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The Photovoltaic Effect in Striated ZnS Single Crystals

by **Walter J. Merz**

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Abstract. The photovoltaic effect in ZnS single crystals was studied as a function of wavelength, light intensity and temperature. Voltages of a few hundred volts can be observed if bandgap light is used and if the voltage is measured perpendicular to the striations, that is parallel to the hexagonal [0001] and the cubic [111] axes. These ZnS crystals show a very intimate intergrowth of a cubic and a hexagonal modification which can be seen in the form of striations. Following a suggestion of F. HERMAN and E. E. LOEBNER it is proposed that at each transition from cubic to hexagonal symmetry or vice versa a barrier is formed at which the electron-hole pairs, which are created by the light, are separated and give rise to a photovoltage. Since this voltage can not be larger than bandgap it is assumed that the high values can occur only when all the many barriers show the same asymmetry so that the small voltages add up to a sizeable net voltage. A possible mechanism for this is shown in terms of the structure of the cubic and hexagonal ZnS. From this asymmetry of the barrier follows also the polarity of the measured voltage. The part of the crystal which grows last (i. e., point of needle) is always the negative electrode at 3130 Å.

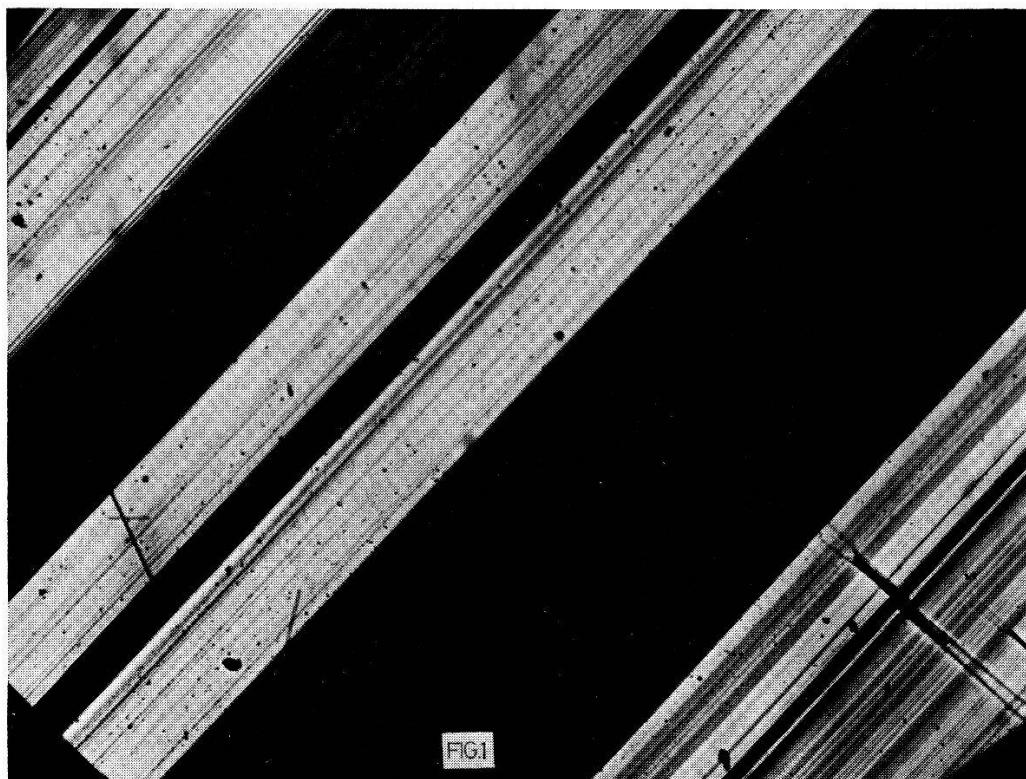
The photovoltage increases first linearly and then logarithmically with light intensity and finally reaches saturation. The voltage increases with decreasing temperature and reaches saturation at a temperature which depends on light intensity. These results can be explained with the proposed model. From the measured curves of photovoltage versus light intensity and temperature the following parameter can be calculated. N , the number of barriers in our needles is about 2000/cm and ΔE , the barrier height is about 0.15 eV.

