

Diffusion of Electrically and Optically Active Defect Centers in II-VI Compounds*

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The diffusion of Cu into doped and undoped ZnSe and ZnS has been studied by radiotracer techniques, accompanied by luminescence and electrical measurements. Both luminescence and radiotracer measurements have shown that the diffusion coefficient of Cu in undoped and Cl-doped ZnSe in the temperature range of 300–570°C obeys the relationship $D = 1.7 \times 10^{-5} \exp(-0.56 \text{ eV}/kT)$. A strong retarding influence on the diffusion of Cu by the presence of Al in the crystals has been interpreted in terms of ion pairing between Al and the in-diffusing Cu. The same effect has also been observed in ZnS. The diffusion of Al into ZnSe has been found to be accompanied by a codiffusion of Zn vacancies. The luminescence patterns, the electrical characteristics and the radiotracer data in partially diffused crystals have been used to correlate the electrical and optical activity of the in-diffused defect centers.

INTRODUCTION

A COMMON procedure in introducing electrically or optically active defect centers into solids is to diffuse the appropriate foreign impurity or stoichiometric excess of a lattice constituent into the material until the whole volume of the specimen is uniformly doped. Often, and this is particularly true in II-VI compounds, rearrangements occur inside the crystal during such a diffusion process. Native defects may diffuse in along with the foreign impurity or the diffusant may associate itself with such defects already present in the crystal. Precipitation or dissolution of a second phase may occur if the diffusant has an influence on the solubility of a defect already present in the crystal.

This paper describes a method which allows us to investigate some of these relationships in II-VI compounds. In this method a radioisotope of the dopant to be studied is diffused approximately halfway into the host crystal. The diffusion profile is determined by appropriate counting methods, and the changes in the electrical and optical properties of the crystal as a function of the distance from the outer edge of the crystal are determined by suitable measurement techniques. By performing the diffusion under various ambient atmospheres, temperatures, and previous dopings, informative relationships between the electrical and optical characteristics of the produced defect centers are obtained.

We have applied this method to the study of some well-known defect centers in II-VI compounds. We have performed most of the measurements with ZnSe, as this compound lends itself well to both electrical measurements as well as luminescence studies in the visible spectral range. A few experiments on other II-VI compounds will also be discussed.

EXPERIMENTAL METHOD

The ZnS and ZnSe crystals used in this study were synthesized by the vapor growth method.¹ The Cl-doped

crystals were prepared by adding SrCl₂ to the ZnSe powder charge. The grown crystals were cut into cube-shaped pieces, approximately 3 mm on the side. In the Al diffusion experiments undoped crystals were fired at 1050°C in a Zn-Al alloy containing 10 mole % Al. The crystals used for the Cu diffusion experiments were first purified by firing in molten Zn at 850°C.² They were then coated with Cu₂Se by immersion in a hot solution of Cu⁺ ions³ and fired at temperatures ranging from 200 to 570°C in quartz vials containing 1 atm of hydrogen. Control crystals that were treated similarly, except for the omission of the Cu₂Se coating, showed no measurable change in their electrical or optical properties. It is believed, therefore, that in these low-temperature diffusion experiments the atmosphere in which the crystals are fired does not significantly influence the stoichiometry of the crystals, and that the native and foreign defects already present in crystals at the start of the diffusion experiment do not undergo significant configurational changes during the diffusion. The effect of the atmosphere begins to be felt, however, above about 600°C, with rapid changes in stoichiometry occurring at 800°C.

The radioisotope diffusion profiles for Cu were obtained by using a Cu⁺ plating solution containing the Cu⁶⁴ isotope. Cu⁶⁴ has a half-life of 12.9 h and decays to the stable isotopes of Ni⁶⁴ and Zn⁶⁴ with the emission of β⁺, β⁻, and 1.34-MeV γ rays. The counting was performed with Nuclear Chicago Model 181A radiation counter. The method used was to perform a γ-ray count on a crystal into which radioactive Cu had been diffused, etch off a known volume with hot 50% NaOH, and repeat the count. This was repeated until the count had decreased to within about 10% of the background. The treatment of the data and the estimated accuracy of the method have been recently described in detail by Woodbury.⁴

The penetration depth of the luminescence into the crystals was obtained by cutting or grinding the crystal

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¹ W. W. Piper and S. Polich, *J. Appl. Phys.* **32**, 1278 (1961).

² M. Aven and H. H. Woodbury, *Appl. Phys. Letters* **1**, 53 (1962).

³ M. Aven and D. A. Cusano, *J. Appl. Phys.* **35**, 606 (1964).

⁴ H. H. Woodbury, *Phys. Rev.* **134**, A492 (1964).

to expose the central area as shown in Fig. 1. The diffusion distance of the luminescent species was taken as the distance between the outer edge of the crystal and the line of demarcation between the luminescent region and the nonluminescent (or differently luminescent) central area. The measurements were done with a microscope provided with a calibrated eyepiece. The diffusion distance values used in the calculations usually represent the averages of eight measurements done on the four edges of each of the two opposite sides of a crystal slab cut as shown in Fig. 1.

