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Impurity Conductivity in Single-Crystal CdS

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The transport properties of electrons in CdS grown with Group I impurities which show the phenomenon of "storage" have been studied to determine the mechanism of conduction. The mobility parallel to the c axis at low temperature is of the order of 1 to 10 cm^2/ volt sec and is very anisotropic, the mobility perpendicular to the c axis being 10 to 30 times that parallel to the c axis. The resistivity of the crystals shows an activation energy of about 0.001 eV at low temperature. The resistivity is very sensitive to either donor or acceptor concentration. These characteristics indicate that the conduction mechanism is not a result of electrons in the normal conduction band but is a result of an impurity conductivity. The activation energy of 0.001 eV is thought to correspond to ϵ_3 in silicon and germanium impurity-conduction theory.

INTRODUCTION

THERE is a certain class of CdS crystals grown with large amounts of Group I impurities which show the property of mechanical stimulation of edge emission.[1] That is, these crystals, when cooled to 77°K in the dark or in the light, give forth a flash of green luminescence when tapped with a hard object. Hence the name "tap" crystals has been given to them.[2] Several other unique properties of these crystals have been investigated by Reynolds and Litton.[2,3] In many crystals of this type, the photoconductive current at low temperatures does not decay when the crystals are put in the dark. Thus, the dark conductivity at low temperature may change irreversibly by as many as 12 orders of magnitude upon exposure to light of 6900 Å or shorter wavelength. The crystals can be returned to the low-conductivity state by warming to about 0°C and recooling in the dark. These crystals have been called "storage" crystals by Litton and Reynolds.[2]

Above a critical current, the crystals exhibit a negative slope in the voltage-current characteristic at helium temperature.

The mechanism of current transport in the high-conductivity state is of prime importance in understanding these crystals. We have studied the Hall mobility and the effect on the electrical properties of doping the crystals with indium—a donor impurity—and of compensation in sulfur. The results of these experiments indicate that the conduction is best described as impurity conduction, and a comparison of the properties of these crystals with those of other crystals known to conduct current by this mechanism is presented.

DATA AND RESULTS

A. Mobility Measurements

Figure 1 shows the mobility, parallel to the c axis, of two "storage"-type crystals and a "normal" CdS crystal in the temperature range 4.2 to 350°K. Characteristically, the mobility of a "normal" CdS crystal increases with decreasing temperature below 300°K, levels off, and finally decreases again at very low temperatures.[4–6] The mobility of the storage crystals, on the other hand, decreases from a maximum at about 320°K as the temperature decreases to about 200°K, then levels off and stays at a low value to helium temperature. Above about 320°K the mobility of the storage crystals behaves very similarly to that of the normal crystals.

At 77°K there is a dependence of the mobility on the number of carriers as shown in Fig. 1. (The number of carriers can be adjusted over several orders of magnitude by the integrated amount of light allowed to fall on the crystal.) The increase in mobility with number of carriers in a photoconductor has been observed by Bube and MacDonald,[7] and they explain it as a result of a decrease in scattering by ionized impurity centers in the upper part of the bandgap which are neutralized because of a rise in the Fermi level.

In our case, however, the mobility is already so very small that this mechanism is not likely. On the other hand, if impurity conductivity is involved, a dependence of mobility on the number of carriers and on the number of impurity centers is expected.[8]

Above a critical current level, these storage crystals have a negative slope in the voltage-versus-current characteristic.[3] This has been interpreted by Litton and Reynolds as a result of double injection. In the crystal shown in Fig. 1 this change in slope takes place at about 20 mA and 50 volts/cm. At 4.2°K the mobility increases as the current is increased past the point where the negative characteristic is observed. These points are shown in the insert in Fig. 1 for currents of 23, 50, and 70 mA.

If one considers that the injected carriers are put

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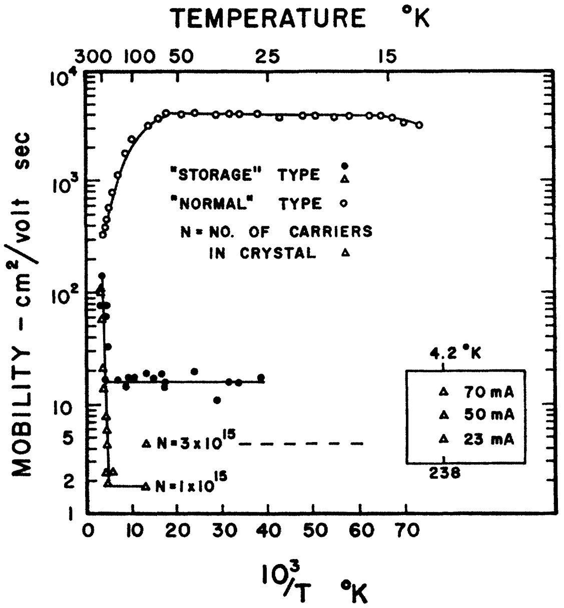

