

determined by chemical analysis or by examining the x-ray data for the lattice parameter.^{6,9} From the data it appears that the tantalum carbide samples previously reported as not superconducting had C/Ta mole ratios lower than 0.84. Such a composition is to be expected for samples which have been arc-melted or heated to very high temperatures under vacuum due to the rapid vaporization of carbon under these conditions. It must be emphasized that true stoichiometry was not attained in the present work, and by reference to the phase diagrams^{7,8} it is apparent that it cannot be attained at the temperatures used for preparation of samples. Carbides of higher carbon content can be prepared in the presence of excess carbon, and therefore transition temperatures higher than 9.7°K for tantalum

⁹ E. K. Storms and N. H. Krikorian, *J. Phys. Chem.* **63**, 1747 (1959).

carbide and 11.1°K for niobium carbide may be attainable.

Now only vanadium carbide of the Group Va carbides remains as a nonsuperconductor. However, vanadium carbide with a molar ratio, C/V, higher than 0.88 cannot be obtained by the usual techniques.¹⁰ It is very possible that this limitation prevents the occurrence of a superconducting transition rather than any fundamental difference between vanadium carbide and the other carbides of this group.

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¹⁰ E. K. Storms and R. J. McNeal (to be published).

Theory of the Anomalous Photovoltaic Effect of ZnS

GERTRUDE F. NEUMARK

Philips Laboratories, Irvington-on-Hudson, New York

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A theory to account for anomalies observed in the photovoltage of faulted ZnS crystals is proposed. The theory assumes that the spontaneous polarization of hexagonal ZnS causes internal fields in these crystals, with opposing fields in cubic and in hexagonal material. If one then considers a unit of one cubic and one hexagonal segment, these fields will cause differences in carrier concentration, and resultant differences in photovoltage at the two band-gap barriers in such a unit. The net photovoltages of such units will be additive along the crystal. It appears that the proposed theory can account for observed photovoltages, both as to their magnitude and their reversal of sign with wavelength.

I. INTRODUCTION

A NUMBER of investigations on ZnS single crystals¹⁻⁵ have established the existence and a number of properties of a so-called "anomalous" photovoltaic effect. The main characteristics of this effect are that the photovoltage is much higher than the voltage corresponding to the band gap,¹⁻⁵ and that it reverses sign with wavelength of irradiation.^{2,4,5} In the region of band-edge absorption (the region of interest in the present paper), the photovoltage is generally of one sign (negative, by convention^{2,4}) until about 3300 Å, then becomes positive until about 3500 Å, and then becomes negative again.^{2,4} At longer wavelengths, there can be still another reversal, with the photovoltage persisting to quite long wavelengths² ($\gtrsim 10\,000$ Å), but this will not be considered here.

It has been established fairly well that this anomalous behavior takes place only in crystals which show at least some stacking disorder (i.e., changes in structure from cubic to hexagonal).^{1,3-5} Early attempted explanations^{1,3} therefore assumed a photovoltage at each structural reversal (estimated experimentally at 0.15 v per reversal³), with these voltages additive along the crystal. However, as was pointed out by Tauc, it is hard to understand such additivity, so that it seems better to assume that each structural "unit," i.e., a unit composed of one segment of cubic structure and one of hexagonal structure, contains opposing barriers (or potential gradients).⁶ Each unit would here have one or more barriers with an increasing potential energy, and opposing barriers with a decreasing potential energy. In addition, one requires some asymmetry in this system, in order to prevent cancellation between the voltages associated with these opposing barriers.⁶ The explanation of the effect proposed by Tauc⁶ does provide appropriate barriers and asymmetry. However, Tauc⁶ proposes that the barriers arise either from impurity gradients,

¹ S. G. Ellis, F. Herman, E. E. Loebner, W. J. Merz, C. W. Struck, and J. G. White, *Phys. Rev.* **109**, 1860 (1958).

² G. Cherooff and S. P. Keller, *Phys. Rev.* **111**, 98 (1958).

³ W. J. Merz, *Helv. Phys. Acta* **31**, 625 (1958).

⁴ A. Lempicki, *Phys. Rev.* **113**, 1204 (1959).

⁵ G. Cherooff, R. C. Enck, and S. P. Keller, *Phys. Rev.* **116**, 1091 (1959).

⁶ J. Tauc, *J. Phys. Chem. Solids* **11**, 345 (1959).

which seems somewhat arbitrary, or, as suggested by Merz, from "intrinsic forces . . . owing to the unidirectivity of the crystal axis," where these forces are left completely unspecified. A more recent theory by Hutson⁷ introduces opposing internal fields produced piezoelectrically by strain gradients, and seems to provide a more reasonable basis for such barriers. The required asymmetry in this model is apparently obtained by differential absorption of light.⁷ Cubic material has a smaller band gap than hexagonal material,⁸ so there will be a wavelength region (relatively narrow) where cubic material absorbs much more heavily than hexagonal. However, it seems hard to see how the required asymmetry is maintained at other wavelengths. We now propose that such internal fields can cause the required asymmetry by changing the carrier concentration at "energy gap barriers" between cubic and hexagonal material. In addition, the present work also differs from Hutson's model by suggesting an alternate possible cause of internal fields, namely the spontaneous polarization of hexagonal ZnS.

