Effect of Photoexcitation on the Mobility in Photoconducting Insulators

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The Hall mobility of carriers in photoconducting insulators can be varied over an appreciable range by the effects of photoexcitation. Such a variation can result either (1) from a change in the density of scattering centers as the result of a change in the occupation of imperfection centers, or (2) from the initiation of two-carrier conductivity. Suitable use of the phenomena involved in the photo-Hall effect can lead not only to knowledge about carrier density, carrier sign, and carrier mobility, but also about the charge on imperfection centers, and to an independent determination of the cross section of imperfection centers. Experiments on CdS and CdSe single crystals with conductivities lying between 10^{-9} and 10^{-1} mho/cm are described to illustrate the potentialities of the technique. The results emphasize both the importance that changes in mobility can play in normal photoconductive processes, and the importance of hole conductivity under suitable circumstances.

INTRODUCTION

IT is a normal assumption in the usual analysis of photoconductivity processes in solids that carriers of one type are dominant and that the mobility of these carriers is independent of light intensity. This is especially true of photoconducting insulators like CdS and CdSe, where true hole conductivity has seldom been observed except in very highly impure samples. The application of the techniques of the photo-Hall effect to such materials provides an opportunity of checking both of these normal assumptions. The results of this paper show that a quantitative re-evaluation of photoconductivity in insulators may be required in many instances in which these assumptions are violated.

The fact that the mobility in an insulator in the imperfection-dominated range is inversely proportional to the density of charged scattering centers leads to the natural expectation that a change in the density of such centers will lead to a change in the mobility. One method of changing the density of scattering centers is to change their effective charge by adding or removing an electron from their environment. Photoexcitation, with its attendant effects on the Fermi level, is one of the means by which such changes in the effective charge of centers can be achieved. Experiments revealing such a change in mobility with light intensity have been confined to date almost exclusively to Ge and Si. Such effects have been associated with the presence of impurities in the Ge or Si which may exist as either double or singly negative centers; such impurities are Fe, Co, Ni, Mn, etc. Mobility measurements were made on *n*-type Ge containing one of these impurities, both in the dark and for high light intensity.[1] An increase in mobility for the high-illumination condition was detected as doubly negative centers became singly negative by capturing photoexcited holes.

The presence of such impurities in Ge and Si has been shown to give rise also to a change in conductivity type with increasing intrinsic excitation.[2–4] Initially *p*-type Ge:Co and Ge:Mn convert to *n* type with increasing light intensity as the impurity centers capture photoexcited holes. Similarly *n*-type Si:Mn converts to *p* type with increasing light intensity as the impurity centers capture photoexcited electrons, Mn being a donor in Si. When the Hall mobility is measured as a function of light intensity for such systems, a marked light-dependence of the mobility is found, first decreasing to zero and then increasing again as the opposite carriers become dominant.

There are thus two ways in which photoexcitation can cause appreciable changes in the Hall mobility: (1) by changing the occupancy of charged scattering centers, and (2) by making the minority carrier in the dark play a more important role in the conductivity process.

In insulators the effect of photoexcitation on the motion of the Fermi level can be many times larger than in semiconductors such as Ge and Si. As subsequent results show, the Fermi level can be swept through as much as 0.4 ev with varying light intensity at fixed temperature in such sensitive photoconductors as CdS or CdSe. Even without varying temperature, therefore, pronounced changes in mobility may be expected as photoexcitation changes the occupancy of scattering centers in such materials.

There is also the possibility in these materials of observing a change in the Hall mobility as holes play a more important role in the conductivity, either as a result of thermal or optical quenching of the photosensitivity. Measurements of the photomagnetoelectric (PME) effect[5] on CdS have indicated roughly comparable electron and hole lifetimes in *insensitive* crystals. The use of the photo-Hall effect in the range where a sensitive crystal is becoming an insensitive

[1] W. W. Tyler and H. H. Woodbury, Phys. Rev. **102**, 647 (1956).

[2] W. W. Tyler and R. Newman, Phys. Rev. **98**, 961 (1955).
[3] H. H. Woodbury and W. W. Tyler, Phys. Rev. **100**, 659 (1955).
[4] R. O. Carlson, Phys. Rev. **104**, 937 (1956).
[5] H. S. Sommers, R. E. Berry, and I. Sochard, Phys. Rev. **101**, 987 (1956).

crystal as the result of thermal or optical quenching, therefore provides an opportunity to directly estimate the contribution of holes in a way not previously exploited.

Mobility changes at room temperature by factors as large as 6 have been measured for CdS and by factors of more than 20 for CdSe. In those cases where the change in mobility can be attributed to changes in occupancy of scattering centers, the analysis of the dependence of these changes in mobility with location of the Fermi level permits an independent determination of the cross section of the centers involved; the sign of the mobility change permits a determination of the effective charge of the scattering center.

THEORY

Cross Section

A simple expression for the capture cross section of an imperfection center can be derived by equating the Coulomb attraction energy to the thermal energy of an electron:

$$Ze^2/\epsilon r = kT, \tag{1}$$

Z is the number of electronic charges on the center, r is the center radius, and ϵ is the dielectric constant of the material. This criterion gives for the cross section of the center:

$$S_0 = Z^2\pi e^4/\epsilon^2 k^2 T^2. \tag{2}$$

A somewhat more detailed expression for the cross section can be derived from the Conwell-Weisskopf[6] equation for the mobility resulting from Coulomb scattering in a solid:

$$\mu_I = \frac{2^{7/2}\epsilon^2 (kT)^{\frac{3}{2}}}{300\pi^{\frac{3}{2}} e^3 m_e^{\frac{1}{2}} N_I} \frac{1}{\ln[1+(3\epsilon kT/e^2 N_I^{\frac{1}{3}})^2]}. \tag{3}$$

Here N_I is the density of singly charged imperfection centers. An expression for the cross section S_{CW} can be derived from (3) by the following process:

$$S_{CW} = \frac{1}{L^* N_I} = \frac{1}{v\tau N_I} = \frac{m_e^{\frac{1}{2}}}{(2kT)^{\frac{1}{2}} N_I} \frac{1}{\tau}, \tag{4}$$

and

$$\mu_I = (300 m_e/e)\tau, \tag{5}$$

L^* is the mean-free-path of the electron, v its thermal velocity, and τ the time between scattering events. The resulting expression for the scattering cross section can be written:

$$S_{CW} = \Gamma_{CW} S_0 \tag{6}$$

for a singly-charged center, where

$$\Gamma_{CW} = \frac{\pi^{\frac{1}{2}}}{16} \ln\left[1+\left(\frac{3\epsilon kT}{e^2 N_I^{\frac{1}{3}}}\right)^2\right]. \tag{7}$$

As N_I varies between 10^{12} and 10^{18} cm^{-3}, Γ_{CW} varies between 1.4 and 0.4, respectively, assuming $\epsilon = 10$ and $T = 300°$K. Thus the absolute value of S is varied only slightly by the more detailed Conwell-Weisskopf calculation.

