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High-Temperature Hall Effect Measurements in Indium-Doped Cadmium Sulfide in Sulfur Vapor*

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High-temperature Hall effect measurements on indium-doped cadmium sulfide in cadmium and sulfur vapor, combined with the results of similar measurements on undoped CdS lead to the parameters of the equilibrium constant of Schottky disorder

$$K''_{\mathrm{S}} = 410 \exp(-4.09\,\mathrm{eV}/kT)\,\mathrm{site\,fr}^2$$

vacancy formation,

$$K''_{\mathrm{CdV}} = 3.56 \times 10^9 \exp(-2.34\,\mathrm{eV}/kT)\,\mathrm{site\,fr},$$

and pairing of V''_{Cd} with $\mathrm{In}^{\cdot}_{\mathrm{Cd}}$

$$K_P = 6.7\,(\times/:)\,25 \exp(0.47 \pm 0.3\,\mathrm{eV}/kT)\,\mathrm{site\,fr}.$$

Introduction

Recent studies of CdS indicate that the high-temperature conductivity of undoped crystals under both reducing (*1–3*) and sulfurizing (*4–6*) conditions is controlled by the presence of a doubly ionized native donor defect. This evidence along with Cd and S self-diffusion data (*2*, *7*) indicate that the dominant defect is a doubly charged sulfur vacancy; singly ionized Cd interstitials are also present but at smaller concentrations. Previous work on donor-doped crystals indicated that doubly charged acceptor defects, probably V''_{Cd}, are present under sulfurizing conditions (*7*, *8*). The present study of the high-temperature Hall effect as a function of P_{Cd} and P_{S_2} for indium-doped samples was undertaken to verify the above defect models and to check the reported parameters of thermodynamic equilibrium constants involved. Comparison with results reported in (*7*) is particularly meaningful since the experiments were carried out on samples cut from the same single-crystal boule.

Experimental

Measurements of the Hall effect of indium-doped cadmium sulfide crystals in equilibrium with cadmium or sulfur vapor at high temperatures were made in an apparatus described previously (*1*). Square plate-shaped samples (5 × 5 × 1 mm) were cut from high-purity single crystals obtained from Clevite and Eagle Picher corporations. Lightly doped samples containing $<10^{19}$ In/cm^3 were prepared by evaporating a layer of indium onto the surface of the sample prior to a diffusion anneal. Heavily doped samples were prepared by pressing a piece of indium of the proper weight onto the sample surface. To effect in-diffusion, the samples were annealed in quartz ampoules for 4 to 7 days at 950°C under a sulfur pressure of 3 atm. After the diffusion anneal, the samples were lapped and etched with 50% HCl to remove any excess of indium sulfide from the sample surface. The samples were then notched in a cloverleaf shape for electrical measurements using the van der Pauw technique (*9*).

For measurements under Cd vapor, ohmic contacts were made by pressing four graphite electrodes against the sample with 0.010-in. diameter tungsten wires. This arrangement serves to keep the crystal in place and provides lead wires at the same time