FIG. 1. Hall mobility versus $1/T$ for two "storage" crystals in the high-conductivity state, and one "normal" CdS crystal. Inset shows mobility in "negative resistance" region at 4.2°K.

directly into the conduction band and valence band, then the system becomes a three-carrier type and very complicated behavior can be expected. The Hall coefficient was virtually unchanged but the mobility showed a sizeable increase (from 4.5 to 12 volt cm/sec²) as the current increased in the negative resistance region.

The mobility parallel and perpendicular to the c axis was investigated for anisotropy. In normal CdS, Piper and Halsted[5] have shown that the mobility is isotropic within experimental error. Hopfield and Thomas[9] have shown that the electron effective mass is also isotropic but that the hole effective mass is anisotropic with $m^*_{h\parallel}/m^*_{h\perp}$ of the order of 6. Table I shows the results of several measurements on three crystals using the geometries sketched, in Fig. 2. It should be remarked here that similar experiments performed in this laboratory on Eagle-Picher pure crystals and on Cl-doped crystals show no anisotropy within the experimental error, which is less than ±10%.

TABLE I. Anisotropy in the Hall mobility of "storage" crystals of CdS.

Crystal	Configuration (see Fig. 2)	ρ[a] (Ω cm)	N_e (cm^{-3})	$\mu_\perp$[b] (cm²/Vsec)	$\mu_\parallel$ (cm²/Vsec)
5	A Entire	4×10^3	9.5×10^{14}		2
		17	6.0×10^{15}	70	
A-2	B Entire	550	2.0×10^{15}		5.5
	a[c]	100	1.7×10^{15}	30	
	b	800	2.0×10^{15}		4
	c	450	2.5×10^{15}		5.4
	d[c]	16	2.5×10^{15}	150	
A-3	C Entire	1000	2.7×10^{15}		2.3
	a	20	1.6×10^{15}	20	
	b	60	5.0×10^{15}	20	
	c	35	5.5×10^{15}	30	
	d	16	1.0×10^{16}	34	

[a] All values at 77°K in high-conductivity state.
[b] Perpendicular to c axis.
[c] Mass-spectrographic analysis shows impurities nearly identical except Li, Na, and K, for which the concentrations (in ppm atomic) in crystals a and d, respectively, are as follows: Li, 1.5 and 6.0; Na, 70 and 190; K, 2.9 and 0.6.

The very low mobility and the very large anisotropy in the mobility indicate that the mechanism of conduction in the storage crystals is different from that in the normal CdS crystals. Impurity conduction is very strongly suggested.[8] Several pecularities in the transport properties of silicon, germanium, and semiconducting compounds are observed when this mechanism is involved. Often the magnetoresistance shows large and anomalous effects.[10] However, transverse magnetoresistance measurements with the crystal current parallel and perpendicular to the c axis show no effect of the magnetic field on crystal resistance in the high-conductivity state for fields up to 45 kG.

Uniaxial stress along different axes may change the resistivity as much as several orders of magnitude when impurity conductivity is involved.[11] Uniaxial-stress experiments on these crystals in the high-conductivity state with stress applied parallel to the c axis reveal two very large effects. First, there is an irreversible increase in the crystal resistance with stress. This is associated with the return of the crystal to the low-conductivity state from the storage state. The storage effect is not destroyed permanently, since exposing the crystal to light at zero stress returns the crystal to the high-conductivity state. The second effect is a reversible one. As the stress is removed, the crystal resistance decreases one to two orders of magnitude from its maximum value, then increases again to a value somewhat less than the maximum. For example, a certain crystal with a resistance of 10^3 Ω increased in resistance to 8×10^8 Ω at 2×10^9 dyne/cm², As the stress was reduced again, the resistance decreased to 4×10^7 Ω at 7×10^8 dyne/cm², then increased to 4×10^8 Ω as the stress was

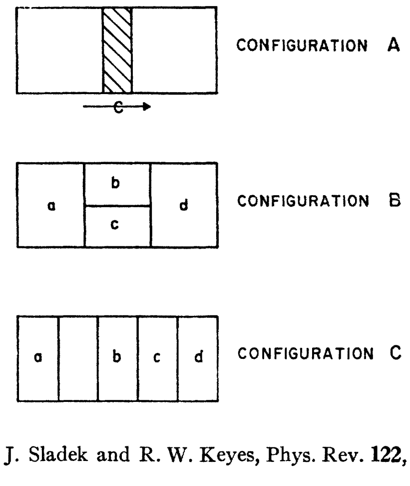

FIG. 2. Method of sectioning crystals for anisotropy experiments.

