Diffusion of Cd in CdS†

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The self-diffusion of Cd in CdS has been measured under a variety of doping and firing conditions. Under saturated Cd pressure the diffusion coefficient is given by $D=3 \exp(-2.0 \text{ eV}/kT)$. Under sulfur pressure at 800°C the diffusion coefficient is found to be linearly dependent on the donor-impurity concentration. A new mechanism for diffusion is proposed to explain the results. No evidence for interstitial Cd was observed and it is suggested that Cd and sulfur vacancies (Schottky defects) are the dominant native defects in CdS.

I. INTRODUCTION

NATIVE defects are known to play important roles in the properties of the II-VI semiconductors. However, the characteristics of these defects in specific experiments are little understood and the identity of the defects which are important is usually decided by hypothetical models. To gain further insight into the behavior of single crystalline CdS when it is heat treated in an excess of Cd or sulfur, the diffusion of radioactive Cd in CdS has been measured under a variety of conditions. Section II describes a relatively simple technique that was used in these studies. The results, described in Sec. III, indicate that a normal self-diffusion takes place which is more rapid under Cd pressure than under sulfur pressure for undoped crystals. The diffusion rate is enhanced under certain doping conditions. These results are discussed in Sec. IV, where it is concluded that interstitial Cd diffusion is not an important process and that a very rapid diffusion of vacancies is the dominant process that occurs when CdS is heat treated. A new mechanism of diffusion is suggested to explain the experimental results. It is further suggested that under sulfur pressure the total Cd vacancy concentration is impurity controlled in the presently available materials.

II. EXPERIMENTAL PROCEDURE

The general procedure employed in these experiments was as follows: Good quality single crystal material[1] was cut into cubes, 2–4 mm on a side, and etched in HCl. The cubes were sealed in quartz ampoules with the radioactive Cd, nonradioactive Cd or sulfur, and impurities as desired. A general description of the firing procedure has been given.[2] In the present experiments, firings were carried out in Cd or sulfur vapor (slight excess) as well as in liquid Cd or sulfur (large excess). In some experiments the radioactive Cd,[3] either Cd^{115m} or Cd^{109}, was added to the quartz

ampoules in the form of the, as received, $Cd(NO_3)_2$ solution which would be vacuum dried and usually oxidized to CdO in the ampoules before sealing off. In other experiments it was added as metallic Cd which was prepared by adding nonradioactive $Cd(NO_3)_2$ carrier to the as-received solution which was then dried, converted to CdO, and reduced with H_2. The final step was a vacuum distillation.

After being fired, the samples were weighed, etched in concentrated HCl, and weighed again. The etchant was diluted to a fixed volume in a standard size test tube and counted with a deep-well scintillation counter for the radioactive Cd content. This procedure of weighing the crystal, etching, counting the amount of radioactive Cd removed, weighing the crystal, etc., was continued until the counting rate was down to background. The counting rates of the etchant were normalized by dividing by the weight loss of the crystal after each etching. A simpler method was also employed which was to count just the crystal before and after each etching and use the difference in the crystal count in place of the etchant count. This method was somewhat less reproducible, probably because the counting geometry was less reproducible and because of self-absorption of the gamma radiation by the sample. Of course, this latter method could not be used if the radioactivity of the sample was high enough to jam the counter. In general, the distance etched was calculated from the weights of the crystal before and after each etching assuming that the cubes etched uniformly (see below).

CdS is a hexagonal crystal of the wurtzite structure in which each Cd atom is surrounded tetrahedrally by four sulfur atoms and vice versa. An anisotropy in the diffusion coefficient would, in general, be expected. Although no attempt was made to directly measure an anisotropy, there were no indications of a large anisotropy and none will be assumed. It is noted that the method of measurement would weight the results in favor of the fastest component of any anisotropy and the results can be so interpreted.

If the surface of the sample is in equilibrium with the added Cd during the firing and if the firing times are kept short $[(Dt)^{1/2} \ll \text{sample dimensions}]$, one would expect for samples fired as described above a diffusion profile corresponding to the diffusion into a semi-

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[1] Unless specified, the crystals used were undoped, UHP grade material obtained from Eagle-Picher Co., Cincinnati, Ohio.

[2] H. H. Woodbury, Phys. Chem. Solids 24, 881 (1963).