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TABLE I

QUASI-CHEMICAL DEFECT REACTIONS AND THE CORRESPONDING MASS ACTION RELATION FOR INDIUM-DOPED CdS

1.	$\mathrm{Cd(g)} \rightleftarrows \mathrm{Cd}_{\mathrm{Cd}}^{\times} + V_{\mathrm{S}}^{\cdot\cdot} + 2e'$	$[e']^2[V_{\mathrm{S}}^{\cdot\cdot}] = K_{\mathrm{S}V}'' P_{\mathrm{Cd}}$	(1)
2.	$\mathrm{Cd}_{\mathrm{Cd}}^{\times} + e' \rightleftarrows V_{\mathrm{Cd}}'' + \mathrm{Cd(g)}$	$[V_{\mathrm{Cd}}']/[e'] = K_{\mathrm{Cd}V}' P_{\mathrm{Cd}}^{-1}$	(2)
3.	$\mathrm{Cd}_{\mathrm{Cd}}^{\times} + 2e' \rightleftarrows V_{\mathrm{Cd}}' + \mathrm{Cd(g)}$	$[V_{\mathrm{Cd}}'']/[e']^2 = K_{\mathrm{Cd}V}'' P_{\mathrm{Cd}}^{-1}$	(3)
4.	$0 \rightleftarrows V_{\mathrm{S}}^{\cdot\cdot} + V_{\mathrm{Cd}}''$	$[V_{\mathrm{S}}^{\cdot\cdot}][V_{\mathrm{Cd}}''] = K_{\mathrm{S}}''$	(4)
5.	$V_{\mathrm{Cd}}'' + \mathrm{In}_{\mathrm{Cd}}^{\cdot} \rightleftarrows (V_{\mathrm{Cd}}\mathrm{In}_{\mathrm{Cd}})'$	$[(V_{\mathrm{Cd}}\mathrm{In}_{\mathrm{Cd}})']/[V_{\mathrm{Cd}}''][\mathrm{In}_{\mathrm{Cd}}^{\cdot}] = K_{\mathrm{P}}$	(5)
6.	$\mathrm{CdS} \rightleftarrows \mathrm{Cd(g)} + \frac{1}{2}\mathrm{S_2(g)}$	$P_{\mathrm{Cd}} P_{\mathrm{S}_2}^{1/2} = K_{\mathrm{CdS}}$	(6)
7.	$0 \rightleftarrows e' + h^{\cdot}$	$[e'][h^{\cdot}] = K_i$	(7)

(*1*). Under sulfur vapor, the samples were pressed against four stationary graphite electrodes by quartz springs. Platinum wires, 0.020 in. diameter, were used for lead wires and were found to hold up quite well under sulfur vapor up to temperatures as high as 900°C. Electron concentrations are calculated from the Hall constant R using $R = f(1/[e']q)$, q being the unit of charge, and f a constant which is taken equal to $3\pi/8$ for nondegenerate samples and 1 for degenerate samples (i.e., samples with $[e'] > N_c$, the density of states in the conduction band. $N_c = 2(2\pi m_e^* kT/h^2)^{3/2} = 4.85 \times 10^{15} T^{3/2}(m^*/m)^{3/2}$, which for $m_e^* \approx 0.2$ m is 15×10^{19} cm^{-3} at 800°C and 1.74×10^{19} cm^{-3} at 900°C.

Results and Discussion

The equilibrium between indium-doped CdS and Cd or S_2 vapor can be formulated with the aid of quasi-chemical reactions, see, e.g., (*8*, *10*). The pertinent reaction equations and the corresponding mass action relations are summarized in Table I. It has been assumed that the indium occupies Cd lattice sites and that all the $\mathrm{In}_{\mathrm{Cd}}$ are ionized at the temperatures of measurement. Consideration of the possibility of association of indium and metal vacancies is necessary since some of the samples were quite heavily doped. For easier comparison of data from samples annealed under S_2 or Cd vapor, all equations have been written in terms of P_{Cd}. Since the S vapor consists almost entirely of S_2 molecules under the conditions of the experiment, the corresponding S_2 pressure for a given Cd pressure can be calculated from Eq. (6) where, according to (*11*),

$$^{10}\mathrm{Log}\, K_{\mathrm{CdS}} = -17\,029/T + 10.302.$$

Asymptotic solutions for the various defect concentrations can be obtained from Eq. (1)–(7) by making appropriate approximations to the neutrality condition. Table II summarizes the expressions for the electron concentration obtained for five different neutrality approximations. The Cd vapor pressure dependence of the electron concentration given by these expressions can be compared to the experimental data and the dominant electrically active defects can then be determined. For an exact interpretation, use of the complete neutrality is necessary, however.