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TABLE II. Symmary of doping experiments.

	Conditions (°C)	(hours)	ρ(before)[a] (Ω cm)	ρ(after)[b] (Ω cm)	μ(before)[a] (cm^2/Vsec)	μ(after)[b] (cm^2/Vsec)	Remarks (after heat treatment)
Indium	400	200	3.5×10^2	1.0×10^8			No storage
	600	150	1.3×10^2	4.9×10^3	13	43	
	700	100	2.0×10^4	6.5×10^2	2.0	53	
	750	100	1.6×10^2	0.5	10	1320	
Sulfur	400	2	4.2×10^2	4.5×10^8			No storage
Vacuum	300	100	3.6×10^2	6.4×10^4 [c]			Still stores
	400	2	8.0×10^3	8.0×10^6 [c]			Little storage effect

[a] High-conductivity state at 77°K.
[b] Dark at 77°K.
[c] High-conductivity state.

released completely. Details of these experiments will be published in a subsequent article.

B. Donor and Acceptor Doping Experiments

Another characteristic of impurity conduction is that the conductivity in the impurity region is very sensitive to small changes in donor and acceptor concentrations. Table II shows the results of a series of doping experiments with storage crystals. In all cases the resistivity of the crystals when cooled to 77°K in the dark was of the order of 10^8 Ω cm. In detail, it is seen that in the case of indium doping at 400°C and sulfur compensation at 400°C, the storage effect is destroyed even though the dark resistivity is not appreciably changed. Vacuum baking also largely destroys the storage capability, but the detailed effect of this treatment is unknown. In the case of Eagle-Picher pure crystals, the resistivity is often increased several orders of magnitude by such a treatment, indicating that a compensating effect takes place. Of particular interest is the 750°C heat treatment with indium. Following this treatment, the mobility of the crystal goes to a value representative of a normal but impure crystal. The mobility-versus-1/T curve then looks very much like that of the normal crystal, shown in Fig. 1. On the basis of the number of carriers frozen out at the indium level there are about 10^{16} indium atoms per cm^3 in the crystal after this heat treatment.

C. Resistivity versus $1/T$: Activation Energy

Finally, the effect of temperature on the resistivity is expected to show a very low but positive activation energy. Figure 3 shows the resistivity as a function of $1/T$ for crystal B. This crystal shows a linear change in log (resistivity) versus $1/T$ over a large temperature range. Two slopes are evident, the first corresponding to an activation energy of about 0.001 eV and the second to one of about 0.0007 eV. These are much too shallow for an isolated donor level which Piper and Halsted[5] set at about 0.032 eV. Measurements of the energy of the Ga, In, and Cl donor levels by Kroger[4] have shown these levels to be in the vicinity of 0.030 eV. In various other storage crystals evidence of traps in the vicinity of 0.020 eV is observed,[12] but below about 10°K only one or both of the shallow slopes are apparent.

D. Transition to Impurity Conduction in Chlorine-Doped "Tap" Crystals

Many of the crystals originally selected for the "tapping" properties are of low resistance. Subsequent mass-spectrographic and electrical-property analysis showed chlorine to be the donor contributing to the low resistivity. These crystals, when cooled to temperatures below 4.2°K, exhibit the shallow slope in ρ versus $1/T$ seen in the "storage" crystals. The resistivity and Hall mobility as functions of $1/T$ in the low-temperature region are shown in Fig. 4. It is clearly evident that as the number of carriers in the conduction band becomes less, the slope of the resistivity versus $1/T$ approaches a value corresponding to 0.001 eV and the mobility decreases to a value very nearly that observed in the "storage" crystals. In the case of the indium-doped crystal mentioned in Sec. B, the residual number of carriers in the conduction band at 4.2°K was considerably higher, the slope corresponding to 0.001 eV was not observed, and the mobility did not decrease below a value of about 700 at 4.2°K. This behavior would be expected if the number of indium donors exceeded the number of vacant levels in the impurity "band."

