Se SELF-DIFFUSION IN CdSe AND THE DEFECT STRUCTURE OF THE II-VI COMPOUNDS*

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It has been found that the diffusion coefficient of Se in CdSe is inversely proportional to the Cd partial pressure for most of the CdSe solidus region. This simple relation implies interstitial Se as the diffusing defect. Other diffusion studies indicate that a similar situation prevails in all of the II-VI compounds.

The native defect structure of compounds such as the Zn and Cd chalcogenides is of basic importance to a complete understanding of their electrical and optical behavior. However, in these compounds, it has been difficult to determine experimentally the nature of the defect structure. E.g., considering the simplest defects, isolated interstitials and vacancies, it is often impossible to demonstrate whether a particular shift from stoichiometry or the self-compensation of an electrically active impurity arises from interstitials of one component or vacancies of the other component without invoking unproven, but "reasonable arguments." In this Letter we will present evidence for the existence of an appreciable concentration of interstitial chalcogens at the normal firing and growing temperatures of these materials and indicate some of the implications of this.

A radio-tracer[1] and etching technique[2] was used to determine the diffusion profiles of Se. The partial pressures of Se_2 and Cd in the sealed firing ampoules were calculated assuming the perfect gas law, from the weight of added Se or Cd. It was necessary to take into account the various polymers of Se in these calculations. The crystals[3] were undoped and subsequent doping with donors (up to 10^{19} cm^{-3} Cl and 7×10^{19} cm^{-3} In) made no difference in the diffusion profiles. Also, no consistent differences were seen in Ag- or Na-doped samples over undoped samples.

The results are summarized in Fig. 1 by a log-log plot of the diffusion coefficient of the Se in CdSe, D_{Se}, versus the cadmium partial pressure, P_{Cd}, at the temperatures indicated. For each given temperature, D_{Se} obeys the relation (except near the maximum P_{Cd} region)

$$D_{\text{Se}} = K_T P_{\text{Cd}}^{-1}. \tag{1}$$

Evaluating K_T for each temperature indicated in Fig. 1 and plotting $\log K_T$ vs $1/T$ yields a straight line which may be expressed in the form

$$K_T(\text{cm}^2\ \text{sec}^{-1}\ \text{atm}) = (1.3\times10^5)\exp(-4.43\ \text{eV}/kT).$$

Two well-defined cases of interest are the situations under minimum total pressure ($P_{\text{Cd}} = \frac{1}{2}P_{\text{Se}_2}$) and minimum P_{Cd} (saturated Se). The diffusion coefficients for these situations, expressed in cm^2 sec^{-1}, are given by

$$D_{\text{Se}}(\text{mimimum total pressure}) = (2.2\times10^{-2})\exp(-2.2\ \text{eV}/kT),$$

$$D_{\text{Se}}(\text{minimum } P_{\text{Cd}}) = (2.6\times10^{-3})\exp(-1.55\ \text{eV}/kT).$$

Self-diffusion in a solid is intimately related to its defect structure with the two simplest cases involving the motion of vacancies or in-

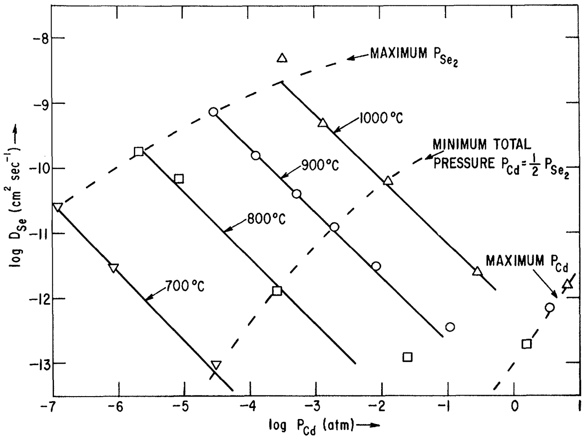

FIG. 1. A log-log plot of D_{Se} vs P_{Cd}. The value of P_{Cd} to the left of the minimum pressure line is calculated from the selenium partial pressure using the equilibrium constant [L. R. Shiozawa et al., Fifth Quarterly Report under Contract No. AF 33(657)-7399 with Aeronautical Research Laboratory, Wright-Patterson Air Force Base, Ohio, 1963 (unpublished)], $K_D = P_{\text{Cd}}^2 P_{\text{Se}_2}$.

