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High-Temperature Hall Effect Measurements on CdS in Cd Vapor*

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The incorporation of excess Cd into CdS was studied by performing Hall effect and resistivity measurements on single-crystal samples in equilibrium with known partial pressures of Cd vapor at temperatures between 400 and 1000°C. The carrier concentration varies as $p_{Cd}^{1/3}$ at temperatures of 700°C and above. This is interpreted in terms of a doubly ionized native donor, probably a sulfur vacancy. The incorporation energy of the doubly ionized defect into the CdS lattice is found to be 1.70 eV. The second donor ionization energy is estimated to be ≤ 0.24 eV, probably ≈ 0.12–0.16 eV. The Hall mobilities $\propto T^{-1.4}$ for $400°C \leq T \leq 1000°C$. This agrees fairly well with the theoretical temperature dependence calculated by reciprocally combining mobilities calculated by considering polar scattering by longitudinal optical modes, deformation potential scattering, and piezoelectric scattering by acoustic modes.

1. Introduction

The influence of native defects on the electrical and optical properties on II–VI compound semiconductors has been the subject of many investigations. Due to the divalent nature of the chemical components, native defect centers should be expected to act as double donors or acceptors. Evidence to support the existence of doubly charged native donor centers has been reported for CdS(1–3), CdSe (4–6), CdTe (*7*, *8*), and ZnS (*9*). Single native donors were found in ZnSe (*10*).

Boer et al. (*11*) and Boyn et al. (*1*) performed conductivity measurements on CdS under S_2 and Cd vapor at temperatures between 400 and 700°C. Their results indicate the formation of doubly ionized native donors at high Cd vapor pressures for sample temperatures above 550°C. At temperatures below 550°C they observed a change in the Cd vapor pressure dependence of the conductivity which was attributed to a compensation of the native donors ($Cd_i^{\cdot\cdot}$), by native acceptors (V''_{Cd}) formed as a result of Frenkel disorder.

Whelan and Shaw (*2*) observed a dependence of the electronic conductivity $\sigma_e \propto p_{Cd}^{1/3}$ at 900°C indicating again a doubly ionized donor, but found a weaker dependence at lower temperatures, probably due to the presence of foreign donors.

The work reported in this paper was undertaken to test the double donor model for CdS over a wide range of temperatures (400–1000°C) and was designed to yield quantitative results. Both Hall effect and resistivity measurements were performed while the sample was in equilibrium with known partial pressures of Cd vapor. Undoped, as well as donor or acceptor doped samples were used. Acceptor doping was intended to check whether the low-temperature deviations assigned to Frenkel disorder could possibly be due to acceptors present as impurities. Al donor doping was used to investigate the solubility of this donor.

2. Experimental Procedure

2.1. Crystal Material

The CdS samples were cut into parallel plates of square or rectangular shape with dimensions from 5–10 mm on a side by 0.5–1 mm thick. The samples were notched on four sides in a cloverleaf pattern for resistivity and Hall effect measurements by the Van der Pauw technique (*12*). The majority of the samples were cut from a single crystal purchased from the Clevite Corporation. One sample (R-8), however, was a vapor grown platelet with a thickness of 0.034 mm supplied through the courtesy of Dr. D. C. Reynolds at the Wright Air Development Center. Prior to insertion in the apparatus, the

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TABLE I

IMPURITY CONCENTRATIONS IN CdS IN ppm (ATOMIC) AS DETERMINED BY MASS SPECTROGRAPHIC ANALYSES[a]

Element	Detection limits[b]	Clevite crystal	Reynolds crystal
H	0.2	0.52	—
Li	0.003	0.005	Not detected
C	0.01	1.3	10
N	0.01	0.063	0.3
F	0.03	Not detected	Not detected
Na	0.003	0.061	0.55
Si	0.1	Not detected	Not detected
Cl	0.03	0.10	Not detected
K	0.003	0.0062	0.56
Ca	0.007	0.01	0.22

[a] Carried out at the Bell and Howell Research Center, Pasadena, California.

[b] Detection limits for Reynolds sample are 30 times those given.

samples were washed with hot toluene, etched with 1:1 HCl:H_2O, and cleaned in boiling deionized water.

Table I lists the concentrations of foreign elements present in the sample as determined by mass spectrographic analysis. The analyses were made after the samples had been in the apparatus at high temperatures for several weeks. Carbon, indicated by the analysis, was found at similar concentrations in cut samples which had not been in the apparatus prior to the analyses. It is probably due to a residue of wax left on the crystal's surface after cutting and washing.