I. Introduction

It is known that ZnS crystals occur in two crystallographic modifications, in the hexagonal wurtzite structure and in the cubic sphalerite structure. At room temperature the cubic modification is stable whereas above 1020° C the hexagonal one becomes more stable. Although it is not very hard to grow ZnS single crystals it is extremely difficult to obtain crystals which are completely cubic or completely hexagonal. Usually the crystals consist of very many cubic and hexagonal regions. The intimate intergrowth of these two modifications can be seen easily with a polarizing microscope in the form of a very pronounced striation,

a typical picture of which is shown in Figure 1. By X-ray it has been established¹⁾ that the stacking is such that the hexagonal *c*-axis[0001] and the cubic [111] axes are aligned and perpendicular to the striations. Needles of ZnS crystals have their axes along the hexagonal [0001] (cubic [111]) axis and the striation can be observed in form of rings around them.

The possible electronic properties of these cubic-hexagonal stacking faults interested a number of people at the RCA Laboratories at Princeton. In particular, F. HERMAN and E. E. LOEBNER proposed that, because of the upset in periodicity, there might exist an extra electric polarization localized near the fault planes, hence a barrier exhibiting a



Picture of a ZnS crystal plate. Striations can be seen in form of dark and light lines.

photovoltage. They speculated that the successive barriers might give additive photovoltages because the same atomic species always appear on the same side of each fault plane. These ideas were spurred by L. PENSAK's discovery²⁾ of a very large photovoltaic effect in evaporated CdTe films and by B. GOLDSTEIN's³⁾ subsequent study of their electric properties.

Experiments on ZnS single crystals show an extremely large photovoltaic effect (a few hundred volts) when the crystals are illuminated with ultraviolet light and when the voltage is measured perpendicular to

the striation. These preliminary results were reported in a short communication⁴). In the present paper more detailed results about this remarkable effect are given and discussed.

II. Experimental

The experimental set up is extremely simple. A ZnS crystal is exposed to ultraviolet light and the resulting photovoltage is measured with an electrometer. Since the impedance of the samples is of the order of 10^{14} Ω or more one has to be careful that the photovoltage is not partially shortcircuited by the instrument. For this reason a bucking voltage is applied so that the crystal sees a nearly infinite external impedance when the photo voltage is compensated. For the same reason it is necessary to keep the crystals dry; a thin film of water reduces the photovoltage much. Most of our experiments were therefore performed in vacuum. Usually we used gallium electrodes because they make ohmic contacts to ZnS. However, the electrode problem is not very critical since contact barriers of a few tenths of a volt do not affect our measured values of hundred of volts.

III. Experimental Results

ZnS has a forbidden gap with an energy of 3.7 eV which corresponds to about 3400 Å. We have found that a large photovoltaic effect can usually be observed only when the wavelength of the light is smaller than 3400 Å. As expected, it shows that the photovoltage is due to the fundamental absorption of light which is caused by the transfer of electrons from the valence band to the conduction band (electron-hole pair formation). For convenience we usually used in our experiments the strong 3130 Å Hg line. The neighboring 3660 line did usually not give any photovoltage. However, we observed that this line causes partial quenching of the voltage; the full mercury spectrum creates less photovoltage than the much weaker 3130 Å line alone. If a crystal is exposed to the 3130 Å line for a long time it is sometimes also sensitive to longer wavelength whereby the polarity is reversed.

Since a large photovoltaic effect can be observed only when the voltage is measured perpendicular to the striations one suspects that it should be proportional to the number of them. Although it is not easy to count them we found that the voltage increases with the number of striations.

The polarity of the voltage is well defined. We found that without exception the part of the crystal which grew last, for example the point of a needle, shows the negative polarity, whereas the base of the needle shows the positive polarity. The consequences of this observation at 3130 Å are discussed later.

The photovoltage increases first linearly with light intensity and at higher intensities, logarithmically as shown in Figure 2. This behavior is quite normal, as is discussed later. However, the absolute values and the slopes of the curves are unusually high. Voltages of a few hundred volts could be detected. At extremely high light intensities saturation can be reached, especially at low temperatures.

