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OPTICAL STUDY OF COPPER DIFFUSION
IN CADMIUM SULFIDE SINGLE CRYSTALS

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Optical Study of Copper Diffusion in Cadmium Sulfide Single Crystals

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The diffusion of copper in cadmium sulfide single crystals has been studied by optical transmission in the temperature range 500°–700°C. Diffusion was made parallel to the c axis. The intensity of the monochromatic light beam ($\lambda = 5230 \pm 20$ Å) transmitted through a small section of the sample was monitored along the diffusion profile. The relationship between the light transmission T and the penetration distance x has been derived and applied to the geometry employed in the experiments. From the slope of the plot $\ln\ln(1/T)$ vs x^2, the diffusion coefficient has been determined and the activation energy for the copper diffusion along the c axis has been calculated ($\Delta E = 13.4$ kcal/mole).

Light absorption by the doped crystals is primarily due to the copper acceptor centers and defects which are generated by the copper diffusion via the self-compensation mechanism. Scattering of light by copper precipitate aggregates has also been considered. The results of the several diffusion studies may be explained assuming that copper diffuses interstitially in the cadmium sulfide lattice and there is an equilibrium between interstitial and substitutional copper during the diffusion. The solubility of substitutional copper which occupies cadmium sites must be greater than the solubility of copper interstitials. The results of the optical studies of copper diffusion compare favorably with diffusion studies using radiotracer techniques. Since it is a nondestructive method, under certain conditions it should be more useful than other types of diffusion analysis.

INTRODUCTION

STUDIES of impurity interactions in many high-purity single crystals can be carried out at room temperature by rapid quenching of the samples from the diffusion temperature in any phase of the reaction. Thus, one can "freeze in" the nonequilibrium distribution of the diffusants which can conveniently be studied by suitable room-temperature physical measurements.[1–3] This experimental technique can be applied to those diffusion-controlled solid-state reactions in which the diffusants exhibit negligibly slow diffusion rates at room temperature. If the physical measurements in such studies are nondestructive, the reaction may be monitored by periodic quenching of the specimen as a function of reaction time.

In this paper we introduce a new nondestructive method for measuring the concentration profile of diffusing impurities and the diffusion coefficient. This technique utilizes the optical properties of semiconducting single crystals which undergo changes due to impurity penetration. The method involves the measurement of light transmission through a thin section of the single crystal, perpendicular to the direction of the diffusion of an optically active impurity. By traversing the crystal in the direction normal to a collimated light source we can monitor the changes of light intensity of the transmitted light and, thus, the impurity concentration along the crystal. We have employed this technique in studying copper diffusion in cadmium sulfide single crystals.

The optical method of studying the diffusion of impurities in semiconductors is sensitive to low concentrations of the diffusants, and can be used to obtain information about the nature of the diffusing species as well. It may also be used in studies of diffusion in ionic solids.[4]

[1] R. M. Barrer, *Diffusion In and Through Solids* (Cambridge University Press, Cambridge, England, 1951).
[2] B. I. Boltaks, *Diffusion in Semiconductors* (Academic Press Inc., New York, 1963).
[3] N. B. Hannay, *Semiconductors* (Reinhold Publ. Corp., New York, 1959).
[4] R. Reisfeld, A. Glasher, and A. Honigbaum, J. Chem. Phys. **42**, 1892 (1965).

DIFFUSION PROCESS

Consider a semi-infinite solid ($0<x<\infty$), of uniform cross section, which is free of impurities and on which an infinitesimally thin layer of diffusant is placed. The initial and boundary conditions may be written as

$$\partial N/\partial x=0, \qquad \text{at } x=0,\ t\geq 0;$$

$$N(x,0)=0, \qquad \text{at } x>0,\ t=0; \tag{1}$$

where $N(x,t)$ is the concentration of the diffusant. The solution of Fick's equation with these boundary conditions[5,6] is

$$N(x,t)=N_0/(\pi Dt)^{\frac{1}{2}}\exp(-x^2/4Dt), \tag{2}$$

where N_0 is the total amount of diffusant and is given by

$$N_0=\int_0^\infty N(x,t)\,dx. \tag{3}$$

Therefore, if we can experimentally measure the relative concentration as a function of the penetration distance x, a plot of $\ln N$ versus x^2 will yield the diffusion coefficient. We may also test the applicability of Fick's law for the diffusion process by noting any deviation from linearity of our plots.