As mentioned, the anomalous photovoltaic effects have been observed only on ZnS crystals with mixed cubic and hexagonal structure. Also, it is known from absorption edge data⁸ that the energy gaps of the cubic and the hexagonal ZnS structures differ by about 0.1 eV, so that there must be resultant barriers at each transition. The theoretical basis for such changes in energy gaps and resultant barriers has already been discussed.⁹ The model we now propose then follows, essentially, from two additional factors. First, hexagonal ZnS has a spontaneous internal polarization¹⁰; we propose that due to the adjoining cubic parts, this polarization is not neutralized "properly," but leads instead to internal fields (see Sec. II). Second, it can be shown from basic considerations that the photovoltage associated with a change in band gap depends on the carrier concentration at the transition region (Sec. III). Then, since the postulated internal fields lead to differences in carrier concentration at the two energy gap barriers associated with each structural unit, there will be a net photovoltage across each unit. It should also be mentioned that the generation of the band-gap photovoltage discussed in Sec. III requires formation of minority carriers. The present theory can therefore account for photovoltages only as long as there is some carrier pair generation, and is thus presumably restricted to wavelength regions in and near the band edge.

Voltage additivity, giving the possibility of voltages higher than band gap, is readily obtained from the proposed model. Since the carrier concentration differences will be in the same direction in each structural unit, the potential difference across the units will be additive along the crystal.

The photovoltage reversals can be accounted for (at least in the band-edge region) by differences in absorption, since the photovoltage will depend mainly on the fields in the regions with the heaviest absorption (Sec. IV).

II. INTERNAL FIELDS IN FAULTED ZnS CRYSTALS

In the hexagonal (wurtzite) form of ZnS the c axis is a polar axis, i.e., there is a net permanent electric moment along this axis.¹⁰ In general, such net moments are neutralized by free charge at the surfaces of the crystals, and can be detected only when they are changed, as for instance by heating (pyroelectricity). For wurtzite, this neutralization would require free charge at each end of the c axis. In faulted ZnS crystals, there is an alternation of hexagonal and of cubic structural segments along this c axis.¹¹ Thus, for "proper" neutralization of the moment of a hexagonal segment, one would require free charge at each interface between hexagonal and cubic material ("improper" neutralization will of course take place on the crystal surface—see below and Appendix I). However, it seems unlikely that adequate free charge would be adsorbed at such a boundary either during growth, or migrate in afterwards (at least within the time scale of the existing measurements). Therefore, we postulate that proper neutralization does not occur, and that there is a net charge density σ_H at each cubic-hexagonal interface. This possibility has already been discussed,⁹ but without mention of resultant opposing fields in cubic and hexagonal regions. Such opposing potentials would result since, if hexagonal regions have $+\sigma_H$ at the right side (and $-\sigma_H$ at the left side), the corresponding charge for the cubic regions will be $-\sigma_H$ and $+\sigma_H$. Charge layers located further away from a given segment should not change this characteristic. Such layers will generally tend to neutralize each other in pairs and even without complete pair neutralization they should not influence the direction of the slope of the potential (i.e., the direction of charge motion) since their charge is, after all, further away. These characteristics are clearly shown by the results in Appendix I, where illustrative quantitative calculations are given for the potential along the line in the center of the crystal.

It also appears that "improper" surface neutralization will not essentially change the above discussed result of a periodic potential. For the geometry of the crystals employed in photovoltage measurements (thin rods) such neutralizing surface charge can presumably consist of rings of line charge around each structural boundary along the length of the rod (which will be referred to as "neutralization on top"), or of area charge at the ends. The two cases are illustrated in Figs. 1(a)

⁷ A. R. Hutson, Bull. Am. Phys. Soc. (II) **6**, 110 (1961).

⁸ See, for example, J. A. Beun and G. J. Goldsmith, Helv. Phys. Acta **33**, 508 (1960); F. A. Kröger, Physica **7**, 1 (1940).

⁹ J. L. Birman, Phys. Rev. **115**, 1493 (1959).

¹⁰ See, for example, A. von Hippel, Z. Physik **133**, 158 (1952).

¹¹ For a recent discussion of the crystallography of ZnS see, for example, H. Samelson and V. A. Brophy, J. Electrochem. Soc. **108**, 150 (1961).