The samples were not analyzed for Au, O, Mn, Fe, and Zn due to the use of an Au sample holder in the mass spectrometer and interference from background lines of S and Cd. The Reynolds sample split during sparking in the spectrometer and was not analyzed for H.

2.2. Preparation of Doped Samples

Samples doped with Al and Au were prepared by first evaporating a thin layer of the metal onto the surface of a CdS platelet followed by an anneal to effect in diffusion. The diffusion anneal for Al was carried out at 1000°C in a sealed quartz ampoule containing Cd vapor at a pressure of 1 atm. The Au was in diffused with the sample at 750°C in a stream of H_2S. The Li doped sample was prepared by heating a CdS platelet buried in Li doped CdS powder at 800°C under flowing H_2S. An Sb doped polycrystalline sample was grown from doped CdS powder by the method of Piper and Polich (*13*).

2.3. Apparatus and Electrical Measurements

A regulated pressure of Cd vapor was established by the technique proposed by van Doorn (*14*) for KCl under K pressures and previously applied to ZnTe by Thomas and Sadowski (*15*). The apparatus of reference (*15*) was modified slightly by adding at the bottom of the tube a reservoir heated by a separate furnace. This allowed a pool of Cd (approximately 100g) to be maintained at its boiling point so that the Cd reflux could be sustained for a long period of time even when Cd was lost by crystallization in the cold zone of the apparatus. The contacts on the sample consisted of graphite feet mounted on tungsten wire springs. Bare tungsten wire was found to be unsatisfactory as a black nonconducting surface layer—probably tungsten sulfide—formed on the ends of the wires near the sample. The contacts were checked for ohmic behavior on each sample. The Hall effect and resistivity measurements were made using a Leeds and Northrop K-3 type potentiometer. The magnetic field and current were reversed to eliminate thermal voltages and noncommuting effects.

3. Experimental Results

3.1. Measurements on Undoped Samples

After inserting a sample in the apparatus, it was found advisable to heat the sample to 900°C for a period of 4 or 5 hr before attempting measurements at lower temperatures. This induction period is necessary to stabilize the carrier concentration; any acceptor impurities that may be present are extracted from CdS by Cd vapor (*15, 16*). A sample would normally be maintained at temperatures above 400°C for a period of 2–6 weeks while the measurements were being performed. It was found that the processes responsible for the variation in carrier concentration were reversible and independent of the sequence of measuring temperatures or applied Cd vapor pressures. The adjustment to equilibrium after a change in Cd vapor pressure was quite rapid for temperatures between 800 and 1000°C. The time constant for this approach to equilibrium appeared to be smaller than the time required to change P_{Cd} in the apparatus (5—20 min).

The Cd vapor pressure dependence of the carrier concentration is plotted in Fig. 1 for three different samples C-4, C-7, and R-8 with thicknesses of 0.85, 0.90, and 0.034 mm, respectively. The relationship between log n and log P_{Cd} is approximately

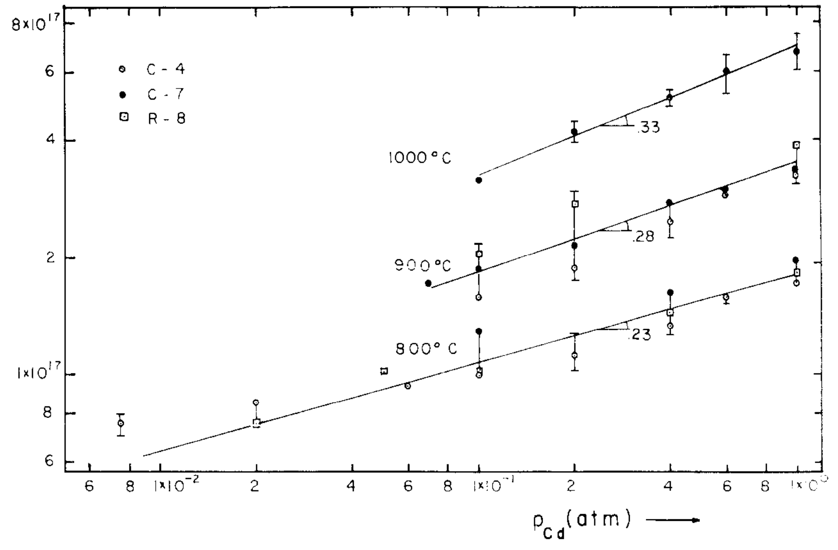

FIG. 1. Cd vapor pressure dependence of the carrier concentration for three different samples at fixed temperatures.