One other calculation of scattering is that of Brooks-Herring,[7] which is a quantum-mechanical treatment including explicitly a variation of scattering with shielding of scattering centers by free carriers. The Brooks-Herring equation for the mobility is identical with the expression of Eq. (3) except for the second multiplying factor. The scattering cross section can be expressed therefore:

$$S_{BH} = \Gamma_{BH} S_0 \tag{8}$$

for a singly-charged center, where

$$\Gamma_{BH} = \frac{\pi^{\frac{1}{2}}}{16}\left[\ln(1+b) - \frac{b}{1+b}\right], \tag{9}$$

where b contains the density of free electrons, n:

$$b = -\frac{6\,\epsilon m_e (kT)^2}{\pi\, n\hbar^2 e^2}. \tag{10}$$

As n varies from 10^8 to 10^{18} cm^{-3}, Γ_{BH} varies from 2.8 to 0.3, respectively, assuming $\epsilon = 10$ and $T = 300°$K.

For all practical purposes, therefore, we may consider the cross section to be given within a factor of order unity by Eq. (2), which at room temperature gives

$$S = 10^{-10}/\epsilon^2 \approx 10^{-12} \text{ cm}^2 \tag{11}$$

for a singly charged center.

Two-Carrier Hall Effect

When both carriers are making an appreciable contribution to the conductivity, the measured Hall constant has the following form:

$$R = \frac{\sigma_n^2 R_n + \sigma_p^2 R_p}{(\sigma_n + \sigma_p)^2}, \tag{12}$$

where σ_n and σ_p are the conductivities contributed by electrons and holes, respectively, and R_n and R_p are the Hall constants for electrons and holes, respectively. Assuming a correlation factor of unity between the Hall mobility and the true mobility, as we shall do throughout this paper in the interest of simplicity, Eq. (12) may be rewritten:

$$R = \frac{p\mu_p^2 - n\mu_n^2}{e(n\mu_n + p\mu_p)^2}. \tag{13}$$

The Hall mobility, $\mu_H = \sigma R$, is therefore given by

$$\mu_H = \frac{p\mu_p^2 - n\mu_n^2}{p\mu_p + n\mu_n}. \tag{14}$$

[6] E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950).

[7] H. Brooks and C. Herring, quoted by P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).

The relative values of p and n for which the Hall mobility goes to zero are dependent on the mobility ratio. Figure 1 shows the dependence of Hall mobility in an n-type material as the density of free holes contributing to the conductivity increases. If the electron mobility is 10 times the hole mobility, for example, the concentration of holes must be 10 times that of electrons to reduce the Hall mobility by a factor of 2. The Hall mobility goes to zero when $p\mu_p^2=n\mu_n^2$.

Dependence of Scattering on Occupancy

A number of simple typical cases in which a change in mobility is associated with a change in the occupancy of an imperfection center are summarized in Fig. 2. They result principally from the fact that under photoexcitation the steady-state electron Fermi level approaches the conduction band and the steady-state hole Fermi-level approaches the valence band.[8]

Consider first Fig. 2(a) representing the existence of positively charged centers (ionized donors for example) lying above the electron Fermi level in the dark. As the Fermi level rises with increasing photoexcitation, these centers become filled with electrons, their charge is removed, and their scattering decreases strongly. This process can be expressed as follows:

$$1/\mu=\beta/\tau_0+\beta v S_+(N_+-n_+), \tag{15}$$

where β is the proportionality factor between mobility and time between scatterings, as given by Eq. (5) and equal in magnitude to 5.7×10^{-16} in practical units, β/τ_0 represents the scattering due to all other processes such as lattice scattering, etc., v is the thermal velocity of an electron, S_+ is the scattering cross section of the positively charged center, N_+ is the density of imperfection centers, and n_+ is the density of electrons in imperfection centers. Now n_+ is determinable from the Fermi distribution function, so that

$$(N_+-n_+)=\frac{N_+}{1+2\exp[(E_+-E_{fn})/kT]}, \tag{16}$$

where E_+ is the energy difference between the bottom of the conduction band and the imperfection level, and E_{fn} is the energy difference between the bottom of the conduction band and the electron Fermi level, both taken as positive quantities. If $1/\mu$ is plotted as a function of E_{fn}, a curve of the type (a) shown in Fig. 3 is obtained. When E_{fn} is much less than E_+, only scattering from the term β/τ_0 remains; when E_{fn} is much greater than E_+, all the scattering terms of Eq. (15) are effective. The difference between $1/\mu$ for small E_{fn} and large E_{fn} gives directly $\beta v S_+ N_+$. If N_+ is known by an independent measurement, as for example from thermally stimulated current data, the value of the cross section S_+ may be calculated. $E_{fn}=E_+$ when $\Delta(1/\mu)=(\beta v S_+ N_+/3)$, and the slope at $E_{fn}=E_+$ is given by:

$$\left.\frac{d(1/\mu)}{dE_{fn}}\right]_{E_{fn}=E_+}=\frac{2\beta v S_+ N_+}{9kT}. \tag{17}$$

Figure 2(b) presents the case of a center lying above the electron Fermi level in the dark which is neutral, but which becomes negatively charged under photoexcitation. Similar considerations apply, of course, to a center which might be singly negative in the dark and become doubly negative under photoexcitation. For this case

$$1/\mu=\beta/\tau_0+\beta v S_- n_-, \tag{18}$$

where S_- is the scattering cross section of a center when negatively charged, and n_- is the density of occupied centers. A value of n_- is calculable from the Fermi distribution:

$$n_-=\frac{N_-}{1+\frac{1}{2}\exp[(E_{fn}-E_-)/kT]}. \tag{19}$$

A representative curve is shown as curve (b) in Fig. 3. $E_{fn}=E_-$ when $\Delta(1/\mu)=(2\beta v S_- N_-/3)$.

It is clear that the case of Fig. 2(a) is similar to that which would be encountered for a negatively charged level lying below the hole Fermi level, and that the case of Fig. 2(b) is similar to that for a neutral or positively charged level lying below the hole Fermi level. Figure 2(c) presents a composite case, representable by the following equation:

$$\frac{1}{\mu}=\frac{\beta}{\tau_0}+\beta v S_+(N_+-n_+)+\beta v S_- n_-. \tag{20}$$

Experimentally, two separate step-wise increases in mobility will in general occur [in form like curve (a) of Fig. 3], depending on the actual location of the levels concerned in the forbidden gap, one corresponding to the filling of the positively-charged centers with electrons and the other corresponding to the emptying of electrons from the negatively-charged centers (i.e., filling with holes).

Figure 2(d) shows another possible case in which negatively charged levels are located between the two steady-state Fermi levels in the dark.

$$\frac{1}{\mu}=\frac{\beta}{\tau_0}+\beta v S_- n_-. \tag{21}$$

Assume first that only free electrons result from photoexcitation, the photoexcited holes being captured at the negatively charged centers to make them neutral. Then $n_-=(N_--n)$, and a typical curve of the behavior of $1/\mu$ is given by curve (d) in Fig. 3.

