Effects of Polarized Light on Photocurrents and Photovoltages in ZnS

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The anomalous short circuit photocurrents in ZnS have been measured using polarized light. In spite of the fact that for a given wavelength, light polarized perpendicular to the c axis is more strongly absorbed than light polarized parallel to the c axis, there are wavelength regions in which the absolute magnitude of the short circuit photocurrents are smaller for perpendicularly polarized light. The data are consistent with a double valence band model.

PHOTOVOLTAGES larger than the energy gap have been reported for hexagonal ZnS.[1-4] In addition, the sign of the open circuit photovoltage (and the short circuit current) reverses with wavelength.[2,4] Similar reversals have been reported for CdS.[5] From measurements of the pyroelectric effect made in this laboratory and by Lempicki,[4] it has been definitely established that the sign of the photovoltage at a given wavelength is associated with the polarity of the c axis. These phenomena are related to general effects of the crystal symmetry on interactions with light.

Another type of measurement falling into this category involves the polarization of light absorbed or emitted by the crystal. As an example we cite the work done on the dichroic optical absorption of ZnS and CdS[6-8] as well as the work on fluorescent measurements.[7,9] The results of the absorption measurements show that light polarized perpendicular to the c axis is more strongly absorbed than light polarized parallel. This is consistent with the optical selection rules derived theoretically by Birman[10] and Casella.[11]

Since the electrical and optical properties are related to the crystal symmetry, it is reasonable to measure the electrical properties with polarized light. This has been done for the photoconductivity of CdS[12] with externally applied fields. We have measured the short circuit photocurrent as a function of the wavelength of incident light for the two directions of light polarization for ZnS. This communication presents the results.

EXPERIMENTAL RESULTS AND DISCUSSION

The measurements have been made by adding a polarizer to instrumentation which together with the

sample preparation has been described in reference 2. It is important to discuss in some detail the nature of our crystal samples. Among workers in the field[2-4] there is some difference of opinion as to the role that crystalline disorder plays in the various properties of hexagonal ZnS. In an attempt to relate crystal disorder, such as inclusions of stacking faults and cubic phase, we have examined many samples for these inclusions. Sixty-five single crystals of hexagonal ZnS (40 unactivated and 25 activated with various combinations of Cu, Al, and Mn) were analyzed by x-ray diffraction techniques. (The x-ray radiation had no effect on the electrical properties.) Most of the crystals were about 4 mm long and exhibited uniform birefringent banding. With these, a one-mm spot in the middle of the crystal was chosen for x-ray examination. With crystals that exhibited heavy banding at one or more points, the one-mm spot included a heavily banded region. A few crystals were examined at several points.

The x-ray patterns were analyzed for relative amounts of stacking faults and cubic phase present. The unactivated crystals show large variations in the amounts of stacking faults and cubic phase present, ranging from none of each to large amounts of each. The activated crystals exhibited much less or no stacking faults and no cubic phase. It appears that the presence of Cu minimizes the density of stacking faults.

In general, the results for the unactivated samples show only a slight correlation between the magnitude of the photovoltages and the stacking fault density. There was no correlation between the photovoltages and the amount of cubic phase present. The activated crystals exhibit a slight correlation between the stacking faults and the photovoltage in the uv but not in the visible region of the spectrum. In all wavelength regions the activated crystals appeared to have larger photovoltages than the unactivated samples with about the same density of stacking faults. Lempicki[4] reported results for only unactivated samples and his results indicate better correlations than do ours.

About 25% of the crystals examined with x-rays were examined further for the effects of polarized light on the short circuit photocurrent, I_{sc}. The samples were selected at random from those crystals that had appreciable photocurrents. Figure 1 presents the results obtained for the unactivated samples. We have plotted

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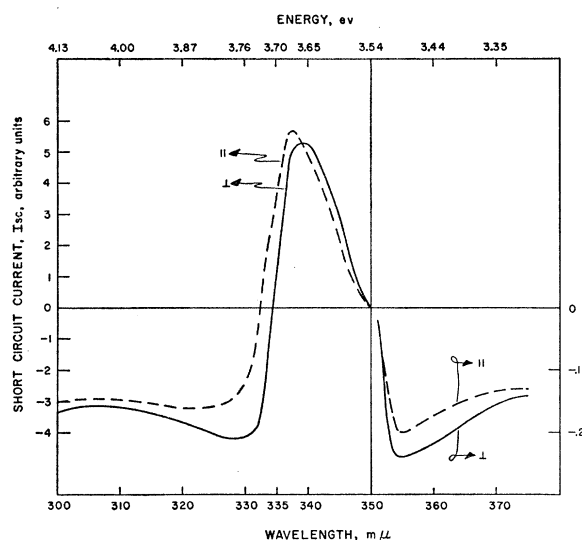[12] R. L. Kelly and W. J. Fredericks, Phys. Rev. Letters 2, 389 (1959).