The electrical diffusion profiles were obtained by measuring the resistance of the crystal between two In contacts on the surface of the crystal as a function of the amount of material ground off the crystal between each measurement. The quantitative values of the carrier concentration were obtained by performing Hall measurements on uniformly diffused bar-shaped, single-crystal specimens.

RESULTS

If the surface of a sample used in the Cu diffusion experiments is in equilibrium with an excess of the chemically formed Cu₂Se during the diffusion, and the penetration of the diffusion front is small compared to the sample dimensions, one would expect to observe a diffusion profile corresponding to the diffusion into a semi-infinite medium from a source of constant concentration. The solution of the diffusion equation for these boundary conditions is given by⁵

$$C = C_0 \left[1 - \operatorname{erf} \frac{x}{(4Dt)^{1/2}} \right], \tag{1}$$

where C_0 is the surface concentration, i.e., the concentration of the diffusant in the crystal near the surface;

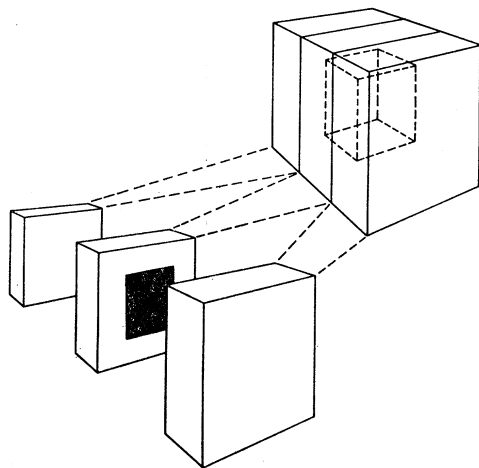


Fig. 1. Method of sectioning partially diffused crystals to expose the luminescence boundary.

⁵ See, for example, J. Crank, *The Mathematics of Diffusion* (Clarendon Press, Oxford, England, 1956), pp. 18, 19.

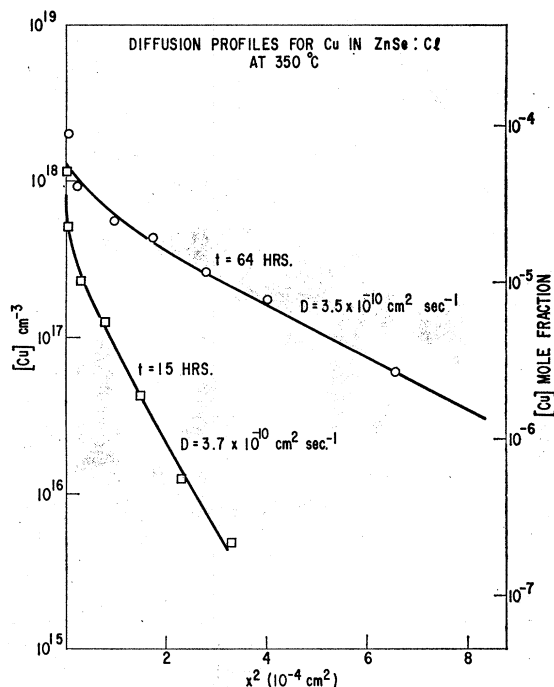


Fig. 2. Diffusion profiles for Cu in Cl-doped ZnSe after 15 h (squares) and 64 h (circles) diffusion at 350°C.

C is the concentration at distance x after time t ; and D is the diffusion coefficient.

Figure 2 shows the diffusion profile for Cu in ZnSe doped with $2 \times 10^{19} \text{ cm}^{-3}$ Cl at 350°C. The diffusion times for the two sets of measurements are 15 and 64 h, respectively. The solid lines drawn through the experimental points represent the functional relationship between C and x as given by Eq. (1). It can be seen that, except for very small x , the fit between the experimental points and the error function curves is satisfactory. The discrepancies at small x may be due to surface irregularities. The fact that diffusion coefficients calculated from the 15- and 64-h data, respectively, are fairly close to each other indicate that the time dependence of Fick's law is obeyed within the experimental accuracy of the measurements.

Figure 3 shows the luminescence pattern of a slab cut from a Cl-doped ZnSe crystal into which Cu had been diffused at 570°C. The light frame on the photograph corresponds to green luminescence of Cu-activated ZnSe, peaking at approximately 2.36 eV. The radiocopper diffusion profile obtained on a similar crystal is shown in Fig. 4. The position of the green-luminescent frame on the photograph in Fig. 3 is indicated by the region labeled "Luminescent domain" in Fig. 4. These data show that the green luminescence occurs in a region in the crystal where the concentration of Cu is roughly between 10^{-5} and 10^{-4} mole fraction (2×10^{17} and $2 \times 10^{18} \text{ cm}^{-3}$). The green luminescence is absent in regions where the Cu concentra-