linear with slope $d(\log n)/d(\log P_{Cd}) \simeq \frac{1}{3}$. In Fig. 2 n is plotted versus P_{Cd} for sample R-8 for temperatures varying from 400 to 900°C. At 400°C n is seen to be independent of P_{Cd} for the accessible range of pressures, limited with the reflux method to $P_{Cd} >$ the partial pressure of Cd at its triple point.

The temperature dependence of the carrier concentration measured with the Cd vapor pressure held constant is plotted in Fig. 3 for three different values of P_{Cd}. The curve for $P_{Cd} = 0.1$ atm shows a definite deviation between the data of the thick and thin samples at temperatures below 800°C. The flattening of the curves for two of the samples at $P_{Cd} = 0.1$ atm is probably due to the presence of $\approx 10^{17}$ cm^{-3} donor impurities in these samples.

3.2. Measurements on Doped Samples

Li, Au, and Sb doped samples were used in attempts to obtain acceptor compensated samples: results were negative or inconclusive in all three cases. Carrier densities in Li and Au doped samples were found to $\propto P_{Cd}^{1/3}$ with magnitudes slightly greater than observed in undoped samples. Either Li is almost completely self compensating with a

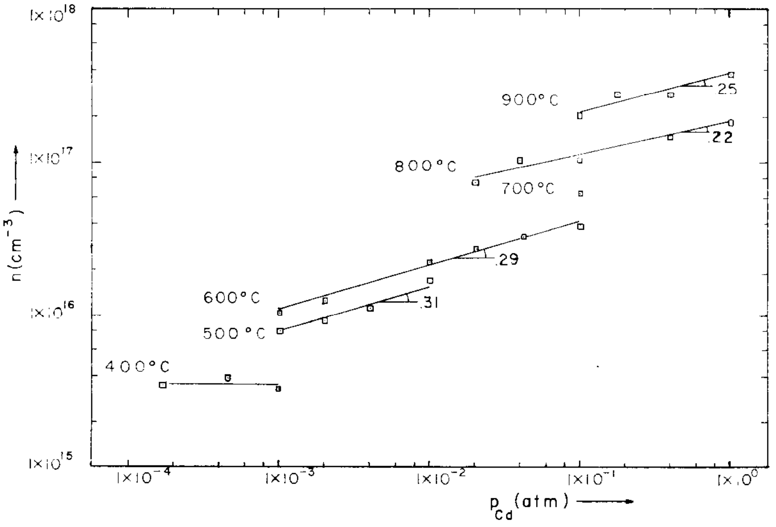

FIG. 2. Cd vapor pressure dependence of the carrier concentration for the thin sample, R-8, at fixed temperatures.

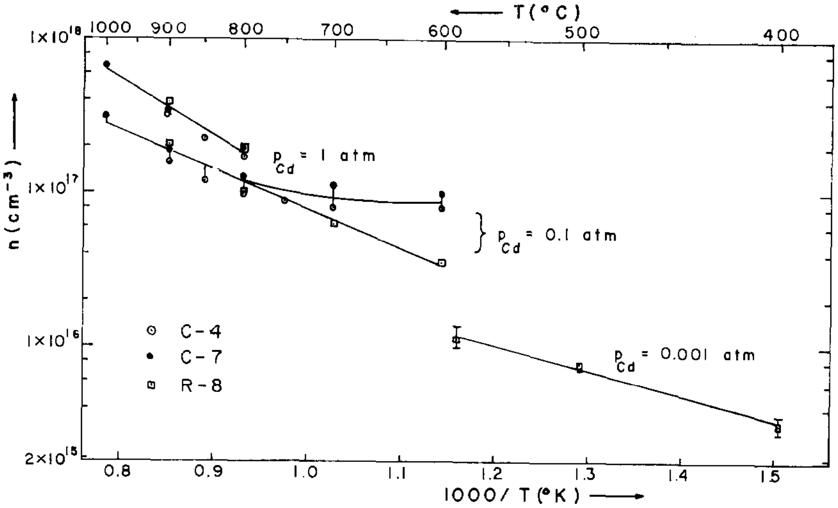

FIG. 3. Temperature dependence of the carrier concentration for three different samples at fixed Cd vapor pressures.

