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Electron Mobility and Shallow Impurity Levels in In- and Cu-Doped CdS†

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Electrical-conductivity and Hall-effect measurements were made between 300 and 4.2 °K on In-doped ($\sim 6\times10^{17}$ cm^{-3}) CdS single crystals. Normal band conduction was observed between 300 and 20 °K, while impurity-hopping conduction in a shallow-donor state (E_{D2}) dominated the conduction mechanism for $T < 20$ °K. In the normal-band-conduction region, the best theoretical fit was obtained by using a two-shallow-impurity-level model. The result yields $E_{D1} = 0.033$ eV for the In level with $N_{D1} = 6\times10^{17}$ cm^{-3} and $E_{D2} = 0.007$ eV for a level with unknown origin with $N_{D2} = 1.3\times10^{17}$ cm^{-3}. The Hall mobility vs temperature was studied for both Cu- and In-doped CdS between 4.2 and 300 °K. It was found that the longitudinal optical phonons dominate the scattering of electrons for $T > 200$ °K and $\mu_L \cong 110(e^{(300\pm10)/T} - 1)$ cm^2/V sec. A brief discussion of the scattering mechanism for $T < 100$ °K is given for both In- and Cu-doped CdS.

I. INTRODUCTION

Although a considerable amount of work has been done on the photoconductive and luminescent properties in II-VI compounds, only a small part of this work has been on the conventional transport properties.

Much of the work on CdS has been concerned with the intrinsic scattering mechanism. Kroger *et al.*[1] attempted to fit their data to a simple expression for optical-mode scattering. Migazawa *et al.*[2] also attempted to fit their data with a combination of optical-mode and impurity scattering. Devlin[3] used the variational method to find the effect of two simultaneous scattering mechanisms on the Hall mobility. Fugita *et al.*[4] measured the Hall mobility under pulsed illumination using the Redfield[5] technique. Monikowa[6] measured the Seebeck coefficient of several n-type CdS crystals having room-temperature carrier concentrations of the order of 10^{15} cm^{-3}, and gave a value of 0.024 eV as the shallow-donor ionization energy. Woodbury[7] reported a double acceptor 0.09 eV below the conduction-band edge. Bradberry and Spear[8] observed trapping effects in their drift-mobility measurement due to a level 0.16 eV below the conduction band. They attributed this level to native defects, tentatively singly ionized sulfur vacancies. Buget and Wright[9] measured the temperature dependence of the carrier concentration in n-type CdS and found it determined by unknown donors with ionization energies of 0.45, 0.63, and 0.82 eV in different crystals.

Kroger and Vink[1] have studied the effect of additions of Cl and Ga which act as shallow donor after firing in Cd atmosphere, but the defects were in such high concentration that the samples were degenerate or indicated impurity-band conduction. Piper and Halsted[10] observed a donor level at 0.032 eV in samples with carrier density of 10^{15} cm^{-3}, which is sufficiently low to avoid impurity banding or screening effects. This energy is in close agreement with the value predicted on the assumption that the donor is hydrogenlike. Itakura and Toyada[11] measured the Hall effect in undoped CdS in which two donor levels were found: one 0.014 eV and the other 0.007 eV below the conduction-band edge.

The transport measurements reported in the literature so far yield a relatively well-understood knowledge with regard to the intrinsic scattering mechanism in CdS. Longitudinal optical- and acoustical-mode scattering dominate the scattering of electrons at high temperatures, while piezoelectric scattering dominates the scattering mechanism at low temperatures. Identification of impurity levels in CdS is still far from ideal owing to the fact that native defects resulting from nonstoicheometry and residual impurities exist in the crystal, controlling the electrical properties of such a material.

In this paper, we attempt to identify the impurity levels in In-doped CdS from a study of electrical-conductivity and Hall-effect measurements between 4.2 to 300 °K. The doping density of indium is chosen such that the material is nondegenerate in certain temperature ranges. An elaborate study of carrier concentration vs temperature between 4.2 and 300 °K is made for In-doped CdS samples. A two-impurity-level model is proposed to interpret the observed results. In addition, the conductivity and the Hall-effect measurements are also studied for Cu-doped CdS. This allows us to draw conclusions with regard to the scattering mechanism as well as shallow impurity states in In-doped CdS.

II. EXPERIMENTAL DETAILS

The undoped CdS crystal was supplied by the Clevite Corporation, and has the following impurities before doping with indium or copper:

Fe < 0.1 ppm, Ni < 0.5 ppm, Zn < 30 ppm,
Cu < 0.1 ppm, Pb ~ 5.0 ppm, Cl < 5 ppm.