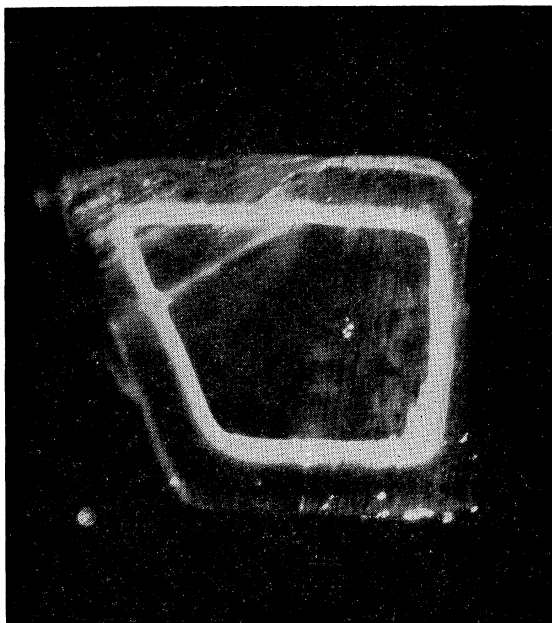


FIG. 3. Luminescence pattern obtained under 3650 Å ultraviolet excitation of a slab cut from a Cl-doped ZnSe crystal into which Cu was diffused at 570°C. The bright band corresponds to green luminescence peaking at 2.36 eV.

tion is below 10^{-5} mole fraction because there is evidently not enough Cu centers to successfully compete with other luminescence and "killer" centers present in the crystal.⁶ The falloff of the luminescence intensity in regions where the Cu concentration is above 10^{-4} mole fraction is probably due to concentration quenching.

It can also be seen in Fig. 4 that the experimental points above about 4×10^{18} cm⁻³ Cu, corresponding to a diffusion distance of approximately 0.5 mm, deviate significantly from the error function curve. This behavior has been observed for Cu diffusion experiments carried out at approximately 400°C and higher. At lower temperatures this apparent saturation phenomenon is absent, and the experimental data follow the error function curve down to much lower values of x (Fig. 2). It has also been observed that in the crystals where the Cu diffusion was carried out at 400°C or higher, the region where the deviation from the error function curve becomes apparent is brown under visual observation. This finding is suggestive of precipitation of Cu selenide within the crystal.

⁶ The sharpness of the inner luminescence boundary may arise from a superlinear relationship between the intensity of the green luminescence and the Cu concentration. Such a relationship would obtain, e.g., if the green luminescence center consisted of several associated entities, or if the recombination cross section of the green center depended on the position of the Fermi level. The variation of the luminescence intensity in the direction perpendicular to the Cu diffusion front could then be substantially faster than the exponential variation of Cu concentration with x^2 shown in Fig. 4 and account for the abrupt termination of the green luminescence at its inner boundary.

Figure 5 shows the temperature dependence of the diffusion coefficients obtained by the Cu⁶⁴ diffusion experiments in ZnSe:Cl in the range of 200 to 570°C. The straight line drawn through the experimental points corresponds to the equation

$$D = 1.7 \times 10^{-5} \exp(-0.56 \text{ eV}/kT). \quad (2)$$

In Fig. 5 are also plotted the results of luminescence diffusion measurements on ZnSe:Cl crystals from the same boule. The treatment of the luminescence data was performed by the method suggested by Dunlap.⁷ According to this method, if a sudden change in some physical property, e.g., luminescence or electrical conductivity, occurs when C reaches a critical value C_i , the diffusion coefficient can be obtained by measuring the penetration distance x_i , corresponding to the critical concentration C_i . For this case a modification of Eq. (1) gives

$$D \log(C_0/C_i) = x_i^2/9.2t. \quad (3)$$

The luminescence data in Fig. 5 are plotted as $D \log C_0/C_i$ versus temperature. It can be seen that above approximately 300°C ($10^3/T = 1.85 \text{ 1}/K^\circ$) the experimental points fall close to the line corresponding to Eq. (2). This means that the diffusion coefficients obtained from the luminescence measurements can be brought to coincide with the values obtained from the Cu⁶⁴ diffusion measurements in this temperature range

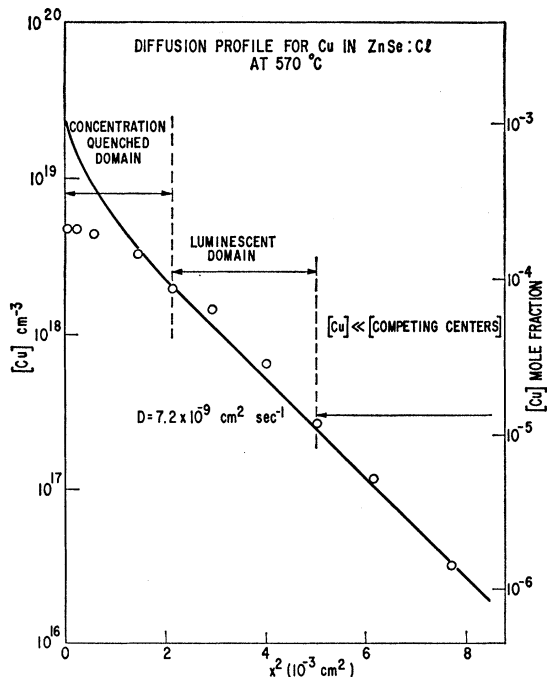


FIG. 4. Diffusion profile for Cu in a Cl-doped ZnSe crystal fired at 570°C. The region labeled "Luminescent domain" corresponds to the green-luminescent band on the crystal shown in Fig. 3.