In actual experimental situations we have a finite solid with free surfaces. Diffusion along these surfaces may, in many instances, become an important factor and may introduce an error in our measurement of the concentration profile.[7] In general, the activation energy for surface-diffusion processes is lower than the activation energy for bulk diffusion. Therefore, surface diffusion is especially important at low temperatures. Fisher[7] has proposed and analyzed a model for calculating the penetration of impurities due to surface diffusion. He finds that the logarithm of the concentration in the bulk varies linearly with penetration as opposed to the square of the distance of penetration for the case of true volume diffusion. Whipple[8] has also analyzed the surface-diffusion problem, and by making fewer assumptions, he finds that $\ln N$ varies as the $\frac{4}{3}$ power of x.

We found that by suitable surface preparation of our cadmium sulfide single crystals (lapping, polishing) we could remove that part of our samples which showed the effect of surface diffusion. This treatment had no effect on the concentration profile of copper which is due to bulk diffusion. Therefore, we did not have to take into account any model for the surface-diffusion component.

[5] H. S. Carslaw, J. C. Jaeger *Conduction of Heat in Solids* (Clarendon Press, Oxford, England, 1959), 2nd ed.
[6] W. Jost, *Diffusion in Solids, Liquids and Gases* (Academic Press Inc., New York, 1952).
[7] J. C. Fisher, J. Appl. Phys. **23**, 74 (1951).
[8] R. T. P. Whipple, Phil. Mag. **45**, 1225 (1954).

CORRELATION BETWEEN LIGHT TRANSMISSION AND THE DIFFUSION COEFFICIENT

The intensity of light I, at any point z, in a conducting medium is[9]

$$I=I_0\exp(-\alpha z), \tag{4}$$

where α is the absorption coefficient and I_0 is the initial intensity.

There are several mechanisms by which a semiconductor absorbs light.[10,11] Some of the more important processes are (a) excitation of electrons across the band gap, (b) free-carrier absorption, (c) excitation of holes and electrons between impurity or defect energy levels and the valence or conduction bands, (d) excitation of lattice vibrations, and (e) scattering by precipitated impurities or large defects in the solid matrix.

In order to avoid the very large absorption from band-gap excitation (a), only light of wavelength longer than that corresponding to the room-temperature band gap of CdS is used ($\lambda>5100$ Å for CdS). Since our experiments are carried out with high-resistivity crystals, free-carrier absorption (b) is not an important factor. Absorption due to lattice vibration (d) is also negligible since we do not use long-wavelength radiation where phonon absorption can be dominant. We are mainly interested in Processes (c) and (e) because these processes are dependent on impurity concentration. Copper in CdS is known to be an acceptor with impurity states ≤ 0.6 eV from the top of the valence band.[12] We can safely assume a linear relationship between the absorption coefficient α_i and the impurity concentration N for absorption from electronic transitions from the impurity levels to the conduction band[10]; thus

$$\alpha_i=KN. \tag{5}$$

A similar linear relationship results if the primary absorption mechanism is by free-carrier absorption[11] or if the light is scattered by precipitated particles which are present in the solid matrix in low concentrations.[13]

We now assume a model in which ideal Fick's law diffusion of an optically active impurity has occurred along the length of a thin rectangular slab of material of thickness d, because we attempt to obtain these conditions in our experiments. The optical properties of any particular section of our crystal is characterized by its absorption coefficient and by its reflection coefficient R. The transmission through a thin slab can be found by considering a single beam of monochromatic

[9] J. M. Stone, *Radiation and Optics* (McGraw-Hill Book Co., Inc., New York, 1963).
[10] H. Y. Fan, Rept. Progr. Phys. **19**, 107 (1956).
[11] T. S. Moss, *Optical Properties of Semiconductors* (Butterworths Scientific Publications Ltd., London, 1955).
[12] R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960).
[13] H. C. Van De Hulst, *Light Scattering by Small Particles* (John Wiley & Sons, Inc., New York, 1957).