The last three elements are greatly reduced in the process of vacuum sintering and growing the crystal. The indium-doping density is chosen such that its concentration is high enough to control the electrical properties of the sample by indium atoms alone, rather than by native defects or residual impurities. In addition, the material has to be nondegenerate in a wide temperature range so that the study of the shallow impurity states can be made in such materials. The optimum concentration chosen for In and Cu is about 5×10^{17} cm^{-3} for the purpose of this study. The sample was cut into a rectangular bar with dimensions $5\times3\times1$ mm^3, after chemical etching. In-Ga paste was used for Ohmic contacts, and is found to be satisfactory over the measuring temperature range. The electrical and the Hall-effect measurements were performed between 4.2 and 300 °K, using standard techniques. An AC-310 liquid-helium refrigeration system was used for low-temperature measurements. The magnetic fields used were between 1 and 8 kG. To assure that no irreversible changes had occurred in the bulk of the crystals or the electrodes during the thermal cycling, several of the crystals were remeasured over the entire covered temperature range. A few crystals were removed from the cryostat, provided with electrodes, and remeasured. It was found that the maximum fluctuation was less than 3%.

III. RESULTS AND ANALYSIS

The Hall-effect and electrical-conductivity measurements were made between 4.2 and 300 °K on In- and Cu-doped CdS single crystals. Detailed analyses of the Hall-coefficient and electrical-conductivity data will be given for the In-doped CdS. For Cu-doped CdS, only qualitative descriptions will be given owing to the nonconclusive results obtained from the present measurements.

A. Single-Donor-Level Model for In-Doped CdS

In analyzing carrier-concentration data vs temperature for In-doped CdS, we first try a single-donor-level model and use the well-known formula[12] for nondegenerate statistics, e.g.,

$$n(n+N_A)/(N_D-N_A-n)=(N_c/g)\,e^{E_D/kT} \qquad (1)$$

for the electron concentration n. Here $N_c = 2(2\pi m_e kT/h^2)^{3/2}$, m_e being the density-of-states electron mass and g the degeneracy factor which depends on the nature of the impurity states and the band edge involved. Later, when considering the carrier concentration associated with two shallow-donor states, we set up the generalization of Eq. (1) appropriate to that case. The electron concentration is assumed to be given by $|R_He|^{-1}$ for simplicity, where R_H is the Hall constant and e is the electronic charge. The factor $r=\mu_H/\mu_d$ (the ratio of Hall-to-drift mobilities) is thus taken to be unity. This is, in fact, a fairly good approximation for CdS moderately doped with indium impurity. We take the electron effective mass ($m_e=0.2\, m_0$) for calculating the donor level from Eq. (1), which is the most acceptable value obtained so far[3] for CdS. If Eq. (1) were used for calculating the shallow impurity level in In-doped CdS, a linear slope with $E_{D1}=0.0154$ eV was obtained for $77<T<300$ °K from a $\ln[n(n+N_A)/(N_D-N_A-n)T^{3/2}]$ vs $1/T$ plot.

The assumed values for N_D and N_A for this case are $N_D=5\times10^{17}$ cm^{-3} and $N_A=1\times10^{17}$ cm^{-3}, respectively.[13] The ionization energy $E_{D1}=0.0154$ eV obtained from this curve fit for In level is about two times lower than the reported values.[14] In addition, the experimental points deviated considerably from the theoretical curve for $T<77$ °K, indicating the inadequacy of using a single-impurity-level model for In-doped CdS. In fact, this discrepancy can be eliminated if a two-donor-level model is used to fit the electron-concentration data between $300>T>20$ °K.

B. Two-Donor-Level Model for In-Doped CdS

Figure 1 shows the electrical conductivity and Hall coefficient vs $1/T$ for In-doped CdS, for $4.2<T<300$ °K. It is noted from the conductivity vs $1/T$ curve, shown in Fig. 1, that normal-band conductivity was observed for $300>T>20$ °K, and impurity-band hopping conductivity was observed for $T<20$ °K. In the normal-band-conductivity region where nondegenerate statistics hold, we use