The temperature dependence of the photovoltage for a fixed light intensity of the 3130 Å line is shown in Figure 3. From -140°C to about $+60^{\circ}\text{C}$ we find in this case a linear decrease of the voltage. At higher temperatures the decrease is slower and at about 160°C the photovoltage reaches a value of almost zero. The curved part can be represented by $\ln V \sim 1/T$ as also shown in Figure 3. With a very strong light source it is possible to reach saturation. The stronger the light, the higher the temperature at which saturation can still occur. At temperatures below the saturation temperature the photovoltage is decreasing (Fig. 4). Both the light intensity – and the temperature – dependence of the photovoltage are discussed in the next paragraphs.

IV. A Model for the Bandstructure

Since the high photovoltage increases with the number of striations and since it can be observed only when the voltage is measured perpendicular to them it becomes clear that it is due to the structural changes in the crystal. The maximum photovoltage which can be created at any junction or barrier is of the order of the bandgap energy. We thus have to assume that, although each of the very many junctions gives only a small voltage, hundreds of volts can be obtained when many barrier voltages are in series. Following HERMAN and LOEBNER's suggestion we propose that at each transition from cubic to hexagonal structure or vice versa a barrier is formed at which the electron-hole pairs which are created by the light are separated and give rise to a voltage. What kind of a band picture do we have to assume? Since the sample is chemically uniform and since the observed voltages are extremely high we can not assume a series of regular p - n junctions. We have to find a band structure in which there are asymmetric barriers all of which are alike so that the voltages add up. A possible type of band structure is shown in Figure 5. In all the cubic and hexagonal sections the electrons are pulled to the left and the holes to the right, thus at each barrier a voltage is generated. All the barriers show the same shape, and thus the voltages add up. Since the details of the bandstructure are not known Figure 5 should not be taken literally; it demonstrates only the general type of a bandstructure we have to assume.

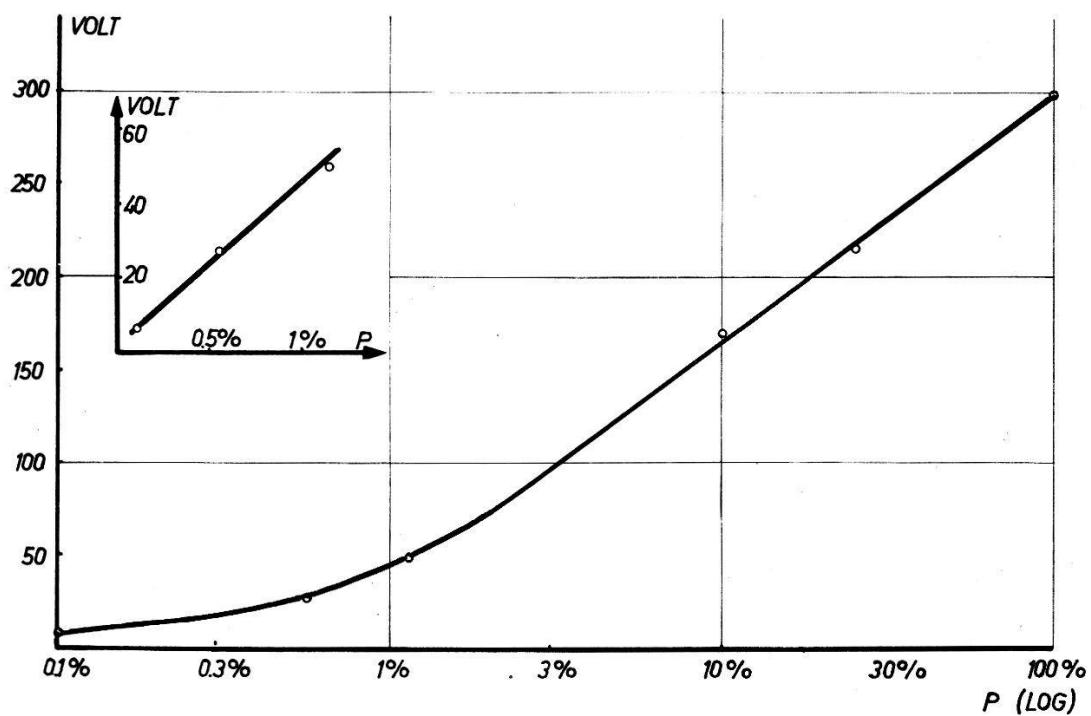


Fig. 2
Photovoltage V versus light intensity P .