[3] The radioactive Cd was obtained from Oak Ridge National Laboratories in the form $Cd(NO_3)_2$ in a HNO_3 solution. The term radioactive Cd is used in the text to mean any Cd containing radioactive Cd and not the carrier free radioisotope.

infinite medium from a source of constant concentration. The solution of the diffusion equation for these boundary conditions is given by[4]

$$C = C_0 \operatorname{erfc}\frac{x}{(4Dt)^{1/2}}, \qquad (1)$$

where C_0 is the concentration at the surface, C is the concentration at distance x after time t, and D is the diffusion coefficient.

It was consistently observed that the samples were never in equilibrium with the liquid or vapor in which the samples were fired for the normal firing times. For example, characteristic experimental results are given in Fig. 1 by the plotted points for a sample fired at 800°C for 53 h in radioactive Cd with an activity that would correspond to a surface concentration of 1.5×10^6 counts/mg. If Eq. (1) is fitted over the approximately straight line portion of the data shown in Fig. 1, the value of C_0 obtained is a few percent of what is expected. All other samples showed similar behavior indicating a nonequilibrium surface situation. A solution of the diffusion equation for a surface rate limiting condition is discussed by Crank[5] whose equations for the case discussed here reduce to

$$C = C_0 \left\{ \operatorname{erfc}\frac{x}{(4Dt)^{1/2}} \right.$$
$$\left. - e^{hx}e^{h^2 Dt} \operatorname{erfc}\left[\frac{x}{(4Dt)^{1/2}} + h(Dt)^{1/2}\right] \right\}, \qquad (2)$$

where h is a parameter relating to the rate of equilibration of the surface with its environment. For $h = \infty$, Eq. (2) reduces to Eq. (1) while $h = 0$ represents no surface exchange or reaction and hence no diffusion into the crystal. The solid curve in Fig. 1 is a plot of Eq. (2) with $h = 3$ cm^{-1} and matched to fit the approximate straight–line portion of the data. Equation (2) with this value of h (within a factor of 3) fits the observed radioactive Cd concentrations in the crystals relative to the radioactive Cd concentrations in the firing ampoules over a wide range of firing times and firing temperatures. The actual shape of the diffusion profile on the semilog plot such as Fig. 1 is little affected by the value of h and the tail can be just as well fitted with Eq. (1). However, the values of D obtained by fitting Eq. (1) to the tail are about 10% lower than those obtained by fitting Eq. (2). The actual procedure employed in these experiments was to visually match the experimental data plotted as in Fig. 1 to a set of master curves derived from Eq. (2) from which the ratio $(x^2/4Dt)$ was obtained.
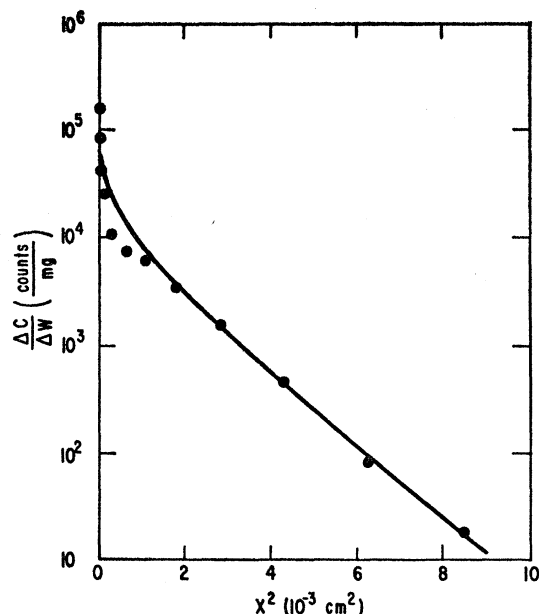

FIG. 1. Diffusion profile for a CdS sample fired in radioactive Cd at 800°C for 53 h. The ordinate gives the radioactive count per milligram of material removed at a distance x from the surface. The curve is Eq. (2) with $h = 3$ cm^{-1} and C_0 adjusted to best fit the tail.