Figure 2(e) is an extension of Fig. 2(d), in which the

[8] A. Rose, RCA Rev. **12**, 362 (1951); Phys. Rev. **97**, 322 (1955).

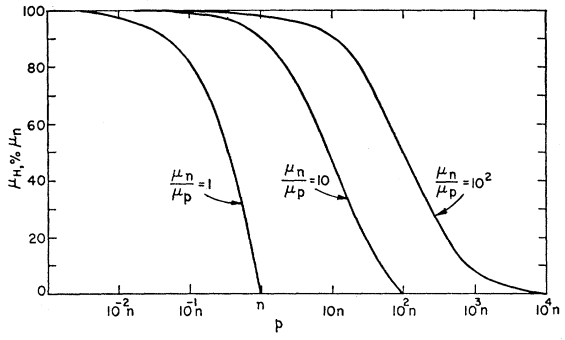

FIG. 1. Theoretical curves for the dependence of Hall mobility, plotted as percent of the electron mobility, on hole concentration, in a system with two-carrier conductivity.

photoexcited electrons are mainly captured at positively charged centers.

$$\frac{1}{\mu}=\frac{\beta}{\tau_0}+\beta v S_+(N_+-n_+)+\beta v S_-(N_--n_+). \quad (22)$$

Rearrangement of terms yields

$$\frac{1}{\mu}=\frac{\beta}{\tau_0}+\beta v(S_+N_++S_-N_-)-\beta v n_+(S_++S_-). \quad (23)$$

All of the variation of scattering with Fermi level derives from the n_+ term, which can be expressed in terms of Eq. (19). A single step in $1/\mu$ is found, with $\Delta(1/\mu)=\beta v N_+(S_++S_-)$. The analogous case where the level above the Fermi level becomes a scattering center when filled is shown in Fig. 2(f). Again a single step in $1/\mu$ is found with $\Delta(1/\mu)=\beta v N_-(S_{n-}-S_{p-})$, where S_{n-} is the scattering cross section of the centers which become negative when filled by the photoexcitation, and S_{p-} is the cross section of the centers which are negative in the dark.

As an example of the type of behavior which might be expected in a possible situation analyzed in previous publications, consider the phenomenon of thermal quenching of photoconductivity which also manifests itself as a variation of photocurrent with a higher-than-unity power of light intensity at fixed temperature. This process involves the changeover of sensitizing centers from recombination centers to hole trapping centers with either increasing temperature at fixed light intensity or with decreasing light intensity at fixed temperature.[8,9] Since sensitizing centers are those which are negatively charged in the dark, capture of photoexcited holes decreases the density of scattering centers. Such capture is effective only as long as the centers are acting as recombination centers, i.e., the hole demarcation level is below them. A previous analysis[9] provides the data from which to calculate the expected change in mobility and its effect on the measured conductivity.

[9] R. H. Bube, J. Phys. Chem. Solids **1**, 234 (1957); Proc. Inst. Radio Engrs. **43**, 1836 (1955).

TABLE I. Analysis of data of Tyler and Woodbury[a] on Ge:Mn.

	Sample 77*F*	Sample 73*F*
Temperature chosen for calculations, °K	20	30
Electron mobility in the dark, cm²/volt sec	10^4	10^4
Electron mobility in the light, cm²/volt sec	6×10^3	3.3×10^3
$\Delta(1/\mu)$, volt sec/cm²	6.7×10^{-5}	2×10^{-4}
Mn concentration, cm^{-3}	5×10^{14}	8×10^{14}
Cross section, S_{-2}, cm², calculated from Eqs. (25) and (26)[b]	3.7×10^{-10}	5.5×10^{-10}
Cross section, S_{-2}, cm², calculated from Eq. (2)[c]	3.6×10^{-10}	1.6×10^{-10}

[a] See reference 1.
[b] Calculated assuming that the light was intense enough to change the occupancy of all Mn centers. To the extent that this was not the case, the values of cross section should be larger. An effective mass, m_c^*, of 0.12 m_0 was used.
[c] For the temperature of the measurement, with $Z=2$, and $\epsilon=16$.

The scattering equation is

$$\frac{1}{\mu}=\frac{\beta}{\tau_0}+\beta v S_- n_-, \quad (24)$$

where n_- is the density of electrons in sensitizing centers, i.e., the density of sensitizing centers which have become hole traps. Values of n and of n_- as a function of excitation intensity, as given in the previous publication,[9] are used to give the calculated curves of Fig. 4. For the sake of the calculation of this figure, β/τ_0 was taken as 10^{-3} volt sec/cm², and S_-N_- was taken as 9×10^6 cm^{-1}. The corresponding values of conductivity, such as would be measured in an experiment, have been calculated and included in Fig. 4. The choice of the constants, and a discussion of their interpretation, will be included in a later section in comparison with experimental results.

The experiments involving the change of mobility with photoexcitation in Ge:Mn[1] are expressible in the framework of this analysis. In this case:

$$\frac{1}{\mu}=\frac{\beta}{\tau_0}+\beta v S_- n_-+\beta v S_{-2} n_{-2}, \quad (25)$$

$$n_-+n_{-2}=N_{Mn}. \quad (26)$$

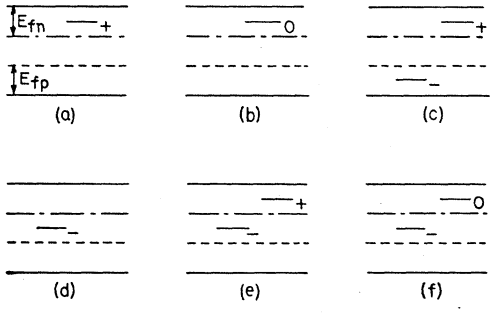

FIG. 2. A number of possible cases in which a change in occupancy of a level as the result of photoexcitation will result in a change in mobility.

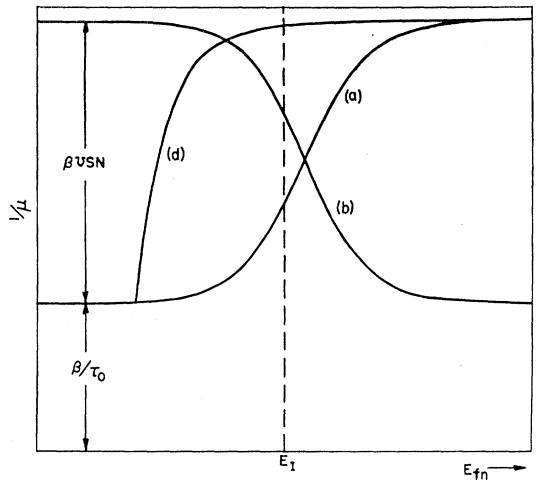

FIG. 3. Theoretical curves for the dependence of $1/\mu$ on the location of the electron Fermi level for three cases with corresponding letters in Fig. 2.