light of intensity I_0 in normal incidence onto the front surface of the slab. A fraction RI_0 will be reflected, and $(1-R)I_0$ will be transmitted. The transmitted part of our initial beam is now attenuated by $\exp(-\alpha d)$ as it traverses the crystal. At the back boundary, part of the light is again reflected and part transmitted. The reflected part is again attenuated as it propagates back to the front surface where it is again reflected.[9] Thus, we see the light beam undergoes multiple reflections as it moves through the crystal. An exact analysis of light transmission T through a thin slab of thickness d yields[10]

$$T=\frac{I}{I_0}=\frac{(1-R)^2+4R\sin^2\psi}{e^{\alpha d}-R^2e^{-\alpha d}-2R\cos 2(\phi+\psi)}, \qquad (6)$$

where $\phi=4\pi nd/\lambda$, $\tan\psi=2k/(n^2+k^2+1)$; n and k are the real and imaginary parts of the complex index of refraction. By using radiation which has a broad enough distribution of energy, we can neglect the interference term $2R\cos 2(\phi+\psi)$. If the crystal is not too highly absorbing, which is the case for CdS, then $k\ll n$ and we may neglect the $4R\sin^2\psi$ term. Thus, Eq. (6) will reduce to

$$T=(1-R)^2/[\exp(\alpha d)-R^2\exp(-\alpha d)]. \qquad (7)$$

For large values of αd, which is a good assumption for our case ($d\cong 0.2$ cm, $\alpha\cong 10$ cm^{-1}), we may approximate Eq. (7) by

$$T=(1-R)^2\exp(-\alpha d). \qquad (8)$$

Now the absorption coefficient can be separated into two parts. One part due to the intrinsic absorption of the matrix and the other arising from the optically active impurities. We may therefore rewrite Eq. (8) as

$$T=(1-R)^2\exp(-\alpha_0 d)\exp(-\alpha_i d)=T_0\exp(-\alpha_i d), \qquad (9)$$

where α_0 is the intrinsic absorption coefficient, α_i is the impurity absorption coefficient, and T_0 is the transmission in the absence of impurities. By taking the logarithm of Eq. (9) we have

$$\alpha_i=(1/d)\ln(T_0/T). \qquad (10)$$

α_i is proportional to the concentration of impurities N, which is given by the Fick's law solution described in the previous section. Therefore, by combining Eqs. (2), (5), and (10) in a logarithmic form, we obtain

$$\frac{x^2}{4Dt}=\ln\frac{dKN_0}{(\pi DT)^{\frac{1}{2}}}-\ln\ln\frac{T_0}{T(x)}, \qquad (11)$$

where $T(x)$ is the light transmission which is a function of impurity penetration. For a particular crystal, d, K, and N_0 are constant. By normalizing T_0 to unity, we can write Eq. (11) as

$$x^2/4Dt=C-\ln\ln[1/T(x)]. \qquad (12)$$

Therefore, by plotting $\ln\ln 1/T$ versus x^2 we should have a straight line with slope $-1/4Dt$. Since the diffusion time t is known, we can determine the diffusion coefficient.

EXPERIMENTAL PROCEDURE

All samples of CdS used in the diffusion studies are ultrahigh-purity-grade single crystals obtained from the Eagle-Picher Company. The crystals are n type and have room-temperature conductivities in the range of 0.5–2 $(\Omega\cdot\text{cm})^{-1}$. They were cut in 4×4×8-mm rectangular slabs with the c axis along the length of the slab. After polishing and etching (6N HCl), the crystals were sealed in an evacuated quartz ampule and annealed for 20 h at the anticipated diffusion temperature. The annealing assures that the stoichiometry of the crystal is consistent with the crystal composition at the diffusion temperature.[14]

After annealing, the samples are re-etched and a thin layer of high-purity (99.9999% pure) copper is evaporated onto the c face. The crystal is resealed into a quartz ampule under 10^{-6} torr and placed into a furnace which has been preheated to the diffusion temperature. The diffusion times range from 3 h to 11 days, and the diffusion temperatures are in the 500°-to-700°C range. The furnace temperature is controlled within ±0.25°C. After diffusion, the samples are quenched and again polished for the optical studies. When necessary, opposite faces of the crystal parallel to the c axis are lapped and polished to remove the surface-diffusion components. The crystals are then ready for the optical measurements.

