

the extreme anomalous skin effect are satisfied, the magnitude of the Hall effect is not sensitive to frequency.

The two fluid model predicts an rf Hall effect to be observable in a superconductor. If a Hall field should be detected experimentally, Hall measurements would provide a useful tool for the study of the band structure of superconductors.

ACKNOWLEDGMENTS

The authors would like to thank the Physics Department of Cornell University for providing the stimulating environment where much of this work was accomplished. One of us (M.S.D.) wishes to acknowledge the National Science Foundation for a postdoctoral fellowship.

Some Optical Properties of CdSe Single Crystals

S. P. KELLER AND G. D. PETTIT

International Business Machine Research Laboratory, Yorktown Heights, New York

(Received August 15, 1960)

Optical transmission and reflection measurements were made on a single crystal of CdSe (crystal class C_{6v}) with light polarized parallel and perpendicular to the c axis. The absorption coefficients, μ_1 and μ_{11} , were determined and are presented as functions of incident photon energy, at room temperature. The selection rule, $\mu_1 > \mu_{11}$, expected for all solids in the crystal classes C_{nv} and C_n , where $n=3, 4$, or 6 , is very well obeyed in CdSe. The absorption coefficients are not simple functions of the photon energy, but are nearly exponential and almost follow Urbach's rule.

The fluorescence of the single crystal has been measured at 77°K. It is peaked at 920 m μ and it is slightly polarized perpendicular to the c axis. The results are similar to what has been obtained for hexagonal ZnS.

I. INTRODUCTION

RECENTLY, there have been extensive studies concerning the anisotropic behavior of the fundamental optical absorption processes in crystals possessing a unique direction. CdS has been studied by Dutton,¹ Thomas and Hopfield² and by Gross and Razbirin.³ Piper, Marple, and Johnson,⁴ Lempicki,⁵ and Keller and Pettit⁶ have studied ZnS. Thomas⁷ has reported on ZnO and Casella and Keller⁸ have reported on tetragonal BaTiO₃. For all of these materials it was found that at the absorption edge, light polarized perpendicular to the c axis is more strongly absorbed than light polarized parallel to the c axis. Hopfield⁹ has given a theoretical treatment for ZnO and Wheeler¹⁰ has treated CdS using the exciton picture, Birman¹¹ and Casella¹² independently proposed an explanation of the

CdS and ZnS data by invoking interband transitions. The selection rule follows whether we assume an exciton model or direct interband transitions. There have also been attempts to apply the selection rules to fluorescent emissions resulting from transitions, involving deep lying states.^{5, 6, 11, 13}

Birman¹¹ has based his derivation of the selection rule, $\mu_1 > \mu_{11}$, where μ is the absorption coefficient, on explicit assumptions regarding the detailed symmetries of the valence and conduction bands of ZnS. Casella¹² has noted that, at the absorption edge, the selection rule follows independently of the symmetries of the bands, provided only that they be different. Both of these treatments are pertinent to and are borne out by the data of the previous workers. Birman's model is more amenable to a physical interpretation in that there is deduced from it two closely spaced valence bands derived from a spin-orbit interaction. The double valence band model has afforded an interpretation for measurements of the photoconductivity in CdS¹⁴ and ZnS,¹⁵ using polarized light.

The material CdSe has the wurtzite structure and it allows for the testing of the applicability of the above concepts to another compound in the crystal class C_{6v} . Transmission measurements were made and it has been determined that the selection rule is fairly well obeyed

¹ D. Dutton, Phys. Rev. **112**, 785 (1958); J. Phys. Chem. Solids **6**, 101 (1958).

² D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

³ E. F. Gross and B. S. Razbirin, J. Tech. Phys. U.S.S.R. **27**, 2173 (1957) [translation: Soviet Phys. (Tech. Phys.) **2**, 2014 (1957)].

⁴ W. W. Piper, D. T. F. Marple, and P. D. Johnson, Phys. Rev. **110**, 323 (1958); W. W. Piper, P. D. Johnson, and D. T. F. Marple, J. Phys. Chem. Solids **8**, 457 (1959).

