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# Chemical Diffusion in CdS*

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The coefficient of chemical diffusion in CdS at high Cd activities is determined as a function of temperature and the result is interpreted on the basis of published self-diffusion data.

## Introduction

Recent work on the self-diffusion in pure and donor-doped CdS using radioactive tracers led to expressions for the tracer diffusion coefficients as $f(P_{\mathrm{Cd}}, T)$ and for some defect mobilities as $f(T)$ (*1*). It was established that at high cadmium activities, cadmium diffusion is faster than sulfur diffusion, in spite of the fact that the defect involved, singly ionized interstitial cadmium, $\mathrm{Cd}_i^{\cdot}$, is present in a concentration much smaller than that of $V_{\mathrm{S}}^{\cdot\cdot}$, which is the major native atomic defect under these conditions. This means that Cd, present in excess over the stoichiometric composition, is present mainly as $\mathrm{Cd}_{\mathrm{Cd}}^{\times}$ with an equal concentration of $V_{\mathrm{S}}^{\cdot\cdot}$, but that changes in the composition are brought about by diffusion of $\mathrm{Cd}_i^{\cdot}$. This gives rise to interesting complications in the relation between the coefficients of chemical and tracer diffusion which we shall pursue below.

## Theoretical

Chemical diffusion is the process by which gradients in the chemical potentials of the components of a crystal are removed. The diffusion process may be studied by measuring a property dependent on the chemical potentials, and thus on the composition. For a crystal such as CdS, the electrical conductivity at high temperatures under high Cd pressure is a simple function of the stoichiometric composition (*2*, *3*). Therefore, measurements of the conductivity as a function of time are appropriate to study the diffusion process involved in establishing deviations from stoichiometry. If the electronic conductivity $\sigma_e$, which is proportional to the concentration of electrons $c_e$, is the property that is being changed, then we can define a $D_{\mathrm{chem}}$ for a one-dimensional diffusion process of electrons;

$$\frac{dc_e}{dt} = \frac{d}{dx}\left(D_{\mathrm{chem}}\frac{dc_e}{dx}\right). \tag{1}$$

If a crystal in equilibrium with a certain $P_{\mathrm{Cd},1}$ at time $t = 0$ has $\sigma_e = \sigma_e^0$ and a corresponding $c_e^0$, then a change in $P_{\mathrm{Cd}}$ to $P_{\mathrm{Cd},2}$ will start a process by which the crystal adapts itself to the new conditions. If $\sigma_\infty$ and $c_\infty$ are the equilibrium $\sigma_e$ and $c_e$ under the new $P_{\mathrm{Cd}}$, the change takes place exponentially and is described by a relaxation time $\tau$:

$$\frac{\sigma_e - \sigma_\infty}{\sigma_e^0 - \sigma_\infty} = \frac{c_e - c_\infty}{c_e^0 - c_\infty} = \exp(-t/\tau). \tag{2}$$

If the sample is a flat plate of thickness $d$ with $d \ll$ dimensions of the flat area, $\tau$ is related to $D_{\mathrm{chem}}$ by (*2*):

$$D_{\mathrm{chem}} = \frac{d^2}{\pi^2 \tau}. \tag{3}$$

The establishment of a changed electron concentration involves the migration of equal numbers of electrons and $\mathrm{Cd}_i^{\cdot}$, i.e., $j_e = j_{\mathrm{Cd}_i}$ (ambipolar diffusion). Both are given by

$$j_e = j_{\mathrm{Cd}_i} = -k D_{\mathrm{Cd}_i}(dc_{\mathrm{Cd}_i}/dx). \tag{4}$$

$D_{\mathrm{Cd}_i}$ is the diffusion coefficient for nontracer $\mathrm{Cd}_i^{\cdot}$; $k$ is a constant resulting from the ambipolar character of the diffusion. As shown in Appendix I, $k = 3/2$. Note that the particle currents of $e'$ and