Figure 1 is typical in the lack of fit between the data and the expected diffusion profiles in the first decade drop of counting rate. Many samples gave better fits, some worse. In addition to the normal experimental errors, particularly in measuring the small weight differences for the first few points, some of the more obvious difficulties are the dissolving and thermal etching of the crystal surface during the firing; failure to remove all the excess radioactive Cd from the surface; nonplanar surfaces due to the formation of etch pits; and preferential etching (rounding) of the corners. By far the most serious difficulty is crystallographic differences in etching rates since this also affects the slope of the approximately straight line portion of the data as plotted in Fig. 1, which essentially determines D. In particular, it is observed that the rate of etching of CdS by concentrated (12N) HCl (room temperature) perpendicular to the c axis is approximately 2.3 times the average rate along the c axis. Furthermore, the etching rates of the opposite c faces differ by about 1.5 under the same conditions.[6] Thus, the exact way that any particular cube etches depends on the direction of the c axis relative to the geometry of the sample. It is preferable to have the c axis along the cube diagonal to minimize these differences. (Any shape sample eventually etches to a sliver.) It was observed that hot (250–300°C) phosphoric acid etches more uniformly than the HCl. However, be-

[4] See, for example, J. Crank, *The Mathematics of Diffusion* (Clarendon Press, Oxford, 1956), pp. 18, 19.
[5] J. Crank, *The Mathematics of Diffusion* (Clarendon Press, Oxford, 1956) p. 34.

[6] L. R. Shiozawa *et al.*, Air Research and Development Command Contract No. AF33(657)-7399, Fifth Quarterly Report, 1963 (unpublished).

cause it etches much more slowly than the HCl and because of the inconvenience of handling the hot acid, the phosphoric acid was not used. In the experiments reported in this paper, unoriented cubes were mostly used. The nonuniformity of the etch was checked in a few samples by measurements with a micrometer and corrections were numerically calculated. These corrections changed the value of D as obtained directly from the data (such as shown in Fig. 1) at most by a factor of 2 indicating that the general procedure outlined provides a relatively simple and quick method of obtaining approximate diffusion values.

An interesting observation is noted here, namely, that in heavily Cl-doped crystals the etching rate in concentrated HCl is noticeably less than in other doped or undoped crystals. It was also observed that while single grain boundaries did not appear to affect the measured diffusion rate of Cd, etching along grain boundaries was considerably faster than in the bulk crystalline regions. For this reason, crystals with grain boundaries could not be used.

In order to get a statistically meaningful count above background for the last one or two points on most samples, it was necessary to etch a "large sampling," that is, $\Delta(x^2)/4Dt > 2$. In such cases, the normalized counting rate deviates considerably from the value corresponding to the midpoint of the distance etched. Corrections for such large samplings were numerically calculated for each particular case as was necessary.

In measuring diffusion rates under different conditions, samples were used which were cut with the same orientation from the same crystal. Also, the firing (diffusion) times were varied to give the same general quantitative profile from sample to sample. Hence, although the absolute accuracy of any one sample is probably not better than a factor of 2, the relative accuracy between similar samples could be much better.

A complication that was encountered in these experiments was the presence of variable amounts of radioactive Ag[110] in different shipments of the radioactive Cd. In liquid Cd firings this problem was not too severe since the liquid metal getters the Ag.[7] However, where the radioactive solution was used directly in sulfur firings or in Cd vapor firings, the Ag very rapidly entered the crystal giving a high background count which often made it impossible to analyze the results for the Cd diffusion. Most of the radioactive Ag could be removed by adding nonradioactive Ag metal to the original solution as a carrier and then precipitating the Ag with HCl. This process does not dilute the specific radioactivity of the Cd but it does put the Cd in the form of $CdCl_2$ which, if used directly in the experiments, dopes the crystals with Cl. It was thus necessary to reduce the $CdCl_2$ by back filling the ampoules to which the $CdCl_2$ had been added with H_2

and heating before sealing off. Another purification process was the vacuum distillation used as the final step in the preparation of the radioactive Cd in the metallic form. This was found to remove most of the radioactive Ag.

III. RESULTS

1. Diffusion of Cd in Undoped Crystals

The first experiments were carried out with undoped crystals fired in liquid Cd or saturated Cd vapor. Results showing the typical variations with different crystals and firing times are shown in Fig. 2. These results are interpreted as the self-diffusion of Cd in CdS since (1), the diffusion profiles indicate a normal diffusion process is occurring following Fick's law, and (2), the concentration of the radioactive Cd indicates that all of the Cd atoms in the crystal are involved in the diffusion process.