slight excess of donor activity or else we succeeded in properly dissolving only a slight amount of Li in the sample and this acted as a donor. The Au appeared to be extracted from the sample by the Cd vapor (*16*). Hall measurements performed on an Sb doped polycrystal were somewhat inconclusive as the voltages were usually erratic. The few stable readings which were obtained indicated $n \approx 10^{18}$ cm^{-3} at 900°C, $P_{\mathrm{Cd}} = 1$ atm; a larger value than for undoped samples. Thus, Sb may act as a donor in CdS. The same was reported in Ref. (*17*).

One sample heavily doped with Al was studied. The Al was found to be soluble as a donor in concentrations $\geqq 2.5 \times 10^{19}$ cm^{-3}.

3.3. Electron Mobilities

The experimental Hall mobilities are shown as a function of temperature in Fig. 4. The values plotted are averages of the measurements made at different Cd vapor pressures. The total scatter in data is indicated for the sample with the highest measured mobility (R-8); similar scatter was obtained for the other samples, Some of the data of Piper and Halstead (*18*) are included for comparison. Theoretical mobility curves may be obtained by reciprocally combining the contributions to the mobility by polar scattering by longitudinal optical modes (μ_0), deformation potential scattering by acoustic modes (μ_{dp}), and piezoelectric scattering by acoustic modes (μ_p).

$$\mu_0 = 5.76(\epsilon_\infty^{-1} - \epsilon_0^{-1})^{-1}\left(\frac{10^{13}}{\omega_l}\right)\left(\frac{T}{300}\right)^{1/2}\left(\frac{m}{m^*}\right)^{3/2} \times (e^Z - 1)\,Ge^{-\xi}\ \mathrm{cm^2/v\ sec}\ (18, 19), \qquad (3.3.1)$$

$$\mu_{dp} = 3.0 \times 10^{-5} c_l E_c^{-2}\left(\frac{m}{m^*}\right)^{5/2} (T)^{-3/2}\ \mathrm{cm^2/v\ sec}\ (20), \qquad (3.3.2)$$

$$\mu_p = 400\left(\frac{m}{m^*}\right)^{3/2}\left(\frac{300}{T}\right)^{1/2}\ \mathrm{cm^2/v\ sec}\ (21, 22) \qquad (3.3.3)$$

The symbols used in the above equations are defined as follows: $\xi = \zeta/kT$ where ζ is the Fermi level, ν_l is the vibrational frequency of the polarization waves assumed to be independent of temperature, $Z = h\nu_l/kT$, G is a function of both Z and ξ, E_c is the deformation potential for the conduction band, and $c_l = \rho\langle u_d^2\rangle$ where ρ is the density and $\langle u_d^2\rangle$ is the square of the longitudinal sound velocity averaged over direction. The following values for the constants have been used in Eqs. (3.31.) to (3.3.3):

$$\epsilon_\infty = 5.24\ (23),$$

$$\epsilon_0 = 9.2\ (24),$$

$$Z = \frac{h\nu_l}{kT} = \frac{440°\mathrm{K}}{T},$$

$$c_l = \rho\langle u_d^2\rangle = 8.87 \times 10^{11}\ \mathrm{dyne\ cm^{-2}}\ (26),$$

$$\omega_l = 5.75 \times 10^{13}\ \mathrm{sec^{-1}}\ (25),$$

$$E_c = 18\ \mathrm{eV}\ (27\text{–}29).$$

Onuki and Shiga (*27*) estimate the deformation potential at 15 eV based on the variation of μ with electric field at low temperatures. Saitoh (*28*) using the same data estimates $E_c = 16 \pm 2$ eV. Kobayshi (*29*) has used a value of 19.2 eV. In Fig. 4 we plot mobility values calculated using the upper limit value given by Saitoh, $E_c = 18$ eV. The individual