Figure 1 presents the electron concentration as a function of P_{Cd} at constant sample temperatures of 800 and 900°C for several samples containing different amounts of indium. In all cases, data are given for the same sample heated in cadmium and sulfur vapor, respectively. The range of pressures where measurements can be made is limited due to sample sublimation at medium S_2 or Cd pressures. It can

TABLE II

ASYMPTOTIC SOLUTIONS FOR THE ELECTRON CONCENTRATION

	Neutrality condition	Electron concentration	
I.	$[e'] \cong 2[V_{\mathrm{S}}^{\cdot\cdot}]$	$[e'] = (2K_{\mathrm{S}V}'')^{1/3} P_{\mathrm{Cd}}^{1/3}$	(9)
II.	$[e'] \cong [\mathrm{In}_{\mathrm{Cd}}^{\cdot}] \cong [\mathrm{In}]_{\mathrm{total}}$	$[e'] = [\mathrm{In}]_{\mathrm{total}}$	(10)
III.	$2[V_{\mathrm{Cd}}''] \cong [\mathrm{In}_{\mathrm{Cd}}^{\cdot}] \cong [\mathrm{In}]_{\mathrm{total}}$	$[e'] = \{\frac{1}{2}[\mathrm{In}]_{\mathrm{total}}/K_{\mathrm{Cd}V}''\}^{1/2} P_{\mathrm{Cd}}^{1/2}$	(11)
IV.	$[V_{\mathrm{Cd}}'] \cong [\mathrm{In}_{\mathrm{Cd}}^{\cdot}] \cong [\mathrm{In}]_{\mathrm{total}}$	$[e'] = [\mathrm{In}]_{\mathrm{total}} K_{\mathrm{Cd}V}'^{\,-1} P_{\mathrm{Cd}}$	(12)
V.	$[(V_{\mathrm{Cd}}\mathrm{In}_{\mathrm{Cd}})'] \cong [\mathrm{In}_{\mathrm{Cd}}^{\cdot}] \cong \frac{1}{2}[\mathrm{In}]_{\mathrm{total}}$	$[e'] = \{K_{\mathrm{Cd}V}'' K_P\}^{-1/2} P_{\mathrm{Cd}}^{1/2}$	(13)

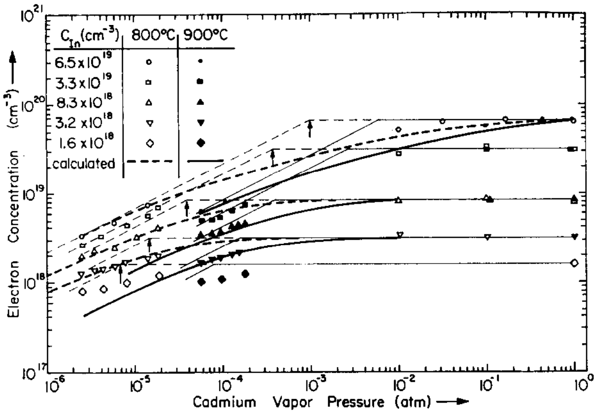

FIG. 1. Electron concentration in indium-doped CdS determined by Hall effect measurements on crystals in equilibrium with Cd or S_2 rich vapors at 800 and 900°C. Thin lines indicate asymptotes, heavy lines give calculated isotherms for samples with 6.5×10^{19}, 8.3×10^{18} and 3.2×10^{18} In cm^{-3}. Arrows mark $(P_{Cd})_{tr}$.

be seen from Fig. 1 that the isotherm for a given sample can be approximated by two straight line segments with different slopes. At high Cd activity, the electron concentration is independent of both temperature and P_{Cd} and is determined only by the indium concentration in the sample. This region corresponds to a condition of impurity controlled conductivity with $[e'] \cong [In_{Cd}^{\cdot}]$, neutrality condition II. Under sulfurizing conditions, the electron concentration is found to be proportional to P_{Cd}^{γ}. The exponent γ varies from approximately 0.5 for the two heaviest doped samples, containing 6.5 and 3.2×10^{19} In cm^{-3} respectively, to approximately 0.2 for a dopant concentration of 1.55×10^{18} cm^{-3}.

