

Photoelectric Hall Effect in KCl at Low Temperatures*

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The Hall effect for carriers released by light has been studied over a temperature range 4° to 114°K in additively colored crystals of KCl containing various concentrations of F centers. A negative Hall signal was observed corresponding to electrons released from F centers by light absorbed in the high-energy side of the F band. The Hall mobility rises steeply below 80°K due to freezing out of the optical modes of lattice vibration. A residual mobility near 4000 cm²/volt sec is found below 30°K in the crystals prepared so far.

A. INTRODUCTION

THE mobility of conduction electrons in the alkali halides is of interest in connection with the polaron problem. In addition, the temperature dependence of the mobility is required in order to properly interpret low-temperature photoconductivity experiments¹ as well as various color-center phenomena. Hall mobility for electrons released from F centers in KCl and KBr has been measured by a variety of different techniques.²⁻⁶ In general, the results indicate a low mobility at room temperature, in the vicinity of 5 to 10 cm²/volt sec which increases steeply as the temperature is lowered, apparently due to the freezing out of optical modes of lattice vibration. Measurements were made on a number of alkali halides down to 80°K by Redfield, using a transient technique⁷ which overcomes difficulties due to high sample impedance, space charge, and small Hall angles. The experiments reported in the present article extend the range of measurements to 4°K and were made using apparatus recently described in the case of AgCl⁸ and AgBr.⁹ Results are given for different F -center concentrations, and the problem of the F center as a scattering center is discussed.

B. RESULTS AND DISCUSSIONS

It has been emphasized¹ that the alkali halide crystals must be freshly colored just before each run if reproducible results on photoconductivity are to be obtained at low temperature. Similar precautions were taken in

the case of the Hall measurements. Harshaw KCl was additively colored using distilled potassium in a sealed Pyrex tube within a double furnace used to control the vapor pressure of the alkali metal independent of the crystal temperature. The crystals were quenched from high temperature by removing the tube from the furnace and wrapping in aluminum foil in air. The M band was barely detectable and only in the most heavily colored crystals. The results of low-temperature photoconductivity tests on these crystals, quenched in air rather than oil, were identical with those described in the preceding work.¹

In the present Hall experiments the longitudinal electric field was provided by voltage pulses applied to a uniform resistance film. Charge induced on the electrodes by the motion of carriers within the illuminated volumes of the crystal was detected by means of a pulse amplifier and oscilloscope.^{8,9} The light source was an intense air spark which was synchronized with the maximum of the electric field pulse. Filters were employed so that carriers were released by light absorbed mainly in the high-energy side of the F band, the K and L regions. The low-field Hall mobility was computed from Eq. (8) of reference 9 using the values of ΔR_T observed at each temperature. The numerical factor G was computed from a solution of the boundary value problem for the electric field in the crystal. Corrections for nonuniform field were kept to a minimum by the use of an uncolored KCl spacer.³

The polarity of the observed Hall effect for light in the wavelength range 350–550 m μ was always negative, indicating the importance of electrons rather than holes. Figure 1 shows the low-field Hall mobility as a function of temperature for widely different F -center concentrations. At 80°K the accuracy of the measurements is low because of a small Hall angle; however, the observed value of 100 cm²/volt sec is in agreement with the results of Redfield.³ As the temperature was lowered, the mobility increased steeply and finally leveled off below 30°K at values near 4000 cm²/volt sec. The experiment became relatively easy below 60°K because of the striking increase in the Hall angle.

There was little difference in the observed mobility for F -center concentrations from 10^{15} to 6×10^{16} cm⁻³, but for a crystal with as many as 3.4×10^{17} F centers per cm⁻³, the residual mobility was in the vicinity of