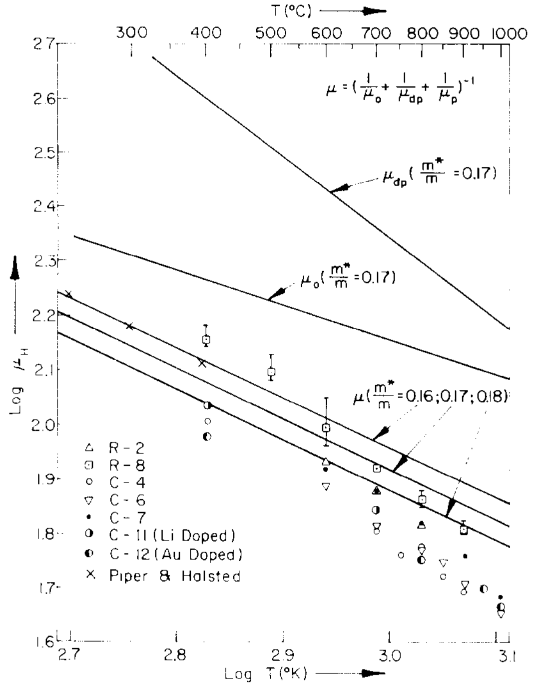

FIG. 4. Temperature dependence of the Hall mobility. The solid lines represent the theoretical mobilities plotted for three choices of m^*/m and the individual contributions of polar optical mode scattering and deformation potential scattering.

contributions μ_0 and μ_{dp} are indicated for $m^*/m = 0.17$; μ_p is almost negligible over the temperature range of interest and gives a correction of less than 1%. The experimental mobilities droop slightly below the theoretical curve at the higher temperatures indicating that an even larger value for E_c would have to be used to improve the fit. Using an increased value for E_c is probably not justified at present due to the large amount of scatter in our data.

4. Discussion

The results presented in Section 3 give strong evidence that the observed cadmium pressure dependence of the carrier concentration at sample temperatures of 700°C and above is due to bulk changes in the native defect concentrations. The good agreement in data for samples with thickness from 0.034 to 1.0 mm. tends to rule out surface effects. The influence of impurities can be excluded because the observed carrier concentrations were at least an order of magnitude larger than the concentrations of foreign constituents found by mass spectrographic analysis.

4.1. Equilibrium Between CdS and Cd Vapor

The equilibrium between a binary compound and the vapor of one of its constituents can be formulated with the aid of quasichemical defect reaction equations and the corresponding mass action relations; see for instance Kröger (*30*) or van Gool (*31*). The incorporation of excess Cd from the vapor into CdS can occur with the formation of sulfur vacancies or Cd interstitials. Both defects would be expected to act as donors and for a similar multiplicity of ionization, the electron concentration would have a similar dependence on the Cd vapor pressure. Recent Cd and S radio-tracer self-diffusion measurements performed by Whelan and Shaw (*2*) and Kumar (*32*) show slopes varying from $\frac{2}{3}$ to 1 for Cd tracer diffusion at high-Cd activities. A slope close to the $\frac{1}{3}$ found for the electron concentration is observed for S tracer diffusion at high-Cd activities. This indicates that doubly ionized S vacancies are the dominant atomic defects. The formation and ionization of these defects can be described by the following reactions and mass action relations:

$$\mathrm{Cd}(g) \rightleftarrows \mathrm{Cd}_{\mathrm{Cd}}^{x} + V_{\mathrm{S}}^{\cdot\cdot} + 2e'; \; H_{\mathrm{Cd}} + E_{d1} + E_{d2} \tag{4.1.1}$$

$$[e']^2 [V_{\mathrm{S}}^{\cdot\cdot}] = K_{\mathrm{Cd}} K_{d1} K_{d2} P_{\mathrm{Cd}} = K'' P_{\mathrm{Cd}}.$$

H_{Cd}, E_{d1}, and E_{d2} represent respectively the enthalpy for the incorporation of a Cd atom from the vapor with the formation of the neutral defect and the first and second ionization energies of the defect.

For $[e'] \simeq 2[V_{\mathrm{S}}^{\cdot\cdot}]$, (4.1.1), gives

$$[e'] \simeq \sqrt[3]{2K''}\, P_{\mathrm{Cd}}^{\frac{1}{3}}, \tag{4.1.2}$$

as observed at high temperatures. Similar P_{Cd} dependencies were reported for electron concentrations and/or conductivities of CdS, CdSe, and CdTe in Refs. (*1–8*).