⁵ A. Lempicki, Phys. Rev. Letters **2**, 155 (1959).

⁶ S. P. Keller and G. D. Pettit, Phys. Rev. **115**, 526 (1959).

⁷ D. G. Thomas, Bull. Am. Phys. Soc. **4**, 154 (1959).

⁸ R. C. Casella and S. P. Keller, Phys. Rev. **116**, 1469 (1959).

⁹ J. J. Hopfield, Bull. Am. Phys. Soc. **4**, 154 (1959).

¹⁰ R. G. Wheeler, Phys. Rev. Letters **2**, 463 (1959).

¹¹ J. L. Birman, Phys. Rev. Letters **2**, 157 (1959); Phys. Rev. **115**, 1493 (1959).

¹² R. C. Casella, Phys. Rev. **114**, 1514 (1959).

¹³ D. M. Warschauer and D. C. Reynolds, Phys. Rev. Letters **3**, 370 (1959).

¹⁴ R. L. Kelly and W. J. Fredericks, Phys. Rev. Letters **2**, 389 (1959).

¹⁵ G. Cheroff, R. C. Enck, and S. P. Keller, Phys. Rev. **116**, 1091 (1959).

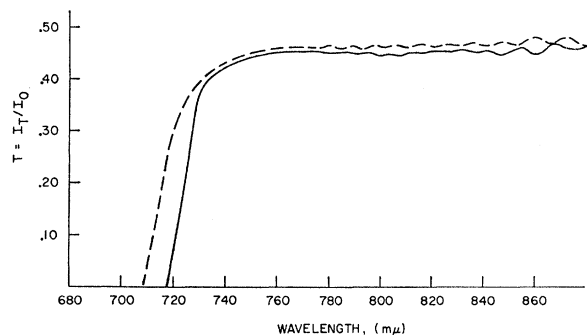


FIG. 1. Transmission, $T = I_T/I_0$, of CdSe. The solid curve is for light polarized perpendicular to the c axis and the dotted curve is for light polarized parallel to the c axis. The wavelength scale is in millimicrons, $m\mu$.

within the absorption edge. There has not been seen the reversal of polarization deep within the edge as has been reported for ZnS⁶ and hinted at for CdS.¹

The fluorescence spectrum has been measured both at room temperature and at 77°K and it is the same as that reported for powders.¹⁶ The emission at 77°K, is slightly polarized perpendicular to the c axis as has been reported for the other materials.^{1,3,5,6,13}

In Sec. II we present a description of the sample preparation and of the experimental setup. The experimental results are presented in Sec. III and a conclusion is given in Sec. IV.

II. CHEMICAL PREPARATION AND EXPERIMENTATION

The crystal preparation is a common one and is similar to that used for ZnS crystal growth. The starting material was G.E. CdSe which has impurities of Al, Cu, Fe, Mn, Pb, and Si between 1 and 10 ppm, and Zn at about 20 ppm.

The powdered CdSe was sealed in a quartz tube and placed in a temperature gradient such that the charge was located in the hottest part of the furnace which was maintained at 950°C. The tube remained in the furnace for about a day. The crystals obtained were either needles or plates. A plate of uniform appearance and of 8 μ thickness was chosen for the measurements. The crystals were not analyzed for impurities due to their dearth. It is assumed that they have roughly the same impurity content as the starting material. (This was true for ZnS.⁶)

The apparatus for transmission and reflection measurements consisted of a Cary Spectrophotometer Model 14. It has a 4 Å resolution in the near infrared region where the measurements were made. Wavelength reproducibility is 0.5 Å and wavelength accuracy is 4 Å. For transmission measurements, the crystal was placed in the sample beam after a Polaroid film. Difficulty was encountered if a Polaroid film was simultaneously placed in the reference beam and so a background was

obtained by removing the crystal and measuring the transmission of the Polaroid film. In this way we corrected for the polarizing effects of the instrument. For reflection measurements, light from an externally mounted tungsten lamp was passed through a Polaroid film and reflected from the sample and focused into the Cary set for single beam operation. A reference signal was obtained by replacing the sample with a mirror. The angle of incidence was less than 10°.