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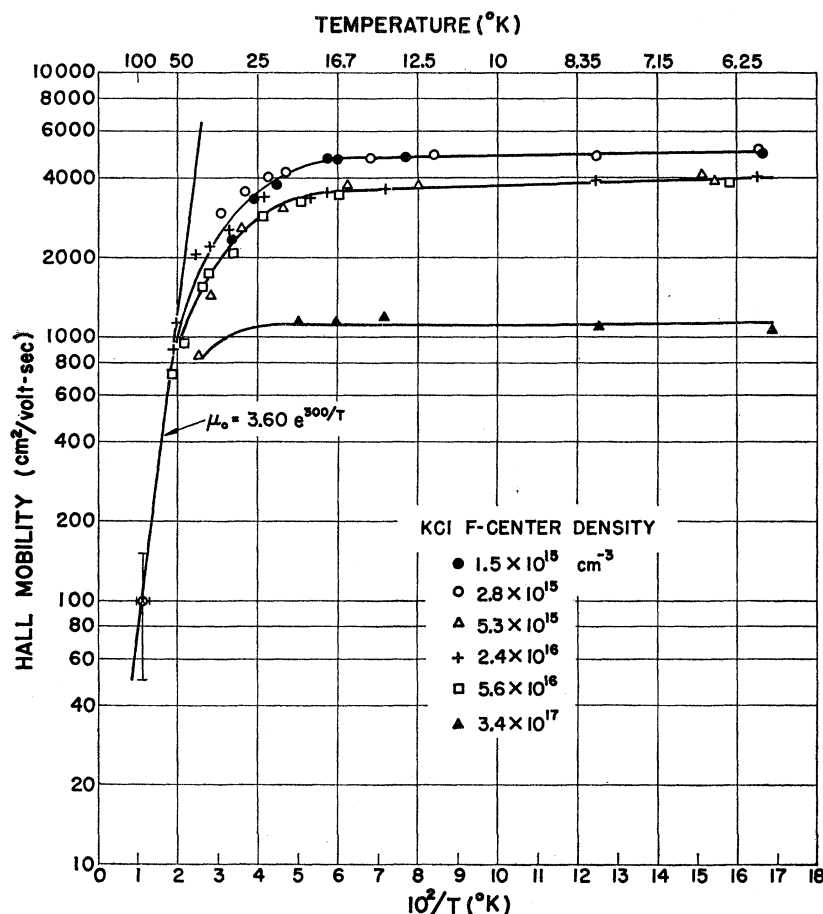


FIG. 1. Low-field Hall mobility as a function of temperature for electrons released by light in crystals with different F -center concentrations as shown. The straight line is the function $\mu_0 = 3.6 \exp(300/T)$ corresponding to optical phonon scattering.

1000 $\text{cm}^2/\text{volt sec}$. This value of mobility indicates that if the F center is the main scattering center in heavily colored crystals, it is a fairly effective one. It would have to be about 10 times more effective than a neutral hydrogen-like impurity according to the formula of Erginsoy.¹⁰ This is surprising considering the localized character of the F center. Another possibility is that there are charged defects associated with the F center which, although present in lower concentration, are more effective scattering centers.

In order to compare mobility in the optical scattering range with theory, it is necessary to compute the Debye $\Theta = \hbar\omega_l/k$ corresponding to the longitudinal optical modes of lattice vibration. The vibrational frequency, ω_l , can be deduced from Reststrahl observations using the relation $\omega_l = (\epsilon/\epsilon_\infty)^{1/2} 2\pi c/\lambda_t$.¹¹ In the case of KCl the static dielectric constant $\epsilon = 4.68$, the high-frequency dielectric constant $\epsilon_\infty = 2.13$, and the wavelength of the transverse optical mode $\lambda_t = 71 \mu$.¹² This gives $\omega_l = 4.0 \times 10^{13}$ and $\Theta = 300^\circ\text{K}$. A detailed calculation of vibrational frequencies assuming equal ion masses has been carried out by Iona.¹³ His highest frequency is

about 4.4×10^{13} so the above value of ω_l is probably not far from right.

The straight-line portion of the mobility in Fig. 1, $\mu_0 = 3.6e^{300/T}$, indicates that optical scattering is predominant above 50°K . The data are at least consistent with a Debye Θ deduced from the vibrational spectrum. Further measurements in the intermediate- and high-temperature range would be desirable and might permit one to obtain Θ directly from the mobility data.

