

Polarization of the Edge Emission in CdS

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The edge emission spectra of CdS has been examined in the temperature range 70°–150°K. In this interval the ratio of the intensity of the light emitted whose plane of polarization is perpendicular to the c axis of the crystal to that parallel to the c axis was determined. The ratio I_{\perp}/I_{\parallel} decreased with increasing temperature. In agreement with an earlier paper assigning the emission as the recombination of a trapped hole and free electron an interpretation is offered in terms of the splitting of the ground state of the center. The splitting is caused by the presence of the crystal field in a manner similar to that observed for the valence band. However, from the present experiment alone an equally satisfactory explanation can be offered in terms of the recombination of a trapped electron with holes possessing a thermal distribution among the valence band levels. In either case a splitting of $\Delta E=0.014$ eV is obtained.

INTRODUCTION

FOLLOWING the initial observation of fluorescence in CdS by Kroger,¹ this material has received almost continuous attention. A summary of the work up to 1956 is available² and recently a fairly extensive bibliography has been given in a review article.³ Fluorescence from CdS has been observed in several regions of the visible and infrared, e.g., emission due to exciton decay ≈ 4900 Å,⁴ edge emission near 5200 Å and emission at various chemical impurity sites.^{5,6} However, only that component near 5200 Å, the "edge emission," will be discussed here. This fluorescence lies just to the long wavelength side of the fundamental absorption edge, and is characterized at low temperatures by a series of equally spaced peaks. Several models^{2,7} for the mechanism of the edge emission have been advanced; the most recent⁷ suggests that it is due to the radiative recombination of a free electron and trapped hole at a sulfur vacancy. Dutton⁸ realizing that the presence of non-cubic crystal fields, due to the ionic nature of the bonding, might effect the luminescence looked for and observed in CdS a preferential polarization of the edge emission with respect to the c axis of the crystal.

It is the purpose of the present paper⁹ to extend the measurements of Dutton to other temperatures and to give an interpretation based on the effect a split valence band has on a recombination level within the forbidden energy gap.

EXPERIMENTAL

The experimental arrangement used to measure the ratio of the intensity of light emitted with its plane of polarization perpendicular to and parallel to the c axis of the crystal is shown schematically in Fig. 1. By the use of filters (6-mm Corning No. 9863) and baffling the reflected exciting radiation was not allowed to enter the detecting apparatus. Unusual care was necessary in this since the 5460 Å line or the continuum always present in a Hg arc, although unimportant in observing the spectral shapes, could easily affect the measured ratio of the two modes of polarization.

A 1P21 photomultiplier was used as the detector in the monochromator and sheets of polaroid, placed between the sample and any optical parts, formed the polarizer. Corrections were made for the polarization properties of the monochromator and optics. The samples of CdS were mounted with pressure contacts against the bottom of the Dewar. A thermocouple in contact with a free surface of the sample was used for the temperature determination. Samples for these studies were cleaved from single crystals of CdS grown at the Wright Air Development Center and supplied by Dr. B. Kulp and Dr. D. C. Reynolds.

It was noted that the ratio of light emitted polarized perpendicular to the c axis and parallel to the c axis showed a gradual decrease with time after cleavage. Whether this represented a deterioration of the surface through the condensation of vacuum pump vapors or a more basic mechanism was never clear. Completely re-

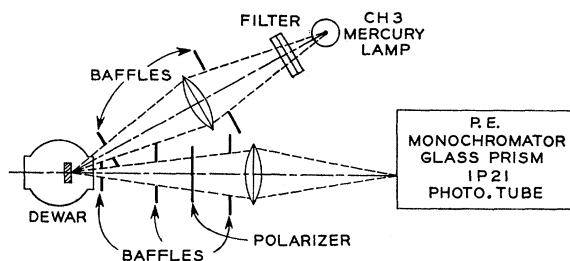


FIG. 1. Experimental arrangement.

¹ F. A. Kroger, *Physica* **7**, 1 (1940).

² J. Lambe, C. Klick, and D. Dexter, *Phys. Rev.* **103**, 1715 (1956).

³ J. Lambe and C. Klick, *Progress in Semiconductors* (John Wiley & Sons, New York, 1958), Vol. 3.

⁴ M. Bance-Grillot, E. F. Gross, E. Grillot, and B. S. Razbirine, *Compt. rend.* **248**, 86 (1959). D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **116**, 573 (1959).

⁵ C. C. Klick, *Phys. Rev. Letters* **2**, 418 (1959).

⁶ D. Warshaw and D. C. Reynolds, *Phys. Rev. Letters* **3**, 370 (1959).

⁷ R. J. Collins, *J. Appl. Phys.* **30**, 1135 (1959).

⁸ D. Dutton, *J. Phys. Chem. Solids* **6**, 101 (1958).

⁹ See also R. J. Collins and J. J. Hopfield, *Bull. Am. Phys. Soc.* **4**, 323 (1959).

producible results could be obtained by measurement of the ratio on freshly cleaved surfaces without regard for what initial crystal was used as long as the crystal did show edge emission.

