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A Comparison of Photovoltages in ZnS and CdS

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Abstract. A model is proposed for ZnS single crystals in order to account for the anomalously large photovoltage. This model is suggested by the resemblance of the photovoltage observed in CdS crystals, which shows the same characteristic sign reversals as a function of wavelength and light intensity as they are known to occur in ZnS. This photovoltage is generated across an internal field between surface and volume and the sign reversal of the photovoltage is explained by a reversal of this field by majority carrier generation in the volume at high intensity and large penetration depth of the incident light. The elementary photovoltaic battery in the striated ZnS crystal is not formed at the transitions from the cubic to the hexagonal phase. These transitions, however, provide an asymmetric potential distribution which leads to a mechanism to connect the elementary surface-volume batteries in series, thus giving rise to a large photovoltage.

I. Introduction

The anomalous photovoltage in ZnS single crystals is characterized by two main features:

1. An observed photovoltage reaching values of the order of hundreds of volts at room temperature for a uniformly illuminated sample with electrode distance of about 1 cm.
2. One or several sign reversals of the photovoltage as a function of wavelength with the shortest wavelength sign reversal occurring at the absorption edge.

There is general agreement among all observers of the anomalous photovoltage that the effect is linked with the existence of transitions from the cubic to the hexagonal phase in ZnS and can only be observed perpendicular to the striations which indicate the crystallographic transitions. Consequently, in any attempt to account for the effect one is faced with the logical and physical problem how a sequence of alternating cubic and hexagonal phases can give rise to a potential distribution which explains the two above-mentioned first-order observations.

All models developed so far attempting to account for the photovoltage in ZnS crystals have in common that barriers are assumed to exist at the cubic-hexagonal interface. The models differ by the physical arguments by which the barrier is intro-

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duced. MERZ¹⁾ proposed a barrier connected with the change in short range periodicity of the Zn and S sequence in the crystallographic transition region. TAUC²⁾ assumed the existence of an impurity concentration gradient tilting the band structure. HUTSON³⁾ assumed barrier formation due to piezoelectric strain, and NEUMARK⁴⁾ made an analysis in terms of the influence of different carrier concentrations in both phases. The different models have in common that the elementary photovoltaic battery is localized at the cubic-hexagonal interface. The internal field across which the photovoltage is generated is perpendicular to the interface.

All of these models are specific to a material with an interchanging crystallographic phase structure or an otherwise regularly disordered periodical structure. Since both the anomalously large magnitude of the photoeffect and the peculiar sign reversal as a function of wavelength are ascribed to the transition barriers the occurrence of those effects would not be expected in a uniform material.

It is the purpose of this note to describe some experimental results on photovoltaic effects obtained with CdS-crystals and to compare them with those obtained on ZnS. The strong resemblance suggests a similar mechanism in both cases which is, however, incompatible with models localising the elementary photovoltaic battery at the crystallographic transition barrier. Since the results indicate that the observed photovoltages arise between surface and volume a model is proposed for the anomalous photovoltage in ZnS which is an alternative to all existing models. In this model the cubic-hexagonal phase boundaries only provide a mechanism to connect the elementary surface-volume batteries in series, this connection giving rise to the anomalously large photovoltage in ZnS crystals.

II. Experimental Results

A photovoltage is observed when a CdS single crystal (unactivated, dark resistivity $> 10^{12}$ ohm \cdot cm) is contacted and illuminated as indicated in Figure 1 (upper right corner). The lower half of the crystal is shielded from light so that only the upper half is illuminated. The photovoltage is observed with an electrometer connected to the two contacts. In the graph of Figure 1 the photovoltage is shown as a function of wavelength of the incident light. The positive voltage in the graph

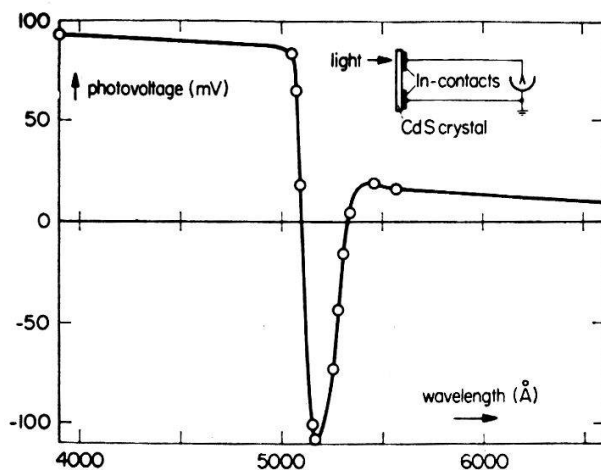


Fig. 1

Photovoltage versus wavelength in CdS

corresponds to positive voltage at the upper electrode. No photovoltage was observed when the crystal was uniformly illuminated (lower half of the crystal unshielded from light).