Samples fired in CdO consistently gave lower values for the diffusion coefficient than samples fired in liquid Cd or saturated Cd vapor. Between 750 and 1000°C, diffusion coefficients 1/4 to 1/40 of the value shown in Fig. 2 were measured. This observation is interpreted as a dependence of the diffusion coefficient on Cd pressure. The partial pressure of Cd over the CdO-CdS system at 800°C is estimated to be 1.5×10^{-3} atm and at 1000°C to be 0.12 atm.[8] The saturated Cd pressure at these two temperatures is 1.4 and 8.2 atm, respectively. The values of the diffusion coefficient were not very reproducible probably because the preparation of the CdO containing the radioactive Cd was not carried out in a consistent manner resulting in variations in the completeness of the oxidation of the Cd and hence variations in the Cd pressure at the firing temperatures.

To check the effects of further decreasing the Cd pressure (or increasing the sulfur pressure) on the diffusion, the following experiment was performed. A crystal was fired for 15 min at 800°C with radioactive Cd in a saturated Cd vapor. This crystal was then fired for 2 h at 900°C under a saturated sulfur pressure. It was then etched and counted in the usual manner.

The observed radioactive profile was characteristic of the short 15-min Cd firing indicating that essentially no additional diffusion took place during the longer sulfur firing. The results are also consistent with the fact that the radioactive Cd is in normal lattice sites since Cd in other sites (in particular, as interstitials) might be expected to be removed in the sulfur firing. This experiment also indicates that a process more rapid than the self-diffusion takes place by which the bulk crystal senses the firing atmosphere since no appreciable smearing of the radioactive profile took place during the sulfur firing. This will be discussed further in Sec. IV.

[7] M. Aven and H. H. Woodbury, Appl. Phys. Letters 1, 53 (1962).

[8] This assumes stoichiometry of CdO and CdS. The basic reaction of importance is $CdS + 2CdO \rightarrow 3Cd + SO_2$. The partial pressure of Cd over CdS alone is estimated to be 2.4×10^{-4} atm at 800°C and 5×10^{-2} atm at 1000°C.
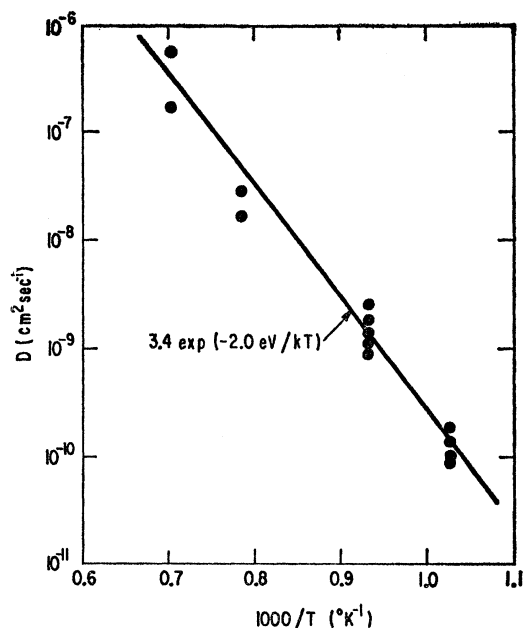
Fig. 2. The diffusion coefficient of Cd in CdS under saturated Cd pressure as a function of temperature. The slope of the line (2.0 eV) corresponds to 46,000 cal/mole.

Several other experiments were carried out in which a stoichiometric excess of sulfur over the radioactive Cd was sealed in the firing ampoules with undoped samples. After being fired, the samples were cleaned of excess sulfur in warm CS_2 and then etched and counted for the radioactive Cd as described above. The results indicated that at 800°C, the diffusion of Cd under these conditions is 10^{-2}–10^{-3} of that shown in Fig. 2 at the same temperature. This will be discussed further after discussing the effects of chemical impurities.

2. Preparation and Characteristics of Doped CdS

Experiments were carried out to ascertain if there was any dependence of the Cd diffusion on impurities or on the position of the Fermi level. In this section the preparation of some doped CdS systems will be described and some qualitative observations made on their electrical and optical characteristics. In the following qualitative discussion, samples with dimensions of 1–2 mm and firing temperatures of 800°C will be assumed unless otherwise noted.

If high purity CdS crystals[1] are fired in sulfur, they become insulating ($\sigma < 10^{-12}$ ohm^{-1} cm^{-1}) whereas if they are fired in Cd, they show n-type conductivity (carrier densities of the order of 10^{16} cm^{-3} at room temperature). The source of the conductivity is not certain although Al is a known donor impurity in sufficient concentration to give rise to the observed conductivity.

