of superconducting lead were made in the temperature range 2.5°K to 7.0°K. The values obtained demonstrate the inadequacy of the assumption of a parabolic or cubic critical magnetic field for lead, but are consistent with the assumption of a quartic critical field approximation. The latent heat data obtained are used to derive expressions for the normal and superconducting electronic specific heat.

INTRODUCTION

In the presence of a magnetic field a superconductor exhibits a latent heat of transition between the superconducting and normal states. This latent heat is a direct measure of the entropy change involved and thus affords a sensitive method for determining the electronic entropies in both the normal and superconducting states. Measurements have been performed on the latent heat of transition of superconductors.[1,2] However, the results were not utilized to estimate the electronic entropies. This paper is a report of an experimental measurement of the latent heat of transition of superconducting lead utilizing eddy current heating. The measurements are in accord with previous observations of the entropy difference between the superconducting and normal states,[3] permit evaluation of the electronic specific heats, and with the assumption of a quartic critical magnetic field equation, give a consistent description of the calorimetric and magnetic properties.

EXPERIMENTAL PROCEDURE

Eddy current heating, induced by the abrupt application of a magnetic field, was balanced against the latent heat of transition from the superconducting to the normal state to yield an isothermal magnetization of a superconducting sphere. The magnetic fields were applied as step functions of time, the rise time being of order 0.01 second. Assuming an ideal isothermal magnetization curve for the superconducting sphere, the eddy current heating was calculated for that applied field yielding supression of superconductivity and zero temperature change. As the measurements were conducted under adiabatic conditions, this eddy current energy required for the transition from the superconducting to the normal state with no change in

---

[1] W. H. Keesom and J. A. Kok, Physica 1, 595 (1934).

[2] W. H. Keesom and P. H. Van Laer, Physica 4, 487 (1937).

[3] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937).