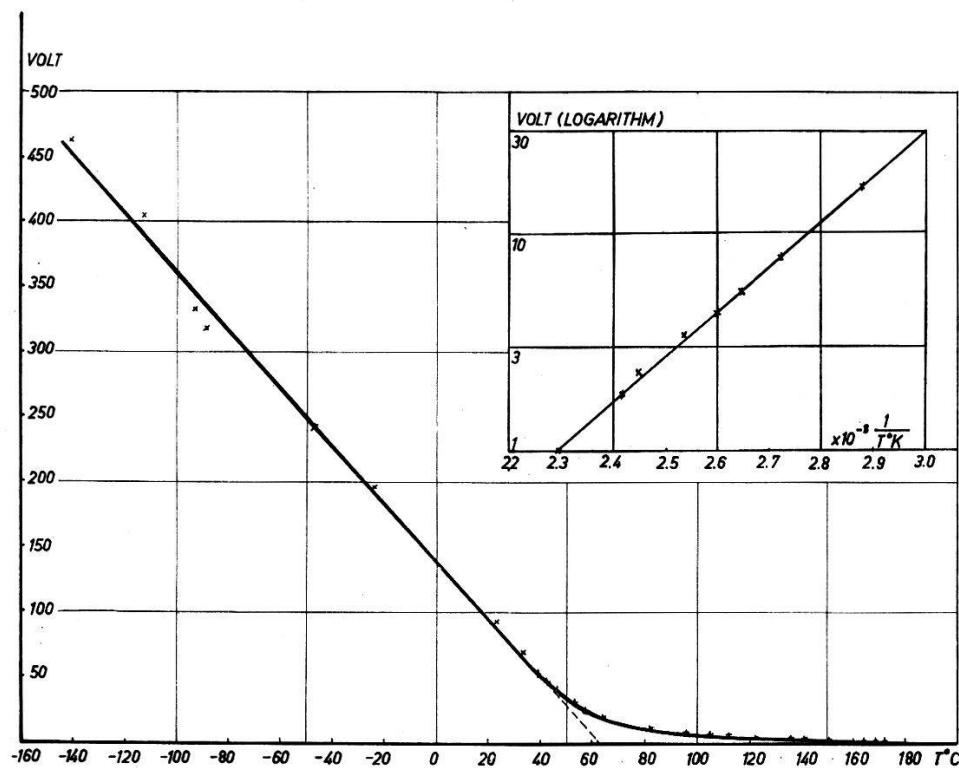


Fig. 3
Photovoltage V versus temperature T .

The main difficulty, of course, is to understand why the barriers have the same asymmetry whether we move from the cubic to the hexagonal structure or vice versa from the hexagonal to the cubic one.

The difference between the cubic and hexagonal structure in ZnS can be seen when one looks along the cubic [111] and the hexagonal [0001]