⁷ W. C. Dunlap, Jr., Phys. Rev. 94, 1530 (1954).

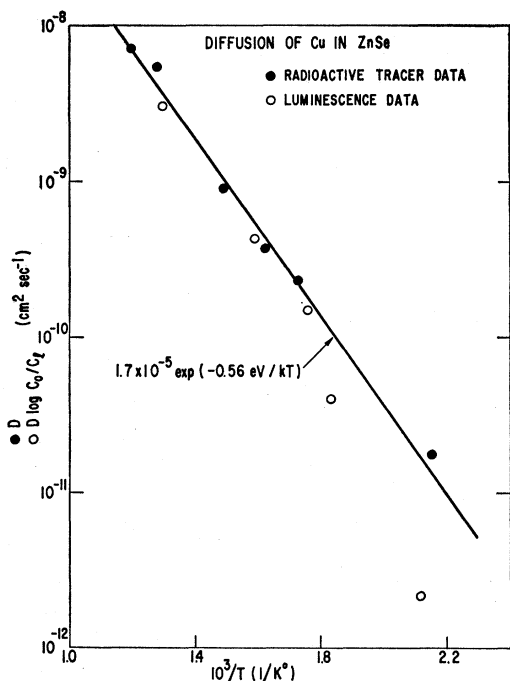


FIG. 5. Temperature dependence of the diffusion coefficient for Cu in Cl-doped ZnSe. Filled circles—radiotracer data; open circles—luminescence data. The luminescence data are plotted as $D \log(C_0/C_i)$ versus $10^3/T$ [see Eq. (3)].

if we set $\log C_0/C_i \approx 1$. This is not unreasonable, as the data in Fig. 4 show that the apparent saturation, which can be taken as approximately equal to the "surface concentration" C_0 , and the concentration of Cu at the luminescence boundary C_i , differ by roughly a factor of 10.

Below 300°C the data points obtained from the luminescence measurements show a systematic deviation from the Cu⁶⁴ data. As very long diffusion times (several weeks) had to be used to obtain measurable luminescence diffusion at these low temperatures, it is possible that a deviation from Fick's law is responsible for this discrepancy. It is also possible, however, that the quantity $\log C_0/C_i$ itself is temperature-dependent. The divergence of the data points at low temperatures may thus be due to the fact that in Fig. 4 the measurements with Cu⁶⁴ are represented by the diffusion coefficient D , while the luminescence measurements are given as the quantity $D \log C_0/C_i$.

Figure 6 shows the resistance profile of a ZnSe:Cl crystal into which Cu was diffused at 460°C up to the depth of 0.305 mm, as judged by the inner boundary of the green luminescence. It can be seen that a drop in resistance by almost a factor of 10^{10} occurs between 0.295 and 0.316 mm from the surface, indicating that the green-luminescent region coincides closely with the high resistance region in the crystal. This finding suggests that in the green-luminescent region at least

a part of the Cu acts as an acceptor, and is therefore located in substitutional sites.

All of the above-described Cu diffusion experiments were performed on Cl-doped ZnSe containing $2 \times 10^{19} \text{ cm}^{-3}$ Cl by chemical analysis. A few experiments with undoped ZnSe yielded diffusion coefficients and luminescence patterns very similar to those found for ZnSe:Cl. It appears, therefore, that most of the Cl contained in the ZnSe:Cl crystals exists in a form that does not interact with the in-diffusing Cu. The inactive nature of the Cl contained in such crystals is also demonstrated by the luminescence spectrum of ZnSe:Cl and ZnSe:Cu,Cl. If the Cl present acted as a part of a luminescence center, the ZnSe:Cl crystals should have shown yellow self-activated luminescence, equivalent to the self-activated blue luminescence in ZnS:Cl.⁸ Similarly, ZnSe:Cl into which Cu was diffused should have exhibited the presence of the red centers, equivalent to the green Cu-Cl centers in ZnS:Cu,Cl.⁹ Yet the ZnSe:Cl crystals used in the present study were weakly blue-luminescent, and ZnSe:Cl to which Cu was diffused showed green luminescence (Fig. 3). Most of the $2 \times 10^{19} \text{ cm}^{-3}$ Cl is also electrically inactive, as Hall coefficient measurements on the ZnSe:Cl crystals have indicated the presence of only $8 \times 10^{15} \text{ cm}^{-3}$ donors and $5 \times 10^{15} \text{ cm}^{-3}$ acceptors. The diffusion, the luminescence, and the electrical characteristics of ZnSe:Cl are, there-