If Eq. (26) is inserted in Eq. (25), it is seen that $\Delta(1/\mu)=\beta v N_{Mn}(S_{-2}-S_{-})=\frac{3}{4}\beta v N_{Mn}S_{-2}$. The experimental data of this work are analyzed with the results summarized in Table I, to give a feeling for the magnitudes of the quantities previously encountered. The cross sections calculated from the experimental data using Eqs. (25) and (26) are quite comparable to those estimated from Eq. (2).

EXPERIMENTAL

All measurements were made on single crystals of CdS or CdSe with melted indium end contacts and melted indium probe and Hall contacts. An electromagnet was used with 1.5-in. pole pieces, capable of producing a magnetic field of 3925 oersteds with the gap of 1.5 inches used in these measurements. A current of 1.5 amp was supplied to the magnet by a Lambda regulated power supply. The voltage applied to the crystal was supplied by batteries, and the crystal current was measured with an RCA ultrasensitive dc microammeter. The difference of potential between probes on the side of the crystal, and also the Hall voltage itself, were measured with a Cary 31–31V vibrating-reed electrometer with a 10^{12}-ohm input resistor and critical damping. Photoexcitation was with a focused No. 1497 microscope lamp operated at 6 volts; to remove infrared quenching and heating effects, the light from the lamp was passed through a 5-cm path of a 2% water solution of $CuCl_2$ in most measurements with CdS, and through a 5-cm path of water alone for most measurements with CdSe. Where indicated, Bausch and Lomb interference filters were used for monochromatic excitation. Variations in light intensity were achieved by interposing calibrated neutral filters made from stainless steel mesh, accurate over seven orders of light intensity.

The spectral response curves of the crystals of CdS and CdSe used were sharply peaked at the respective absorption edges of 5150A and 7300A. Even when a relatively broad-band of excitation radiation is used, therefore, over 90% of the response comes from a narrow band within a couple of hundred Angstroms of the absorption edge. Since the maximum response occurs for that wavelength of light which is just able to penetrate the volume of the crystal, use of a broad-band excitation, as in these experiments, assures a reasonably homogeneous excitation of the crystal, with only minor contributions to the measured current from strongly absorbed light at the surface. Since higher light intensities are obtainable with the broad-band excitation, considerable use has been made of it. The existence and the magnitude of the effects have also been corroborated, however, by the use of monochromatic excitation, as described in more detail further on in this paper. Surface excitation makes an appreciable contribution to the total measured photoconductivity only when strongly absorbed monochromatic radiation is deliberately chosen.

The apparatus was capable of reliably measuring a minimum potential difference of 0.1 to 1 millivolt at a crystal resistance of 10^9 ohms. Measurements were ordinarily made with fixed voltage drop in the crystal as measured by the potential difference between the voltage probes. Hall voltages were measured for both directions of applied field and for both directions of magnetic field; in general only minor differences were observed and the average was used in the calculations.

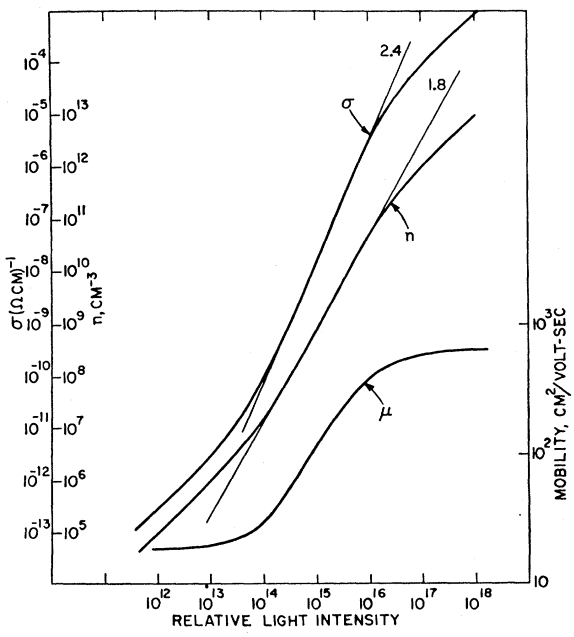

FIG. 4. Theoretical curves for the dependence on light intensity of conductivity, electron density, and mobility, using the data of a previous publication describing the variation of photocurrents with a higher-than-unity power of light intensity.[9]

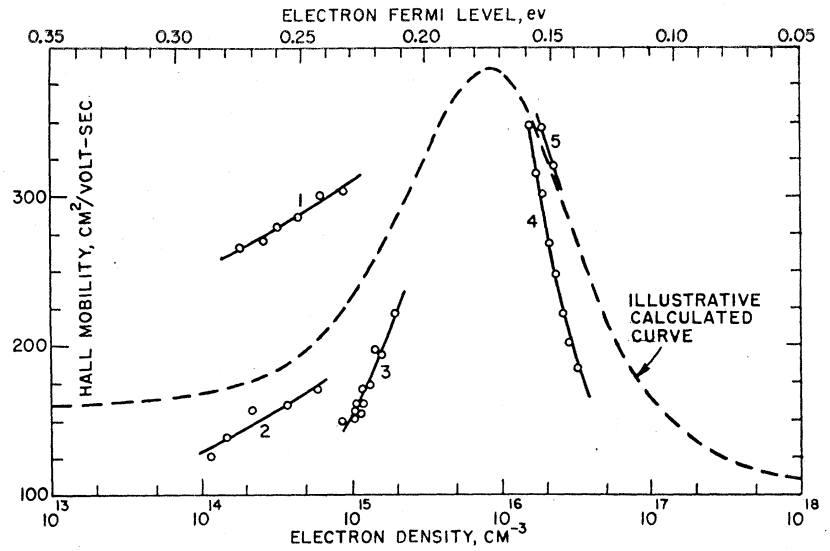

FIG. 5. Experimental curves for the variation of Hall mobility with electron density, as varied by photoexcitation, for five crystals of high-conductivity CdS. The dashed curve is an illustrative theoretical curve indicating how two centers could produce the observed effects.

A number of checks were made to determine the dependence of Hall voltage on the magnitude of the magnetic field; a linear dependence was always found, as is illustrated for one particular case later in this paper. The Hall voltage varied linearly with electric field across the probes from about 1 to 500 volts/cm.

RESULTS AND DISCUSSION

High-Conductivity CdS Crystals

A number of measurements were made on a series of high-conductivity CdS:Cl crystals, for which photoexcitation made only relatively small changes in conductivity. The results for five such crystals are shown in Fig. 5. Changes in electron density result from photoexcitation. For crystals with electron densities below about 3×10^{15} cm^{-3}, the mobility increases with photoexcitation, whereas for those with electron densities above about 3×10^{15} cm^{-3}, the mobility decreases with photoexcitation. The dashed curve shown in Fig. 5 is a purely illustrative calculated curve showing how such behavior could result from the existence of two levels, the deeper of which is charged when the Fermi level is below it, and the shallower of which is charged when the Fermi level is above it. The data used for drawing the dashed curve are: $\beta/\tau_0=10^{-3}$ volt sec/cm^2, $E_+=0.20$ ev, $S_+N_+=9\times10^5$ cm^{-1}, $E_-=0.10$ ev, $S_-N_-=1.5\times10^6$ cm^{-1}. If the values of the cross sections are to be of the order of 10^{-12} cm^2, according to Eq. (11), N_+ and N_- must be of the order of 10^{18} cm^{-3}. Since the value of N in these crystals is more likely to be of the order of 10^{16} cm^{-3}, a large cross section of the order of 10^{-10} cm^2 is suggested.

