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Electric Field Induced Light Absorption in CdS

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A shift of the band edge in CdS has been brought about by application of a high electric field to CdS crystals. High fields are produced at the rectifying junction between a conducting CdS crystal and an electrolyte solution. A shift of the band edge of 70 A was observed for an applied emf of 120 volts. The effect is reversible and the absorption spectrum of the crystal after removing the field is identical with that before the field was applied. The absorption parallel to the crystal c axis and the absorption perpendicular to the c axis are affected in the same way by the applied field. The enhanced absorption at the band edge is believed to be the result of photon-assisted tunneling of electrons from valence band to conduction band in the high-field region within the crystal.

INTRODUCTION

THE effect of a strong electric field on the absorption of light by a crystal of an insulator has been discussed by Franz and by Keldysch.[1] They predict that the electric field will cause the band edge for fundamental absorption to shift toward longer wavelengths. Some recent experiments reported by Böer, Hänsch, and Kümmel[2] have demonstrated a shift of the absorption edge within localized regions in CdS crystals when an electric field was applied. In these experiments two gold electrodes were used and the crystals were photographed by transmitted light which was monochromatic and whose wavelength was slightly longer than that where fundamental absorption begins. On the application of an emf of about 1000 volts there appeared dark ringlike regions which moved from cathode to anode as the voltage was increased. These were attributed to the type of field induced absorption discussed by Franz and Keldysch. This paper describes some experiments which demonstrate a similar field induced light absorption. The technique used here for producing high fields gives a uniform darkening of the crystal with much lower applied voltages and facilitates quantitative study of the effect.

Application of a high electric field to an insulator has the result that electrons with a given total energy exist in states which lie in the filled band at one point in space and in the conduction band at another point in space. This is the situation which leads to Zener emission.[3] A barrier to electron motion is set up but the barrier may be traversed by quantum mechanical tunneling under certain conditions. There is then a finite electron density in states lying in the forbidden energy gap. Figure 1 is a schematic illustration of this state of affairs, using the conventional one-dimensional band picture of an insulator. The slope of the bands shows the effect of an externally applied electric field. An electron in the filled band at point A has available to it states of the same energy which lie in the conduction band but are spatially limited to coordinates lying to the right of point B. Free motion of the electron from A to B along the line of constant total energy is prevented by the triangular potential barrier, ACB. Tunneling into the barrier gives a finite electron density at points in the forbidden zone such as D. Light absorption by such an electron may occur, raising the electron to state E. The electron then moves through the conduction band as indicated.

Use of Electrolyte Solution to Obtain High Fields

Observation of field induced absorption requires electric fields within the crystal of 10^5 volt/cm or larger.[1] It has been found possible to obtain high fields in CdS crystals by making use of the rectifying contact which occurs between CdS and a water solution of an ionic salt such as KCl. A study has been made of the properties of such contacts and a full account will be given elsewhere. The brief discussion which follows will suffice to explain the general features of the observed behavior. The CdS crystals which were used contained small amounts of chlorine which was incorporated during their growth in an atmosphere containing HCl. Chlorine in CdS forms a shallow donor level lying

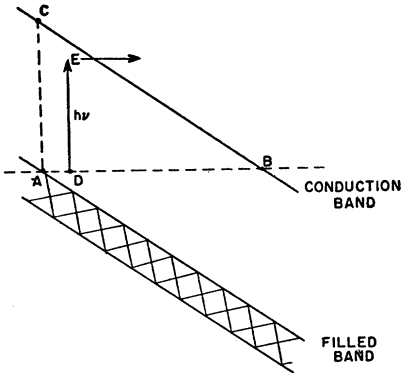

FIG. 1. Energy bands of an insulator in an electric field.

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[2] K. W. Böer, H. J. Hänsch, and U. Kümmel, Z. Physik **155**, 170 (1959); K. W. Böer, Z. Physik **155**, 184 (1959); also unpublished experiments of W. Ruppel.

[3] C. Zener, Proc. Roy. Soc. (London) **A145**, 523 (1934).

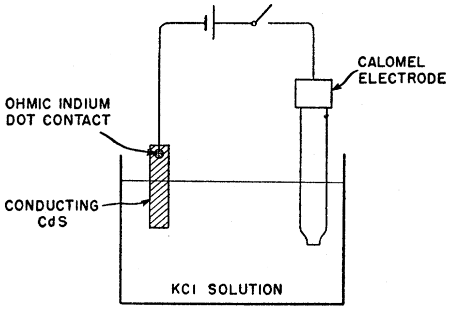

FIG. 2. Experimental arrangement for obtaining high electric fields in CdS crystals.