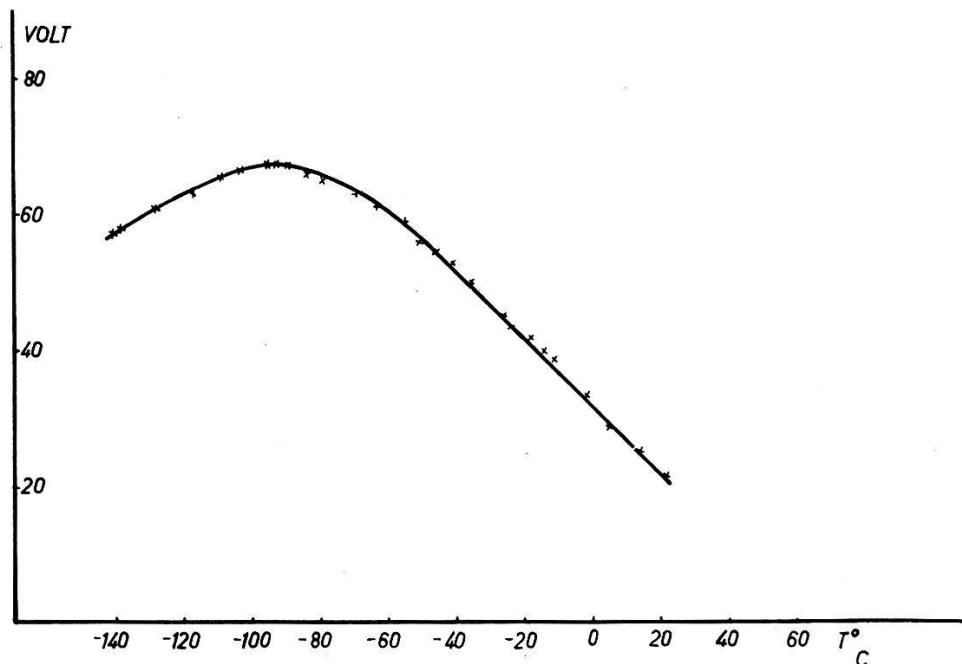


Fig. 4

Saturation of photovoltage versus temperature for high light intensity.

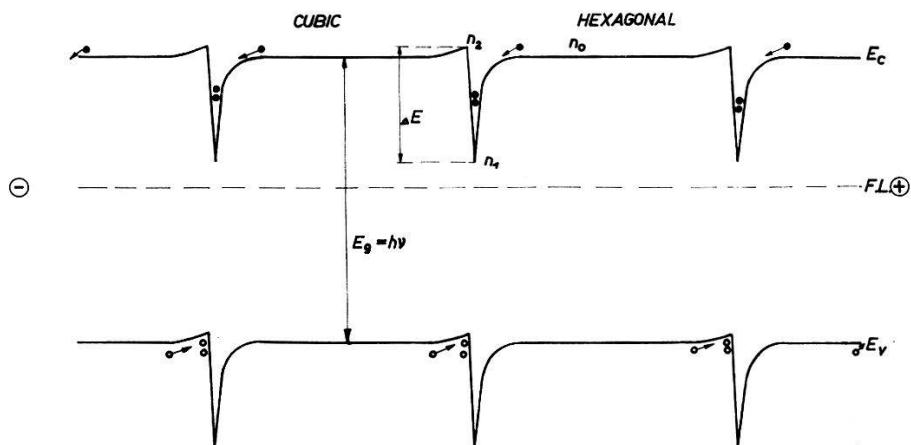


Fig. 5

Proposed bandstructure for cubic-hexagonal ZnS.

axes respectively. As in the case of a cubic and a hexagonal closed packed lattice one finds that in the cubic system the fourth layer coincides with the first one, whereas in the hexagonal system already the third layer coincides with the first one. To go from one structure to the other, one

has to rotate a ZnS tetrahedron around the Zn-S bond along the hexagonal axis by 60° (Fig. 6). This rotation changes the short range periodicity and we assume that this causes a band curvature as shown in Figure 5. It is interesting to note that the bandgaps for cubic and for hexagonal ZnS are the same within a few hundreds of an electron volt⁵). However, by changing the periodicity a band bending is caused which amounts to about a tenth of a volt as we will see later. The surprising fact still remains that we obtain the same sign of voltage regardless of whether we go from cubic to hexagonal symmetry or vice versa. However, the threefold symmetry of the cubic [111] axis and the sixfold symmetry of the hexagonal [0001] axis tells us that it makes no difference whether we turn a ZnS tetrahedron clockwise or counter clockwise