Photosensitive Insulating CdS Crystals

The data reported in this section were obtained with a typical photosensitive crystal of CdS, sensitized by the incorporation of trace proportions of chlorine. The conductivity in the dark was 10^{-8} mho/cm; this conductivity could be increased to 6.6×10^{-3} mho/cm at the highest light level used ($\sim6\times10^3$ ft-c). The variation of Hall mobility with electron density, as varied by photoexcitation, is shown in Fig. 6 for electron densities ranging from 5.3×10^8 cm^{-3} to 1.4×10^{14} cm^{-3}. The Hall mobility increases from about 110 cm^2/volt sec in the dark to a value of 295 cm^2/volt sec under full illumination, in three well-defined steps.

The same data are replotted in a way more susceptible to analysis, in terms of $1/\mu$ vs E_{fn}, in Fig. 7. The simplest interpretation is to propose the existence of three levels, positively charged in the dark, the scattering effect of each of which is given by Eq. (15):

$$\frac{1}{\mu}=\frac{\beta}{\tau_0}+\beta v\sum_i S_i(N_i-n_i). \tag{27}$$

When interpreted in this way, the data of Fig. 7 provide values for the E_i and the S_iN_i. The next natural step

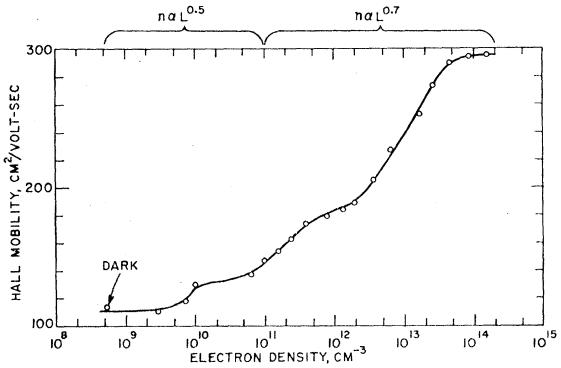

FIG. 6. Hall mobility for a crystal of CdS as a function of free electron density, as varied by photoexcitation, from the dark to excitation with an intensity of about 6000 ft-c.

TABLE II. Summary of imperfection parameters.

Imperfection No.	Trap depth from therm.-stim. current, ev	Trap depth from mobility effect, ev	Density from therm.-stim. current, cm^{-3}	Scattering cross section, cm^2
1	0.20		2.2×10^{15}	
2	0.25		9.1×10^{15}	0.7×10^{-10}
3	0.40	0.35	10^{15}	4×10^{-10}
4	0.46	0.46	3.0×10^{15}	1.1×10^{-10}
5	0.55	0.54	3.3×10^{15}	0.8×10^{-10}

is to look for independent evidence of the existence of such levels, their E_i and their N_i. This was done through the measurement of thermally stimulated current with the results shown in Fig. 8. Traps numbered 3, 4, and 5 in Fig. 8 have trap depths very close to those derived from the mobility data of Fig. 7. The thermally stimulated current data allows in addition the calculation of the densities of these various traps. These densities can then be combined with the mobility data giving the product of density and cross section, to determine values for the cross section. A summary of these determinations is given in Table I. It is found that all scattering cross sections come out of the order of 10^{-10} cm^2, or about 10^2 times larger than expected from the previous considerations. A correlation exists in addition between the measured scattering cross sections and the distance between these imperfections as calculated from their measured density (Table II). The comparison is summarized in Table III.

A theoretically expected variation of $1/\mu$ with E_{fn} was calculated using the values of trap depth, trap density, and capture cross section from Table I, substituting in Eq. (21), with $\beta/\tau_0=3.35\times10^{-3}$ volt sec/cm^2. The resultant calculated curve is compared with the experimental points in Fig. 9. The fit is excellent except for the higher values of E_{fn}; these represent the measurements taken in the highest resistivity range and have a greater margin of possible error.

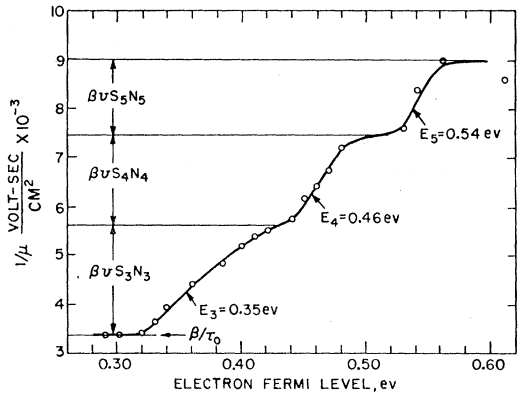

FIG. 7. The data of Fig. 6 replotted in terms of $1/\mu$ as a function of the location of the electron Fermi level to facilitate interpretation.

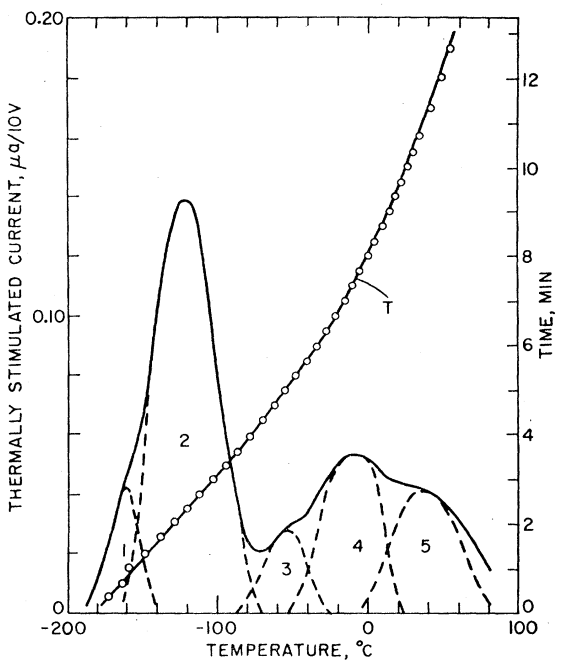

FIG. 8. Thermally stimulated current for the crystal of Figs. 6 and 7, showing 5 trap depths.