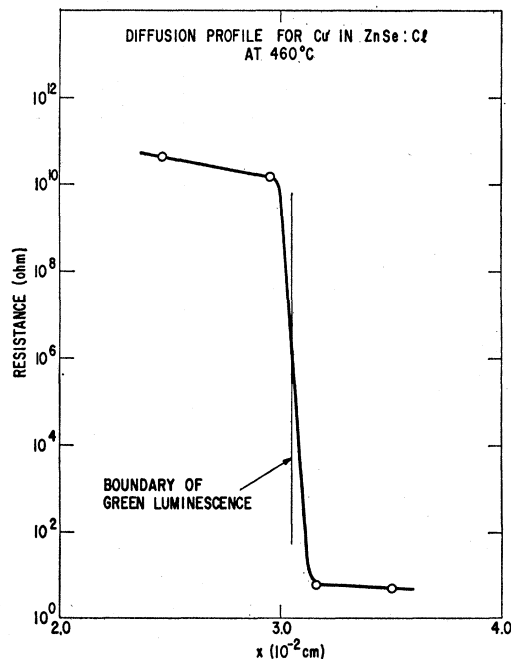


FIG. 6. Electrical resistance profile of a Cl-doped ZnSe crystal into which Cu was diffused at 460°C.

⁸ J. S. Prener and D. J. Weil, *J. Electrochem. Soc.* **106**, 409 (1959).

⁹ F. F. Morehead, Jr., *Phys. Chem. Solids* **24**, 37 (1963).

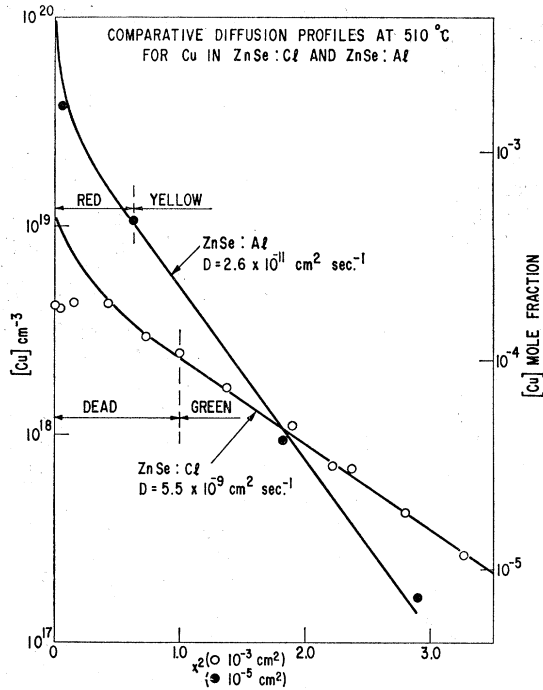


Fig. 7. Comparative diffusion profiles for Cu in Cl-doped and Al-doped ZnSe at 510°C. Filled circles—ZnSe doped with 2×10^{19} cm^{-3} Al; open circles—ZnSe doped with 2×10^{19} cm^{-3} Cl.

fore, consistent with the assumption that the Cl is present in the ZnSe:Cl crystals in an inactive form.

In contrast to Cl-doped ZnSe, very profound changes in the diffusion of Cu is observed in Al-doped ZnSe. Figure 7 shows the diffusion profiles of Cu in ZnSe doped with 2×10^{19} cm^{-3} Cl and 2×10^{19} cm^{-3} Al, respectively, for equivalent diffusion times and temperatures. It can be seen that the diffusion coefficient of Cu in Al-doped ZnSe is less than in Cl-doped (or undoped) ZnSe by about a factor of 200. Also, while the diffusion of Cu into undoped or Cl-doped ZnSe resulted in the production of green luminescence centers, the diffusion of Cu into ZnSe:Al results in red luminescence, peaking at 1.95 eV.

Because of the strong effect the presence of Al in ZnSe has on the Cu diffusion rate and luminescence spectrum, the diffusion of Al into ZnSe was investigated. Figure 8 shows a half-slice cut out of a rectangular ZnSe crystal slab after firing in an Al-Zn alloy at 1050°C. The photograph was taken under ultraviolet excitation. The diffusion front can be seen as the line of demarcation between the yellow-luminescent edge region and the virtually nonluminescent central area. The yellow luminescence band peaks at 2.07 eV. The luminescence center responsible for this band is equivalent to the self-activated blue-luminescence center in ZnS, and has been proposed to consist of a Zn vacancy associated with a halogen or a group III donor.⁸ The yellow-luminescent edge region was found to have a resistivity

of 10^{-2} $\Omega\text{-cm}$, while the central portion of the crystal had a resistivity in excess of 10^4 $\Omega\text{-cm}$. Hall measurements on bars cut out of the edge region showed electron concentrations of about 2×10^{18} cm^{-3} . The analytically determined concentration of Al in crystals that had been fired under similar conditions until the whole crystal was doped uniformly was found to be 2×10^{19} cm^{-3} .