terstitials. Elementary considerations of defect chemistry[4] lead to the conclusion that increasing P_{Cd} over the CdSe increases the selenium vacancy concentration $[V_{\mathrm{Se}}]$ and decreases the selenium interstitial concentration $[\mathrm{Se}_i]$. Clearly a selenium vacancy mechanism for the Se self-diffusion is incompatible with (1) since the diffusion coefficient decreases with increasing P_{Cd}, opposite to the change in $[V_{\mathrm{Se}}]$. (Under extreme P_{Cd} conditions, it is felt that a vacancy mechanism is operative.) The simplest model to explain (1) is to assume the presence of a neutral, rapidly diffusing interstitial Se defect[5] which interacts sufficiently with the lattice to maintain interstitial-substitutional local equilibrium (e.g., via an interstitial-vacancy-substitutional equilibrium or an interstitialcy[6] type process).

Diffusion measurements[7] have been carried out on four of the remaining five Zn and Cd chalcogenides (ZnS being the exception) and these are all consistent with the results outlined here. It appears that the same basic physical model is applicable to all of these compounds.[8] In particular, these results make untenable the "covacancy" model for the diffusion of Cd in[2] CdS, since that model would require the self-diffusion of S to be at least as rapid as the self-diffusion of Cd under excess of Cd. It is suggested that the "anomalously high" rate of diffusion of Cd in CdS under excess Cd is due to interstitial Cd.

A simple interstitial diffusion process with interstitial-substitutional local equilibrium can be treated as a case of an instantaneous chemical reaction.[9] The observed, or effective, diffusion coefficient for such an interstitial-substitutional self-diffusion process is given by

$$D_{\mathrm{Se}}(\mathrm{obs}) = D_i \Big/ \left(\frac{1}{[\mathrm{Se}_i]} + 1\right) \approx D_i[\mathrm{Se}_i], \qquad (2)$$

where $[\mathrm{Se}_i]$ is the mole fraction of interstitial Se, or, in this context, the ratio of freely diffusing Se (interstitials) to immobilized Se (substitutionals or normal lattice atoms). A relation similar to (2) would hold for a Cd interstitial process. Taking as a reasonable upper limit a value of 10^{-5} cm^2 sec^{-1} for the uninhibited interstitial diffusion, D_i, it is apparent that the interstitial concentration could be appreciable (10^{18}-10^{20} cm^{-3}) in the Cd chalcogenide compounds. The lack of electrical activity of this magnitude in undoped quenched samples cannot be taken as definitive evidence that these postulated interstitials are neutral, since it is probable that they would be unstable at room temperature. They may, in fact, be the source of the precipitates that can be readily produced in these materials. However, there is no experimental evidence for impurity compensation or electrically active complexes, which would be expected to be stable, involving native interstitials. The independence of the chalcogen self-diffusion on doping is consistent with this and provides positive evidence for the electrical inactivity of chalcogen interstitials. It is thus suggested that in the II-VI compounds, the only electrically active native defects are vacancies, but that the chemical equilibrium and deviations from stoichiometry may be dominated by neutral interstitials.

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[1] The Se^{75} (labeled Se-75-P-2) was obtained from Oak Ridge National Laboratory.

[2] H. H. Woodbury, Phys. Rev. 134, A492 (1964).

[3] CdSe single crystals were obtained from the Clevite Corporation and the Harshaw Chemical Company, both of Cleveland, Ohio.

[4] See, e.g., F. A. Kröger, The Chemistry of Imperfect Crystals (North-Holland Publishing Company, Amsterdam, 1964), Chap. 13.

[5] The simple relationship indicated by (1) and the independence of D_{Se} on doping suggests that charge neutrality does not play an important role in the physical chemistry of the pertinent defects. The simplest assumption is to consider the defects neutral, which leads directly to $[\mathrm{Se}_i] \propto P_{\mathrm{Cd}}^{-1}$.

[6] See, e.g., P. G. Shewmon, Diffusion in Solids (McGraw-Hill Book Company, New York, 1963), pp.151-155.

[7] R. A. Reynolds, thesis, Stanford University, Department of Material Science Report No. 65-32, 1965 (unpublished); H. H. Woodbury, Scientific Reports Nos. 3 and 5, and R. B. Hall, Scientific Report No. 6, under Contract No. AF-19(628)-4976 with U. S. Air Force Cambridge Research Laboratory, 1965-1966 (unpublished); plus unpublished work by the authors on the diffusion of Se and Te in CdTe.