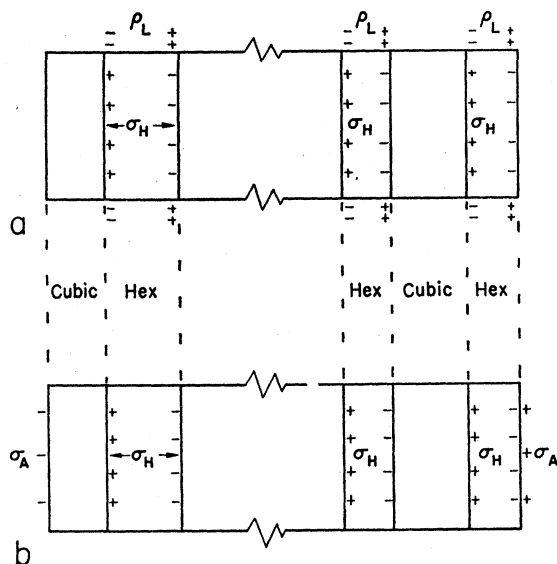


FIG. 1. Proposed model of the charge distribution in disordered ZnS crystal. Figure 1(a) applies to the case where the charge (σ_H) at the hexagonal-cubic boundary is "neutralized" by free line charge (ρ_L) around the perimeter of the boundary, ("neutralization on top"), Fig. 1(b) applies for "neutralization" by an area charge (σ_A) at the ends of the crystal.

and 1(b), respectively. For neutralization at the ends, the surface charge will be too far removed from most of the crystal to greatly affect the potential there, although it may cause some reduction (although not inversion) of the potential near the ends. For neutralization on top, the potential will still vary periodically from cubic to hexagonal regions, although one will here also have to consider the variation of potential with depth, where this latter variation will be superimposed on the periodic variation. The change of potential with depth would be expected to occur since near the surface the direction of the slope of the potential is determined mainly by a concentrated line charge (ρ_L) rather than by the relatively diffuse area charge σ_H . On the other hand, at the center of the crystal one would expect σ_H to dominate the slope, as is confirmed in Appendix I. Thus, since ρ_L and σ_H are of opposite sign, the potentials will vary in an opposite sense near the surface and in the interior of the crystal. The expected resultant potential distribution is shown, schematically, in Fig. 2.

Since V is essentially periodic, one would expect the carrier concentration to also be periodic. Some insight into this can be obtained by considering the continuity equation for the carrier distribution. The appropriate equation for electrons, for a one-dimensional geometry, is

$$D_n \frac{d^2 n}{dx^2} + \mu_n \frac{d(nE)}{dx} + f - \frac{\Delta n}{\tau_n} = 0, \quad (1)$$

where D_n =diffusion constant for electrons= $\mu_n kT/e$, μ_n =electron mobility, τ_n =electron lifetime, f =generation rate of the carriers produced by the light, E =field,

n =electron concentration, Δn =electron concentration above the thermal equilibrium value, and k , T , and e have their usual meaning. With the assumptions $n \approx \Delta n$ and $\tau_n \approx \tau_p \approx \tau$, this equation reduces to

$$\frac{\mu_n kT}{e} \frac{d^2 n}{dx^2} + \mu_n \frac{d(nE)}{dx} + f - \frac{n}{\tau} = 0. \quad (2)$$

To solve this equation we will assume, for mathematical convenience, a series of structural segments all of length d , and a trial function for n of the form:

$$n = n_0 + n_1 \cos(\pi x/d). \quad (3)$$

With this assumed form for n , it is easy to solve for nE , thus obtaining E , and then V . (Note that the reverse process is considerably more difficult.) Substituting and integrating, one obtains

$$nE = \left(\frac{n_0}{\mu_n \tau} - \frac{f}{\mu_n} \right) x + n_1 \left(\frac{d}{\pi \mu_n \tau} + \frac{kT}{e} \right) \frac{\pi x}{d} \sin \frac{\pi x}{d} + c_0. \quad (4)$$

Here, in order for nE not to keep increasing with x , one requires

$$n_0 = \tau f. \quad (5)$$

Also, it can be seen that for $c_0 \neq 0$ one would obtain an increasing potential. Therefore one also requires

$$c_0 = 0. \quad (6)$$

Thus, using

$$\alpha \equiv (d/\pi)^2 (1/\mu_n \tau) + (kT/e), \quad (7)$$

one obtains:

$$E = \alpha_n (\pi/d) \sin(\pi x/d) / ((\tau f/n_1) + \cos(\pi x/d)), \quad (8)$$

and

$$V = \int E dx = \alpha_n \ln[(\tau f/n_1) + \cos(\pi x/d)] + c_1. \quad (9)$$

For $V=0$ at $x=d/2$ (see Fig. 2),

$$c_1 = -\alpha_n \ln(\tau f/n_1),$$

and

$$V = \alpha_n \ln[1 + (n_1/\tau f) \cos(\pi x/d)]. \quad (10)$$

If the field causes only a relatively small perturbation of the carrier concentration, i.e., if $n_1 \ll n_0$ and therefore

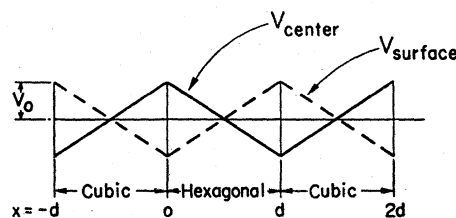


FIG. 2. Expected potential (schematic) in disordered ZnS crystals, assuming neutralization on top.