A crystal can be heavily doped with In by sealing it

in a quartz tube with a small piece of In and firing it 100–300 h. When this is done in excess sulfur with, for example, 0.5% added In, the crystals become deep red in color and show n-type conductivity (carrier densities of the order of 10^{17}–10^{18} cm^{-3} at room temperature). If such crystals are then fired in Cd for 10 min, they turn gray or black and their conductivity increases (carrier densities of the order of 10^{19}–10^{20} cm^{-3} at room temperature). The darkening of the crystals is due to precipitates (presumably In) as thin sections under a microscope show black inhomogeneities in a yellow matrix. If the crystals are less heavily doped (e.g., fired with 0.005–0.05% In), they become lighter red in color when fired in sulfur and tend toward the original yellow CdS color when fired in Cd. They show conductivities between the undoped crystals and the crystals fired in 0.5% In. These color and conductivity changes are reversible with alternate short Cd and sulfur firings. A distinct color boundary can be observed in doped crystals and an estimate of the rate of these changes can be made by observing the distance color boundary has moved after a short firing. One experiment in which an In-doped, sulfur-fired crystal was fired a few minutes in Cd at 800°C gave an estimated diffusion coefficient of 10^{-5} cm^2 sec^{-1} for the entity producing the color change.

Similar results are obtained firing the crystals in sulfur plus $CdCl_2$, although they cannot be as heavily doped with Cl as with In. Presumably the other column III or column VII donors could likewise be introduced into CdS or the other II-VI semiconductors. It is apparent that in the presence of excess sulfur the In or Cl donor impurities are being electrically compensated by native acceptor defects and/or are being incorporated into compensating complexes.

Rapid changes are also observed with Ag-doped samples. For example, Ag-doped samples can be prepared by firing crystals in a Cd, 10% Ag alloy for a day. Such crystals have a dark greenish cast and have conductivities of the same order of magnitude as the original crystals fired in only Cd. If these crystals are fired in S for just a few minutes, they turn black presumably due to precipitated Ag or Ag_2S and become insulating. (If they are doped heavily enough with Ag, they show some conductivity when fired in S. This is believed to be due to conduction along connected precipitates.[9]) Refiring in Cd vapor returns the crystal to its original state. Copper and gold show similar behavior.

When crystals are fired at high temperatures and high Cd pressures other rapid processes occur. One effect is the creation of double-acceptor defects which

[9] A. Dreeben, J. Electrochem. Soc. 111, 174 (1964); M. Aven and H. H. Woodbury, Air Force Cambridge Research Laboratories Contract No. AF19(604)-8512, Scientific Report No. 2, 1962 (unpublished).

are produced in a few minutes firing.[10,11] In undoped crystals,[1] their concentration increases with firing temperature and Cd pressure and at 1000°C under saturated Cd pressure the defect has an easily measurable concentration of $\sim 7 \times 10^{15}$ cm^{-3}. At this temperature it is estimated that the defect results in part from an entity with a diffusion coefficient (if Fick's law holds) of the order of, or greater than, 10^{-5} cm^2 sec^{-1}.

It is also observed that firing crystals at 900°C in liquid Cd or in saturated Cd vapor results in a pronounced darkening of the samples which occurs as rapidly as the introduction of the double-acceptor defect. At higher firing temperatures and pressures, the samples become black. This color change is reversible with lower temperature or pressure Cd firings or by firing in sulfur. The Cd pressure dependence of these effects demonstrates that defects are involved that diffuse from or to the surface of the crystal. The blackening of the crystals is due to precipitates, presumably Cd. If it is Cd, the source of the excess Cd is not from the surface since no appreciable diffusion of Cd is observed in the short firing times employed. (Note the value of the Cd diffusion coefficient given in Fig. 2.)

It is noted here that when samples are fired at 1000°C in liquid sulfur ($P_{S_2} \sim 100$ atm), they show "clear" precipitates, presumably sulfur although they may be voids.

The main point to be emphasized in describing these qualitative experiments is that there are defect processes that occur 10^2–10^6 times faster than the observed diffusion of Cd. The significance of this conclusion is discussed in IV.

3. Diffusion of Cd in Doped Crystals

To test whether a rapidly diffusing interstitial Cd defect plays any part in the color and conductivity changes described above, In- or Cl-doped crystals were first fired in sulfur and then fired in radioactive Cd vapor for times sufficient to produce the changes described above. The upper limit for the radioactive Cd concentration inside such fired crystals indicated an added Cd concentration less than 1/10–1/1000 the impurity concentration. It is thus concluded that none of the rapid changes that can occur in crystals fired in Cd arise from Cd diffusing in from the surface.