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$\text{Cd}_i^{\cdot}$ are equal in spite of the fact that their concentrations are not equal. Writing $c_{\text{Cd}}$ and $c_V$ for the concentrations of $\text{Cd}_i^{\cdot}$ and $V_S^{\cdot\cdot}$, respectively,

$$c_e = c_{\text{Cd}} + 2c_V \approx 2c_V, \tag{5}$$

$$(c_{\text{Cd}})_{\text{excess}} = c_{\text{Cd}} + c_V \approx c_V. \tag{6}$$

The proper flux equation for the establishment of nonstoichiometry, reconciling (1), (4), and (6), is

$$j_{\text{Cd}_i} = j_e = -D_{\text{chem}}[d(c_{\text{Cd}} + c_V)/dx]. \tag{7}$$

This amounts to the introduction of a quasi particle current for $V_S^{\cdot\cdot}$—quasi because $V_S^{\cdot\cdot}$ is not diffusing to an appreciable extent, but is formed as a result of a chemical reaction (see below). A more sophisticated approach leading to the same final result is given in Appendix II. Combination of (4) and (7) gives

$$D_{\text{chem}} = kD_{\text{Cd}_i}(1 + dc_V/dc_{\text{Cd}})^{-1}. \tag{8}$$

An expression for the variation of $c_V$ with $c_{\text{Cd}}$ is obtained by considering the process by which inside the crystal $\text{Cd}_i^{\cdot}$ is transformed into $V_S^{\cdot\cdot}$; this is by a combination of

$$\text{Cd}_i^{\cdot} + V_{\text{Cd}}'' \rightarrow \text{Cd}_{\text{Cd}}^{\times} + e',$$

and the Schottky disorder reaction taking place at dislocations. The total reaction is

$$\text{Cd}_i^{\cdot} \rightleftarrows \text{Cd}_{\text{Cd}}^{\times} + \text{V}_S^{\cdot\cdot} + e'. \tag{9}$$

If we assume local equilibrium for (9),

$$c_V\, c_e/c_{\text{Cd}} = K. \tag{10}$$

Differentiation after elimination of $c_e$ using (5) gives

$$dc_V/dc_{\text{Cd}} = c_V/2c_{\text{Cd}} = [V_S^{\cdot\cdot}]/2[\text{Cd}_i^{\cdot}]. \tag{11}$$

Here the square brackets indicate concentrations expressed as site fractions. Since the tracer diffusion constant $D^*_{\text{Cd}_i} = D_{\text{Cd}_i}[\text{Cd}_i^{\cdot}]$, combination of (8) and (11), with $k = 3/2$ gives

$$D_{\text{chem}}/D^*_{\text{Cd}} = \frac{3/2}{(\frac{1}{2}[V_S^{\cdot\cdot}] + [\text{Cd}_i^{\cdot}])} \approx \frac{3}{[V_S^{\cdot\cdot}]}. \tag{12}$$

For

$$[e'] = 2[V_S^{\cdot\cdot}], [V_S^{\cdot\cdot}] = (K''_{SV}/4)^{1/3} P_{\text{Cd}}^{1/3},$$

with $K''_{SV}$ the equilibrium constant for the formation of $V_S^{\cdot\cdot}$ and two electrons; as reported in Ref. (*3*),

$$K''_{SV} = 1.14 \times 10^{-7} \exp(-1.75\,\text{eV}/kT)\,\text{site fr}^3\,\text{atm.}^{-1} \tag{13}$$

According to Ref. (*1*),

$$D^*_{\text{Cd}} = 7.29 \times 10^{-5} P_{\text{Cd}}^{2/3} \exp(-1.26\,\text{eV}/kT)\,\text{cm}^2\,\text{sec}^{-1}. \tag{14}$$

Therefore,

$$(D_{\text{chem}})_{\text{calcd}} = 7.26 + 10^{-2} P_{\text{Cd}}^{1/3} \exp(-0.68\,\text{eV}/kT). \tag{15}$$

For a logarithmic average $\bar{P}_{\text{Cd}} \approx 10^{-2}$ atm (corresponding to the conditions of our experiments)

$$(D_{\text{chem}})_{\text{calcd},\, \bar{P}_{\text{Cd}}=10^{-2}\,\text{atm}} = 1.56 \times 10^{-2} \exp(-0.68\,\text{eV}/kT). \tag{16}$$

## Experimental

Relaxation experiments were done at the high Cd pressure side of the CdS stability range. These experiments were confined to the determination of relaxation times and no attempt was made to determine the electron concentration or mobility. A simple two electrode technique was used to observe the relaxation of the sample resistance in response to a step-wise change in $P_{\text{Cd}}$. The measured variable was the voltage across a constant resistance which was connected in series with the sample and a constant voltage supply. The constant resistance used was 0.2 ohms, much smaller than the sample resistance (~100 ohms), to maximize the relative change in current between the two steady states.