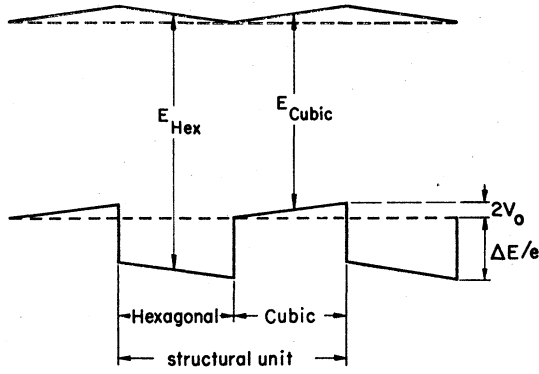


FIG. 3. Schematic of the postulated band edges, with the change (ΔE) in band gap between cubic and hexagonal material shown in the valence band due to the assumption (Sec. III.) of a constant density of ionized donors.

by Eq. (5) ($n_1/\tau f \ll 1$) (see Appendix II), one then obtains

$$V \approx \alpha_n (n_1/\tau f) \cos(\pi x/d). \quad (11)$$

This is not quite of the form shown in Fig. 2, but is close enough for our present purpose. If the potential is written in the form

$$V = V_0 \cos(\pi x/d), \quad (12)$$

then

$$n_1 \approx V_0 (\tau f / \alpha_n). \quad (13)$$

It follows from Eqs. (3) and (5) that

$$n = \tau f [1 + (V_0/\alpha_n) \cos(\pi x/d)]. \quad (14)$$

Within the limitation of the various assumptions which have been made, one has now obtained an expression for the carrier concentration in terms of the voltages caused by the postulated internal fields.

It should still be noted that, strictly speaking, V_0 will depend, via the Poisson equation, not only on σ_H but also on n_1 and p_1 (assuming n_0 and p_0 to be generated in equal amounts and thus to cancel). However, when appropriate values are selected for the various parameters, it can be shown that the fields due to n_1 and p_1 are negligible (see Appendix II).

III. PHOTOVOLTAGE OF A STRUCTURAL UNIT

The effect of the periodic potential on the photovoltage at two otherwise equivalent band-gap barriers will now be discussed. The energy gap difference between cubic and hexagonal material^{8,9} causes a variation in the potential acting on the carriers, which is superimposed on this periodic potential, so that a carrier might "see" a potential something like the one sketched in Fig. 3. The carrier concentration at a "band-gap" barrier will thus be different, depending on whether the barrier is on a hill or in a valley of the electrical potential.

Equations for the photovoltage associated with a

change in band-gap have been derived by Tauc.^{12,13} We will here briefly sketch his derivation, in order to obtain an equation for the photovoltage in a form appropriate to show the effect of a difference in carrier concentration at otherwise equivalent barriers. (The final equation of Tauc assumes $\Delta n = \Delta p$, a condition which we do not wish to enforce in the present problem.)

By using the condition of zero current Tauc derives, for a photovoltage (U) associated with a change in band gap¹³:

$$U = -\frac{1}{e} \int (l_n d\zeta_n - l_p d\zeta_p), \quad (15)$$

where we have used a slight change in notation from the one used by Tauc,^{12,13} with

$$l_n = \frac{\mu_n n}{\mu_n n + \mu_p p}, \quad (16)$$

$$l_p = \frac{\mu_p p}{\mu_n n + \mu_p p},$$

where p = hole concentration, μ_p = hole mobility,

$$\Delta\zeta_i = \zeta_i - \zeta_{i0} \quad (17)$$

ζ_i = chemical potential of the assembly of electrons (or holes) under illumination, and ζ_{i0} = chemical potential in the dark. In addition, one has the subsidiary equations^{12,13}

$$n = A_n \exp(\zeta_n/kT), \quad (18)$$

$$p = A_p \exp(\zeta_p/kT),$$

$$-\frac{1}{n_e} \frac{dn_e}{dx} + \frac{1}{p_e} \frac{dp_e}{dx} = -\frac{1}{kT} \frac{dE_g}{dx}, \quad (19)$$

where A_i = density of states, E_g = energy gap, and n_e, p_e = equilibrium carrier concentrations. With the use of Eqs. (16)–(18) one can obtain Eq. (15) in terms of derivatives of the carrier concentrations. However, to simplify the resultant equation, we will make two assumptions. First, we will assume that the number of carriers generated by the light will be approximately constant in the vicinity of the energy gap change,¹² i.e., that $d\Delta n/dx \approx d\Delta p/dx \approx 0$. This assumption means (1) that in the immediate vicinity of the energy gap barrier one is neglecting the spatial variation in the carrier concentration caused by the internal fields, and (2) that one is considering, strictly speaking, only the photovoltage in wavelength regions where cubic and hexagonal material have roughly equal absorption¹⁴

¹² J. Tauc, Revs. Modern Phys. **29**, 308 (1957).

¹³ J. Tauc and M. Závětová, Czech. J. Phys. **9**, 572 (1959).