In order to extend the information about the effects of photoexcitation on the Hall mobility of this crystal of CdS still further, the mobility was measured as a function of light intensity for various monochromatic excitations. (See Fig. 10.) Here the observation is that mobility increases with increasing light intensity for volume-absorbed light as previously indicated, but decreases with increasing light intensity for surface-absorbed light. If correction is made for the difference in absorption coefficients, however, the data may be consistently interpreted. If we assume an absorption constant of 10^6 cm^{-1} for the wavelengths shorter than the absorption edge, the fact that the thickness of the crystal is 1.25×10^{-2} cm, suggests that the equivalent electron density for the surface-absorbed light is about 10^4 times that for the volume-absorbed light. If this correction to the electron density for surface-absorbed light is made, all the data on this crystal can be plotted together as in Fig. 11 to give a continuous variation of mobility with Fermi level. In addition, Fig. 11 shows a calculated theoretical curve, identical with that of Fig. 9 above $E_{fn}=0.30$ ev, but calculated for smaller E_{fn} assuming that imperfection number 2, with trap depth and density determined from thermally stimulated current data, has a scattering cross section of 0.7×10^{-10} cm^2 and is negatively charged when the Fermi level lies above it. Most of the experimental data can reasonably be fitted, therefore, by a single theoretical curve. Points which fall rather far from the curve are those for 6330A excitation, corresponding to direct excitation of imperfection centers. This departure may

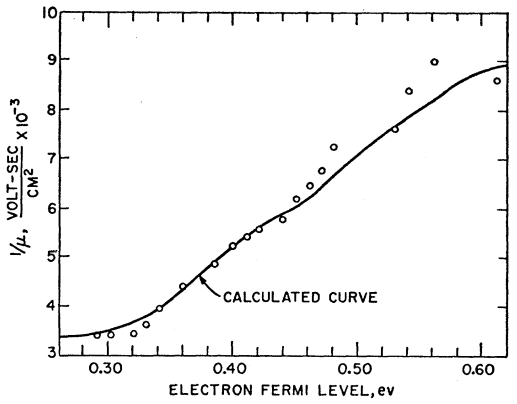

FIG. 9. Comparison between the theoretical curve for scattering by traps 3, 4, and 5 of Fig. 8 with the experimental points. Parameters in the calculation are given in Table II.

be interpreted as indicating that such excitation is restricted to a smaller portion of the crystal near the surface, as has been previously shown to be the case in certain CdSe:I:Cu crystals.[10]

All of the above considerations have been concerned with changes in mobility resulting from motion of the electron Fermi level with photoexcitation. It is well known, however, that there are negatively-charged sensitizing centers in CdS, lying about 1.0 ev above the top of the valence band, as was mentioned earlier in this paper. Under photoexcitation, these centers capture photoexcited holes and become neutral. In CdS these captured holes are thermally stable at room temperature, but they can be removed by optical excitation from the valence band, i.e., by initiating infrared quenching of photoconductivity. Experiments were performed using a primary exciting radiation of 5170A (volume-absorbed) and a quenching radiation consisting of a microscope lamp passed through a Corning 2540 filter, giving all wavelengths beyond about 1 micron. The intensity of the quenching radiation was varied to produce various degrees of quenching as indicated in Fig. 12(a). Simultaneously the Hall mobility was measured with results shown in Fig. 12(b); the mobility varies from 235 cm²/volt sec in the absence of quenching to 41 cm²/volt sec for 99.8% quenching. In the process of infrared quenching, however, the electron Fermi level is also lowered, and the change in mobility due to the lowering of the electron Fermi level must be distinguished from the change in mobility due to optical freeing of holes from sensitizing centers. In order to do this, the mobility was measured with the quenching radiation turned off, equivalent currents being obtained by decreasing the intensity of the primary radiation. Figure 12(c) then compares the variation of mobility with $1/eR$ purely as the result of the motion of the electron Fermi level, with the total variation of mobility resulting from both the motion of the electron Fermi level and of optical freeing of holes from sensitizing centers. Not only does the optical freeing of holes have a definite and distinct effect, but its magnitude is even larger than that associated with motion of the electron Fermi level. The ratio of the mobilities is plotted in Fig. 12(d). The magnitude of the change in mobility with optical freeing of holes is such that S_-N_- would have to be of the order of 4×10^6 or larger if the mobility change were to be due to a change in scattering resulting from the freeing of holes with the accompanying creation of scattering centers. Even with $S_-=10^{-10}$ cm², a value of $N_-=4\times10^{16}$ cm^{-3} or larger would be required. On the other hand, the observed decrease in Hall mobility might be attributed to an increased participation of holes in the conductivity process, as a result of being optically freed from sensitizing centers. Assuming an electron mobility about 10 times the hole mobility, this means that at the lowest value of $n=1/eR$ shown in Fig. 12(d), where the mobility has been decreased by a factor of 5 by optical freeing of holes, the actual density of holes (see Fig. 1) must be about 30 times the density of electrons.

The linearity of the Hall voltage with magnetic field intensity under a condition of 92% quenching of the primary excitation, as described above, is shown in Fig. 13. This condition was chosen as a fairly complicated situation where nonlinearities would be most likely to become evident.

TABLE III. Comparison of measured cross sections with distance between imperfections.

Imperfection No.	Sign of charge	Measured S, cm² as given in Table II	$\pi(N_I^{-\frac{1}{3}})^2$, cm²
2	−	0.7×10^{-10}	0.72×10^{-10}
3	+	4×10^{-10}	3.1×10^{-10}
4	+	1.1×10^{-10}	1.5×10^{-10}
5	+	0.8×10^{-10}	1.4×10^{-10}

Photosensitive Insulating CdSe Crystals

Photosensitive insulating CdSe crystals were obtained by vacuum annealing of insulating crystals as previously reported.[10] Because the sensitizing centers in

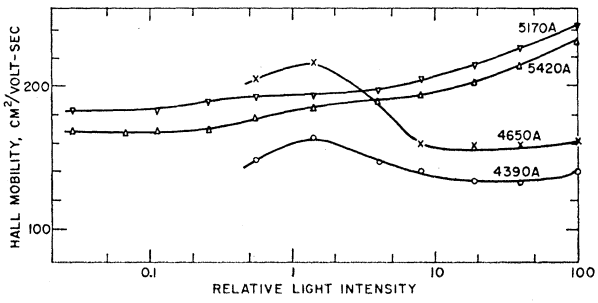

FIG. 10. Hall mobility as a function of light intensity for volume-absorbed excitation (5170 and 5420A), and for surface-absorbed excitation (4390 and 4650A).

[10] R. H. Bube and L. A. Barton, J. Chem. Phys. **29**, 128 (1958).