The experimental set-up is shown in Fig. 1. The sample S, approximately $0.1 \times 1 \times 1$ cm$^3$, and from the same boule of pure CdS single crystal used in self-diffusion and Hall effect experiments reported on earlier (*1*, *3*) is supported on four pointed graphite feet F, passing through four holes in a 1/8-in. thick quartz plate. The graphite feet move freely within the holes and are individually pressed against the sample with quartz springs, G, fused to one side of the plate, while the sample is pressed against the feet by two more quartz springs on the other side of the plate. The plate is connected to the end of a four-bore quartz rod (.1969 × 32 in. long), through which four W wires are passed and are vacuum sealed within the rod at three points along its length for about 1 in. at each point, as shown in Fig. 1. Each wire is connected at the plate end to one of the graphite feet by passing it through a fine hole drilled across the foot and then bending it. The pointed graphite feet and the W wires provide the contacts and the leads, respectively, to connect the sample to the outside circuit. Only two of the four available probes were used for these measurements.

The assembly is enclosed under vacuum in a 20-in. long quartz tube of 18 mm i.d., 20 mm o.d. About a gram of high-purity Cd metal was added to the tube before vacuum sealing. The rod carrying the wires is sealed to the tube at one end, while the sample holder (the quartz plate) is near the other

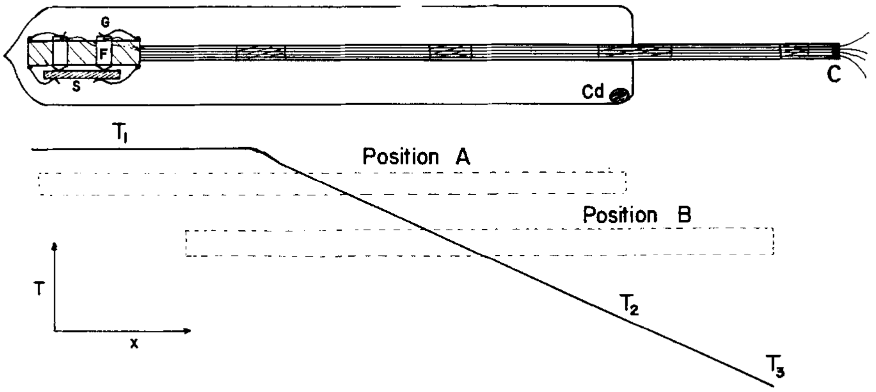

FIG. 1. Apparatus for the relaxation experiments, and the temperature profile in which it is placed.

end (where the tube is finally vacuum-sealed). Thus, about 12 in. of the rod carrying the W wires sealed in it sticks out of the tube. The wires emerge at the end, and are again sealed to the rod at C by using some epoxy resin; this is possible because this end of the apparatus remains at room temperature. The use of epoxy was found necessary in order to seal the tube completely off from the atmosphere; the W wires could not be perfectly sealed inside the four-bore quartz rod. The small leaks between the W wires and the quartz rod automatically seal during the experiment as Cd condenses there.

To study relaxation at a temperature $T_1$, between Cd pressures corresponding to temperatures $T_2$ and $T_3$, a temperature profile of the form shown in Fig. 1 is established in a 36-in. long furnace. The sample is allowed to equilibrate while the tube is held in position A inside the furnace. When a steady resistance is recorded, the tube is quickly shifted to the position B. This changes the temperature of the Cd end and, therefore, $p_{Cd}$ in the tube. The sample resistance is recorded till a new steady state is attained. A thermocouple attached to the colder end is used to measure the temperature at this end and its variation when the tube is shifted to a new position. The time constant $\tau$, and the fractional change in resistance, are calculated from the recorded relaxation curve (Fig. 2).

Using the expression for exponential decay, $R = R_0 \exp(-t/\tau)$, $\tau$ was taken to be the time difference between points where $R = R_0$ and where $R = R_0/e$; the resistance to be approached in the new steady state being the reference $R = 0$. It was found from the recorded temperature of the Cd end that about 90% of the temperature drop occurred in the first minute; after this there was a very slow change. Keeping this in mind, $\tau$ was calculated from the part of the relaxation curve recorded at least 1 min after the start of the experiment. Values of $\tau$ were obtained from at least three different points of the curve. These were found to be within 10–15% of one another. This scatter shows itself in the reported $D_{\text{chem}}$ (Fig. 3).

Because, at higher temperatures, the relaxation time is smaller, whereas the time for attaining the changed temperature at the colder end is about the same, the results from high temperatures are not representative of the crystal equilibration process.