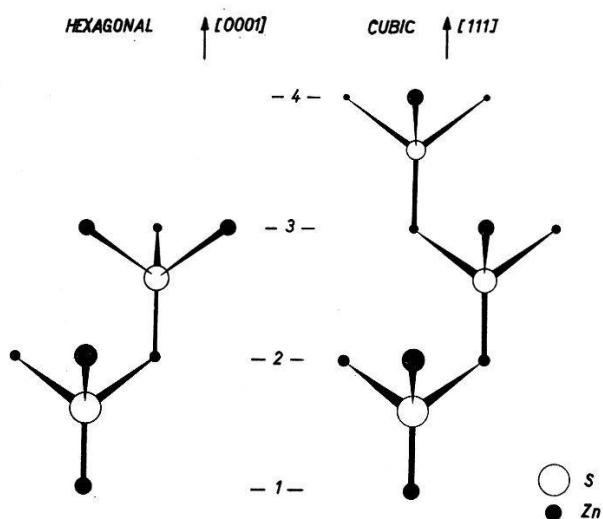


Fig. 6
Crystallographic structure model of cubic and hexagonal ZnS.

ally 60° . Since all the bonds along these axes always go from Zn to S or bways from S to Zn, but never both, we perform the same operation whenever we go from one structure to the other. Thus this might be the key to why the sign is the same and why all the voltages can add up to very high values. This is possible only because the cubic and the hexagonal structures of ZnS can be transformed into each other by the same mechanism.

The polarity of the photovoltage is therefore determined by the sequence of the atoms, that is, whether the bonds along the cubic [111] and hexagonal [0001] axes go from Zn to S or from S to Zn. Since all the crystals show the same polarity (point of needle is always the negative pole) it follows that the crystal growth along this axis can have only one sense. In Figure 7 we show four possible atomic arrangements. In cases

A and *C* the bonds along the cubic [111] and hexagonal [0001] axes grew from Zn to S in cases *B* and *D* from S to Zn. On the other hand, in cases *A* and *B* the first bond to the substrate is vertical in cases *C* and *D* not.

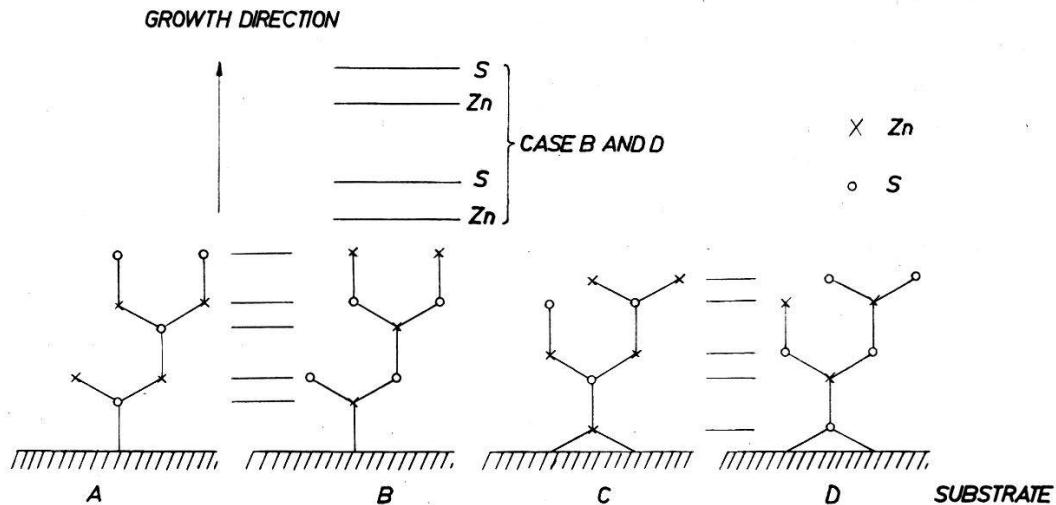


Fig. 7
Four possible growth patterns of ZnS.