The apparatus used in our optical studies of the copper diffusion profile in CdS single crystals consists of three major parts: (a) light source and monochromator, (b) crystal holder and slit system, and (c) detector. Schematic representation of the experimental equipment is shown in Fig. 1.

A Bausch & Lomb grating monochromator is used. The light intensity is $I_0\cong 25$ μW/cm^2. The light is collimated by a system of two consecutive slits. The width of the light beam impinging on the crystal is 50±5 μ.

In order to traverse the crystal past the light beam, the sample is mounted on a movable micrometer stage. A voltage proportional to the displacement of the crystal with respect to the slit is obtained by coupling the micrometer lead screw to a helipot acting as a voltage divider for a 1.35-V mercury battery. This voltage is fed to the X axis of a Mosely X–Y recorder. The intensity of the transmitted light beam, after passing through the crystal, is monitored by a detector (RCA 1P21 photomultiplier tube, Keithely 610A electrometer). The electrometer output, which is proportional to the transmitted light intensity, is monitored on the Y axis of the X–Y recorder. Thus, we

[14] G. A. Somorjai and J. E. Lester, J. Chem. Phys. **42**, 4140 (1965).

can monitor directly the intensity of the monochromatic light transmitted by the crystal as a function of the distance x from the edge of the crystal ($x=0$).

During polishing, the edges of the crystal became slightly rounded instead of square. Thus, incident light near the edge ($x=0$) of the crystal was scattered at an angle, and the light transmission showed an anomalous decrease. By using careful polishing techniques, the region of anomalous transmission in our crystals could be limited to the first 300 μ from the edge of the crystal. The transmission data for penetration of less than 300 μ have not been reproduced in our graphs.

Possible errors which are due to the use of finite slit-width instead of slits of infinitesimally small width were negligible.[15] Uncertainties in normalizing the light transmission through the CdS crystals were unimportant in determining the slope, $-1/4Dt$, from the transmission data.[15]

PRECIPITATION OF COPPER

After copper diffusion and subsequent quenching of the cadmium sulfide single crystals, all samples showed marked discoloration. The yellow crystals turned reddish-brown or even black at one end of the samples where in-diffusion of the evaporated copper film occurs. Under higher magnification, the presence of precipitate particles in certain portions of the copper diffusion profile is clearly visible. The aggregates are platelets of 1–10 μ in length and are all oriented along the c axis. Particles of submicroscopic size may also be present in the samples but have not been studied at present. The composition of these aggregates may vary from Cu_2S to pure copper. Cuprous sulfide is known to precipitate in CdS in micron-size platelets along the crystal defects,

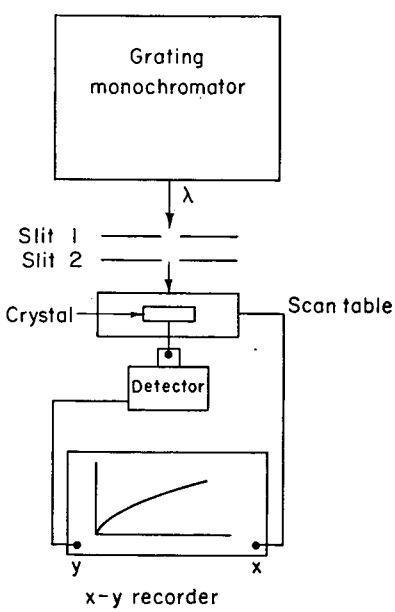

FIG. 1. Apparatus for the optical transmission studies.

[15] W. Szeto, thesis, University of California, Berkeley, 1965.