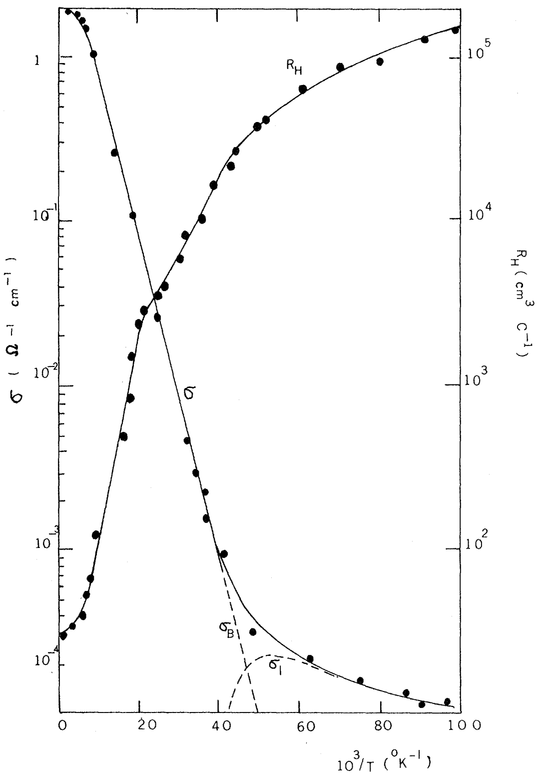

FIG. 1. Electrical conductivity σ and Hall coefficient R_H vs $1/T$ for In-doped CdS, for $4.2 < T < 300\ ^{\circ}K$. For $T < 25\ ^{\circ}K$, the conductivity data σ is decomposed into two parts (dashed line); one due to normal-band conduction and the other due to the impurity-hopping conduction. The indium concentration is $N_D \simeq 6 \times 10^{17}\ cm^{-3}$, and $\sigma = \sigma_B + \sigma_I$ for $T < 25\ ^{\circ}K$.

the two-donor-level model to perform the curve fit from the electron-concentration data vs $1/T$. The results indicate that the indium-donor level is responsible for the electron conduction between 300 and 77 °K (range I), while another unidentified donor state dominates the conduction mechanism for temperatures between 20 and 77 °K (range II). In order to analyze the electron-concentration data for the above temperature regions, we start with the charge-neutrality equation, and assume that N_{D1} and E_{D1} are the indium density and ionization energy, respectively; N_{D2} and E_{D2} are the density and ionization energy of the unknown defects, respectively. The acceptor density for this sample is assumed to be N_A. The electron-concentration data can be analyzed in two temperature regions, using nondegenerate statistics as given by Eq. (1). For range I, the following expression is obtained for n vs T:

$$\frac{n(n+N_A-N_{D2})}{N_{D1}+N_{D2}-N_A-n} = \frac{n[n/N_A-(N_{D2}/N_A-1)]}{N_{D1}/N_A-n/N_A+(N_{D2}/N_A-1)}$$

$$= \frac{1}{g} N_c e^{E_{D1}/kT}. \qquad (2)$$

In this temperature region, the second donor state E_{D2} is assumed completely ionized, while the first donor state E_{D1} is partially filled. In range II, the first donor state is assumed compleIely filled and the second donor state is partially ionized. The relationship between n and T in this temperature range is given by

$$\frac{n(n+N_A)}{N_{D2}-N_A-n} = \frac{1}{g} N_c e^{E_{D2}/kT}. \qquad (3)$$

Since $n \ll N_A$ and $n \ll N_{D2}-N_A$ for $T < 77\ ^{\circ}K$, Eq. (3) can be reduced to

$$n \cong (N_c/g)\,(N_{D2}/N_A-1)\,e^{E_{D2}/kT}. \qquad (3')$$

With the aid of Eqs. (2) and (3′), E_{D1}, E_{D2} and N_{D1}, N_{D2} can be determined by assuming values of N_A, g, and using values of n determined from the Hall constant. The procedures for determining these parameters are indicated in the legend of Fig. 2.