¹⁴ For other wavelength regions it is difficult to obtain the magnitude of the corresponding photovoltage, since the simultaneous variation of Δn and E_g complicates the evaluation of the necessary integrals.

(also see the next section). Second, we will assume that the ZnS is an n -type semiconductor and that it has an approximately constant density of ionized donors along its length; this means that, again neglecting spatial variations due to the internal fields, one has $dn_e/dx \approx 0$ in the band-gap region. With these approximations and with use of Eqs. (16)–(19), Eq. (15) then reduces to:

$$U \approx -\frac{1}{e} \int \frac{\mu_p \Delta p}{\mu_n n + \mu_p p} \frac{dF_0}{dx} dx.$$

Due to the assumptions that Δn , Δp , and n_e are approximately constant this equation can be integrated readily and one obtains, per barrier:

$$U_B \approx -\frac{1}{e} \frac{\Delta p}{bn + p} \Delta E, \quad (20)$$

where ΔE = energy gap difference and $b = \mu_n/\mu_p$. It should be noted that here p is the concentration of minority carriers so that, as usual,¹² the presence of minority carriers is required for the observation of a photovoltage. This requirement thus limits the present theory to the photovoltages observed in and near the intrinsic (band gap) absorption region.

Having obtained an expression for the photovoltage per barrier, one can now readily obtain the photovoltage for a structural unit. Each such unit will contain two barriers, one of $+\Delta E$, the other of $-\Delta E$, and the photovoltage of the unit will be the sum of the opposing photovoltages of these two barriers. The carrier concentration at each barrier will be given, within the approximations of Sec. II, by Eq. (14). For one barrier at $x=0$ and the other at $x=d$, one has

$$\begin{aligned} n(0) &= \tau f[1 + (V_0/\alpha_n)], \\ n(d) &= \tau f[1 - (V_0/\alpha_n)]. \end{aligned} \quad (21)$$

Assuming an equal generation rate of holes and electrons, i.e., absorption in or at least very near the band-gap region, the expressions for p will be similar, but with the opposite phase, i.e.,

$$\begin{aligned} p(0) &= \tau f[1 - (V_0/\alpha_p)], \\ p(d) &= \tau f[1 + (V_0/\alpha_p)]. \end{aligned} \quad (22)$$

A negligible concentration of dark carriers has already been assumed in Sec. II, so that one also has $\Delta p \approx p$. Thus, the net photovoltage of a structural unit (U_N) will be

$$\begin{aligned} U_N &= -\frac{1}{e} \frac{[1 - (V_0/\alpha_n)]}{b[1 + (V_0/\alpha_n)] + [1 - (V_0/\alpha_p)]} \Delta E \\ &\quad + \frac{1}{e} \frac{[1 + (V_0/\alpha_n)]}{b[1 - (V_0/\alpha_n)] + [1 + (V_0/\alpha_p)]} (-\Delta E). \end{aligned}$$

Using $(V_0/\alpha) \ll 1$ (which follows from the assumption

$n_1 \ll n_0$ used in Sec. II), this reduces, approximately, to

$$U_N \approx -\frac{\Delta E}{e} 2bV_0 \left(\frac{1}{\alpha_n} + \frac{1}{\alpha_p} \right) / (b+1)^2. \quad (23)$$

For $b \gg 1$ (which is probably the case in ZnS), this reduces to

$$U_N \approx -\frac{\Delta E}{e} \frac{2V_0}{b} \left(\frac{1}{\alpha_n} + \frac{1}{\alpha_p} \right). \quad (24)$$

As already mentioned, these photovoltages will add all along the crystal, since the differences in carrier concentration will always be in the same direction in each unit.

IV. PHOTOVOLTAGE REVERSAL

We will now discuss how the present model can account for the photovoltage reversals in the band-edge region. Essentially, the proposed explanation depends on the reversals of the internal fields, coupled with the variation of absorption with wavelength. Since two possibilities for field reversals have been suggested, one with length (cubic to hexagonal), and one with depth, there appear to be two corresponding possibilities for photovoltage reversals. These will now be discussed in sequence.

For field reversal with length, we assume that for roughly equal absorption of light in cubic and hexagonal regions, the photovoltage is due to the mechanism which has just been presented, i.e., due to the differences in carrier concentration at the barriers. However, in the band-edge region of absorption there will be a wavelength region with heavy absorption by cubic material, due to its smaller band-gap, and much less absorption by the hexagonal material, and this has already been suggested as an explanation for the photovoltage reversals.^{6,7,9} In the present model, it would seem likely that in this wavelength region one can have a photovoltage due to the electric potential in the cubic regions, with a sign opposite to the net band-gap photovoltage. This latter field induced photovoltage would not be expected to give any appreciable contribution for roughly equal absorption, since in that case it should be balanced by an equal and opposite voltage in the hexagonal regions. This situation would thus lead to a photovoltage reversal: for short λ , i.e., for wavelengths well within both intrinsic absorption regions, there would presumably be roughly equal absorption in the two regions, and one would have the ("negative"^{2,4}) photovoltage of the band-gap barriers; at a slightly longer λ , where hexagonal ZnS no longer absorbs heavily but cubic ZnS still does, the "cubic" ("positive"^{2,4}) photovoltage would dominate; at still longer λ , for exciton or impurity absorption, one would probably again have regions of roughly equal absorption, with resultant renewed domination of the band-gap photovoltages (although only as long as the absorption some how still generates minority carriers—cf. Sec. III.).