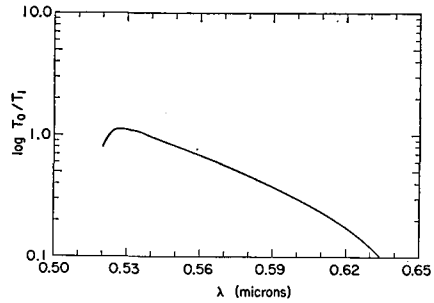

FIG. 2. The ratio of light transmission between pure and copper-doped CdS crystals, T_0/T_i, as a function of wavelength λ.

and its precipitation characteristics have been investigated recently.[16]

Enhanced diffusion at the crystal boundaries were clearly visible in the samples; such diffusion can be controlled to some degree by careful surface preparation, repeated fine polishing, and etching treatments which minimizes the surface damage. It could be removed entirely by lapping after diffusion as noted previously.

RESULTS

In Fig. 2 we have plotted the logarithm of the ratio of light transmission by the pure and copper-doped cadmium sulfide samples, $\log_{10}(T_0/T_i)$, as a function of wavelength λ. Here T_i is defined as $T_i=(1-R)^2 \exp(-\alpha d)$. The quantity $\log_{10}(T_0/T_i)$ is proportional to the difference in the absorption coefficients, $\alpha-\alpha_0$, of the doped and undoped crystals. There is a broad absorption maximum for the copper-doped crystal at $\lambda=5230$ Å. There is little absorption at this wavelength from the matrix itself since the wavelength corresponding to the band-gap energy of CdS is $\lambda=5100$ Å at room temperature.[17] Therefore, all of the light-transmission data on copper-diffused CdS crystals were taken at $\lambda=5230$ Å.

Light transmission T through the doped crystals was measured as a function of penetration x by the technique described above. From these data the natural logarithm of the normalized inverse light transmission, $\ln(1/T)$, and the square of the penetration x^2 were calculated and displayed on a semilog plot for each of the samples which were copper doped for different times and temperatures. Representative transmission curves are shown in Fig. 3. It is seen that the diffusion profile along the c axis is well represented by a straight line on the $\ln\ln(1/T)$-vs-x^2 plots in the temperature range of our studies. Such a linear relationship is predicted by our diffusion model. The copper concentration varies an order of magnitude along the diffusion profile, while the intensity of the transmitted light varied over four to six orders of magnitude from one end of the crystal to the other. Our data, therefore, are very sensitive to even

[16] A. Dreeben, J. Electrochem. Soc. **111**, 174 (1964).
[17] D. Dutton, Phys. Rev. **112**, 785 (1958).

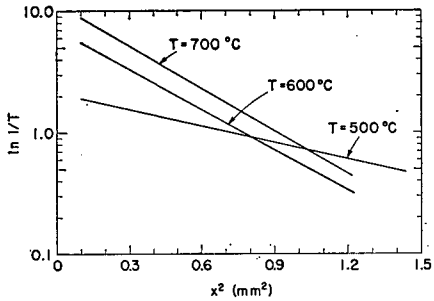

FIG. 3. Representative curves of the light transmission by doped CdS crystals as a function of copper penetration plotted as $\ln\ln(1/T)$ vs x^2.

small variations of the copper concentration along the diffusion profile.

From the slope of the light-transmission data we have calculated the diffusion coefficients D_T at the different temperatures and tabulated representative values from several measurements at each temperature in Table I along with those values which were obtained by Clarke[18] using radiotracer technique. Our values are within a factor of 2 and are somewhat lower than those reported by Clarke throughout the experimental temperature range. There are several differences between our treatment of the CdS single crystals and the copper-diffusion data and that of the work by Clarke which may account for this deviation. We have annealed our single crystals in vacuum, which may give rise to vacancy concentrations of different magnitude. We did not have to correct our diffusion profile in order to take into account the surface-diffusion component, as was the case in other measurements. By suitable lapping of the crystals after diffusion, we were successful in entirely removing the effect of surface diffusion. Finally, our sample geometry and surface preparation differed greatly from the methods used by Clarke.[18] The probable experimental error in D_T is 15%.