In Figure 2 the photovoltage is shown for two opposite directions of illumination. Again only the upper half of the crystal is illuminated but the photovoltage is measured for illumination from both sides as indicated in Figure 2.

The speed of response is faster for short wavelengths than for long wavelengths. In general, the response with respect to a change in wavelength is much faster than with respect to a change in intensity of illumination. The response is particularly fast with respect to a change in wavelength in the region of the shortest wavelength sign reversal (around $\lambda = 5100 \text{ \AA}$). At wavelengths beyond the absorption edge ($\lambda > 5100 \text{ \AA}$), the response both to a change in wavelength and to a change in light intensity is so slow that ac-detection of the photovoltage with an electrode separated from the crystal was impracticable.

The sign reversal of the photovoltage does not only depend on the wavelength of the incident illumination but also on its intensity. In Figure 3 is shown how the wavelength of the short wavelength sign reversal changes as a function of light intensity. To the left of the curve the photovoltage is positive while to the right of the curve it is negative.

The dependence of the anomalous photovoltage in ZnS on the wavelength is already described in the literature⁵⁾⁶⁾⁷⁾. By some authors⁵⁾⁶⁾ it was also noted that in the vicinity of the zero photovoltage wavelength a sign reversal occurs when the light intensity is changed. Quantitative measurements of this effect were made on ZnS and are plotted in Figure 4 in an analogous way to the results shown for CdS in Figure 3.

III. Discussion

The dependence of the photovoltage in CdS on wavelength has a striking resemblance to that observed for the anomalous photovoltage in ZnS⁵⁾⁶⁾⁷⁾. While the magnitude of the photovoltage in ZnS is anomalously high the magnitude of the photovoltage in CdS does not exceed some tenths of a volt. The similarity of the peculiar dependence of the photovoltage on the wavelength in the two materials but the different order of magnitude of the voltage can be reconciled if one assumes that the elementary photovoltaic battery exhibiting the peculiar wavelength dependence is based on an identical mechanism in both materials, but that only in ZnS many of these batteries are connected in series.

Apart from the fact that the CdS crystals used were flawless and apparently also crystallographically homogeneous the observation that uniform illumination of the CdS crystals does not yield any photovoltage excludes the possibility that the photovoltage in CdS is generated at a barrier arising at a crystallographic interface, as has been proposed for ZnS¹⁻⁴⁾. Further, the photovoltage in CdS can not be generated between a metal contact and the CdS crystal since the results of Figure 2 show that the sign of the photovoltage depends on the direction of the incident light. The sign of a photovoltage originating at the metal contact would be independent of the direction of illumination; only the magnitude of the effect would vary in accordance with the different amount of light absorbed before it reaches the contact-crystal interface through either the CdS crystal or the transparent metal contact.

The different sign of the photovoltage in CdS for opposite directions of the incident light can, however, be accounted for by the assumption that the photovoltage is generated between the free surface and the volume of the CdS crystal. The photovoltage represented by the full dots in Figure 2 would be generated across the internal field between the left free surface and the volume of the crystal in the experimental arrangement shown in Figure 2. The photovoltage for the direction of incident light indicated by the open circles would correspondingly originate between the right free surface and the volume of the crystal.

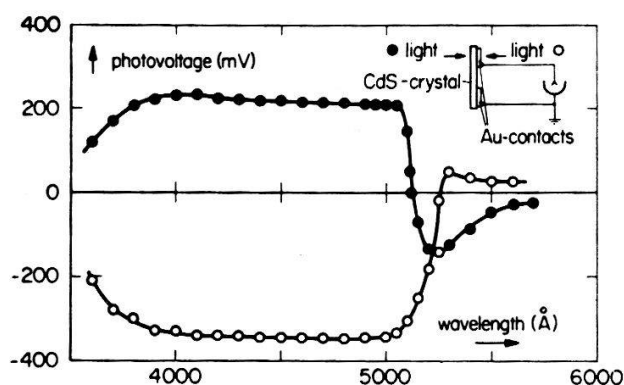


Fig. 2

Photovoltage versus wavelength in CdS for two opposite directions of illumination

A direct confirmation of this assumption would be the measurement of the photovoltage by a conventional ac-surface photovoltage detection system with distant electrodes. As already pointed out, the long response time of the photovoltage, particularly at long wavelengths, does not permit the measurement of the photovoltage over the same wavelength range as covered by the employed dc-method with electrodes attached to the crystal.