For temperatures below 20 °K, the impurity-

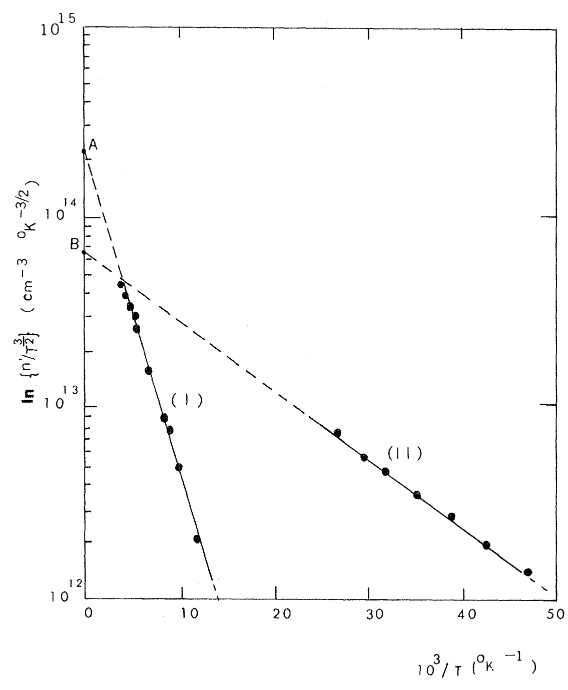

FIG. 2. Region (I) is a plot of $\ln\{n[n+N_A-N_{D2}]/[N_{D1}+N_{D2}-N_A-n]\ T^{3/2}\}$ vs $1/T$. The slope of this straight line yields $E_{D1}=0.033$ eV, and the extrapolation of this line to the intercept of the ordinate is $A=(2/g)(2\pi m_e k/h^2)^{3/2} = 2.1\times10^{14}$, which yields $m_e = 0.2\ m_0$. Region (II) is a plot of $\ln[n/T^{3/2}]$ vs $1/T$. The slope of this line yields $E_{D2}=0.007$ eV and the intercept of this line with ordinate is $B=A(N_{D2}/N_A-1)=6.4\times10^{13}$. Assuming $g=2$, $N_A = 1\times10^{17}\ cm^{-3}$, $N_{D1}=6\times10^{17}\ cm^{-3}$ and $N_{D2}=1.3\times10^{17}\ cm^{-3}$.

band hopping-conduction process dominates the conduction mechanism; this is shown in Fig. 1. For $T < 20\,^\circ\mathrm{K}$, the indium levels are completely filled and the second donor state (E_{D2}) is partially filled. Presumably, the electron conduction is by hopping from one filled state to the nearest empty state in this level. The hopping conductivity for $T < 20\,^\circ\mathrm{K}$ is shown by the dashed line in Fig. 1 for In-doped CdS. The low electron mobility for $T < 10\,^\circ\mathrm{K}$ is more evidence for the hopping conduction in this material (e.g., for $T = 10\,^\circ\mathrm{K}$, $\mu_H \approx 10$ $\mathrm{cm^2/V\,sec}$). The hopping-conductivity activation energy observed from conductivity–vs–inverse temperature curve for $T < 20\,^\circ\mathrm{K}$ is found to be 0.000 35 eV.

Electron mobilities of In- and Cu-doped CdS were determined from the conductivity and Hall-effect measurements between 4.2 and 300 °K, as is shown in Fig. 3. The present results are adequate to permit a study of the dominant scattering mechanisms. From the near equality of the mobilities for $T > 200\,^\circ\mathrm{K}$ for samples with different doping, and from their fairly rapid increase with decreasing temperature, it appears that the μ_H for $T \geq 200\,^\circ\mathrm{K}$ are determined by the intrinsic properties of the two samples and not by the crystal defects. The scattering of electrons in this temperature range is most likely by the longitudinal optical phonons.[1] The best fit of the mobility data for $T > 200\,^\circ\mathrm{K}$ is given by $\mu_L \cong 110(e^{(300\pm10)/T} - 1)$. For both In- and Cu-doped CdS samples, the electron mobiblity reaches a maximum at $T = 80\,^\circ\mathrm{K}$, and then decreases with decreasing temperatures. The doping density of both copper and indium is approximately equal to $5\times10^{17}\ \mathrm{cm^{-3}}$. The significant difference in electron mobility for both samples for $T < 100\,^\circ\mathrm{K}$ depends mainly on the effectiveness of the ionized impurity scattering of electrons by both centers. Since indium atoms introduce a shallow donor level in CdS with a single positive charge when it is ionized, the electrons experience a Coulomb attractive potential while being scattered by such centers. On the other hand, the copper atoms introduce a deep acceptor level, and it will stay as $\mathrm{Cu}'_{\mathrm{Cd}}$, with a single negative effective charge. The electrons similarly will experience a Coulomb repulsive potential while being scattered by such centers. In general, the scattering cross section for the former is much greater than the latter.[15] As a result, the electron mobility in Cu-doped CdS is much higher than that of In-doped CdS for $20 < T < 100\,^\circ\mathrm{K}$. For In-doped CdS, the electron mobility decreases exponentially with temperature for $T < 15\,^\circ\mathrm{K}$, indicating a hopping-type conduction takes place in the localized states.

In addition to the conductivity and the Hall-effect measurements reported above, we have done an optical-transmission measurement on the In-doped CdS sample in the wavelength interval 2.5–40 μm. A strong absorption peak was observed at 7.14 μm, corresponding to a defect level at 0.175 eV below the conduction-band edge (neglecting Franck-Condon shift). No conclusion can be drawn regarding the type of defect involved without further investigation.