[8] The close similarity of these results to the self-diffusion of S in PbS is also noted [M. S. Seltzer and J. B.

Wagner, Jr., J. Phys. Chem. Solids 26, 233 (1965)], where native defect concentrations up to 10^{19} cm^{-3} are observed.

[9] See, J. Crank, The Mathematics of Diffusion (Oxford University Press, New York, 1964), Chap 8.

ELECTRIC-FIELD MODULATION OF THE VIBRATIONAL ABSORPTION OF OH^- IN KBr†

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Most experimental measurements of the effects of the lattice on the OH^- impurity in alkali halides have been done at low temperatures. Kuhn and Lüty[1] have shown that the OH^- dipole is aligned along [100] directions in KCl at low temperatures; Feher, Shepherd, and Shore[2] and Bron and Dreyfus[3] have studied the paraelectric resonance of OH^-; and Wedding and Klein have determined the depth of the wells in the [100] directions for several alkali-halide lattices by measuring the vibrational and librational modes of OH^-.[4] Except for optical-absorption and thermal-conductivity measurements at low temperatures for OH^- in KCl reported by Chau, Klein, and Wedding,[5] most of the data support the model of a dipole in an octahedral field first worked out by Devonshire.[6] We present further experimental evidence, based on electric-field modulation of the OH^- vibrational absorption line, that the Devonshire model does not fully explain the properties of OH^- in alkali-halide lattices at room temperature.

The experimental apparatus is similar to that used in many electroabsorption measurements.[7] A voltage at 1700 Hz was applied to the crystal and the variation in transmitted light intensity was phase-sensitively detected at twice the frequency. The electric field, of magnitude about a few times 10^4 V/cm, was normal to the incident radiation, and measurements were made with light polarized both parallel and perpendicular to the electric field as is shown in the inset of Fig. 1. Figure 1(a) shows the OH^- vibrational absorption near 3610 cm^{-1} at zero electric field. Figure 1(b) shows the change in absorption, $\Delta\alpha$, of the vibration line of the OH^- dipole in KBr with a [100] field orientation, for both parallel and perpendicular polarizations of the transmitted light. Figures 1(c) and 1(d) show similar results on KBr crystals with the electric field oriented in [110] and [111] directions. These samples were all cut from the same crystal, which had a doping of about 540 ppm of OH^-. Although not shown, qualitatively similar results were obtained for KCl:KOH for fields in the [100] direction. Figure 2 shows that the variation of the peak heights with field is quadratic.

Due to the small fractional changes in absorption (~10^{-5}) with electric field, the noise levels were high as indicated on the curves of changes in absorption. For this reason the line shapes are to be considered uncertain to this extent when quantitative comparisons are made. This leads to an uncertainty in the precise location of the peaks, as well as uncertainties in the ratio of the peak heights for parallel and perpendicular polarization for a given orientation. It is impossible to determine whether $\Delta\alpha$ for perpendicular polarization changes sign in the wings as does $\Delta\alpha$ for parallel polarization, although we believe that it does not. An additional error is introduced by the small depolarizing effect of the light scattering from the surface caused by its reaction with the atmosphere.

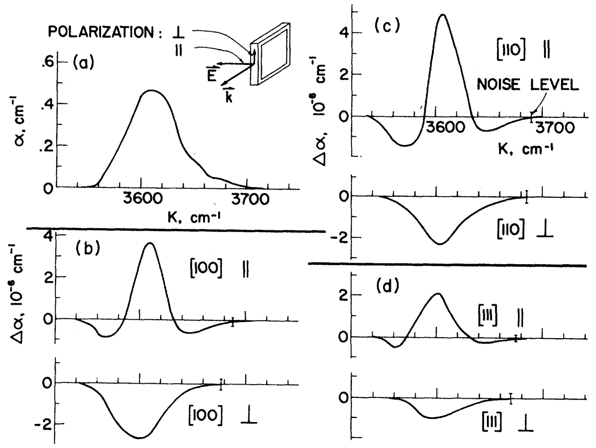

FIG. 1. The absorption and electric-field-induced change of absorption of the OH^- vibrational level in KBr for parallel and perpendicular polarizations of the incident light, for fields along [100], [110], and [111] crystal directions.