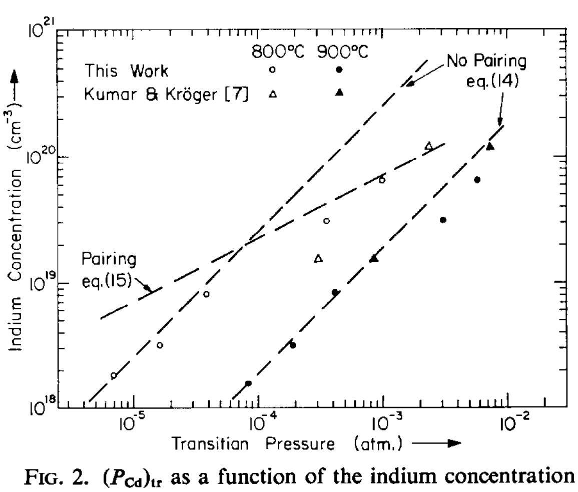

FIG. 2. $(P_{Cd})_{tr}$ as a function of the indium concentration at 800 and 900°C. Dashed lines give the variations expected on the basis of Eq. (14) and (15).

The value of $\gamma = 0.5$ as found for the strongly doped samples can be explained by a compensation mechanism of the form of either $[In_{Cd}^{\cdot}] \cong 2[V_{Cd}'']$ or $[In_{Cd}^{\cdot}] \cong [(V_{Cd}''In_{Cd}^{\cdot})']$, see Table II. The reason for the smaller slopes found in the weakly doped samples is to be found in the closeness of the range boundary. Differentiation between the various compensation models mentioned above can be made by studying the variation with dopant concentration of the Cd pressure $(P_{Cd})_{tr}$, marking the intersection of the two asymptotic solutions for $[e']$ valid, respectively, for high and low Cd activity. Expressions for $(P_{Cd})_{tr}$ can be derived by equating the expressions for $[e']$ valid under neutrality approximations II and III or II and V.

$$(P_{Cd})_{tr\,II,\,III} = 2[In_{Cd}^{\cdot}]\,K_{CdV}'' \tag{14}$$

$$(P_{Cd})_{tr\,II,\,V} = [In_{Cd}^{\cdot}]^2\,K_{CdV}''\,K_P \tag{15}$$

$(P_{Cd})_{tr}$ for each sample at 800 and 900°C, was determined graphically by drawing lines with the asymptotic slope of 0.5 through the low P_{Cd} data. The placement of these lines for the three lightly doped samples is somewhat arbitrary. It is based on the view that the proximity of a range boundary tends to lower the points below the asymptotes determined by the approximation of the neutrality condition characterizing the range. Figure 2 shows values for $(P_{Cd})_{tr}$ as a function of the indium concentration for 800 and 900°C. Transition pressures determined from Cd self-diffusion data (Kumar (7)) are included in Fig. 2 for comparison.

It is seen that although the 900°C data are in reasonably good agreement with Eq. (14), the 800°C data show a concentration dependence somewhat between that expected on the basis of (14) and (15). This indicates that pairing is important, at least at the higher concentrations.

The temperature dependence of the electron concentration of the various samples at a sulfur pressure of one atmosphere is given in Fig. 3. Note that a constant sulfur pressure means a varying cadmium pressure. The decrease in slope with decreasing indium concentration from 0.775 to 0.324 eV is to be attributed to the same effect that was the cause of the decrease in γ, viz., the approach of the boundary with range II where $[e'] = [In_{Cd}^{\cdot}]$, independent of both temperature and cadmium pressure. Only the most heavily doped samples are sufficiently far from the boundary to make an approximate solution for the appropriate low P_{Cd} valid. However, in this case pairing will come into the picture. A simple interpretation of the observed slopes is therefore not possible.