An alternate possibility for photovoltage reversal is given by field reversals with depth (for neutralization on top). For heavy absorption, most of the absorption takes place near the upper surface, and the photovoltage sign would be determined by the surface fields. With lower absorption, more of the absorption would take place in the interior of the crystal; the effect of the inside, opposite fields could then dominate over the surface fields, leading to a photovoltage reversal. Finally, with still less absorption, the lower surface of the crystal would also contribute; with both surfaces active, the surface fields could then again dominate. These considerations provide a second possible explanation for photovoltage reversals of the type observed. (It should be noted that if this type of reversal takes place, one would expect a dependence of the reversal wavelength on the crystal thickness, and it may thus be of interest to look for such an effect.)

V. DISCUSSION

A rather satisfying aspect of the present theory of ZnS photovoltages is that, assuming internal fields, either of the type postulated here or elsewhere,⁷ the various photovoltage properties (i.e., the net segment photovoltages, the additivity of these net photovoltages, and the photovoltage reversals) appear to follow in a relatively straightforward manner. Although the equation [Eq. (24)] describing the net band-gap photovoltage of a unit has been based upon a number of assumptions (e.g., $\Delta n \approx n$, $dn_c/dx=0$, $n_1 \ll n_0$ etc.), these assumptions should only affect the quantitative relations, with a net photovoltage obtained basically as a consequence of the fields and the resultant differences in carrier concentrations. Similarly, both the additivity of the net photovoltages and the photovoltage reversals follow qualitatively from the existence of these fields.

It thus seems appropriate at this point to consider whether the proposed model can also account for the magnitude of observed photovoltages. As mentioned, there is an experimental estimate of ≈ 0.15 v per barrier.³ The present model predicts a voltage per unit of at most $\Delta E/e$, i.e., of ≈ 0.1 v. This is of the same order of magnitude as the experimental estimate, although somewhat on the low side. However, there is some question concerning the reliability of the experimental value of 0.15 v. This value was derived by dividing the observed voltages by the estimated number of barriers in the crystals. This number, in turn, was obtained in two ways, first by determining the number of lines visible under polarized light and assuming that each line corresponded to a barrier; and secondly by comparing the observed photovoltage with that to be expected from a single contact or *p-n* junction barrier. The result of neither method appears conclusive. Thus, it is known that under polarized light disordered ZnS crystals contain bands of relatively uniform birefringence, with sharp lines (presumably the lines counted in reference 3) at the ends

of these regions^{11,15}; however, judging by the birefringence of the bands it appears quite likely that each of these bands is of mixed structure, with a possibility of a large number of structure reversals per band.¹⁵ The number of energy gap barriers per crystal could thus easily be considerably larger than the number of lines visible under polarized light. The second method of estimating the number of barriers makes use of the equation (for high light intensity) of the photovoltage per barrier for contact- or *p-n* junction barriers³:

$$U \approx (kT/e) \ln f + \text{const}, \quad (25)$$

which predicts a slope of kT/e when plotting U vs $\ln f$. On making such plots in connection with multiple barrier cells, the number of barriers is presumably obtained by dividing the observed slope by kT/e . However, no such dependence is predicted by Eq. (20),¹⁶ so that if the present theory is correct it does not appear feasible to use this slope method to estimate the number of barriers.

It will now be shown that if one disregards the above estimate of ≈ 0.15 v per barrier, the proposed theory seems quite adequate to account for observed photovoltages (ranging up to ≈ 400 v/cm of crystal³). If the assumptions leading to Eq. (24) are valid, one obtains, for the voltage per cm of crystal:

$$U_c = \frac{2V_0}{b} \left(\frac{1}{\alpha_n} + \frac{1}{\alpha_p} \right) \frac{1}{2d} \frac{\Delta E}{e}. \quad (26)$$

To estimate α [Eq. (7)] we will assume that $\tau \sim 10^{-7}$ – 10^{-8} sec, and $\mu \sim 10$ – 100 cm²/v sec. For d , we will use Merz's³ result of ≈ 200 birefringent bands/cm, and assume that for crystals with high photovoltages one has ten or more structure reversals per band, giving $d \lesssim 5 \times 10^{-5}$ cm for such crystals. With these values, one obtains, at room temperature:

$$(d/\pi)^2 (1/\mu_n \tau) \lesssim 2.5 \times 10^{-3} \ll (kT/e). \quad (27)$$

Consequently,

$$\alpha_n \approx \alpha_p \approx (kT/e). \quad (28)$$

With this simplification and with the use of the internal field:

$$E_0 = V_0(\pi/d), \quad (29)$$

one obtains

$$U_c \approx (2eE_0/\pi b kT)(\Delta E/e). \quad (30)$$

It is worth noting that as long as the inequality (27) holds, this photovoltage is no longer dependent on the

¹⁵ L. W. Strock, V. A. Brophy, and T. E. Peters, Enlarged Abstracts of the Electronics Division, Electrochem. Soc. Spring Meeting, p. 61 (1958).