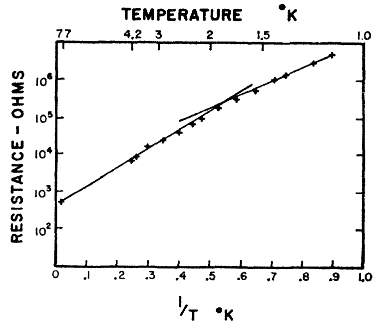

FIG. 3. Resistance versus $1/T$ for a good storage crystal.

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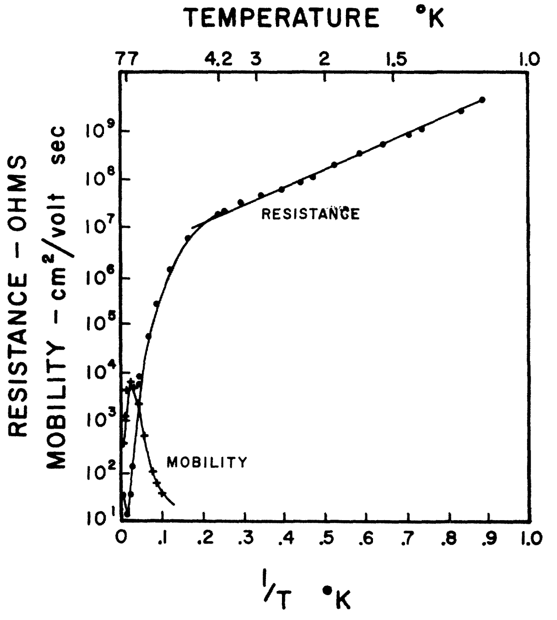

FIG. 4. Resistivity and mobility of a chlorine-doped "tap" crystal.

DISCUSSION

The transport properties of the cadmium sulfide crystals described here can be explained on the basis of impurity conduction.

Impurity conduction generally takes place when the wave functions of the impurity atoms overlap sufficiently for the electrons to hop or tunnel from one atom to another. At moderate impurity concentrations, $5\times10^{15}/\mathrm{cm}^3$ in germanium, compensation is necessary and an activation energy of a few millielectron volts is observed. At high concentration, above about $10^{17}/\mathrm{cm}^3$ in germanium, metallic-like conduction is observed and the activation energy goes to zero. In the case of silicon and germanium, impurity conduction sets in as the temperature is decreased. The electrical properties can be described by three activation energies, thus[12]:

$$\sigma=C_1\exp(-\epsilon_1/kT)+C_2\exp(-\epsilon_2/kT)+C_3\exp(-\epsilon_3/kT).$$

The energy ϵ_1 represents the energy of the donor level which, at low temperature, provides the impurity "band." ϵ_2 is the activation energy in a transition region at moderate impurity concentration and is not clearly characterized even in silicon or germanium. ϵ_3 is the activation energy for impurity conduction in the region before metallic-like conduction sets in. This energy is constant over a wide range of impurity concentrations but tends to zero as the concentration exceeds a critical value and conduction becomes metallic-like. The critical concentration is characteristic of the impurity and the host lattice. It is greater in silicon than in germanium because the Bohr radius of the impurity wave functions in silicon is of the order of $\frac{1}{3}$ of that in germanium.

The temperature at which impurity conduction is observed is higher in silicon than in germanium (for comparable impurity concentration) because the donor energy ϵ_1 in silicon is about 5×10^{-2} eV and only 1×10^{-2} eV in germanium.

In the case of the CdS crystals described here, the activation energy ϵ_1 is not observed except in the case of the chlorine-doped crystals. The electrons for the conduction process come from a deep trap (1.75 eV from the conduction band) and are trapped in the impurity band. It is not known at the present time whether only one impurity is involved, that is, whether a particular impurity atom changes its ionization state to form the impurity band. Two impurities may be involved, one to supply the electrons (by changing its ionization state) and another to form the band. Both mass-spectrographic analysis and analysis of thermally-stimulated-current curves[13] show an abundance of impurities available for compensation or for contributing to the conduction mechanism.

Litton and Reynolds have shown that a Group-I impurity is responsible for the "tap" effect. The Bohr radii of these atoms are Na, 70 Å; Li, 85 Å; and K, 110 Å. In all the "storage" crystals which have been analyzed, the concentration of these elements is of the order of $(10\text{ to }100)\times10^{16}\ \mathrm{cm}^{-3}$. The number of carriers obtained from the Hall coefficient, however, is of the order of $(0.5\text{ to }1)\times10^{16}\ \mathrm{cm}^{-3}$. It should be noted, though, that the number of carriers can be adjusted to any value up to the maximum stated above by varying the total integrated amount of light shined on the crystal. Furthermore the additional accidental trapping centers described in Ref. 13 can cause the number of electrons contributing to the conduction to vary over a wide range, independently of the number of centers forming the impurity band. The relative size of the wave function and the measured concentrations of impurities are well within the expected limits for the observation of impurity conduction. It has not been possible as yet to produce metallic-like conduction by the addition of a higher concentration of Group-I atoms.