4.2. Evaluation of Equilibrium Constants and Energy Levels

The equilibrium constant for the $V_{\mathrm{S}}^{\cdot\cdot}$ formation reaction (4.1.1) has been calculated using both the data of Fig. 3 and Ref. (*1*) with

$$\begin{aligned} K'' &= K_{\mathrm{Cd}} K_{d1} K_{d2} \\ &= K_0'' \exp - \left(\frac{H_{\mathrm{Cd}} + E_{d1} + E_{d2}}{kT} \right) \\ &\simeq \frac{[e']^3}{2P_{\mathrm{Cd}}}. \end{aligned} \tag{4.2.1}$$

The temperature dependence of this constant is plotted in Fig. 5. The scatter caused by using the highest and lowest values of carrier concentration

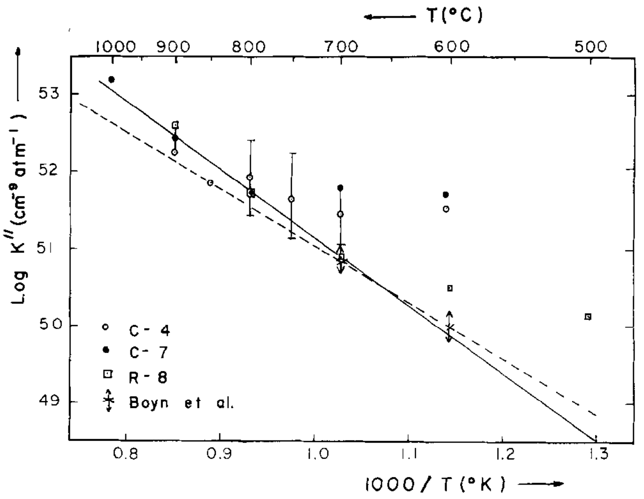

FIG. 5. Temperature dependence of the equilibrium constant (K'').

measured at each temperature is indicated. The values for the data of Boyn et al. (*1*) were obtained by converting their conductivities to carrier concentrations using our experimental mobilities; the uncertainty in this calculation due to the scatter in μ is also indicated. For the thin sample R-8 it has been assumed that

$$[e'] \cong 2[V_S^{\cdot\cdot}] + [D^{\cdot}] - [A'] \qquad (4.2.2)$$

with

$$[D^{\cdot}] - [A'] \cong 3.5 \times 10^{15}\ \mathrm{cm}^{-3} \cong [e']_{400^\circ\mathrm{C}},$$

a value based on the observation that $[e']$ was independent of P_{Cd} at 400°C. The assumption of such a fixed concentration of impurity donors does not bring the 500 and 600°C values onto the temperature dependence curve defined by the data for higher temperatures: the bend remains. It cannot be due to nonequilibrium. In the 500°C measurements, the sample R-8 was maintained at each set of conditions for 6 to 8 hr. The time constant for this sample at 500°C, calculated using the data of Ref. (*1*), is 6.1 min. Therefore, the sample should have reached equilibrium. It is possible that the bend results from the presence of two defect donor species, say sulfur vacancies and interstitial Cd atoms. Owing to the scarcity of low-temperature data, a definite conclusion cannot be reached at present.

Table II summarizes the values obtained for the equilibrium constant (K'') for CdS, CdSe, and CdTe. The first expression represents the best fit between the data of this work and that of Ref. (*1*).

The first defect donor ionization energy is known to be approximately $E_{d1} \cong 0.042$ eV (*33*). An upper limit for the second ionization energy of the S vacancy can be estimated by considering the ratio of the concentration of doubly to singly ionized defects, i.e., say $[V_S^{\cdot\cdot}]/[V_S^{\cdot}] \geqq 2$. This yields an upper limit of 0.24 eV; assuming $[V_S^{\cdot\cdot}]/[V_S^{\cdot}] > 5$ gives an upper limit of 0.12 eV. The latter value is probably the closest to E_{d2} since the carrier concentration did not exhibit a greater P_{Cd} dependence than a $\frac{1}{3}$ power law which would indicate that $[e']/[V_S^{\cdot}]$ must be $\geqslant 10$. For comparison the hydrogenic approximation yields values $E_{d1} \cong 0.048$ eV and $E_{d2} \cong 0.158$ eV.

Many authors have reported for CdS levels 0.03–0.04 eV and 0.10–0.25 eV below the conduction band. In particular, Nicholas and Woods (*33*) reported that the trap densities for the levels which they measured as 0.05 and 0.14 eV were much greater in Cd-rich crystals than in Cd-poor crystals, indicating that these levels are due to a native defect.