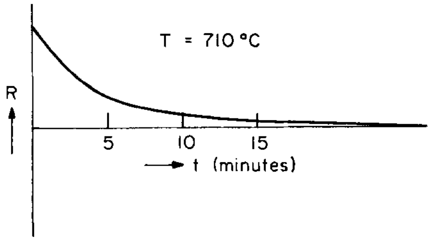

FIG. 2. Experimental relaxation curve of the sample resistance.

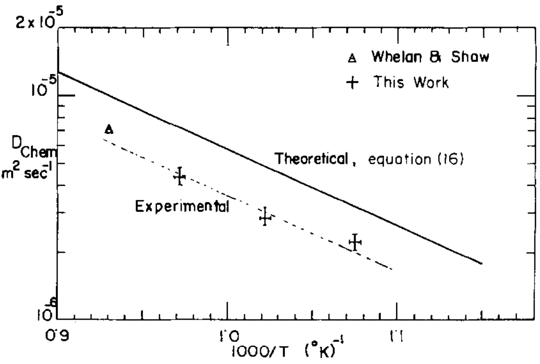

FIG. 3. Comparison of experimental and calculated values for $D_{\text{chem}}$.

At lower temperatures, on the other hand, the assumption of $V_S^{\cdot\cdot}$ being the majority defect is probably no longer valid. This is especially true in impure crystals if small concentrations of donors are present and the crystal is likely to be dominated by the foreign donors. Due to these restrictions, data were obtained only at 660, 710, and at 760°C. The sample temperature was not exactly equal in the two positions A and B, there being $\simeq 7°$ difference. The value of $P_{\mathrm{Cd}}$ for a particular experiment was taken to be the logarithmic average of the $P_{\mathrm{Cd}}$ values at the temperatures $T_2$ and $T_3$. The temperature differences used, $\Delta T = T_2 - T_3 \approx 100°\mathrm{C}$, gave pressure ratios of $\approx 10$.

## Results and Discussion

The initial and final values of the resistivities measured before and after the change in $P_{\mathrm{Cd}}$ showed the expected dependence $\propto P_{\mathrm{Cd}}^{-1/3}$. Values of $D_{\mathrm{chem}}$ deduced from the relaxation experiments at various temperatures are shown in Fig. 3. The figure also contains a point deduced from a relaxation time $\tau \leqslant 1$ min for a 1-mm thick crystal at 800°C at $\bar{P}_{\mathrm{Cd}} \approx 7 \times 10^{-4}$ atm reported by Whelan and Shaw (*5*). Correcting for the difference in the cadmium pressure at which their and our data were taken, their $D_{\mathrm{chem}} = 1.7 \times 10^{-5}$ cm² sec⁻¹ changes to $D_{\mathrm{chem}} = 7 \times 10^{-6}$ cm² sec⁻¹, the point shown in Fig. 3 which is in good agreement with our data. Our data were also consistent with the estimated time for equilibration reported in Ref. (*3*).

It is seen that there is agreement with the theoretical line calculated from self-diffusion data using (16) as far as the slope is concerned; the absolute values differ by no more than a factor of $\approx 1\,1/2$. This may be considered good agreement and supports both the experimental data on which the result was based and the model used to relate $D_{\mathrm{chem}}$ to $D_{\mathrm{Cd}}^*$.

Relaxation experiments carried out by Boyn *et al.* (*2*) at $T \leqslant 650°\mathrm{C}$ may be represented by

$$(D_{\mathrm{chem}})_{\mathrm{Boyn}} = 3.4 \times 10^{-5} \exp(-0.62\,\mathrm{eV}/kT). \qquad (17)$$

A pressure dependence is not mentioned. This expression is markedly different from (16) and predicts values which at 660°C are 100 times smaller than our experimental point at this temperature. The reasons for this discrepancy are not clear.

## Appendix I

### The Ambipolar Coefficient $k$

The only species with appreciable mobility are $\mathrm{Cd}_i^{\cdot}$ and $e'$. The diffusion of these species takes place according to the particle current expressions

$$j_{\mathrm{Cd}_i} = -D_{\mathrm{Cd}_i}\, dc_{\mathrm{Cd}}/dx + (c_{\mathrm{Cd}}\, D_{\mathrm{Cd}_i} q/kT)\frac{d\phi}{dx}, \qquad \text{(a)}$$

$$j_e = -D_e\, dc_e/dx - (c_e\, D_e q/kT)\frac{d\phi}{dx}, \qquad \text{(b)}$$

$d\phi/dx$ represents the strength of the internal electric field built up as a result of differences in the diffusion terms of (a) and (b). The space charges necessary to keep $j_{\mathrm{Cd}_i}$ and $j_e$ in balance are small, and, therefore the assumption $j_{\mathrm{Cd}_i} = j_e$ is a good approximation. This leads to