The polarizing films were commercial HR Polaroid films which are useful in the near infrared. For work at shorter wavelengths, HN 32 Polaroid films were used. The efficiency of the Polaroids was almost 100% in the wavelength region of interest.

The fluorescence data were obtained with the same apparatus that was described in reference 6. A 7102 RCA photomultiplier tube as well as a PbS cell were used as the detectors and a 1000w tungsten projection lamp was used as the light source. The polarization measurements were made with the Polaroid films described above and were made at 77°K where the intensity of emitted light was higher than at room temperature since at room temperature the intensity was so low that no meaningful data were obtainable.

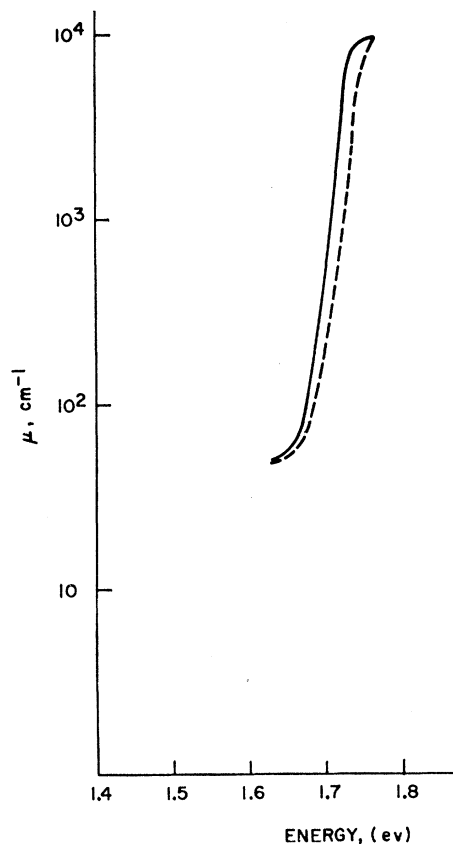


FIG. 2. The absorption coefficient, μ , plotted as a function of incident photon energy in electron volts. The solid curve denotes μ_I and the dotted curve denotes μ_{II} .

¹⁶ G. F. J. Garlick, Proc. Phys. Soc. (London) **B67**, 442 (1954).

III. EXPERIMENTAL RESULTS

A. Transmission Results

In treating our data we have used the well-known expressions:

$$I_T = I_0 \left\{ \frac{(1-R)^2 e^{-\mu t}}{1-R^2 e^{-2\mu t}} \right\}, \quad (1)$$

and

$$I_R = I_0 R \left\{ 1 + \frac{(1-R)^2 e^{-2\mu t}}{1-R^2 e^{-2\mu t}} \right\}, \quad (2)$$

where I_0 , I_T , and I_R are the intensities of the incident, transmitted, and specularly reflected light, respectively, μ is the absorption coefficient, R is the reflection coefficient, and t is the crystal thickness. In the present paper, I_T , I_0 , and I_R and t were all measured and Eqs. (1) and (2) were programmed on the IBM-704 computer. The quantities μ and R were determined as functions of photon energy for the two directions of light polarization.

Figure 1 presents a plot of the transmission, $T = I_T/I_0$, versus wavelength of light in $m\mu$ for the two directions of polarization. The long-wavelength structure is due to multiple-reflection interference effects. Figure 2