RESULTS AND DISCUSSION

The results of the measurements are shown in Figs. 2 and 3. Figure 2 gives the spectrum emitted in the two modes of polarization at 78°K. The ratio could be measured over the temperature range 135°K to 71°K and is plotted against I/T in Fig. 3. It was unfortunate that the decreasing intensity of the green edge emission with increasing temperature was so pronounced that the measurements could not be extended to higher temperatures. The lower end of the temperature scale was reached at the equilibrium temperature established by pumping on solid nitrogen.

An interpretation of these results is possible in terms of the model¹⁰ for the CdS band structure, which suggests that the valence band is a P band and the conduction band is an S band. In this partially ionic hexagonal crystal the presence of both crystal field and spin-orbit coupling will split the otherwise threefold degenerate valence band as shown in Fig. 4. The symmetry¹¹ of each component of the bands is given on the side of the figure. Also shown are the results of the earlier paper¹⁰ on the selection rules for the emission process. If the recombination of a trapped hole⁹ and free electron occurs at a site of high enough symmetry that " P_x, P_y " states are not mixed with " P_z " states then the selection rules will be the same as for band-to-band processes.

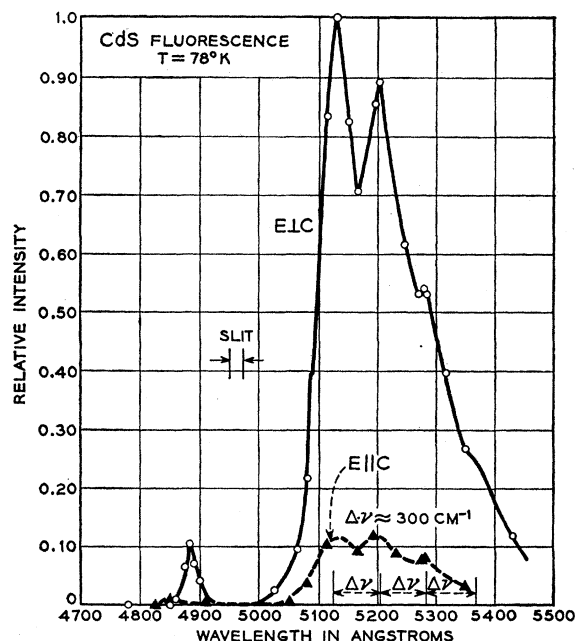


FIG. 2. Edge emission spectrum of CdS at 78°K.

¹⁰ J. J. Hopfield, J. Phys. Chem. Solids **10**, 110 (1959).

¹¹ J. L. Birman, Phys. Rev. Letters **2**, 157 (1959).

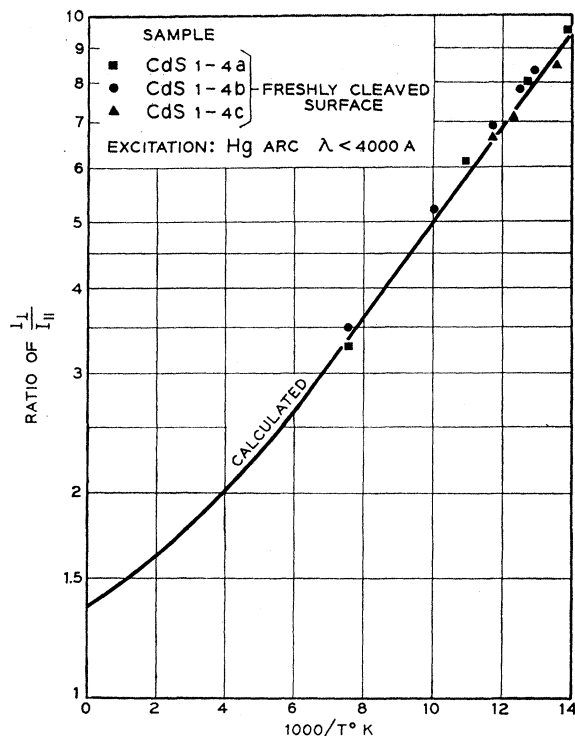


FIG. 3. Ratio of intensity of radiation emitted with E_{\perp} to c axis to that emitted with E_{\parallel} to c axis, as a function of $1/T$. The points are experimental and the solid curve calculated from

$$\frac{I_{\perp}}{I_{\parallel}} = \left(\frac{H_{\perp}}{H_{\parallel}} \right)^2 \left(\frac{\frac{1}{2} e^{\Delta E/kT} + \epsilon}{1 - 2\epsilon} \right),$$

with $\epsilon = 0.28$ $(H_{\perp}/H_{\parallel})^2 = 0.72$ and $\Delta E = 0.014$ ev.