ENERGY, ev

FIG. 1. The short circuit current, I_{sc}, for unactivated crystals, plotted against the wavelength of light in millimicrons and the energy in ev. The wavelength scale is linear. The solid curve represents data obtained with light polarized perpendicular to the c axis and the dashed curve represents data obtained with light polarized parallel to the c axis. 30% of the crystals exhibit the properties shown to the right of the solid line which indicates a change in the I_{sc} scale. The remainder of the crystals show no separation for the two curves.

the short circuit current as a function of the wavelength of incident light for light polarized perpendicular and parallel to the c axis. With 70% of the crystals measured there was no separation between the two curves at wavelengths longer than 350 mμ, while 30% show the separation as indicated. Figure 2 presents the results for the activated crystals.

As mentioned previously it has been found experimentally for ZnS that for a given wavelength, light polarized perpendicular to the c axis is more strongly absorbed than light polarized along the c axis both in the fundamental and in the impurity absorption regions, in agreement with theory. Since I_{sc} is proportional to the amount of light absorbed[2] we expected that perpendicular light would lead to a larger absolute value of the short circuit current, $|I_{sc}|$, than parallel light in the spectral regions shown in Figs. 1 and 2.

The data for unactivated crystals shown in Fig. 1 have the expectation fulfilled in the region within the absorption band (less than 333 mμ) and at the absorption edge (between 338 and 350 mμ). Only 30% of the samples have the expected results at the long wavelength side of the edge (between 352 and 375 mμ) whereas $|I_{sc}|_{\perp} \leqslant |I_{sc}|_{\parallel}$ for the region between 333 and 338 mμ and between 350 and 352 mμ for all the crystals, contrary to the results expected from absorption data. The data for the activated crystals are shown in Fig. 2. The expectation, from absorption data, is fulfilled in the region deep within the absorption band (less than 333 mμ), at the absorption edge (between 336 and 342

mμ), at the long wavelength side of the edge (between 362 and 400 mμ), and in the visible region (around 540 mμ). However, these data show that at wavelengths shorter than the gap (between 333 and 336 mμ) and at wavelengths longer than the gap (between 342 and 362 mμ) $|I_{sc}|_{\perp} < |I_{sc}|_{\parallel}$, contrary to expectation.

One can regard most of these data as consistent with the absorption data if one views the two curves presented in Fig. 1 at wavelengths shorter than 350 mμ as a displacement in wavelength of one from the other. In the case of Fig. 2, the two curves appear displaced from each other at all wavelengths shorter than 400 mμ. We see that in the two figures the short circuit current peaks for parallel polarization are separated by about 0.03 ev from the peaks for perpendicular polarization. This separation is approximately equal to the displacement of the absorption edges for the two directions of polarization as reported in reference 6. The two curves might be amenable to interpretation in terms of Birman's model of a double valence band[10] if one assumes there are two absorption edges associated with the two valence bands.

We have measured similar effects (reversals with wavelength[5] and shifts with light polarization) in CdS. However, the phenomena are more complicated in that preliminary measurements indicate the effects to be transitory.