LOCATION OF THE IMPURITY LEVEL

The very large anisotropy which is observed in the mobility indicates that the impurity levels are not tied to the conduction band. The valence bands in CdS do show a large anisotropy in the same direction as the impurity band studied here. However, several bits of information indicate that the band is nearer the conduction band. Following partial stimulation, the technique of thermally stimulated current shows that many electron traps are emptied as the Fermi level moves away from the conduction band. In other crystals in the "storage" state, electron trapping levels are filled as the crystal is cooled to 4.2 from 77°K (see Fig. 10 of Ref.

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13). In the case of the chlorine-doped crystal discussed in Sec. D, it appears that the impurity conductivity sets in as the chlorine level is filled. It should be remarked that the decrease in mobility as the temperature is lowered is a characteristic of CdS.[4–6] Piper and Halsted[5] have shown a direct correlation between the temperature at which the mobility decreases and the gallium donor concentration. Therefore it is not really certain that the impurity in the chlorine-doped crystal is the same as that in Group-I-doped material.

CONCLUSION

The transport properties in "storage"-type crystals of CdS indicate that electrical conduction takes place via an impurity mechanism. On comparing the situation with the better understood materials silicon and germanium, it appears that the activation energy ϵ_3 is being observed and that it is about 0.001 eV. The second energy observed at 0.0007 eV may be the contribution of a second impurity, since mass-spectrographic analysis shows several elements present in sufficient concentration to permit impurity conductivity.

The exact mechanism for the formation of the impurity band is not known even to the extent of uniquely identifying the element involved. All that is known is that Group-I atoms are necessary, but not sufficient. Further work involving crystal growth and doping techniques will be needed to more accurately characterize the crystals.

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Magneto-Optic Experiments on the *F* Center and *A* Center in KCl[†]

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We report the measurement of the magnetically induced circular dichroism in the optical-absorption bands of the *F* center and *A* center in KCl performed to test theoretical productions of Henry, Schnatterly, and Slichter based on the method of moments. It is found that a magnetic field can alter the area of an optical-absorption band, but only at the expense of other optical-absorption bands of the center; the total area due to all the optical-absorption bands of the center remains constant. The magnetic field causes the *F* band to shift in energy. The shift is found to be greater in the peak than in the tails of the *F* band. Depending upon the orientations of the *A* centers, the magnetic field causes either a shift in the *A*2 band, or an increase in the area of the *A*2 band and equal and opposite decrease in the area of the *A*1 band. These results are in good agreement with the predictions of Henry, Schnatterly, and Slichter. We show that the signals from paramagnetic circular dichroism in the *K* band and *F* band occur with the same spin-lattice relaxation time, confirming that the *K* band is an excited state of the *F* center. The ratios of the coupling to the cubic and noncubic lattice modes of the *F* center and the ratios of the spin-orbit coupling constants of the *A* center are also evaluated.

I. INTRODUCTION

RECENTLY, magneto-optic experiments on the *F* band have led to a determination of the spin-orbit coupling in the first excited state of the *F* center.[1,2] Stimulated by these experiments, Henry, Schnatterly, and Slichter (HSS) performed a detailed analysis of the effect of a magnetic field (and other perturbations) on the optical properties of color centers, applying these results to the *F* center and *A* center.[3] Calculating the optical-absorption line shape of the *F* center and the effect of a magnetic field on the line shape is extremely difficult owing to the large electron-lattice coupling, the orbital degeneracy of the excited state, and the presence of a strong spin-orbit interaction. In spite of these difficulties, HSS showed that the moments of the optical-absorption band and the changes which occur in these moments when a magnetic field is applied may be computed quite simply and with rigor. Their analysis shows that by measuring the second moment and the magnetically induced changes in the first and third moments of the *F* band, one could evaluate not only the spin-orbit coupling constant, but also the orbital *g* factor of the first excited state of the *F* center and several parameters describing the electron-lattice interaction of this state.

HSS applied their results to analyze the magneto-optic experiments of Margerie and Romestain[4] on the *F* band in CsCl and CsBr. HSS found that the energy separation of the partially resolved transitions to the

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[*] Now at Bell Telephone Laboratories, Murray Hill, New Jersey.

[†] This research was supported in part by the U. S. Atomic Energy Commission, Contract AT(11-1)-1198.

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