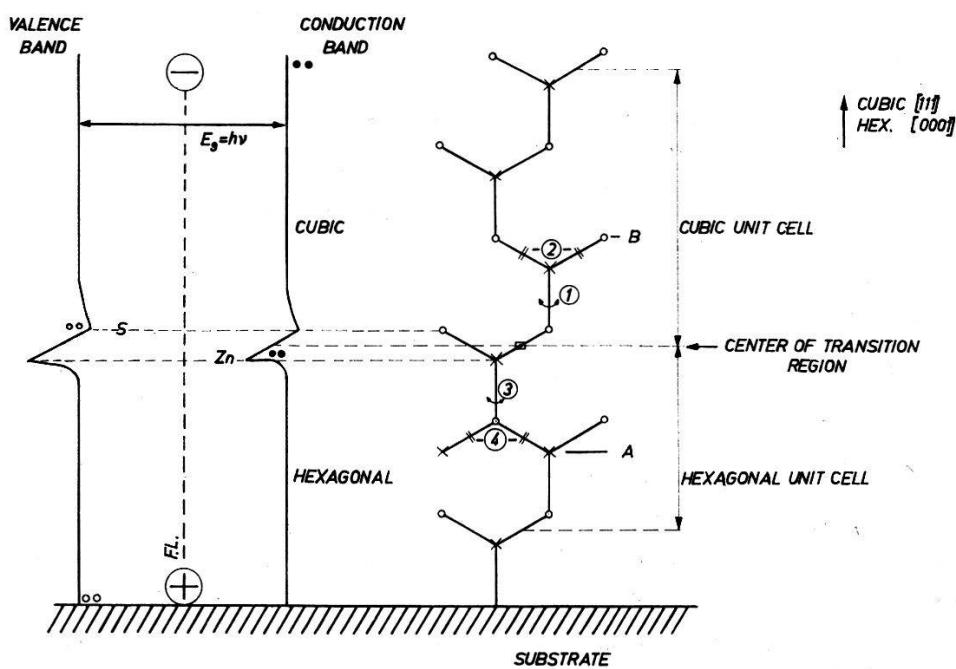


Fig. 8
Crystallographic structure and band structure at a transition from cubic to hexagonal symmetry in ZnS.

X-ray investigations by JOHN WHITE of the Princeton Laboratory¹⁾ showed that only cases *B* and *D* are possible, that is, the bonds along the [111] axis go from S to Zn. This is consistent with the polarity of the measured photovoltage as shown in Figure 8. Coming from the substrate

we turn around bond 1 by 60° in order to change the structure from hexagonal to cubic; bonds 2 are now in a new position. On the other hand, coming from the other side, we turn around bond 3 by 60° in order to make the structure change from cubic to hexagonal and bonds 4 are now in a new position. There is a transition region *A* to *B* where both structures overlap. The center of this region is marked by a square. To the left of this diagram the band structure as discussed before is shown. ZnS is partially ionic where Zn are the positive ions and S the negative ions. It thus seems reasonable to identify the valleys in the conduction band with Zn positions and the hills in the valence band with S positions as shown in Figure 8. The figure shows that the vertical bonds go from S to Zn coming from the substrate because the point of the needle is the negative electrode, and because the center of transition is on a diagonal bond going from Zn to S. Hence both X-ray and electrical measurements agree. Whether case *B* or *D* is the true one can not be decided with these experiments. In favor of *B* speaks the negativity of the oxygen layer of the quartz substrate on which the crystals grew, in favor of *D* speaks the three point initial attachment. Experiments on growing ZnS on different substrates might clear up this question.

V. Photovoltaic Effect

The photovoltaic effect at a metal-semiconductor contact or at a *p-n* junction is reasonably well understood. The maximum voltage one can obtain is in both cases given by ΔE , the barrier height. The maximum voltage we can expect to obtain from our type of a junction is ΔE , the jump of the band at the barrier (Fig. 5).

The open circuit voltage at either type of a barrier is given by⁶⁾

$$V_0 = \frac{kT}{e} \ln \left(1 + \frac{I_L}{I_0} \right) \quad (1)$$

where I_L is the photocurrent created by light and I_0 is the reverse current in the dark. This equation is obtained by equating the photocurrent and the forward current, due to diffusion of the excess carriers in the presence of the voltage V_0 . Equation (1) shows that the open circuit voltage increases with light intensity (I) and decreases with increasing temperature (I_0).