Doping crystals heavily with In or Cl did not change the observed diffusion rate of Cd over that measured in undoped crystals under Cd firing. This was true whether predoped crystals were used or whether the In or Cl was diffused into the crystals at the same time the radioactive Cd diffusion was carried out.[12]

[10] M. R. Lorenz and H. H. Woodbury, Phys. Rev. Letters **10**, 215 (1963); M. R. Lorenz, M. Aven, and H. H. Woodbury, Phys. Rev. **132**, 143 (1963).

[11] M. R. Lorenz, B. Segall, and H. H. Woodbury, Phys. Rev. (to be published).

[12] Although no Cd diffusion process other than the self-diffusion first described above has been observed in the experiments
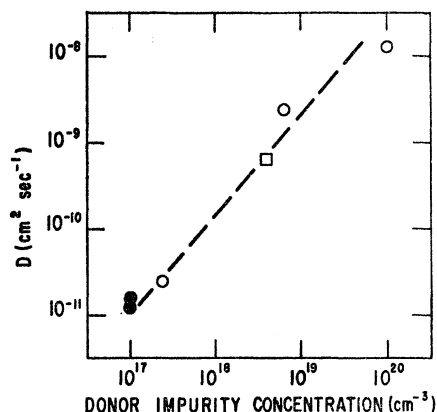

FIG. 3. The diffusion coefficient of Cd in CdS under sulfur pressure at 800°C as a function of the donor-impurity concentration. The open circles indicate data for In-doped samples; the square for a Cl-doped sample; and the filled circles represent two undoped samples containing about 10^{17} cm^{-3} Al.

In contrast to the above, it was observed that under sulfur pressure the diffusion of Cd depended on the donor impurity concentration. This is indicated in Fig. 3 where the measured Cd diffusion coefficient at 800°C is plotted as a function of donor impurity concentration for a series of crystals fired in liquid sulfur (approximately 35 atm pressure). The samples were first doped by firing them in sulfur with small amounts of In or CdCl$_2$ as described above. The donor impurity concentration in the crystals was determined by spectroscopic analysis and/or by firing a companion sample in Cd at 800°C and measuring the room temperature electron concentration. The lowest points in Fig. 3 represent undoped samples but for which spectroscopic analysis indicated about 10^{17} cm^{-3} Al impurities.

Several undoped samples were fired at 800°C in which only a slight excess of sulfur was present. One of these experiments was as follows: An undoped sample was first fired in an excess of sulfur with radioactive Cd for two hours at 800°C. Such a firing is sufficient to cause most of the radioactive Cd to be incorporated into the crystal, probably as CdS grown onto the surface, but is short enough so that essentially no self-diffusion takes place. The sample was then fired for 305 h at 800°C in an ampoule in which the sulfur pressure was estimated to be 1/74 the saturated pressure. This pressure was calculated from the volume of the ampoule and the added excess sulfur and assumed that the sulfur vapor was all in the form

dealing with highly doped samples, an interesting enhancement of the Cd self-diffusion rate with the simultaneous diffusion of Ag was noted. For example, if a 60-mg crystal is fired in 200-mg radioactive Cd with 20 mg Ag for three hours, the apparent Cd diffusion rate is enhanced a factor of approximately 40. The word "apparent" is used since the experimentally calculated diffusion rate depends strongly on the firing time, i.e., the time dependence of Fick's law does not hold. There is little enhancement (less than a factor of 2) if the crystal is predoped by first firing in nonradioactive Cd, 10% Ag alloy.

of S_2. The measured diffusion coefficient was approximately 4×10^{-12} cm^2 sec^{-1}, significantly less than the value measured under saturated pressure (note lowest points, Fig. 3). It is concluded from this and other experiments in which less than saturation conditions prevailed, that in the undoped crystals used the Cd diffusion coefficient at 800°C goes through a minimum at some sulfur pressure less than the saturation pressure.

IV. SUMMARY AND DISCUSSION

This discussion will be presented in three parts: First, the several qualitative observations on the behavior of CdS fired in either excess Cd or excess S will be discussed. Secondly, a new mechanism for self-diffusion in simple compounds will be suggested. Finally, a qualitative model will be presented to correlate the experimental observations presented in this paper.