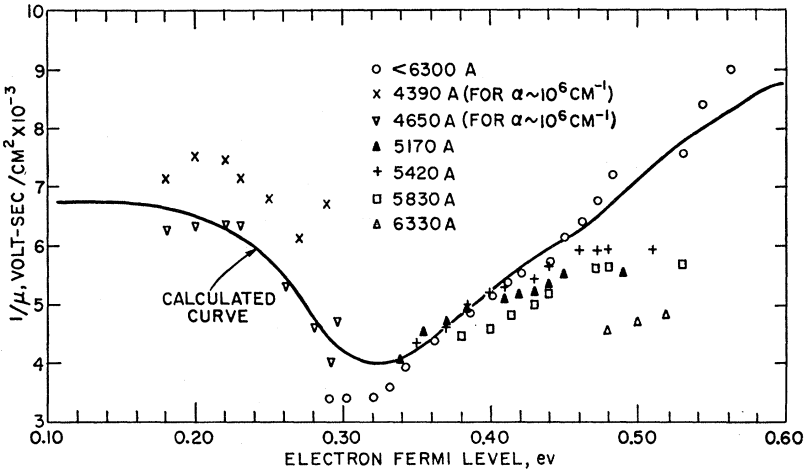

FIG. 11. Comparison between the theoretical curve for scattering by traps 2, 3, 4, and 5 of Fig. 8 with all the experimental points on this CdS crystal. The points for the 4390A and 4650A excitation have been shifted an amount corresponding to a 10^4 higher electron density than if calculated from the current and the width of the crystal. Trap 2 is assumed to be charged when the Fermi level lies above it, as opposed to Traps 3, 4, and 5, which are charged when the Fermi level lies below them.

CdSe lie only 0.6 ev above the top of the valence band, whether they act as recombination centers (and retain photoexcited holes) or as trapping centers (and remain negatively charged) depends on the light intensity at room temperature. We have examined a theoretical example of such a process with the results shown in Fig. 4. Actual experimental data on a crystal of CdSe are shown in Fig. 14. Except for the structure in the mobility curve, the results are quite similar to those indicated in Fig. 4. The mobility decreases from 792 cm²/volt sec at high light intensity to 50 cm²/volt sec at a light intensity about four orders of magnitude lower. The mobility data is replotted in Fig. 15 in terms of the $1/\mu$ vs E_{fn} [11] dependence. The steps in the curve at smaller values of E_{fn} can be simply described in terms of positively charged levels lying above the dark electron Fermi level: one with $E_1=0.36$ ev and $S_1N_1=3\times10^5$ cm^{-1}, and the second with $E_2=0.49$ ev and $S_2N_2=5\times10^5$ cm^{-1}. The sudden steep rise in $1/\mu$, associated with the thermal freeing of holes from sensitizing centers, would require a much larger value of S_-N_- if interpreted in this way. It was previously mentioned in connection with Fig. 4 that a value of $S_-N_-=9\times10^6$ cm^{-1} had been chosen there, producing a similar curve to the experimental curve of Fig. 14. If S_-N_- is calculated from the slope of the curve for large E_{fn} in Fig. 15, according to Eq. (17), a value of about 10^7 cm^{-1} is likewise obtained. Even with values of $S_-=10^{-10}$ cm², large values of N_- are required. On the other hand, if the change in the Hall mobility were due to increased participation of holes in the conductivity process at low light intensities, about 60 times as many holes (see Fig. 1) as electrons would be required to take part in the conductivity.

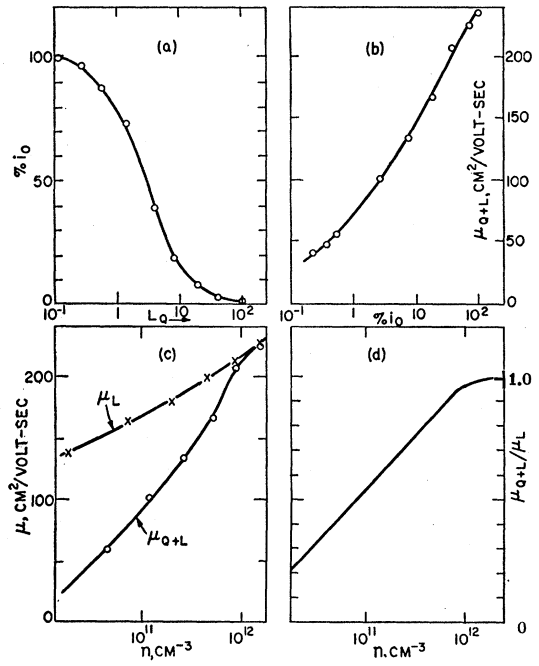

FIG. 12. Infrared quenching data on the CdS crystal. (a) Percent of the original photocurrent excited by 5170A light as a function of the intensity of the infrared quenching radiation. (b) Measured Hall mobility under infrared quenching, μ_{Q+L}, as a function of the percent of the original photocurrent. (c) Measured Hall mobility with decreasing 5170A light intensity in the absence of infrared quenching, μ_L, compared with the measured Hall mobility with constant 5170A excitation and increasing infrared intensity, as a function of $n=(eR)^{-1}$, (d) The ratio of the two mobilities plotted in (c).

Another type of dependence of Hall mobility on light intensity in CdSe, more like curve (d) in Fig. 3, has also been observed and is illustrated in Fig. 16. Although there is a continuous change in Hall mobility with light intensity from 550 cm²/volt sec to a maximum of 735 cm²/volt sec, over three orders of magnitude of light intensity, the electron density is practically independent of light intensity over this range. The latter independence rules out an effect of a moving electron Fermi level, and places the cause for the entire observed effect in this relatively high-conductivity crystal on the capture of photoexcited holes by sensitizing centers with a subsequent decrease in their scattering. As

[11] E_{fn} calculated as if $n=1/eR$.

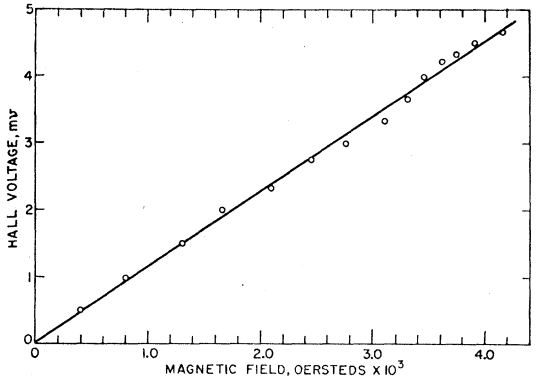

FIG. 13. Dependence of Hall voltage on magnetic field strength under conditions of 92% infrared quenching of original photocurrent.

increasing light intensity produces more and more electron-hole pairs, the effect of the electrons is not observed in the conductivity until the photoexcited density exceeds the density present in the dark, allowing also for the possibility of many of the photoexcited electrons being caught in electron traps. The corresponding photoexcited holes, however, captured at negatively charged centers affect the mobility immediately.

SUMMARY

It has been demonstrated that the Hall mobility can vary by large factors as a result of photoexcitation in insulating photoconductors. Many of the phenomena of photoconductivity should be reinvestigated by means of the photo-Hall effect to truly separate the different functions of carrier lifetime and carrier mobility.

One way in which photoexcitation can change the mobility is to alter the occupancy of scattering centers. When such a process is taking place, measurements of photo-Hall effect can be used to determine both the charge and the cross section of the scattering centers. Reasonable success is shown in fitting experimental data on CdS crystals with such an interpretation, providing that a large scattering cross section of the order of 10^{-10} cm^2 is used in a point-defect scattering model, which corresponds to a radius of about the distance between imperfections.