Since the photocurrent is proportional to the light intensity P equation (1) can be written as follows:

$$\frac{I_L}{I_0} \ll 1 \text{ (low light intensity): } V_0 = \frac{kT}{e} \frac{I_L}{I_0} = \text{const } P \quad (2)$$

$$\frac{I_L}{I_0} \gg 1 \text{ (high light intensity): } V_0 = \frac{kT}{e} \ln \frac{I_L}{I_0} = \frac{kT}{e} \ln P + \text{const.} \quad (3)$$

The voltage thus depends first linearly and then logarithmically on light intensity which agrees with our experimental results (Fig. 2). At very high light intensities saturation sets in and equation (1) is not valid anymore.

The reverse current in the dark increases exponentially with temperature which leads to linear decrease of the photovoltage with increasing temperature at high light intensities. This has been observed experimentally (Fig. 3).

Using the model discussed in chapter IV and using the numerical values described in chapter III we get the following results for N , the number of barriers per cm and ΔE , the barrier height.

A direct optical measurement of N by counting the number of lines (striation) with a microscope using polarized light and also reflected light is difficult since many of the lines are very faint. (See Fig. 1.) Furthermore, plates can show very many or only very few striations. However, surprisingly enough we found that in contrast to the plates all our needles showed about the same line density of the order of about 2000/cm. N can also be calculated from equation (3) that is from Figure 2 where the photovoltage of a needle is plotted versus the logarithm of the light intensity. According to equation (3) the slope of the voltage in the logarithmic range should be $kT/e = 1/40$ Volt at room temperature. But, experimentally we observe values of 40–60 Volts depending on the length of the needle. This, of course, is due to the fact that N barriers are put together in series. We found that the slope in the logarithmic range is independent of the absolute light intensity as it should be. Using ZnS needles with a length between 0.7 and 1.2 cm we obtain for N values of 1700–2100/cm which is in remarkable close agreement with the direct optical measurement of $N \approx 2000/\text{cm}$. It is interesting to note that B. GOLDSTEIN³) obtained very similar results in CdTe films.

The saturation voltage V_{sat} is the product of the number of barriers N times the barrier height ΔE . Depending on the length of the samples we find values for V_{sat} between 63 Volts and 450 Volts. Using the corresponding N values we obtain for ΔE an average value of 0.15 eV (between 0.12 and 0.18 eV).

VI. Summary

The experimental results agree quite well with the band model proposed in section IV, at least in a qualitative way. The light intensity – and temperature – dependence of the photovoltage follows the equations presented in section V. The voltage increases first linearly and then logarithmically with light intensity and reaches saturation at high light level. On the other hand, the voltage decreases first linearly and then exponentially with increasing temperature. At low temperatures saturation

can be observed. Furthermore, the polarity of the voltage can also be explained by the proposed band model. However, it is clear that this model is too simple in order to get good quantitative results. The value for the number of striations in needles comes out reasonable and also the barrier height of 0.15 eV. The small decrease of photovoltage below the saturation temperature might be explained by a change of the barrier height ΔE with temperature which of course could also influence the numerical values at higher temperatures.

Due to the high impedance in the order of $10^{14} \Omega$ the power output of the ZnS single crystal photovoltaic cell is less than 10^{-8} watt. A semiconductor with similar type of stacking faults and with the same type of intergrowth of two crystallographic modifications might give a much more efficient photovoltaic cell.

VII. Acknowledgment

In the course of this work I enjoyed the cooperation of a number of people. In particular I am thankful to Drs. F. HERMAN, M. A. LAMPERT, E. E. LOEBNER, D. O. NORTH, and A. ROSE of the Princeton laboratories of RCA for many discussions during the initial stages and to Dr. W. RUPPEL of this laboratory and Prof. F. STOECKMANN during the final stages of this work. I also would like to thank Drs. J. G. WHITE and S. G. ELLIS for their X-ray work and Mr. C. W. STRUCK for the preparation of the crystals.

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