The activation energy for the copper diffusion which was calculated from the temperature dependence of the diffusion coefficient D_T is $\Delta E = 13.4$ kcal/mole. This value is somewhat lower than the reported value for copper diffusion along the c axis using the radioactive-tracer method[18] (17.8 kcal/mole).

Woodbury[19] has reported that in the presence of low copper surface concentration the diffusion rate of copper in CdS is more rapid than at high surface concentrations. Similar results were obtained for silver diffusion in CdS as well. In the experiments using low surface concentrations, the presence of rapidly diffusing interstitial copper or silver atoms can be detected. In our experiments and in that of Clarke's, high surface concentrations of the copper impurity were used. The diffusion rates are much slower than those reported by Woodbury. We could not detect the presence of any high-diffusivity component of the copper concentration gradient which may have superimposed on the diffusion profile, within the sensitivity of our measurement. The low activation energy, however, which we have found for copper diffusion is indicative of an interstitial mechanism.

MECHANISM OF COPPER DIFFUSION IN CdS

The following statements summarize the experimental information which may be used to propose a mechanism for copper diffusion in CdS single crystals:

(a) The activation energy for copper diffusion in CdS is $\Delta E = 13.4$ kcal/mole, as measured by our optical technique. The observed diffusion profile is indicative of a single mechanism of copper penetration in the temperature range of our study, 500°–700°C.

(b) The diffusion rate of copper in CdS is surface concentration dependent.[19] At high surface concentration the diffusion rate is markedly lower than for low copper concentration.

(c) Copper is an acceptor in the CdS crystal lattice.[20] Although its presence greatly increases the resistivity of the n-type single crystals, CdS remains n type throughout the diffusion experiments. CdS cannot be made p type by copper diffusion or by the introduction of other acceptors.

(d) The vacuum evaporation rate of pure CdS is drastically affected by the presence of copper.[21] The vaporization experiments on the doped crystals indicate the generation of sulfur vacancies V_{S^+} during the in diffusion of copper. The diffusion rates of vacancies in CdS are much higher than the diffusion rates of copper measured by this study in the temperature range of interest.[22,23]

Our experimental results and those of others[18,19] can be explained if we assume that copper diffuses interstitially into CdS with an insterstitial–substitutional equilibrium superimposed on the diffusion process. Such a model was discussed by Frank and Turnbull[24] for copper diffusion in germanium. It is proposed that copper diffusion occurs interstitially so rapidly that, to the first approximation, the diffusivity of substitutional

TABLE I. Diffusion coefficient of copper in cadmium sulfide.

T (°C)	D_{exptl} (cm²/sec)	D_{Clarke} (cm²/sec)
500	1.53×10^{-8}	1.51×10^{-8}
600	3.07×10^{-8}	5.58×10^{-8}
700	0.893×10^{-7}	1.61×10^{-7}

[18] R. L. Clarke, J. Appl. Phys. **30**, 957 (1959).
[19] H. Woodbury, J. Appl. Phys. **36**, 228 (1965).
[20] R. H. Bube, Phys. Rev. **128**, 532 (1962).
[21] G. A. Somorjai and H. B. Lyon, J. Chem. Phys. **43**, 1456 (1965).
[22] G. A. Somorjai and D. W. Jepsen, J. Chem. Phys. **41**, 1394 (1964).
[23] H. H. Woodbury, Phys. Rev. **134**, 492 (1964).
[24] F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956).

copper in CdS can be neglected. The interstitial impurity Cu_i reacts with the ionized cadmium vacancies V_{Cd}^- according to the reaction

$$Cu_i + V_{Cd}^- \rightleftarrows Cu_s^-. \quad (13)$$

This way copper ions Cu_s^- substitute for the acceptor cadmium vacancies. The solubility of substitutional copper ions, however, is much higher than that of cadmium vacancies in the undoped crystal. Therefore, when the V_{Cd}^- concentration has been reduced, copper dissolves in the lattice by the self-compensation mechanism[21,25,26]

$$Cu \rightleftarrows Cu_s^- + V_S^+. \quad (14)$$

The copper acceptors in excess of the concentration of cadmium vacancies must be compensated for by the generation of donors, such as V_S^+, or other defects in the CdS lattice. The exchange between copper and substitutional cadmium ions takes place in the presence of sulfur vacancies. Self-compensation is a well-known property of large-band-gap IIA–VIB semiconductors. It accounts for the fact that CdS cannot be made p type by copper diffusion[25] for the pressure dependence of cadmium diffusion in cadmium sulfide[23] and for the evaporation characteristics of CdS.[22]