A question arises as to the cause of the residual mobility in the lightly colored crystals. It is not likely that this is due solely to scattering by acoustic lattice vibrations. Little is known about ordinary deformation potential scattering in these materials, but it is most likely greater than the observed values. The acoustic-polar interaction described by Meijer and Polder¹⁴ is very small because of the near equality of ion masses for KCl. Probably imperfections such as impurities play the major role. For example, it has been found by activation analysis that Harshaw KCl may contain as much as 10^{18} atoms of Br and of the order of 5×10^{16} atoms per cm^3 of Ni and S.¹⁵

As mentioned in the previous article, the photo-

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¹⁵ S. Anderson, J. S. Wiley, and L. S. Hendrichs, J. Chem. Phys. **32**, 949 (1960).

conductivity $\eta a w_0$ only begins to reflect the rise in mobility as the temperature is lowered because of the existence of shallow traps in the crystals studied to date. These traps are most effective at temperatures below 25°K where the mobility has leveled off. It seems reasonable that these defects are scattering as well as trapping centers at low temperature. One might inquire as to the relative probability for scattering as compared to that for trapping. For most defects in semiconductors, the scattering cross section is larger than the trapping cross section.¹⁶ A comparison below 25°K in the present case gives the trapping time $\tau_t = w_0/\mu \approx 1.5 \times 10^{-10}$ sec ($w_0 \approx 6 \times 10^{-7}$ cm²/volts¹) whereas the scattering time is of the order of magnitude $\tau = \mu m/e = 2.5 \times 10^{-12}$ sec.

¹⁶ M. Lax, Phys. Rev. **119**, 1502 (1960).

The difference seems large enough to justify our interpretation of the transient Hall experiment in terms of mobility and relaxation time τ .

It would be interesting to pursue the matter of the relative scattering and trapping times further, perhaps by a direct measurement of trapping time as a function of temperature. Several other points for future study suggest themselves. For example, it is important to improve the accuracy and extend the Hall measurements to other alkali halides having different coupling strengths and Reststrahl wavelengths. The origin of the scattering below 30°K is unknown but it would be interesting to see if the residual mobility can be increased by crystal purification as has been found to be the case for the silver halides.

Diffusion in Compound Semiconductors*

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Self-diffusion in single crystal InP and GaAs has been measured, together with the diffusion of the acceptors Cd and Zn and the donors S and Se in GaAs. Radioactive isotopes of these elements were used as tracers. The diffusions of In and P in InP are characterized by activation energies of 3.85 ev and 5.65 ev, respectively; those for Ga and As in GaAs are characterized by activation energies of 5.60 ev and 10.2 ev, respectively. The marked differences in both activation energies and diffusion rates of the constituent atoms in these materials indicate that the basic mechanism of the self-diffusion is one of migration within a specific sublattice.

The impurity diffusion measurements in GaAs suggest that the concept of sublattice diffusion be extended to include impurity diffusion when the impurities enter the lattice substitutionally. The activation energy of the diffusion of both Cd and Zn in GaAs is about 2.5 ev, while that of the diffusion of both S and Se in GaAs is about 4.1 ev. Experimental details of interest include the observation of GaS compound formation when GaAs is heated in S vapor, and the formation of glassy layers on the surface of GaAs due to Se.

I. INTRODUCTION

THIS paper presents and discusses measurements of self-diffusion in single crystal indium phosphide and gallium arsenide and the diffusion of cadmium, zinc, sulfur, and selenium in GaAs. Radioactive isotopes of these elements were used as tracers. The work was undertaken to determine primarily the diffusion constants and activation energies, and by so doing to determine, if possible, the specific mechanism of the diffusion in these materials.

InP and GaAs belong to the class of intermetallic compound semiconductors comprised of elements from columns IIIb and Vb of the periodic table. The properties of these materials which make them interesting as host matrices for diffusion studies are (1) their structure, which consists of two interpenetrating face

centered cubic lattices, each of which is composed of one of the constituent atomic species, (2) the stoichiometry of the constituent atoms which is better than 1 part in 10⁵, and (3) the fact that their electrical properties provide knowledge of the way in which certain impurities enter the lattice. For example, in GaAs cadmium and zinc are acceptor impurities known to replace gallium while sulfur and selenium are donor impurities known to replace arsenic.¹

The measurements to be reported here plus the work of others indicate strongly that the basic mechanism of substitutional diffusion in these materials is one of atomic migration within one of the sublattices.²⁻⁴

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