The several observations of bulk changes in CdS crystals which occur more rapidly than the measured Cd diffusion rate are summarized as follows: (1) The abrupt halting under sulfur pressure (relative to the normal diffusion rate when Cd fired) of the Cd self-diffusion in undoped samples which are first Cd fired. (2) The rapid color and conductivity changes in highly doped samples which are alternately Cd fired and sulfur fired. (3) The creation of a double-acceptor defect uniformly throughout an undoped crystal under Cd firing in times of a few minutes. (4) The darkening of crystals when fired in Cd above 900°C.

The rapid and reversible character of the above described phenomena under Cd vapor firing and then sulfur vapor firing indicate that they must be due to deviations from stoichiometry. In terms of the simplest native defects[13] a stoichiometric excess of Cd in CdS can be created in several ways when a crystal is fired in Cd. One possibility is the diffusion of interstitial Cd (Cd$_i$) into the crystal from the surface. The lack of radioactivity inside crystals fired in radioactive Cd for times just sufficient to produce the above phenomena precludes this possibility.

A second possibility is the creation of Cd$_i$ and Cd vacancy (V_{Cd}) pairs (Frenkel defects) with the rapid diffusion of the V_{Cd} to the surface. The Cd$_i$ would have to have a very low diffusion rate if the Frenkel defects were created uniformly throughout the bulk since the high solubility required to produce the effects seen and a diffusion rate comparable to or faster than the self-diffusion would make such a species readily detectable. It is noted that if a high solubility of Cd$_i$ is created under Cd firing, the Cd$_i$ would have to be electrically neutral (or a deep donor) since electrical effects of such a species would otherwise be seen in electrical measurements. A possibility is that the

Frenkel defects are created at impurity sites or at lattice-disorder points which can readily accommodate the Cd$_i$. This is considered further below. In either case, it is the V_{Cd} which must move rapidly.

A third possibility is the creation of sulfur interstitials and sulfur vacancies (V_S) with the sulfur interstitials rapidly diffusing to the surface. Because of its size and ionic character it is difficult to conceive of how interstitial sulfur could play a more important role in these processes than Cd$_i$. This could be tested with measurements of the diffusion of sulfur using the radioisotope, S^{35}. For now, it will be assumed that interstitial sulfur does not play a part in the rapid processes that are observed.

A fourth possibility for creating a stoichiometric excess of Cd during Cd firing is the rapid diffusion of sulfur vacancies (V_S) from the surface into the crystal.

Similar arguments can be made for creating a stoichiometric excess of sulfur under sulfur firing. Again, the complete lack of evidence for Cd$_i$ and assuming interstitial sulfur to be unimportant, it is concluded that the effects must be created by the diffusion of vacancies. Thus, the first general conclusion is that the rapid processes that are seen when CdS is fired in sulfur or Cd are the result of the diffusion of sulfur and/or Cd vacancies.

Self-diffusion is usually thought of as dependent on the concentration and mobility of vacancies. For example, the motion of a vacancy through a lattice must represent the displacement by one lattice site of the corresponding lattice atoms along the path of the vacancy. Thus, in CdS, one concludes that since firing the crystal in sulfur should increase the Cd vacancy concentration, the self-diffusion of Cd should increase. This assumes that there is not an over-riding effect due to the position of the Fermi level. For example, it might be that the mobility of vacancies strongly depends on their charge state.

A second self-diffusion process can be visualized in a compound. Again taking CdS as an example, assume that the Cd atoms surrounding a sulfur vacancy can interchange in times comparable to or less than the time a sulfur vacancy remains at one particular lattice position. Then a self-diffusion of Cd can take place which would be dependent on the sulfur vacancy concentration rather than the Cd vacancy concentration. If this were the only process, firing CdS in sulfur should decrease the diffusion rate. This diffusion process will be referred to as covacancy diffusion.

The rapid interchange of the neighboring Cd atoms surrounding a sulfur vacancy may be objected to on the basis that they are all positively charged ions which normally repel one another. In particular, one might picture that such interchange may be more rapid in the presence of the neutralizing negative sulfur ion. Such objections are met if one postulates a considerable covalent interaction in the crystal which even extends between pairs of Cd atoms surrounding a

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[13] In the following discussion, complexes such as divacancies and disorders such as Cd atoms in sulfur sites and vice versa will not be considered although their possibility should be kept in mind.

sulfur vacancy. Such a covalent interaction has been suggested as a possible explanation of some electrical properties of these II-VI compounds.[11] Alternatively, a ring mechanism of self-diffusion[14] could be operative in which the four Cd atoms about the sulfur vacancy rotate together.