¹⁶ Using $n = n_c + \Delta n$, with Δn and Δp proportional to the excitation density, one can see that Eq. (20) gives a linear dependence on light intensity at low excitation and saturates at high excitation, as is observed experimentally.³ However, a detailed equation for the intensity dependence of the present model seems unwarranted in view of various approximations which have been used. For example, the carrier density at the barriers (Eq. 21) has been derived by assuming a high excitation intensity ($\Delta n \approx n$).

parameters μ , τ , or d , only E_0 , b , and $(\Delta E/e)$ being required. Neither E_0 nor b appear known for ZnS, but if one assumes $E_0 \sim 10^3$ v/cm, $b \sim 10$, and $\Delta E/e \approx 0.1$ ev,⁸ one obtains, at room temperature,

$$U_c \approx 250 \text{ v/cm of crystal.}$$

The selected values for the field and for the mobility ratio appear to be in a quite reasonable range, which means that the proposed theory can account for observed voltages with reasonable values of these parameters. It is also of interest that although the temperature dependence of E_0 and b is unknown, the kT factor can, as such, account for an increase of U_c with decreasing temperature (as is observed experimentally near room temperature^{3,17}).

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APPENDIX I

To illustrate some of the points made in Sec. II, we will now consider both the density of surface charge required for the neutralization of the postulated internal charge σ_H , and then calculate (for neutralization on top) the resultant potential along the line in the center of the crystal.

The density of such surface charge, relative to σ_H , can be estimated by requiring zero field in regions well away from the crystal. In such regions, the various charge densities can be considered, approximately, as dipoles, and the condition for zero field is that the dipole moments cancel. For neutralization by rings of line charge (of density ρ_L), and assuming the crystal to be a circular rod of radius R , this requires:

$$\begin{aligned} \pi R^2 \sigma_H &= -2\pi R \rho_L, \\ \rho_L &= -(R/2)\sigma_H. \end{aligned} \quad (\text{A1})$$

For neutralization at the end of the crystal, one has to consider the moment of all the hexagonal segments before one can obtain the required charge density. For an area charge (of density σ_A) at the ends one now requires:

$$\begin{aligned} \sigma_H D_H &= -\sigma_A D_C, \\ \sigma_A &= -(D_H/D_C)\sigma_H, \end{aligned}$$

where

$$D_H = \sum_i d_H^i,$$

d_H^i is the length of the i th hexagonal segment, and D_C is the length of the crystal.

From the values of the charge densities one now could, in principle, compute the potential at any point in the crystal in terms of σ_H . In practice, this does not appear

¹⁷ G. Cherooff, Bull. Am. Phys. Soc. 6, 110 (1961).

to be possible without elaborate calculation and also appears unnecessary for the further considerations of this paper. We will therefore merely consider, as an illustration, the potential along the line in the center of the crystal. We will here mainly consider the case of neutralization on top, but will mention where conclusions apply to either type of neutralization. The potential along such a line can be obtained fairly readily, especially if one considers only a few charge layers (as will be done here). Thus, the potentials along the axis of a ring of charge (for ρ_L) and of a disk of charge (for σ_H) are known.^{18,19} For a ring of charge, the potential (V_R) is given by¹⁸

$$V_R = (2\pi\rho_L/\epsilon)/[(x/R)^2 + 1]^{\frac{1}{2}},$$

where x is the distance from the center of the ring along the axis, and ϵ is the product of the dielectric constant and the permittivity. This with use of Eq. (A1) becomes

$$V_R = -(\pi\sigma_H R/\epsilon)/[(x/R)^2 + 1]^{\frac{1}{2}}. \quad (\text{A2})$$

The equivalent potential for a disk of charge (V_D) is¹⁹

$$V_D = (2\pi\sigma_H R/\epsilon)\{[(x/R)^2 + 1]^{\frac{1}{2}} - (x/R)\}. \quad (\text{A3})$$

Both V_D and $-V_R$, as well as the sum of these two potentials, are shown in Fig. 4 as functions of x/R . As can be seen, and as was pointed out in Sec. II, the slope of the sum of the two potentials is essentially determined by V_D .

We will next consider the potential in more detail for $x \ll R$, i.e., for regions thin compared to the radius of the crystal. Since the thickness of a structural segment in the disordered ZnS crystals is generally of the order of microns or less,^{3,15} this should approximate the situation in a given segment of these crystals. For this

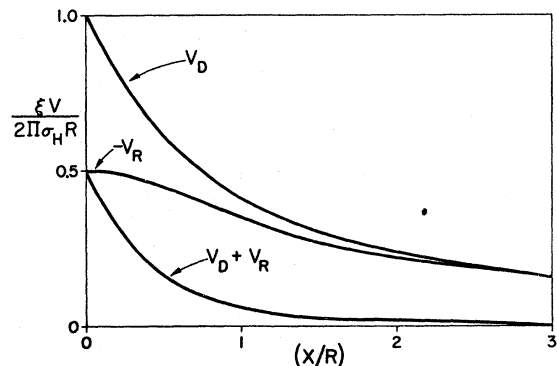


Fig. 4. The potential along the line in the center of the crystal due to a charged layer (V_D), and due to a ring of opposing charge around the edge of the charged layer ($-V_R$). The sum of the two potentials is also shown.