0.04 ev below the conduction band.[4] The chlorine concentration was sufficient to give the crystals resistivities around 10 ohm-cm. When the crystal is in contact with a metal the current across the boundary is carried by electrons just as in the interior of the crystal. This is no longer the case when the crystal makes contact to an ionic solution since the current in the solution is entirely due to the transport of ions. There must be a change in the mechanism of conduction at the boundary in this case. Conduction is accompanied by the transport of ions from the crystal into the solution along with the formation of neutral atoms on the surface. An illustration of this behavior is the experiment shown in Fig. 2. A platelike crystal of conducting CdS is immersed halfway into an ionic solution and forms a portion of an electric circuit such that negative charge flows into the top of the crystal through an ohmic metal-CdS contact[5] and out the bottom of the crystal through a CdS-solution contact. The transport of charge from the crystal into the solution is by negative ions so sulfur ions from the crystal must go into solution. This leaves an excess of cadmium ions on the crystal at its surface. These would soon stop the flow of current were it not for the fact that they may be readily neutralized to cadmium metal by the free flow of electrons through the crystal from the external circuit. The result of the experiment is that with a battery of several volts and the polarity illustrated, the portion of the crystal in the solution blackens with a deposit of metallic cadmium as soon as the switch is closed. If the polarity of applied voltage is reversed, then the situation is quite different. Electrons now flow upward through the crystal and out into the external circuit. There is, however, no ready supply of electrons which can enter the crystal at the contact with the solution. Removal of electrons from negative ions in the solution is a possible source, but there is no evidence of electrolysis even when 140 volts is applied by the battery. This is in agreement with estimates which show that the energy levels of electrons bound to chloride and hydroxyl ions in solution lie quite deep.[6] A more likely source for the electrons seems to be Zener emission from the filled band to the conduction band in a high field region within the CdS near the solution boundary. The fact that no electrolysis of the water occurs with high applied voltage suggests that the greater part of the voltage drop occurs within the crystal. In any event, the CdS-solution contact biased in this way has a high resistance of the order of 10^9 ohms. (Note that the CdS crystal has a resistance of about 100 ohms between ohmic metal contacts and the solution has a resistance of a few hundred ohms. For the calomel electrode, resistance is not well defined since it is not an ohmic conductor. The potential drop across the electrode is approximately independent of the current carried so its differential resistance, dV/di, is negligible.) It appears that the field is concentrated in an exhaustion barrier which is adjacent to the solution and similar to that in a metal-semiconductor rectifying contact. Thus the direction of the field is perpendicular to the surface of the crystal. For observation of the effect of the field on the absorption spectrum of the crystal it is, of course, a great advantage that the solution contact is completely transparent.

EXPERIMENTAL

The crystals of CdS used were in the form of flat plates about 2×10×0.1 mm in their dimensions. They were quite transparent to wavelengths longer than that corresponding to the band edge which lies at about 5200 A. The apparatus shown in Fig. 2 was used with the positive terminal of the applied voltage connected to the CdS crystal through the ohmic indium dot con-

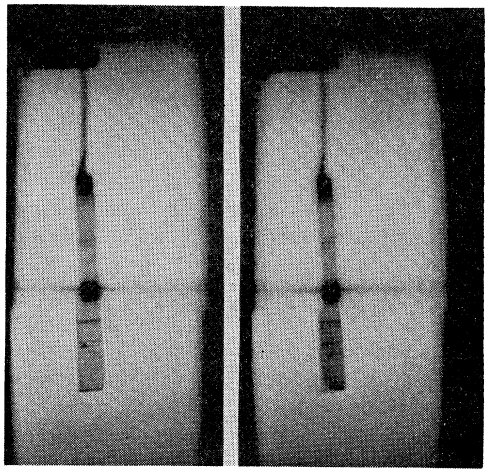

FIG. 3. Photographs of CdS immersed halfway in KCl solution. Left: No applied voltage. Right: 120 volts applied. Top half of crystal is out of focus because the water makes the apparent distance of the bottom half from the camera less than that of the top half.

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[4] R. H. Bube, Proc. Inst. Radio Engrs. 43, 1836 (1955).

[5] R. W. Smith, Phys. Rev. 97, 1525 (1955).