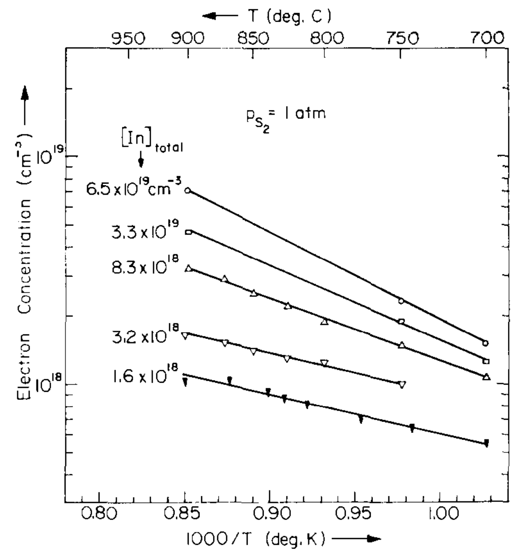

FIG. 3. Temperature dependence of the electron concentrations of samples with different indium content at $P_{S_2} = 1$ atm.

We shall analyze the data on the basis of the assumption that pairing is negligible for the samples doped with 1.6×10^{18} cm^{-3} indium, but has to be taken into account to explain the results for the more highly doped samples.

The neutrality condition and indium balance

$$[\mathrm{In}_{\mathrm{Cd}}^{\cdot}] = [\mathrm{In}]_{\mathrm{total}} = [e'] + 2[V_{\mathrm{Cd}}''], \qquad (16)$$

together with Eq. (1) leads to a quadratic equation in $[e']$ from which, for given $[e']$ and P_{Cd}, $K_{\mathrm{Cd}V}''$ can be found. Low indium concentration data for 800 and 900°C lead to

$$K_{\mathrm{Cd}V}'' = 3.56 \times 10^9 \exp(-2.335\,\mathrm{eV}/kT)\ \text{site fr.} \qquad (17)$$

The data for $[\mathrm{In}]_{\mathrm{total}} = 6.5 \times 10^{19}$ cm^{-3} now are interpreted with the neutrality condition and indium balance:

$$[\mathrm{In}_{\mathrm{Cd}}^{\cdot}] = [e'] + 2[V_{\mathrm{Cd}}''] + [(\mathrm{In}_{\mathrm{Cd}}\,V_{\mathrm{Cd}})'], \qquad (18)$$

$$[\mathrm{In}_{\mathrm{Cd}}^{\cdot}] + [(\mathrm{In}_{\mathrm{Cd}}\,V_{\mathrm{Cd}})'] = [\mathrm{In}]_{\mathrm{total}}, \qquad (19)$$

combined with (3) and (5). For high electron concentrations, $[e']$ in (3), but not in (18), is to be replaced by a_e, the activity of electrons; a_e may be taken from Rosenberg (*12*) who lists a_e as $f([e']/N_c)$. This leads to

$$\begin{aligned}[\mathrm{In}]_{\mathrm{total}} &= 2[(\mathrm{In}_{\mathrm{Cd}}\,V_{\mathrm{Cd}})'] + [e'] + 2[V_{\mathrm{Cd}}''] \\ &= [e'] + 2a_e^{\,2} K_{\mathrm{Cd}V}'' P_{\mathrm{Cd}}^{-1} + \\ &\qquad \frac{2K_{\mathrm{P}} K_{\mathrm{Cd}V}''[\mathrm{In}]_{\mathrm{total}}\, a_e^{\,2} P_{\mathrm{Cd}}^{-1}}{1 + K_{\mathrm{P}} K_{\mathrm{Cd}V}''\, a_e^{\,2} P_{\mathrm{Cd}}^{-1}} \qquad (20)\end{aligned}$$

For $K_{\mathrm{P}} = 0$ and $a_e = [e']$, this equation goes back to the simpler one used above. Application of (20) to the data for the sample with $6.5 + 10^{19}$ cm^{-3} indium, using $K_{\mathrm{Cd}V}''$ arrived at earlier leads to