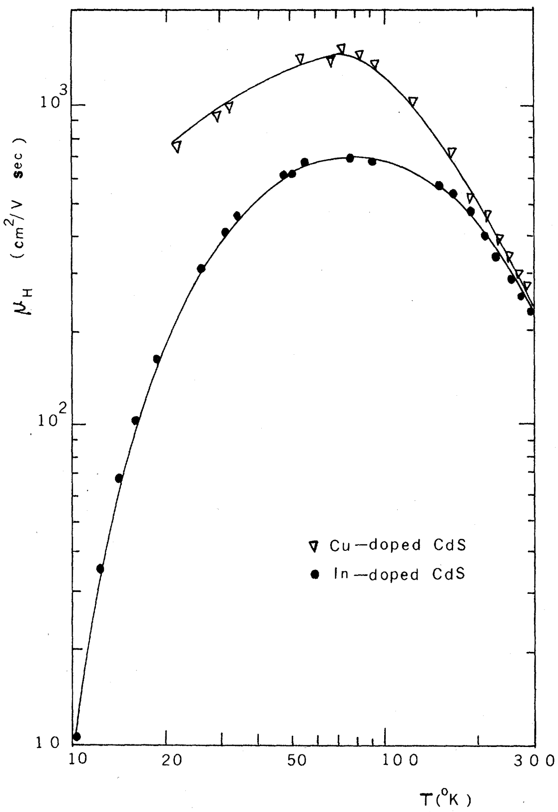

FIG. 3. Electron mobility vs T for In- and Cu-doped CdS. $\mu_L \cong 110(e^{300\pm10/T} - 1)$ $\mathrm{cm^2/V\,sec}$ for $T > 200\,^\circ\mathrm{K}$.

IV. CONCLUSIONS

Electrical-conductivity and Hall-effect measurements have been made between 300 and 4.2 °K on In- and Cu-doped CdS single crystals. A two-donor-level model has been proposed for the In-doped CdS in order to interpret the electron-concentration data between 20 and 300 °K. The results yield $E_{D1} = 0.033$ eV for the In level, which is in excellent agreement with the recent report by Nassau *et al.*[16] The ionization energy observed between 77 and 20 °K for an unknown donor level is $E_{D2} = 0.007$ eV. This energy is smaller than the predicted value by the hydrogenic impurity model which for the case of CdS should be 0.0305 eV. Although we have no adequate explanation in this respect, an unknown donor state with identical ionization energy ($E_D = 0.007$ eV) has been reported by Itakura and Toyada[11] in a high-purity undoped CdS between

50 and 10 °K. It is believed that the low-temperature hopping conduction observed in our In-doped CdS samples is taking place at this unknown donor state because the thermal energy in this temperature range is much smaller than E_{D2}. Optical-transmission experiments revealed another defect level at 0.175 eV below the band edge. The scattering of electrons is independent of the types of impurities for $T > 200$ °K and is mainly due to the longitudinal optical-mode scattering. Impurity-hopping conduction was observed for In-doped CdS for $T < 20$ °K. This was not observed for the case of Cu-doped CdS with the same amount of impurity concentration.

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Light Scattering from Acoustic Plasma Waves and Single-Particle Excitations in Semiconductor Magnetoplasmas*

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A theoretical discussion of inelastic light scattering from acoustic plasma waves and single-particle excitations in a one-component spherical-band semiconductor plasma in a magnetic field is given. A phenomenological relaxation time is used to treat collisional effects. Detailed scattering spectra are computed as a function of magnetic field using physical parameters appropriate for infrared experiments with conduction electrons in indium antimonide. It is shown that screening effects predicted by a simple effective-mass theory are grossly different from those predicted by a more realistic theory which properly treats virtual interband transitions. The general results indicate that the acoustic-plasma-wave damping in high magnetic fields is sufficiently small and the cross section is sufficiently large to yield an unambiguous spectral identification of this wave with currently available experimental apparatus.

I. INTRODUCTION

In the absence of a dc magnetic field $\vec{B}_0$, the cross section for inelastic light scattering from a single-component plasma in a semiconductor exhibits[1] (for long wavelengths) (a) broad quasi-elastic scattering of single particles in the frequency range $0 \lesssim \omega \lesssim q v_c$, where v_c is a characteristic particle speed and q is the scattering wave-vector magnitude, and (b) plasma-wave scattering near $\omega = \omega_p$, the free-carrier plasma frequency.[2] Both of these scattering processes have been observed[3-8] and theoretically discussed.[4,9-14] If a magnetic field is applied to the plasma, the scattering spectra peaks occur in similar frequency bands. However, if one considers a strong field applied to low-temperature (degenerate) carriers, so that Landau orbital quantization is important,