The flux of interstitial copper atoms in the CdS matrix is given by

$$dCu_i/dt = -D_i \nabla Cu_i, \quad (15)$$

where D_i is the diffusion constant for the interstitial diffusion. If there is copper present in substitutional positions, however, the diffusion gradient must be modified and given by $\nabla(Cu_i + Cu_s^-)$. Here (Cu_s^-) is the concentration of substitutional copper ions. Thus, the effective diffusion constant D_{eff}, which is measured in the experiments, is given by

$$D_{eff} = D_i \frac{\nabla Cu_i}{\nabla(Cu_i + Cu_s^-)} = D_i \frac{Cu_i}{Cu_i + Cu_s^-}. \quad (16)$$

That is, D_i is reduced by the fraction $Cu_i/(Cu_i + Cu_s^-)$. When the solubility of substitutional copper ions is larger than Cu_i, D_i would be greatly reduced. Thus, under these conditions the measured diffusion constant should be a sensitive function of the substitutional copper concentration. The concentration dependence of D_{eff} observed by the different investigators and the low activation energy for copper diffusion in CdS indicate that the physical conditions leading to Eq. (16) may have been present in CdS. If the solubility characteristics of copper in CdS are similar to that of silver, a value for a solubility ratio $Cu_s^-/Cu_i \approx 10^3$ would not be unreasonable in the temperature range of our experiments. Thus, there is a marked decrease in the diffusivity of interstitial copper.

The presence of vacancy aggregates in CdS, in addition to point defects, cannot be excluded.[19] The relative ease of the internal precipitation of copper could indicate vacancy clustering as suggested by Fuller[27] recently. It is likely that the interstitial substitutional diffusion mechanism in CdS may apply to other cations such as silver and nickel[19] as well. It is interesting to note the similarity in the mechanism of copper diffusion in Group IVA elements and in IIA–VIB compounds in spite of the great difference of most of the physical–chemical properties of these two groups.

MECHANISM OF LIGHT ABSORPTION BY COPPER-DOPED CdS

The light absorption characteristics of copper-doped crystals displayed in Fig. 2 indicate that the absorbing centers have a broad energy distribution in the forbidden gap of cadmium sulfide. The transmission curves (Fig. 3) are indicative of a single absorption mechanism for the crystals doped at the different temperatures. It was therefore concluded that the dominant light absorption mechanism at $\lambda = 5230$ Å is most likely the excitation of electrons from the copper acceptor centers to the conduction band of cadmium sulfide.

In addition to absorption by impurity centers, light scattering due to the presence of precipitate aggregates of copper or copper compounds Cu_xS_y should also occur. We have noted previously that the precipitate particles are clearly visible as they line up along the c axis. The large ($r > 5230$ Å) precipitate particles seem to form preferentially at certain portions of the copper concentration profile and vary greatly in size. Since our transmission curves are smooth functions of x^2, the copper penetration, it seems unlikely that such a nonuniform distribution of copper aggregates have an important effect on the transmission of light through the samples. Also the usual inverse λ^4 dependence of the light intensity[13] which is characteristic of light scattering by small particles ($r < 5230$ Å) does not hold for the samples investigated. The absorption must be primarily due to copper impurity centers and to defects which are created by the copper diffusion.

ACKNOWLEDGMENT

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[25] G. Mandel, Phys. Rev. **134**, A1073 (1964).
[26] R. F. Brebrick, J. Phys. Chem. Solids **4**, 190 (1958).
[27] C. S. Fuller and K. B. Wolfstien, J. Phys. Chem. Solids **26**, 1463 (1965).