¹⁸ S.e., for example, N. H. Frank, *Introduction to Electricity and Optics* (McGraw-Hill Book Company, Inc., New York, 1940), p. 37.

¹⁹ See, for example, M. Mason and W. Weaver, *The Electromagnetic Field*, (The University of Chicago Press, Chicago, Illinois, 1929), p. 11.

case, one obtains:

$$V_R \approx -(\pi\sigma_H R/\epsilon)[1 - \frac{1}{2}(x/R)^2], \quad (\text{A4})$$

$$V_D \approx (2\pi\sigma_H R/\epsilon)[1 - (x/R) + \frac{1}{2}(x/R)^2], \quad (\text{A5})$$

$$V_D + V_R \approx (\pi\sigma_H R/\epsilon)[1 - (2x/R) + \frac{1}{2}(x/R)^2]. \quad (\text{A6})$$

The voltage in a segment (V_S) due to the charge at each boundary, i.e., $+\sigma_H$ at $x=0$ and $-\sigma_H$ at $x=d$, to the order of the terms linear in x , is thus given by

$$\begin{aligned} V_S &\approx (\pi\sigma_H R/\epsilon)[-(2x/R) + 2(d-x)/R] \\ &= (2\pi\sigma_H/\epsilon)(d-2x). \end{aligned} \quad (\text{A7})$$

As can be seen, this equation gives a potential of the type shown in Fig. 2.

If one assumes that for the next few charge layers away from this segment one still has $x \ll R$, it then becomes easy to consider a few more layers. For an additional charge layer on either side of the segment under consideration, each layer a distance d away [with $(d+x) \ll R$], the terms linear in x in Eq. (A6) cancel, and one has a contribution only from the quadratic terms. The result is

$$V_S = (\pi\sigma_H/\epsilon)(d/R)(d-2x). \quad (\text{A8})$$

The potential is now smaller and has a smaller slope (by $d/2R$) than the potential given by Eq. (A7), but the direction of the slope is still the same.

If one still considers two additional layers (again on either side, a distance d from the preceding layer), then the linear terms in Eq. (A6) do not cancel but are again the main terms. Now, to the order of the linear terms, the two additional charge layers on either side cancel each other, and one obtains the same potential as given by Eq. (A7).

It should still be noted that, for $x \ll R$ and for purposes of the discussion following Eq. (A6), the potential V_D is essentially of the same form as $V_D + V_R$, so that the conclusions of this part of the treatment also hold for V_D alone (i.e., for the case of end neutralization).

APPENDIX II

It will here be shown that the values of the parameters which have been used are consistent with the as-

sumptions used in solving Eq. (2), namely that $n_1 \ll n_0$, and that the field due to n_1 (and p_1) is negligible compared to the internal field. From Eq. (5) and (13) one can see that the requirement for $n_1 \ll n_0$ is

$$V_0/\alpha \ll 1.$$

Use of Eqs. (28) and (29) then gives the requirement

$$eE_0 d/\pi kT \ll 1.$$

For $E_0 \sim 10^3$ v/cm and $d \lesssim 10^{-5}$ cm, one obtains, at room temperature,

$$eE_0 d/\pi kT \lesssim 0.13, \quad (\text{A9})$$

so that the required inequality is here well fulfilled (although a more exact treatment may be required at low temperatures).

To evaluate the field due to the free carriers (E_c), one requires evaluation of the expression

$$E_c = (4\pi e/\epsilon) \int (n-p) \cos(\pi x/d) dx.$$

Assuming $n_0 = p_0$, using Eqs. (5), (14), (28), and (29) and integrating, one obtains

$$E_c = (4\pi e/\epsilon)[2n_0 e E_0 d/\pi kT](d/\pi) \sin(\pi x/d).$$

Use of Eq. (A9) then gives

$$E_c \lesssim 0.26(4e/\epsilon)dn_0.$$

The resistivity, even under strong irradiation, of the ZnS crystals showing the photovoltaic effect is probably $\gtrsim 10^6$ ohm cm, so that, assuming $\mu_n \sim 100$ cm²/v sec, one obtains

$$n_0 = 1/e\mu\rho \lesssim 6 \times 10^{10}.$$

With $\epsilon \approx 8$ and $d \lesssim 10^{-5}$, this gives

$$\begin{aligned} E_c &\lesssim 4 \times 10^{-4} \text{ statvolt/cm} \\ &\lesssim 0.1 \text{ v/cm,} \end{aligned}$$

which is considerably less than the postulated internal field of 10^3 v/cm.