An equilibrium distribution of trapped holes between the levels of the defect characteristic of the lattice temperature will be reached if the relaxation process is shorter than the time required for recombination emis-

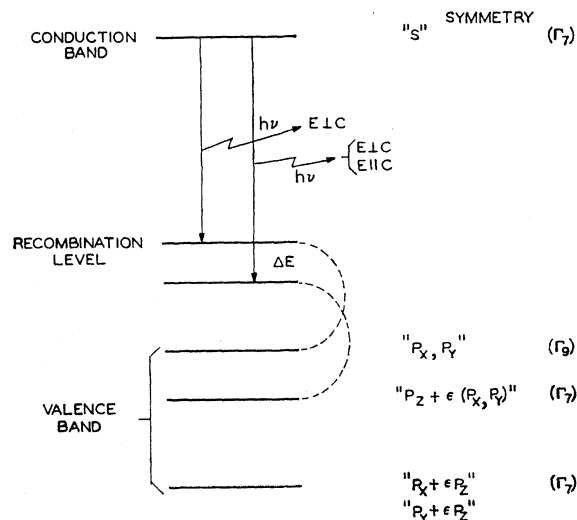


FIG. 4. Energy bands of CdS.

sion. It is known⁷ that at 78°K the light emission, i.e., recombination of free electron and trapped hole, requires times of the order of 10^{-6} second. It seems therefore safe to assume that thermal equilibrium will be reached since the excited carrier should have sufficient time to relax to the lattice temperature.

The intensity of light emitted in the two modes of polarization may be written as:

$$I_1 \propto (H_1)^2 (\frac{1}{2} \text{ population } \Gamma_9 + \epsilon \text{ population } \Gamma_7), \quad (1)$$

and

$$I_{11} \propto (H_{11})^2 [(1-2\epsilon) \text{ population } \Gamma_7], \quad (2)$$

where H_1 and H_{11} are the optical transition matrix elements, and ϵ is fractional mixing of the P_x and P_y wave function with P_z in the lower state. The $\frac{1}{2}$ arises from the normalization. Furthermore, since the ratio:

$$\text{population of } \Gamma_9 / \text{population of } \Gamma_7 = e^{\Delta E/kT}, \quad (3)$$

if ΔE is the separation and a thermal distribution is assumed, then

$$\frac{I_1}{I_{11}} = \left(\frac{H_1}{H_{11}} \right)^2 \left(\frac{\frac{1}{2} e^{\Delta E/kT} + \epsilon}{(1-2\epsilon)} \right). \quad (4)$$

Since the other level is much further removed its contribution will be neglected. From the exciton spectrum analysis⁴ carried out by Thomas and Hopfield a value of $\epsilon=0.28$ can be found (Note: by an unfortunate choice of symbols the ϵ used here differs from Thomas and Hopfield by $\epsilon=\frac{1}{2}-\epsilon_{TH}$.) The term $(H_1/H_{11})^2$ appears only as a sliding scale factor and a value of 0.72 was used to give the best fit in Fig. 3.

Using the two parameters given above the ratio of (I_1/I_{11}) for the edge emission as a function of temperature can be used to determine the energy separation of the levels in the defect by fitting Eq. (4) to the data. The solid curve in Fig. 3 which was the best fit obtained gave a value of $\Delta E=0.014$ ev. This value for the splitting of the levels in the recombination center is in good agreement with the values of the valence band splitting obtained from the exciton analysis.

It should be noted that in accordance with an earlier paper, the edge emission is assigned as the recombination of a free electron with a trapped hole. The present data could equally well be interpreted on the trapped

electron-free hole model in terms of the splitting of the valence band and a thermal distribution of the holes between the different levels within the valence band.

The model of edge emission presented not only gives a temperature dependence of polarization but also predicts that the emission in the two modes shall be displaced in wavelength by $\Delta E \approx 0.014$ ev. Since this is approximately $\frac{1}{3}$ of the longitudinal phonon energy separation between peaks the shift should be observable. Examination of Fig. 2 shows however that except for an apparent loss of resolution the emission polarized parallel to the c axis is not shifted with respect to that polarized perpendicular to the c axis.

The apparent absence of a displacement can probably be understood as a partial mixing, due to some experimental condition, of the two modes of emission. A mixing of a few percent of $E||c$ into $E \perp c$ at 78°K would have almost no effect on either spectral shape of $E \perp c$ or on the ratio since $E \perp c \gg E||c$. On the other hand, a few percent of $E \perp c$ mixed into $E||c$ would contribute a small error to the ratio but more important its first effect would be to cause a loss of resolution in the emission peaks. A possible source for this mixing would be the irregularities present on the cleaved surfaces. Unfortunately, samples were not available which would both fluoresce and contain the c axis in a growth face. Furthermore, optical polishing of the surfaces was not possible since this operation in general destroys edge emission.

In addition the samples available fluoresced so weakly that it was necessary to use fairly wide slits (≈ 0.01 ev) which, being about the same as the shift expected, would make its observation difficult.

It should be pointed out that recently similar measurements on ZnO at Erlangen¹² do show a displacement of the emission polarized perpendicular to the c axis with respect to that emitted parallel to the c axis.

ACKNOWLEDGMENTS

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¹² B. Andress and E. Mollwo, *Naturewiss.* 46, 623 (1959).