Because of the lack of a suitable Al isotope, the Al diffusion could not be measured by the radioisotope method. The value of $D \ln(C_0/C_1)$ [see Eq. (3)], calculated from the distance of penetration of the luminescence boundary into the crystal of Fig. 8 was found to be 3.2×10^{-9} $\text{cm}^2 \text{sec}^{-1}$. The assumptions that C_0 is equal to the saturation concentration of 2×10^{19} cm^{-3} , and that C_1 is determined by competition of the self-activated centers against approximately 2×10^{17} cm^{-3} of other luminescence and "killer" centers present in the crystal (see Fig. 4), lead to a diffusion coefficient of 1.6×10^{-9} $\text{cm}^2 \text{sec}^{-1}$.

This diffusion coefficient is characteristic of the diffusion of Al, and not of the Zn vacancy with which it is associated in the self-activated center. This conclusion is reached on the basis of the finding that the highly conducting ZnSe:Al crystals can be rendered

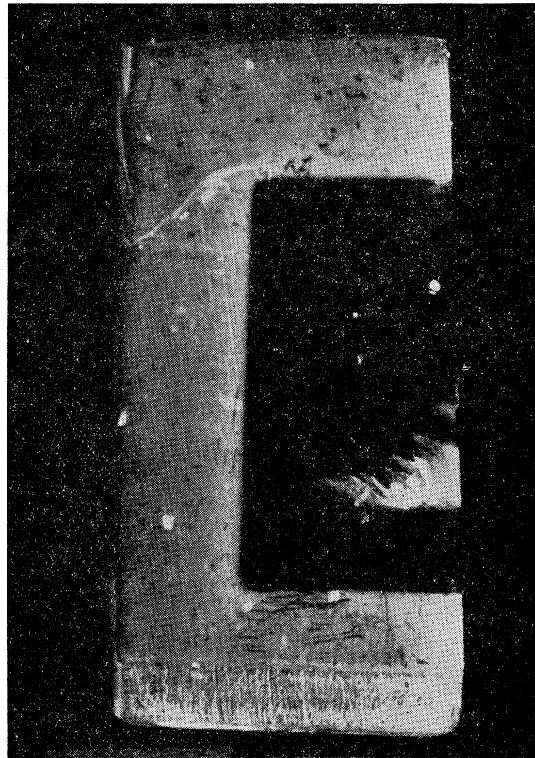


Fig. 8. Luminescence pattern obtained under 3650 Å ultraviolet excitation of a slab cut from an undoped ZnSe crystal into which Al was diffused at 1050°C. The bright edge region corresponds to yellow-luminescence peaking at 2.07 eV. The bright structure within the dark area is due to light trapping by a crack near the surface.

insulating by a brief firing at reduced Zn pressure or 850°C, with complete restoration of the high conductivity after refiring in about 0.5 atm of Zn pressure at the same temperature. This shows that Zn vacancies diffuse in and out of ZnSe very rapidly ($D \approx 10^{-6}$ cm² sec⁻¹), which is consistent with the fast diffusion of Cd vacancies in CdS observed by Woodbury.⁴ It is clear, therefore, that the limiting factor in the rate of formation of the yellow $V_{Zn}Al$ centers, as Al diffuses into the crystal, is the supply of Al atoms rather than Zn vacancies.

Before discussing the significance of these findings, it should be mentioned that experiments similar to the described diffusion work on ZnSe, carried out on ZnS, showed qualitatively similar results. For example, the diffusion of Cu into undoped ZnS single crystals produced a blue-luminescent frame similar to the green-luminescent frame in Fig. 3. The estimated diffusion coefficient at 500°C, assuming the quantity of $\ln C_0/C_1$ to be the same as in ZnSe, was about 1.5×10^{-9} cm² sec⁻¹, i.e., half that for ZnSe. Also, the diffusion of Cu into previously Al-doped ZnSe was found to be much slower than in undoped ZnS. These findings, as well as the parallels between the present work and the Cd self-diffusion experiments by Woodbury referred to earlier, indicate that the described diffusion and interaction phenomena may be generally valid for II-VI compounds.

DISCUSSION

The experimental results have shown that the diffusion of Cu and Al into II-VI compounds is often accompanied by codiffusion of other species, or association between the diffusing species and impurities already present in the crystal. Although the data available are inadequate for arriving at a unified picture for the equilibria and dynamics for all the defect centers involved, several significant correlations between the electrical and optical activity of these centers can be obtained from the results of the present study.