[6] R. W. Gurney, *Ions in Solution* (Cambridge University Press, New York, 1936), p. 189; W. Ruppel, A. Rose, and H. J. Gerritsen, Helv. Phys. Acta 30, 238 (1957).

tact. An image of the slit of a Bausch and Lomb monochromator was focussed on a ground glass plate mounted 1 cm behind the crystal. The uniformly lighted glass plate was viewed through the crystal and was masked so that only light passing through the crystal was observed. For a given wavelength the intensity of the light transmitted with no applied voltage was compared to that transmitted when the voltage was applied. Light intensity measurements were made with a Spectra spot photometer consisting of a photomultiplier and optical system for focussing on the light coming from a small area which was less than that of the crystal face. Monochromator slit widths were 0.3 to 0.5 mm in different measurements giving wavelength bandwidths of 5 to 8 A. The electrolyte was 0.1-molar KCl in water. A saturated calomel electrode was used as the second contact to the solution. For the small currents found here the potential drop across the calomel electrode-solution interface is independent of the magnitude or direction of the current.

CdS crystals have hexagonal structure and the *c* axis lies in the plane of the platelike crystals. Near the band edge the absorption differs for the two polarizations, parallel and perpendicular to the *c* axis. A sheet polarizer was placed between the exit slit of the monochromator and the crystal and separate observations were made for light of the two different polarizations.

RESULTS AND INTERPRETATION

Figure 3 shows a photograph of a crystal mounted as in Fig. 2. Monochromatic light of wavelength 5110 A provides the illumination. The two photographs compare the crystal, viewed by transmitted light, without applied voltage and with applied voltage. It can be seen that the portion of the crystal below the surface of the water darkens uniformly on applying the voltage. The darkening occurs within a tenth of a second on applying the voltage and disappears in a comparable time on removing the voltage. Some crystals deteriorate on the surface after repeated application and removal of the voltage but several showed no apparent change after approximately 100 cycles of applying and removing the voltage. The darkening cannot be explained by Joule heating of the crystal due to current flow. Crystals which carry the smallest currents for a given applied voltage show the most pronounced darkening. As a specific example, one crystal showed a shift in the band edge of 10 A when an emf of 20 volts was applied. The darkening occurred in a time considerably less than one second. A current of 0.02 microampere flowed through the crystal so the total power available for joule heat was 4×10^{-7} watt. The area of the crystal was 0.1 cm^2 and the heat capacity of CdS is 1.8 joule/deg-cc. Assuming the entire heating to occur in a barrier layer next to the surface and having a thickness of 1000 A, the maximum temperature rise in 1 second would be 0.02°C. The band edge in CdS shifts about 1 A/deg C. Thus the observed darkening cannot be a heating effect. Considering the magnitude of the current, it is also clear that the darkening cannot be due to formation of a highly colored material by electrode reaction.

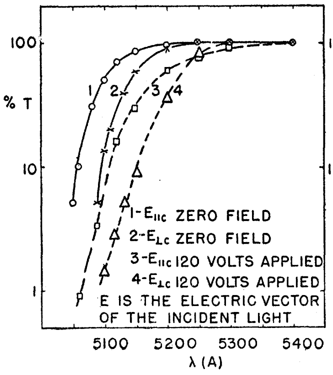

FIG. 4. Percent transmission for light of various wavelengths through a CdS crystal, with and without applied voltage. Separate curves are shown for light polarized parallel and perpendicular to the crystal *c* axis.

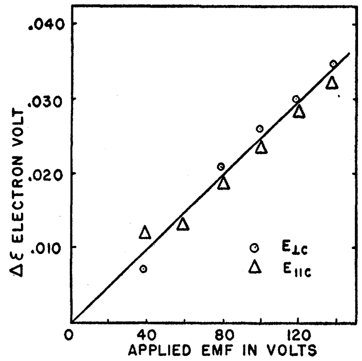

FIG. 5. Shift of band edge as a function of applied voltage.

Figure 4 shows a typical plot of percent transmission vs wavelength for light of two different polarizations, with and without applied voltage. The effect is about the same for each polarization and shows a shift of the band edge of 70 A on applying the voltage. In analyzing the data, reflection losses were corrected by assuming that at 5400 A and at longer wavelengths, the crystal, in the absence of applied field, had no true absorption and that the difference of the observed transmission from 100% was due to reflection losses.

Figure 5 shows a typical plot of the shift of the band edge, in energy units, vs the applied voltage. The band edge was arbitrarily taken as the frequency at which the percent transmission reaches 25%. It is seen that the relation is a linear one.