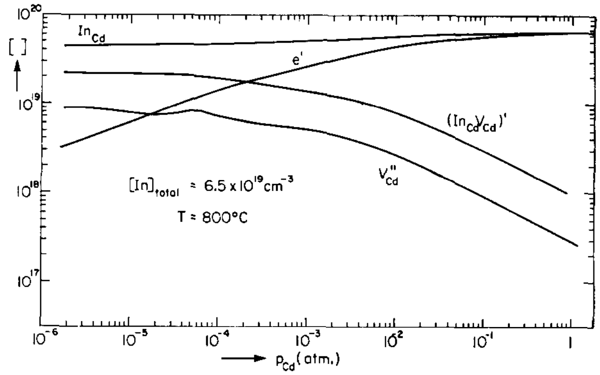

FIG. 4. Defect isotherms for CdS with $[\mathrm{In}]_{\mathrm{total}} = 6.5\ 20^{19}$ cm^{-3} at 800°C, calculated from Eq. (20) using (17) and (21).

$$K_{\mathrm{P}} = 6.7\,(\times/:)\,25 \exp(0.47 \pm 0.3\,\mathrm{eV}/kT)\ \text{site fr.} \qquad (21)$$

These parameters of K_{P}, though not very accurate because of the narrow temperature range, are quite acceptable. The pre-exponential is close to 12, the number of nearest metal sites round a given metal site, the value to be expected if the change in vibrational entropy upon pairing is negligible. The median pairing enthalpy $H_{\mathrm{P}} = -0.47$ eV is somewhat smaller than the coulombic energy $H_{\mathrm{P}} = -2q^2/\epsilon r$, which for an average dielectric constant $\epsilon = 9$ and a nearest metal-metal neighbor distance $r = 4.14$ Å, gives $H_{\mathrm{P}} = -0.77$ eV. A smaller value is to be expected because the sulfur atoms, present between the two attracting defects, have a polarizability considerably larger than that of Cd. As previously shown for the alkali halides (*13*), in such cases, the use of an effective $\epsilon >$ the average ϵ is justified. Note, however, that the coulombic value is inside the indicated margin of error.

Using (21) and (17), we now can calculate from (20) expected values for $[e']$ as $f(P_{\mathrm{Cd}}, T)$ for all concentrations. Figure 4 shows a complete set of defect isotherms for $[\mathrm{In}]_{\mathrm{total}} = 6.5 \times 10^{19}$ cm^{-3} at 800°C. The solid curves in Fig. 1 are arrived at in the same way. It is seen that the agreement between theory and experiment is satisfactory. It is therefore concluded that our data support the model used, including considerable pairing between $\mathrm{In}_{\mathrm{Cd}}^{\cdot}$ and V_{Cd}'' at the higher indium concentrations. Combination of $K_{\mathrm{Cd}V}''$ as given by (17) and K_{SV}'' according to Ref. (*1*),

$$K_{SV}'' = 1.14 \times 10^{-7} \exp(-1.75\,\mathrm{eV}/kT)\ \text{site fr atm}^{-1}, \qquad (22)$$

gives the Schottky constant

$$K''_{\mathrm{S}} = K''_{\mathrm{S}V}\, K''_{\mathrm{Cd}V} = 410 \exp(-4.09\,\mathrm{eV}/kT)\,\mathrm{site\ fr.}^2 \tag{23}$$

In the light of Kumar's work, we must interpret results previously attributed to Frenkel disorder as being due to Schottky disorder. We then have to compare the enthalpy of (23) with the value of 2.5 eV reported for $K''_{\mathrm{F,Cd}}$ (*14*). The much larger $H''_{\mathrm{S}} = 4.09$ eV found by us leads to a situation with the intrinsic electron-hole product $K_i > K''_{\mathrm{S}}$, and therewith, for pure CdS, to a central range governed by $[e'] \approx h^{\cdot}]$ rather than $[V''_{\mathrm{Cd}}] \approx [V^{\cdot\cdot}_{\mathrm{S}}]$ (*15*).

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