The most straightforward of the described diffusion work is the diffusion of Al. It was mentioned earlier that the defect center responsible for the self-activated luminescence in II-VI compounds is believed to consist of a complex between a donor and a cation vacancy, e.g., $V_{Zn}Al$ in ZnSe, which acts as a deep acceptor, whereas the isolated group IIIb elements act as shallow donors. The present data are consistent with this assumption. The yellow diffusion front shown in Fig. 8, which enters crystals fired in Zn-Al alloy, represents the diffusion of Al atoms. The low value of the diffusion coefficient at 1050°C, i.e., $\sim 10^{-9}$ cm²/sec, suggests that the diffusion is not interstitial. Along with the indiffusion of Al, Zn vacancies enter the material and associate themselves with some of the Al. The ratio of the isolated Al to the Al associated with Zn vacancies depends on the vapor pressure of Zn. Crystals contain-

ing 2×10^{19} cm⁻³ Al, for example, are almost completely compensated by firing at 850°C in vacuum or neutral atmosphere, indicating that under these conditions roughly half of the Al is associated with Zn vacancies (it is believed that the concentration of isolated cation vacancies in *n*-type II-VI compounds is very low) and half exists in donor sites. At about 0.5-atm Zn pressure (the approximate vapor pressure of Zn at 850°C) the equilibrium is shifted in favor of isolated Al. The compensation ratio, however, remains quite high, as the excess of isolated Al over the $V_{Zn}Al$ centers (assuming that all the 2×10^{19} cm³ Al is active) is still only 2×10^{18} cm⁻³. This means that the concentration of the $V_{Zn}Al$ centers has been reduced from approximately 1×10^{19} cm⁻³ to 0.9×10^{19} cm³, and explains why there is no great difference in the intensity of the yellow luminescence between insulating and conducting ZnSe:Al crystals. The assumption that the concentration of the yellow-luminescence centers is of the order of 10^{19} cm⁻³ is also consistent with the finding that the switchover from yellow to red luminescence in ZnSe:Al crystals into which Cu⁶⁴ was diffused, occurred at a Cu concentration of approximately 10^{19} cm⁻³ (see Fig. 7).

The relatively fast rate of the diffusion of Cu into undoped ZnSe and ZnSe:Cl, and the low activation energy for diffusion given in Eq. (2) suggest an interstitial diffusion mechanism. However, as both the acceptor activity of Cu as well as the proposed models for the red and green Cu centers require Cu to be in substitutional sites, the interstitial diffusion of Cu must be at least partially accompanied by an interstitial-substitutional exchange mechanism. Consider first the case of undoped (or Cl-doped) ZnSe, into which Cu diffuses fast, produces green-luminescence centers, and completely compensates the available active donors. The actual concentration of Cu that forms luminescence centers cannot be ascertained from the measurements that relate the total concentration of Cu to the position of the luminescence boundaries (Fig. 3). We know, however, that the luminescence front coincides closely to the boundary between the *n*-type conducting and the compensated regions. At such a boundary the concentration of the in-diffused Cu that appears in substitutional sites and can, therefore, act as an acceptor, must be roughly equal to the concentration of uncompensated donors. The substitutional sites into which the Cu enters cannot be species like $V_{Zn}Cl$ or isolated V_{Zn} . These species are already acceptors and, since the crystal was *n*-type before the Cu diffusion, the entry of Cu into either of these would not increase the degree of compensation. We conclude, therefore, that Cu must enter into newly created V_{Zn} sites. Such sites can be produced either by local displacement of Zn, or the indiffusion of Zn vacancies from the surface or from gross lattice imperfections, e.g., dislocations.

The situation is different in Al-doped ZnSe. The

$V_{Zn}Al$ center is the major compensating defect in Al-doped n -type ZnSe. In a crystal containing $2 \times 10^{19} \text{ cm}^{-3}$ Al and showing $2 \times 10^{18} \text{ cm}^{-3}$ free electrons, there must be of the order of 10^{19} cm^{-3} $V_{Zn}Al$ centers, assuming that all of the Al present is in active donor or acceptor sites. There exists, therefore, a large probability for the in-diffusing Cu to enter the Zn vacancies associated with Al. Such an interaction would be expected to significantly decrease the diffusion rate of the diffusant as demonstrated, for example, by the study of Li diffusion in acceptor-doped Ge and Si.¹⁰ The observed retardation of Cu diffusion in ZnSe:Al is thus entirely consistent with the assumption that the in-diffusing Cu is captured by the $V_{Zn}Al$ centers. The simultaneous conversion of the yellow luminescence of $V_{Zn}Al$ to the red Cu luminescence could, therefore, be simply due to the conversion of the $V_{Zn}Al$ centers to CuAl centers. The possibility that, along with the Cu that is captured by the Zn vacancies, some isolated substitutional Cu diffuses in and forms red-luminescence centers, cannot be excluded, however.

The green- and red-luminescence centers in ZnSe are equivalent to the "high Cu blue" and the Cu green centers in ZnS, respectively. Various models have been proposed for these centers. Some workers consider that the same defect center is responsible for both the green and the red luminescence.⁹ Others believe that the green and red luminescences originate in different centers.¹¹ As it has been generally observed that an excess of Cu over coactivator leads to a predominance of green over red luminescence, several models for the green center involve associated pairs of Cu, e.g., Cu_sCu_i (substitutional Cu associated with interstitial Cu). Such an associated pair is sometimes considered to be self-compensated, Cu_s acting as an acceptor and Cu_i as a donor. The Cu_sCu_i combination has also been considered as an acceptor, which may be charge compensated by another Cu_i acting as a donor, or some other donor present in the crystal.