Taking $E_{d1} \cong 0.042$ eV and $E_{d2} \cong 0.14$ eV, $H_{\mathrm{Cd}} \cong 1.52$ eV.

TABLE II

EXPRESSIONS FOR THE EQUILIBRIUM CONSTANT, $K'' = K_0'' \exp(-H/kT)\ \mathrm{cm}^{-9}\ \mathrm{atm}^{-1}$ FOR CdS, CdSe AND CdTe

	K_0'' (cm^{-9} atm^{-1})	H(eV)	Reference
CdS	5.9×10^{59}	1.70	This paper
CdSe	3.8×10^{63}	1.83	(4)
CdSe	1.3×10^{64}	2.10	(6)
CdTe	2.0×10^{59}	1.70	(8)

TABLE III

EXPRESSIONS FOR THE EQUILIBRIUM CONSTANTS FOR CdS

Reaction	Equilibrium constant[a] (expressed in site fractions)
$\mathrm{Cd}(g) \rightleftarrows V_S^{\cdot\cdot} + 2e' + \mathrm{Cd}_{\mathrm{Cd}}^x$	$K'' \cong 7.40 \times 10^{-8} \exp(-1.70\ \mathrm{eV}/kT)$ $s_0(V_S^{\cdot\cdot}) + s_0(\mathrm{Cd}_{\mathrm{Cd}}^x) \cong 18.22\ k$ $s_0(V_S^{\cdot\cdot}) \cong 5.20\ k$
$\mathrm{Cd(g)} \rightleftarrows \mathrm{Cd}_{\mathrm{Cd}}^x + V_S^x$	$K_{\mathrm{Cd}} \cong 9.78 \times 10^{-2} \exp(-1.52\ \mathrm{eV}/kT)$
$V_S^x \rightleftarrows V_S^{\cdot} + e'$	$K_{d1} \cong 1.74 \times 10^{-3} \exp(-0.042\ \mathrm{eV}/kT)$
$V_S^{\cdot} \rightleftarrows V_S^{\cdot\cdot} + e'$	$K_{d2} \cong 4.35 \times 10^{-4} \exp(-0.14\ \mathrm{eV}/kT)$

[a] Preexponential terms evaluated at 900°C with $m^*/m = 0.2$.

The mass action constant for (4.1.1) can be written

$$K'' = \exp -\frac{\Delta G}{kT}$$

$$= \exp\frac{1}{k}\,[s_0(V_S^{\cdot\cdot}) + 2s_0(e') + s_0(\mathrm{Cd_{Cd}}^x) -$$

$$s_0(\mathrm{Cd}_g)]\exp -\frac{\mathrm{H_{Cd}} + E_{d1} + E_{d2}}{kT}. \qquad (4.2.3)$$

Evaluation of the experimental preexponential leads to

$$s_0(V_S^{\cdot\cdot}) - s_0(\mathrm{Cd}_{\mathrm{Cd}}^x) \cong 18.22\ k \text{ at } 900^\circ\mathrm{C}. \qquad (4.2.4)$$

If Latimer's value (*34*) for the entropy of a Cd atom on a lattice site corrected to 1173°K is used, $s_0(\mathrm{Cd}_{\mathrm{Cd}}^x) = +13.02k$, we find $s_0(V_S^{\cdot\cdot}) = +5.20k$. Bloem and Kröger (*35*) found for PbS at 1100°K $s_0(V_S^x) = -8.05k$, while Thomas (*36*) found for ZnO at 800°K $s_0(\mathrm{Zn}_i^{\cdot}) - s_0(V_i^x) = +4.4\ k$.

5. Conclusion

Resistivity and Hall effect measurements were performed on CdS in equilibrium with Cd vapor at high temperatures. Results indicate that at temperatures above 700°C excess Cd is incorporated into the crystal with the formation of a double donor defect, probably an S vacancy. The equilibrium constant for the incorporation of the doubly ionized defect into the crystal, the estimates of individual activation energies and the defect entropies are summarized in Table III.

Hall mobilities were measured over the temperature range 400–1000°C. The experimental values were compared with the theoretical mobility calculated by reciprocally combining the separate contributions considering polar scattering by longitudinal optical modes, deformation potential scattering and piezoelectric scattering by acoustic modes. The experimental values agreed fairly well with the theoretical mobility although the mobilities measured at high temperatures appear somewhat low.

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