According to the picture of field induced absorption elaborated in the introduction, each light quantum absorbed liberates one electron into the conduction band. In the absence of collision ionization there should be a photocurrent directly proportional to the absorbed light intensity. A crystal, mounted as in Fig. 2 was illuminated with light of two different known constant intensities. The wavelength was 5110 A which is in the region where field induced absorption occurs. Photocurrent as a function of applied voltage is shown by

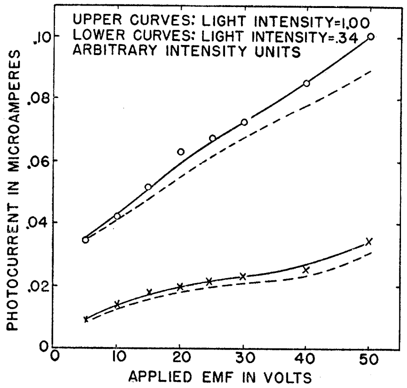

FIG. 6. Photocurrent for constant incident light as a function of applied voltage. Dotted lines correct for the fact that light absorption increases with increasing voltage.

the solid lines in Fig. 6. Absorption increases with applied voltage, and the ratio of transmitted light intensity without applied voltage to that with applied voltage is shown in Fig. 7. These data were then used to obtain the photocurrent per unit intensity of absorbed light which is shown by the dotted lines in Fig. 6. The detailed mechanism of the photocurrent is not yet clear. The existence of a photocurrent is in agreement with the above picture of the light absorption.

These results are interpreted as being an example of the type of electric field induced absorption predicted by Franz. This implies that electric fields of 10^5 to 10^6 volts/cm are set up in the crystal on the application of the modest voltages employed here. Such high fields might also shift the band edge of the crystal by setting up strains which change the interatomic distances. It is difficult to distinguish experimentally between a shift in the band edge due to this process and one due to the process discussed by Franz. Two pieces of evidence suggest that the observed effects are not due to strain. First, the data in Fig. 4 show no obvious differences for light polarized parallel and perpendicular to the *c* axis of the crystal. Second, crystals, mounted as in Fig. 2, were observed between crossed polarizers during the application of an electric field and no effect could be observed though this is a fairly sensitive test for crystal strain.

The voltage drop probably occurs across a barrier layer similar to a Schottky barrier. It is reasonable to expect a barrier width of 10^{-4} cm and this would give an average field of 10^6 volt/cm with 100 volts applied. The direction of the field would be everywhere perpendicular to the surface of the crystal. Franz[1] gives an equation relating the shift of the band edge to the applied field. The data here unfortunately cannot be used as a sensitive test of the validity of this equation. The field in the crystal can be related to the applied voltage only if the shape of the barrier layer is known. Barrier layers of the kind encountered here have not been sufficiently studied to justify the use of a theoretical expression for quantitative purposes. In addition, the width of the barrier layer (and therefore the length of the absorbing path for the field induced absorption) is probably a function of the applied voltage. This complicates the problem of determining the position of the band edge accurately.

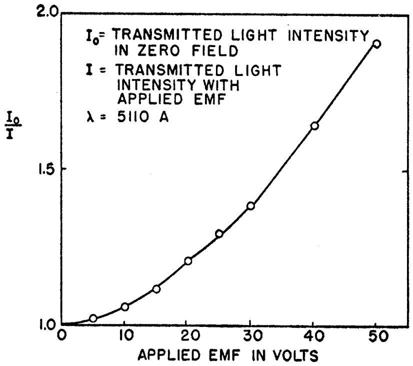

FIG. 7. Ratio of the intensity of transmitted light intensities with and without applied voltage. These data are used to correct the photocurrents in Fig. 6. Without applied voltage the percent transmission is 25%.

CONCLUSIONS

An electric field induced light absorption has been observed in CdS crystals. A high field is produced by utilizing the rectifying contact between CdS and an electrolyte solution. The light absorption is believed to be due to photon assisted tunneling of electrons from the valence band to the conduction band of the crystal.

ACKNOWLEDGMENTS

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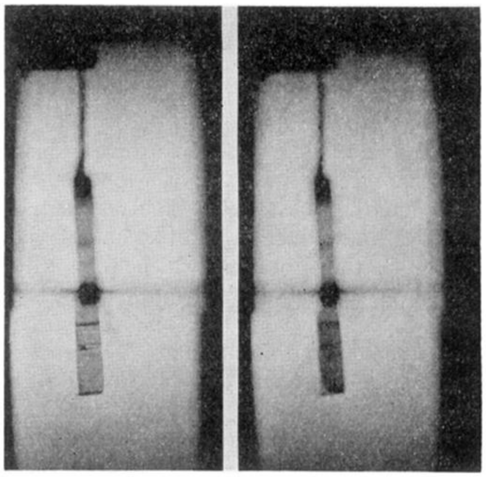

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