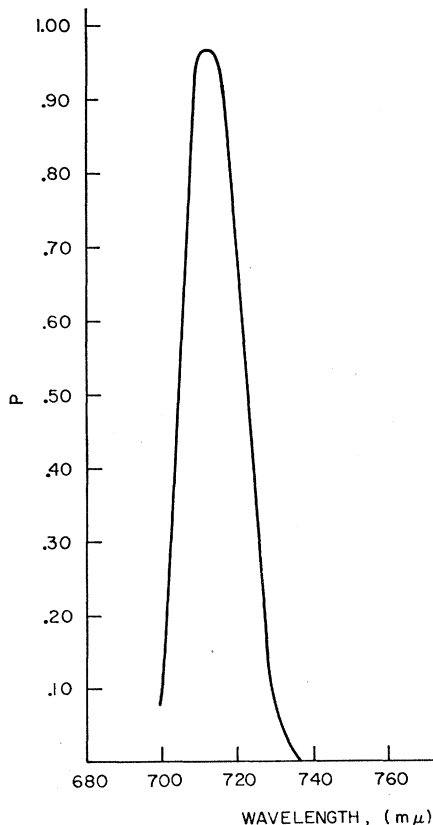


FIG. 3. The degree of polarization, P , plotted against the wavelength, P is defined as $(T_{11} - T_{\perp}) / (T_{11} + T_{\perp})$ where $T = I_T/I_0$. The wavelength scale is in millimicrons.

presents the results of the machine solution where μ_{\perp} and μ_{11} are plotted as functions of incident photon energy. The sample was too small to etch or polish and hence we could not minimize diffuse reflection. As a result in regions of low absorption $I_0 \neq I_R + I_T$. We tried to correct for this but the correction was not perfect which resulted in the value of 50 cm^{-1} for μ at 1.63 eV where the crystal does not absorb.

It can be seen that the μ 's vary between 50 and 10^4 cm^{-1} between 1.65 and 1.77 eV. In this range R_{\perp} and R_{11} vary between 0.23 and 0.32. As can be seen from Fig. 2, the frequency dependences of the absorption coefficients do not follow the integral or half-integral powers predicted by various models. Between 1.69 and 1.74 eV the dependences are nearly exponential, consistent with Urbach's rule.

In Fig. 3 we present the conventional degree of polarization $P = (T_{11} - T_{\perp}) / (T_{11} + T_{\perp})$. The effect is larger here than reported for BaTiO_3 ⁸ and for CdS ¹ and it is just slightly larger than reported for ZnS .⁶ This can also be seen by noting the values of the absorption coefficients in Fig. 2.

B. Fluorescence Measurements

The CdSe crystal is weakly fluorescent at room temperature and more strongly fluorescent at 77°K. The spectrum is the same as that we have measured for powdered samples, which spectrum has been reported earlier.¹⁶ At room temperature the spectrum consists of a single peak at around 1.20μ (1.03 eV). At 77°K, the emission intensity is increased and consists of a peak at $920 \text{ m}\mu$ (1.33 eV) and the one at 1.20μ . The relative heights of these two peaks differ for different samples. In the case of the single crystal the 77°K spectrum showed mainly the $920 \text{ m}\mu$ peak and a trace of the 1.20μ peak. The excitation peak at room temperature is around $725 \text{ m}\mu$ (1.72 eV) and at 77°K it is near $700 \text{ m}\mu$ (1.78 eV). This probably is indicative of an energy gap increase of 0.06 eV. The shift in the gap for these two temperatures is in the same direction but is smaller than that reported for other materials ($\sim 0.20 \text{ eV}$ for ZnS , $\sim 0.15 \text{ eV}$ for CdS , $\sim 0.14 \text{ eV}$ for BaTiO_3). The fluorescence is analogous to the "blue-green" fluorescence in ZnS . We measured the fluorescence of CdSe powders with Cu purposely added in varying amounts. The emission was the same as that manifested by the single crystal and its intensity increased with increased Cu addition.