A real understanding of the significance of this large cross section is not presently at hand; temperature dependence data should be helpful and are planned. One possibility is to retain the point-defect model but to consider multicharged clusters as the scattering centers; such a model would require each cluster to have 100 charges in order to keep (SN) equal to the observed value. Smaller clusters or otherwise ordered imperfections might give rise to crystal strains with apparent scattering cross sections of the magnitude observed. Additional experimental work is required to support more detailed speculation.

Because it does predict a variation of mobility with carrier density, the Brooks-Herring relationship provides an additional mechanism for the type of results observed and therefore deserves consideration. Although it is questionable whether this relationship is valid at the low values of carrier density involved, it

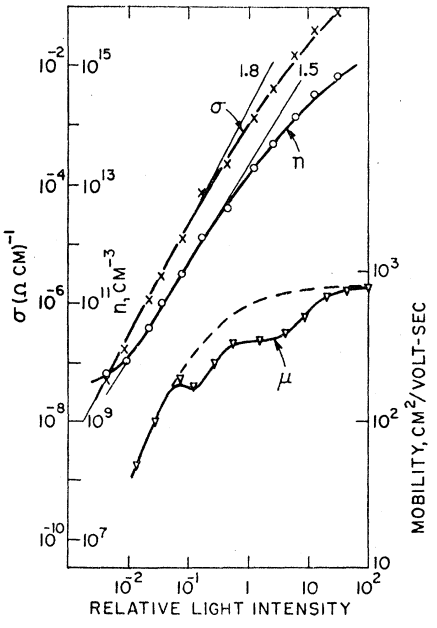

FIG. 14. Experimental variation of conductivity, $n=(eR)^{-1}$, and Hall mobility, with light intensity for a crystal of CdSe; to be compared for similarity with Fig. 4.

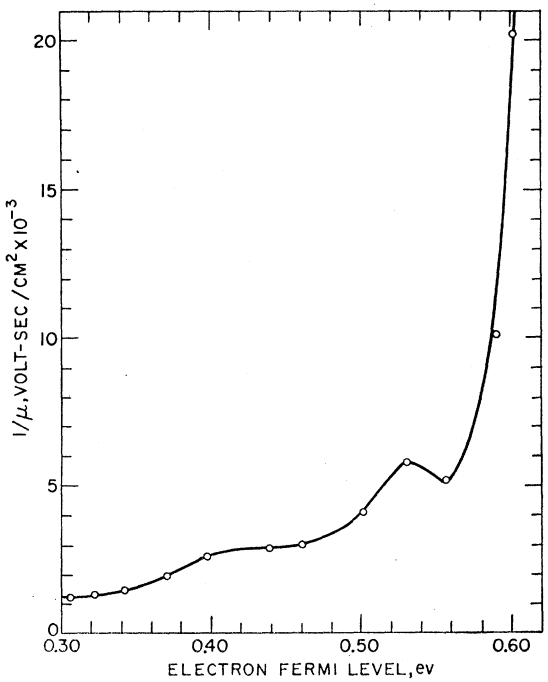

FIG. 15. Mobility data of Fig. 14 replotted as $1/\mu$ as a function of the location of the electron Fermi level, assuming $n=(eR)^{-1}$.

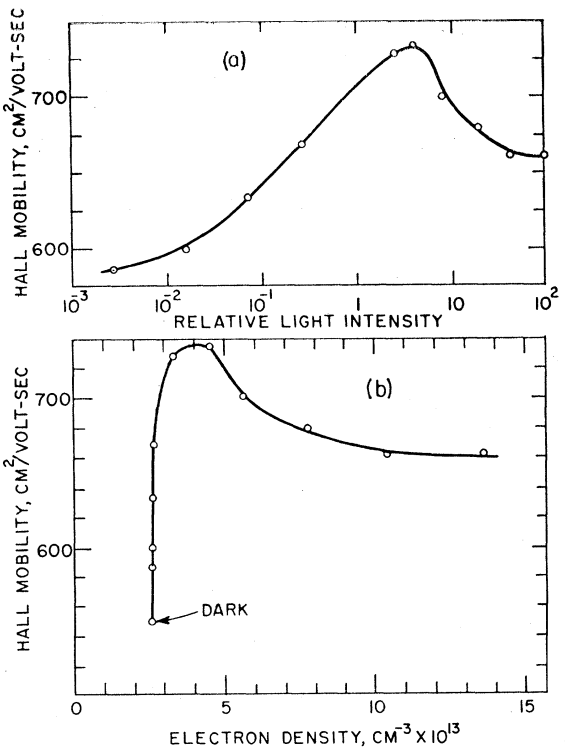

FIG. 16. Hall mobility as a function of (a) light intensity, and (b) free electron density, for a crystal of CdSe with moderately high dark conductivity.

does provide a kind of guide. To see what part of the experimental results may be described in terms of the Brooks-Herring equation, we assume a high density (5×10^{17} cm^{-3}) of shallow ionized donors with a normal scattering cross section of the order of 10^{-12} cm^2. It is also assumed that the observed Hall mobility, μ_H, may be expressed as:

$$\frac{1}{\mu_H}=\frac{1}{\mu_0}+\frac{1}{\mu_I}+\frac{1}{\mu_{BH}}, \tag{28}$$

where μ_0 represents the residual mobility due to lattice scattering or other scattering not affected by the photoexcitation under consideration, μ_I represents the mobility due to charged imperfection scattering with occupancy changing under photoexcitation, and μ_{BH} represents the mobility due to scattering by the shallow ionized donors. It is found that, even if such a $1/\mu_{BH}$ variation is subtracted off, according to the Brooks-Herring relationship, the remaining $1/\mu_0+1/\mu_I$ still exhibits the same type of variation with carrier density. The only difference is that now a cross section of about 5×10^{-11} cm^2 is indicated instead of 10^{-10} cm^2. It is also not possible to take up the whole variation in $1/\mu_H$ with carrier density in a $1/\mu_{BH}$ term. If, for example, μ_0 is taken as 600 cm^2/volt sec, the Brooks-Herring relation predicts a decrease in Hall mobility of 40% as n decreases from 10^{14} to 10^8 cm^{-3}, whereas a decrease of 60% (with structure) is observed.

Another way in which photoexcitation can change the mobility is to make both carriers important in the conductivity process rather than just one. Measurements of infrared quenching in CdS, and of variations of photoconductivity with a higher-than-unity power of light intensity in CdSe, indicate changes in Hall mobility which are too large to be interpreted simply in terms of a change in scattering. When they are interpreted in terms of increased participation of free holes in the conductivity, in agreement with the probable mechanisms involved, they indicate that the density of free holes in the desensitized crystals is 30 to 60 times that of free electrons, i.e., that the conductivity contributions of electrons and holes are of the same order of magnitude.

It is believed that this initial investigation has indicated the potentialities of a new and fruitful technique in the investigation of the nature of imperfections in insulators.

ACKNOWLEDGMENTS

The authors are deeply indebted to both Dr. Richard Williams and to Dr. L. R. Weisberg, with whom helpful discussions were held throughout the work, and who have made appreciable contributions to the interpretation of the work.