If one assumes that the photovoltages observed both in CdS and ZnS originate across the internal electric field between free surface and volume two problems arise: First, how can this photovoltage exhibit one or several sign reversals as a function of wavelength, and second, how can the elementary surface-volume photovoltaic batteries in ZnS be connected in series as to exhibit the observed large magnitude of voltage?

Concerning the sign reversal of the photovoltage as a function of wavelength, an indication for an explanation of the effect is given by the observation that the photovoltage of a CdS crystal with a pressed In point contact exhibits a sign reversal as a function of the incident light intensity⁸). This was accounted for by the change sign of the internal field between surface and volume at high light intensities due to excess carrier generation. In the particular case of an In-contact pressed into a CdS crystal it was assumed that the electron life time in the volume is much larger than that at the surface. If in the dark, due to surface states, the electron concentration at the surface is larger than in the volume this ratio will reverse with increasing light intensity. Consequently, an electron accumulation layer at thermal equilibrium is converted into an electron depletion layer at high light intensities.

The same effect can be expected to occur for any excitation mechanism as soon as the excited excess majority carrier concentration is large enough to modify the

potential distribution between surface and volume. In particular, the volume electron concentration depends strongly not only on the intensity of the incident light but also on its wavelength. At wavelengths longer than that corresponding to the absorption edge considerable volume excitation of electrons occurs. If the internal field between surface and volume in the dark had a sign as to indicate lower volume than surface electron concentration, illumination at wavelengths creating large electron concentrations in the volume will give rise to a reversal of the sign of the internal field and of the observed photovoltage.

This explanation accounts for the two sign reversals as a function of wavelength shown in Figure 1. At wavelengths shorter than that corresponding to the absorption edge the carrier generation in the volume of the crystal is small and the internal field between surface and volume has the same sign as in thermal equilibrium. Beyond the absorption edge electrons are generated in the volume and, as outlined above, internal field and photovoltage change sign. At very long wavelengths as the absorption still decreases the majority carrier excitation in the volume decreases correspondingly and the internal field between surface and volume again assumes the sign which it has at thermal equilibrium. The latter effect accounts for the sign reversal at longer wavelengths.

This explanation is supported by some further observations about the sign reversal as a function of wavelength in ZnS. The short wavelength sign reversal generally coincides with the absorption edge and does not vary from crystal to crystal. On the other hand, the behavior at long wavelengths follows no simple rule. Some crystals do not show any sign reversal beyond the absorption edge, some crystals show even several sign reversals. Since at wavelengths longer than that corresponding to the absorption edge majority carriers are excited from impurities and since the impurity content is different for each crystal a variation of the experimental results among different crystals can be expected. Nevertheless, on the base of the model outlined, a photovoltage with a sign opposite to that due to wavelengths shorter than that corresponding to the absorption edge would be expected in spectral regions which have strong excitation of majority carriers from impurities and a long majority carrier life time. The correlation between the sign of the photovoltage in ZnS at long wavelengths on the one hand and impurity absorption and photoconductivity on the other hand has, however, not yet been experimentally investigated.

In the mechanism leading to a sign reversal of the photovoltage the similar effect of strong light and long wavelength illumination is emphasized since both lead to large majority carrier concentrations in the volume. When this exceeds the surface concentration, internal field and photovoltage reverse sign. The similar action of long wavelength illumination and strong light intensity is illustrated by the experimental results shown in Figure 3 and 4. On the ground of the outlined model strong light is indeed expected to shift the short wavelength sign reversal towards shorter wavelengths, since a majority carrier concentration in the volume equal to that at the surface is reached at a higher absorption constant for strong illumination. The similarity of the results obtained for CdS and ZnS again strongly suggests a similar mechanism for the elementary photovoltaic battery in both materials. The observed shift in wavelength as a function of light intensity is larger in CdS (Fig. 3) than in ZnS (Fig. 4) since the absorption edge in CdS is not as steep as it is in ZnS. If instead of plotting the wavelength at which the photovoltage reverses sign

one plots the corresponding absorption coefficient, the two curves for CdS and ZnS are reduced to almost one curve.