The present results lend little support to the model according to which the red and the green luminescences originate in the same defect center. For, if the lumi-

nescence emission in such a center depended on the position of the Fermi level, with red luminescence favored in more n -type and the green luminescence in less n -type material, the inner edge of the green band in Fig. 3 where the crystal switches from very high to very low resistivity should have exhibited at least some red luminescence. Although no positive identification of the species responsible for the green luminescence can be made on the basis of the available data, the close coincidence between the location of the inner edge of the green-luminescent band and the boundary of the strongly n -type region in the crystal (Figs. 3 and 4) suggests that the green-luminescence center contains a Cu that acts as an acceptor. The present experimental findings would thus support models involving isolated substitutional Cu or nonself-compensated Cu_sCu_i species.

Perhaps the most unexpected finding of the described work is the passive character of Cl in ZnSe:Cl. It was seen that, of the $2 \times 10^{19} \text{ cm}^{-3}$ Cl found to be present in the crystal, only a maximum of about 10^{16} cm^{-3} could be acting as donors. In fact, as the background concentration of Al in ZnSe is usually in the 10^{16} – 10^{17} cm^{-3} range, all the donor activity could be explained by the presence of Al, leaving the Cl completely inactive. It was also shown that the presence of the large concentration of Cl had no effect on the diffusion rate of Cu in ZnSe, nor did it promote self-activated luminescence.

We have, as yet, no adequate explanation for this finding. The simplest inactive complex in which Cl could exist within the crystal is Cl_2 as isolated "molecules" or a separate phase. As such, it could conceivably be detected on the basis of its vibrational frequencies. It is also conceivable that Cl has formed complexes with Sr atoms, as $SrCl_2$ was used as the source of Cl during crystal growth. It is hoped that suitable measurements will, before long, resolve this problem.

ACKNOWLEDGMENTS

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¹⁰ E. M. Pell, J. Appl. Phys. **31**, 1675 (1960).

¹¹ N. Riehl and H. Ortmann, Ann. Phys. (N. Y.) **7**, 3 (1959).

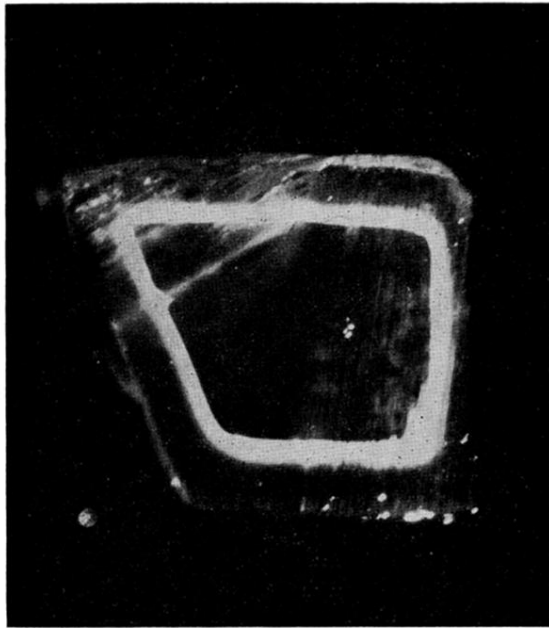


FIG. 3. Luminescence pattern obtained under 3650 Å ultraviolet excitation of a slab cut from a Cl-doped ZnSe crystal into which Cu was diffused at 570°C. The bright band corresponds to green luminescence peaking at 2.36 eV.

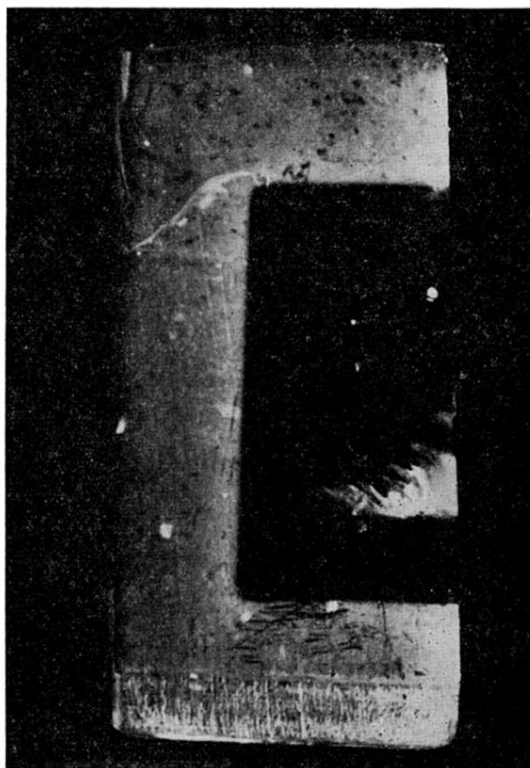


FIG. 8. Luminescence pattern obtained under 3650 Å ultra-violet excitation of a slab cut from an undoped ZnSe crystal into which Al was diffused at 1050°C. The bright edge region corresponds to yellow-luminescence peaking at 2.07 eV. The bright structure within the dark area is due to light trapping by a crack near the surface.