$$\frac{q}{kT} d\phi/dx = (D_{\mathrm{Cd}_i}\, dc_{\mathrm{Cd}}/dx - D_e\, dc_e/dx) \times (D_{\mathrm{Cd}_i} c_{\mathrm{Cd}} + D_e c_e)^{-1}, \qquad \text{(c)}$$

which introduced in (a) and (b) gives

$$j_{\mathrm{Cd}_i} = j_e = -D_{\mathrm{Cd}_i}\{dc_{\mathrm{Cd}}/dx + c_{\mathrm{Cd}}(D_{\mathrm{Cd}_i}\, dc_{\mathrm{Cd}}/dx - D_e\, dc_e/dx) \times (D_{\mathrm{Cd}_i} c_{\mathrm{Cd}} + D_e c_e)^{-1}\}. \qquad \text{(d)}$$

This expression may be simplified by using (5), (6), and (10) and its differentials:

$$dc_e \approx 2dc_V, \qquad \text{(e)}$$

$$c_e\, dc_V + c_V\, dc_e = K dc_{\mathrm{Cd}}, \qquad \text{(f)}$$

and leads to

$$j_{\mathrm{Cd}_i} = j_e = -D_{\mathrm{Cd}_i}\left\{\frac{3}{2} D_e\, c_e/(D_{\mathrm{Cd}_i} c_{\mathrm{Cd}} + D_e c_e)\right\} dc_{\mathrm{Cd}}/dx, \qquad \text{(g)}$$

which for $D_e c_e \gg D_{\mathrm{Cd}_i} c_{\mathrm{Cd}}$ reduces to

$$j_{\mathrm{Cd}_i} = j_e = -\frac{3}{2} D_{\mathrm{Cd}_i}\, dc_{\mathrm{Cd}}/dx. \qquad \text{(h)}$$

Comparison with (4) shows $k = 3/2$.

## Appendix II

### Derivation of (12)

In the presence of sinks and sources—in our case the formation of $V_S^{\cdot\cdot}$ by reaction (9)—Fick's second law for the mobile species $\mathrm{Cd}_i^{\cdot}$ and $e'$ should be extended:

$$dc_{\mathrm{Cd}}/dt = -dj_{\mathrm{Cd}}/dx + (\partial c_{\mathrm{Cd}}/\partial t)_r, \qquad \text{(i)}$$

$$dc_e/dt = -dj_e/dx + (\partial c_e/\partial t)_r. \qquad \text{(k)}$$

The terms with subscript $r$ are due to reaction (9). The stoichiometry of reaction (9) indicates that

$$(\partial c_{\mathrm{Cd}}/\partial t)_r = -(\partial c_V/\partial t)_r = -(\partial c_e/\partial t)_r. \qquad \text{(l)}$$

Further, in (e) and (f)

$$dc_V \equiv (\partial c_V)_r.$$

From (5), (e) and (f)

$$dc_e = (K/c_e)\, dc_{\mathrm{Cd}} \tag{m}$$

Then from (f), (m) and (l)

$$(\partial c_e/\partial t)_r = (1 - c_V/c_e)\, dc_e/dt. \tag{n}$$

Which, introduced into (k), using (h) for $j_e$, gives

$$\begin{aligned} dc_e/dt &= -(c_e/c_V)\, dj_e/dx = -2dj_e/dx \\ &= \frac{d}{dx}(3D_{\mathrm{Cd}_i}\, dc_{\mathrm{Cd}}/dx). \end{aligned}$$

With (m) to relate $dc_{\mathrm{Cd}}$ to $dc_e$, replacing $c_{\mathrm{Cd}}/c_V$ by $[\mathrm{Cd}_i^{\cdot}]/[V_{\mathrm{S}}^{\cdot\cdot}]$ and remembering that $D_{\mathrm{Cd}}^* = D_{\mathrm{Cd}_i}[\mathrm{Cd}_i^{\cdot}]$, we get

$$dc_e/dt = \frac{d}{dx}\left(D_{\mathrm{Cd}}^* \frac{3}{[V_{\mathrm{S}}^{\cdot\cdot}]} dc_e/dx\right), \tag{o}$$

or, comparing with (l),

$$D_{\mathrm{chem}} = \frac{3}{[V_{\mathrm{S}}^{\cdot\cdot}]} D_{\mathrm{Cd}}^*, \tag{p}$$

which is identical with (12).

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