The second main problem is to find an explanation for the anomalously large magnitude of the photovoltage observed in ZnS. If the elementary photovoltaic battery is localized between surface and volume of the ZnS crystal, the photovoltage is detected perpendicularly to the internal field across which it originates. In the following a model will be outlined whose main feature accounts for the adding up of the elementary surface-volume batteries.

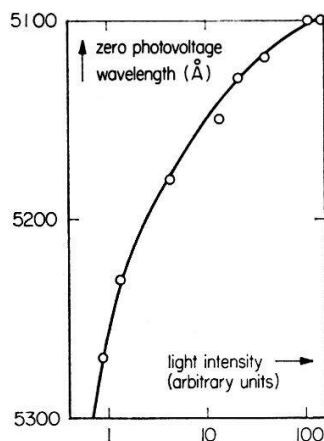


Fig. 3

Wavelength at which sign reversal occurs
versus light intensity for CdS

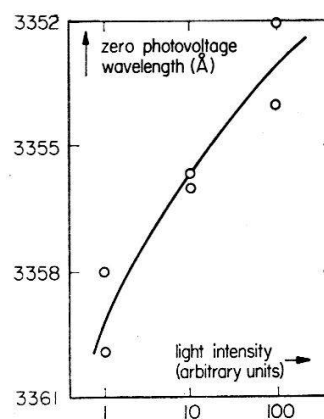


Fig. 4

Wavelength at which sign reversal occurs
versus light intensity for ZnS

The assumption is made that the voltages generated between surface and volume in the cubic and in the hexagonal phase of the crystal are not equal. This is plausible since the absorption in the two phases is different because of a difference of 0.1 eV in band gap⁶⁾ and since also the carrier life times might not be equal due to different impurity contents in both phases.

The hexagonal phase of the ZnS crystal shows a polar axis⁹⁾. The hexagonal axis is directed perpendicular to the cubic-hexagonal phase boundaries, and by pyroelectric measurements it was shown that the direction of polarization is the same for all hexagonal parts of the crystal⁷⁾. The ionic dipole moment of the hexagonal part is completely or partially neutralized at the cubic-hexagonal phase boundaries. The neutralization takes place by the conduction electrons in the ZnS and electrons are correspondingly attracted or repelled at the phase boundaries. The result is a periodic array of electron accumulation and depletion layers, that is low and high resistance parts in the volume of the crystal. At the surface the conductivity is determined by surface boundary conditions independent of volume polarization. The lowest resistance path through the crystal will therefore be as schematically indicated in Figure 5. Since the low resistance path in regions of electron depletion in the volume is shifted more towards the surface than in regions of electron accumulation in the volume the surface-volume photovoltaic batteries V_C in the cubic phase and V_H in the hexagonal phase are connected as indicated in Figure 5. The total voltage V detected across the crystal is

$$V = \sum (V_C - V_H).$$

If $V_C \neq V_H$ the voltage will not cancel and with a sign reversal of the elementary battery voltage V_C or V_H also the total voltage V will change sign.

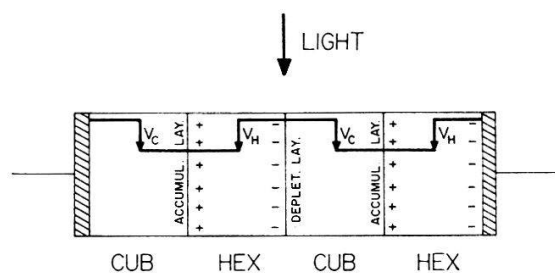


Fig. 5

Proposed model to explain sign reversal and magnitude of photovoltage in ZnS

In conclusion, both the mechanism of the sign reversal of the photovoltage as a function of wavelength and the model of the ZnS crystal to account for the adding up of the elementary voltage are not more than a proposal based on qualitative arguments. They might serve as a working guide to new calculations and experiments which would allow a more detailed model. In particular, to obtain a better understanding of the sign reversal of the photovoltage as a function of both light intensity and wavelength the potential distribution in photoconductors, space charge layers at high excitation rates must be more quantitatively understood. Experimentally, the role of the surface for the photovoltage particularly in ZnS crystals must be investigated, e. g. by studying the influence of different ambients or a field effect electrode arrangement on the photovoltage.

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