The intensity of the room temperature fluorescence, in the single crystal, is so weak that we could not determine meaningfully any polarization effects. However, at 77°K we determined that the light emitted at $920 \text{ m}\mu$ was weakly polarized perpendicular to the c axis. The polarization of the emission, defined as $(I_{\perp} - I_{11}) / (I_{\perp} + I_{11})$ where I is the intensity of the emitted light, is about 0.06. This is the same sign and the same magnitude of the polarization found for

unactivated crystals of ZnS⁶ at 77°K and it is the same behavior that Lempicki reports.⁵

If we assume that the emission is due to Cu which is not unreasonable since, as we stated above, the intensity of the particular emission increases with increasing Cu concentration in the powders, then the data are only partly consistent with that reported for Cu activated ZnS.⁶ In that case the polarization of the emission, at 77°K, was a function of the wavelength of exciting light. With the energy of the exciting light greater than the gap, the fluorescence was polarized perpendicular to the *c* axis and with the exciting light at the long-wavelength side of the gap the fluorescence was polarized parallel to the *c* axis. In the present case the exciting light was within the gap and hence the perpendicular polarization is consistent with the ZnS data. However, these data are not in agreement with those reported by Warschauer and Reynolds¹³ for Cu activated CdS. They report the Cu emission to be polarized parallel to the *c* axis but they do not report if this is a function of the wavelength of exciting light.

IV. CONCLUSION

We have seen that the experimental results for the transmission data agree with the theoretical prediction in that $\mu_i > \mu_{ii}$. If we accept the double valence band picture of Birman,¹¹ we see that the conduction band belongs to the Γ_7 irreducible representation, that the uppermost valence band belongs to the Γ_9 irreducible representation, and the next lowest valence band belongs to the Γ_7 irreducible representation. (We shall ignore the lowest Γ_7 valence band which was derived from a crystal field splitting.) Transitions between the Γ_7 conduction band and the Γ_9 valence band are allowed with the absorption or emission of perpendicularly polarized light and the transitions between the Γ_7 conduction band and the Γ_7 valence band are allowed with the absorption or emission of light with either direction of polarization.

One is tempted to attribute the two apparent transmission spectra shown in Fig. 1 to the existence of the two bands with the separation of the two spectra giving the spin-orbit interaction energy. However,

there are several inconsistencies with such a picture. First, since $\Gamma_7 \leftrightarrow \Gamma_7$ transitions allow both directions of polarization one would expect a positive jog in the T_1 curve at the onset of the $\Gamma_7 \leftrightarrow \Gamma_7$ transitions. This is seen to be untrue in that both curves preserve smooth continuities over the whole wavelength range. From another point of view, since these considerations apply at $\mathbf{k}=0$, one would expect that as one went away from $\mathbf{k}=0$, the selection rules would break down via $\mathbf{k} \cdot \mathbf{p}$ interactions and both curves would merge into each other just to the short wavelength side of their onset. This higher energy region would correspond to transitions from within the valence bands to the conducting bands, which involves transitions at $\mathbf{k} \neq 0$. This merging of the spectra is seen not to be true since both curves maintain their identities over the whole wavelength region. If one ignores these difficulties and pursues the previous ideas, then one arrives at spin-orbit interaction energies of 0.04 eV for ZnS, 0.02 eV for CdS, 0.04 eV for BaTiO₃, and 0.02 eV for CdSe.

Turning to the fluorescent data, we have seen that the emitted light is perpendicularly polarized. Its energy is about 0.45 eV less than the band gap. If this level is due to Cu or to some other imperfection, we see its binding energy (~ 0.45 eV) is appreciable. If one assumes the emitted light is due to a Schon-Klasens type of transition, then we see that the level lies 0.45 eV above the valence band. This binding energy is so large that it is difficult to see why the symmetry of this level is given by the symmetry of the band from which it has been lifted. Similarly, if a Lambe-Klick model is assumed, then the level lies nearer the conduction band and again it is difficult to see why its symmetry should be clearly defined by the symmetry of the conduction band. If one ignores this difficulty then either model applies. It is, of course, possible that since the level is a deep one, then the symmetries of an excited state and the ground state of the center will determine the polarization of the emitted light.

ACKNOWLEDGMENTS

We wish to thank D. Ridgley and J. Kucza for sample preparation and R. Casella for helpful discussions.