The donor-impurity dependence of the Cd self-diffusion when the samples are under sulfur pressure, contrasted with the independence of the diffusion with impurity content when the samples are under Cd pressure, indicate that two different mechanisms are operative under these two different firing conditions. The fact that the diffusion under sulfur pressure can be varied significantly faster than as well as slower than the diffusion under Cd pressure with donor-doping levels indicates that the difference does not simply arise from a possible change in the charge states of pertinent defects. It is thus proposed that in crystals fired in excess sulfur the Cd self-diffusion proceeds via Cd vacancies while in crystals fired in excess Cd, the Cd self-diffusion proceeds via the covacancy mechanism (sulfur vacancies).

The general model that is proposed for CdS is as follows: In the pure crystalline material, V_S and V_{Cd} are the primary defects (Schottky defects).[15] Under sulfur pressure at high temperatures, the stoichiometry of the pure material is shifted by a decrease in the V_S concentration, $[V_S]$, and an increase in the V_{Cd} concentration, $[V_{Cd}]$. The shift of the crystal to a stoichiometric excess of sulfur is very limited compared to the concentration of chemical impurities in the crystals used. (It is possible that the pure material cannot be made sulfur rich, that is, that the sulfur-CdS solidus always lies on the Cd side of the phase diagram. On the proposed model that only Schottky defects are important, this would mean that in the ideal pure material $[V_S]$ is always greater than $[V_{Cd}]$.) However, if donor impurities are present, the formation of V_{Cd} (assumed to be acceptors)[15] will be favored by compensation[16] and in material of present purity, the con-

centration of V_{Cd} is always determined by the donor-impurity concentration. As the sulfur pressure is decreased, the self-compensation of the donors decreases and $[V_{Cd}]$ decreases causing the diffusion rate to decrease. Eventually, as the sulfur pressure is decreased (or Cd pressure increased), the material becomes Cd rich and $[V_S]$ dominates over $[V_{Cd}]$, even in heavily doped material. The diffusion rate then increases with the diffusion proceeding via the covacancy mechanism.

At extreme Cd (or sulfur) pressures, a second, non-equilibrium situation is suggested, namely, the creation of Frenkel defects at lattice imperfections such as grain boundaries, dislocations, internal voids, possibly chemical impurity sites, etc. The vacancies produced would diffuse rapidly to the surface of the crystal leaving the interstitials at the imperfection. This process produces the internal precipitation of Cd[9] (or sulfur) at such imperfections during firing. Such a process does not represent a true stoichiometric shift of the material.

The above model is consistent with the fact that CdS is a good n-type semiconductor but so far has not been made in a p-type form. The problem appears to be the inability to create uncompensated cation vacancies (V_{Cd}). The ability to create such centers appears to be necessary to produce shallow acceptor levels in the II-VI semiconductors.[17]

If the column III donors (which substitute for Cd) diffuse by the same mechanisms as does Cd, then the above model would predict a linear dependence of the rate of diffusion on the concentration of these impurities in CdS under sulfur pressure since the $[V_{Cd}]$ would depend on the total donor concentration. While at high donor concentrations one might expect a fairly high diffusion rate, at low concentrations the model would indicate that the diffusion of these impurities might proceed faster under Cd pressure. Although no single definitive prediction can be made concerning the diffusion of other impurities (singly or as activator-coactivator pairs) the possible implications of the above model are evident.

V. ACKNOWLEDGMENTS

[14] C. Zener, Acta Cryst. 3, 346 (1950).

[15] In the following, no distinction will be made between the possible charge states of these defects although each charge state should be considered as a distinct entity. From electrical evidence (see below) as well as the proposed model, the V_{Cd} are assumed to be acceptors which are always compensated in material of present purity.

[16] The increase in the vacancy concentration and hence the enhancement of self-diffusion by this mechanism was first demonstrated in Ge by W. M. Valenta and C. Ramasastry, Phys. Rev. 106, 73 (1957).

[17] M. Aven and B. Segall, Phys. Rev. 130, 81 (1963); M. R. Lorenz and B. Segall, Phys. Letters (to be published).