As an extension of this work, it may be worthwhile to look for similar optical and electrical effects in a broader class of materials. Casella has generalized his treatment of the optical selection rule in the wurtzite system to include materials in the crystal classes C_{3v}
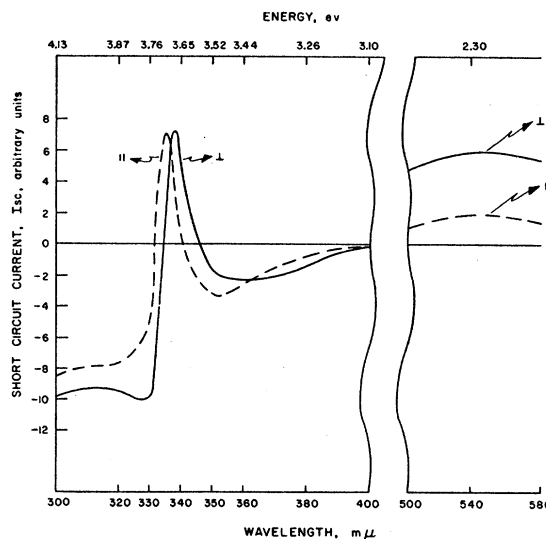
ENERGY, ev

FIG. 2. The short circuit current I_{sc}, for activated crystals, plotted against both the wavelength of light in millimicrons and the energy in ev. The wavelength scale is linear. The solid curve represents data obtained with light polarized perpendicular to the c axis and the dashed curve represents data obtained with light polarized parallel to the c axis. The vertical wavey lines indicate a break in the wavelength and energy scales and the I_{sc} scales are different on the two sides of the break.

and C_{4v} as well as C_{6v}. The theory is in qualitative agreement with experiment with regard to the optical dichroism for poled $BaTiO_3$ in the tetragonal phase.[13]

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[13] R. C. Casella and S. P. Keller (to be published).

Exciton States in Ionic Crystals*

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Exciton states in ionic crystals are analyzed according to configurations allowed by cubic point symmetry. The "excitation" and "electron transfer" models of the exciton structure are reintroduced as two slightly different aspects of the same general group-theoretical problem. Predictions of these models concerning multiplicity of absorption peaks are shown to be essentially identical. A theory of the "halogen atom doublet" appearing in the experimental absorption spectra of certain alkali halide crystals is given and is used in a preliminary interpretation of the electronic structure of low-lying exciton states in these solids.

I. INTRODUCTION

THE ultraviolet absorption spectra of alkali halide crystals were studied at an early date.[1] Hilsch and Pohl and their collaborators measured the spectra up to energies corresponding to 1600 A in the vacuum uv region, and, somewhat later, Schneider and O'Bryan extended the measurements to 1100 A. More recently, the alkali iodides have been studied extensively,[2,3] since the first peak of their fundamental absorption lies in the vicinity of 2000 A, a region of the spectrum which can be reached with conventional uv apparatus. The recent work has, among other things, confirmed that free electrons are not produced when light is absorbed in the region of the first peak of the fundamental absorption, so it is very likely that this process results in the creation of excitons.

The first attempts to interpret the structure of the exciton in alkali halide crystals were made by Hilsch and Pohl[1] and by Mott,[4] who pointed out that most of the spectra of the iodides and bromides exhibit a strong doublet structure, at least in the first absorption peak. The separation of this doublet is about equal to the

separation of the ground-state doublet of the free halogen atom, which is 0.942 ev in iodine and 0.457 ev in bromine. The interpretation of the doublet structure followed the interpretation of spectra of alkali halide vapors: when a photon is absorbed, an electron is ejected from the halogen ion and a neutral atom is left behind. In a crystal, the electron is not set free, but remains associated with the neutral halogen atom, or alternatively speaking, with the p^5 hole present in the halogen ion. If the direct interaction of the electron and hole is small compared to the spin-orbit interaction of the hole, one may have conditions somewhat similar to jj coupling in an atom, i.e., there exist two neighboring states which differ essentially only in the j-value assigned to the hole ($\frac{1}{2}$ or $\frac{3}{2}$). As in the atom, both of these states may be reached by optical transitions from the p^6 ground state, provided the electron is in an s-like state ($j=\frac{1}{2}$).

Recently, attempts have been made to describe the alkali halide exciton on a more quantitative basis. The calculations have centered mainly around two electronic models. In one, which is analogous to the Frenkel exciton model, the unit excitation of the exciton wave is sufficiently localized in a unit cell that it is somewhat characteristic of an excited state of a free atom. This model, which has been studied by Dexter[5,6] and by Muto and co-workers,[7] will be referred to as the "excitation" model. In the other,[1] which was developed by von Hippel,[8] the unit excitation involves the transfer of an electron from a halogen ion to the nearest neighboring positive ion. This model, which has been

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