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ANOMALOUS PHOTOVOLTAIC EFFECT IN ORTHORHOMBIC SULFUR

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Larger than band gap photovoltages have been observed in single crystals of orthorhombic sulfur grown from CS_2 solution or the vapor phase.

ANOMALOUS photovoltages which exceed the band gap by orders of magnitude have been observed in evaporated layers[1] and in single crystal ZnS[2] with the early results and explanations being summarized by Tauc.[3] We report here the observation of an anomalous photovoltage in single crystal orthorhombic sulfur.

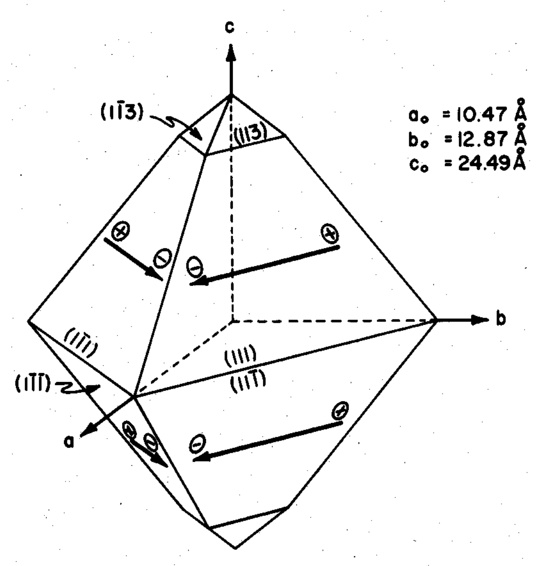

FIG. 1
Schematic representation of a single crystal of orthorhombic sulfur as grown from CS_2 solution or the vapor phase. The arrows show the sign and direction of the maximum photovoltage on the {111} faces.

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Under sufficiently short wavelength radiation, a photo-e.m.f. appears between two points on the crystal. Figure 1 shows the direction and sign of the photovoltage maximum as observed on each of the {111} faces of all samples examined. Maximum open circuit photovoltages more than 100 volts for an electrode separation of 1 cm were found in some cases and in all cases the photovoltage was proportional to the electrode distance. The photo-e.m.f. is independent of the electrode material and appears also when care is taken to shield the contacts from the incident light. For directions other than $<110>$ on the {111} faces the photovoltage is smaller, vanishing in a direction approximately perpendicular to $<110>$. No profound difference in the effect was found between crystals grown from CS_2 solution and those deposited from the vapor phase.

Figure 2 shows the open circuit photovoltage as a function of light intensity. If we subscribe to the hypothesis that the anomalous photovoltaic effect arises from a number of "elemental batteries" connected in series, each battery producing a voltage given by a normal photovoltaic effect, then the photo-e.m.f. can be written as [4]:

$$V = n\,(kT/e)\,\ell n\,(1 + L),$$

where L is proportional to the incident light intensity, n is the number of elemental batteries, and the other symbols have their usual meaning. With the use of the above equation, therefore, n may be deduced along with the average length of a battery. From the data of Fig. 2, we arrive at $n \approx 200$/cm or a mean length of 50μ for this particular sample. Among various other samples, the mean length runs from 10-100μ depending on

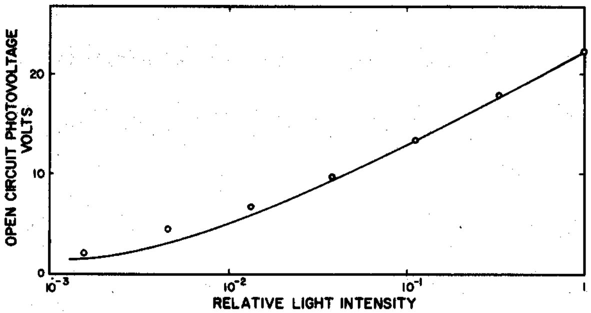

FIG. 2

Open circuit photovoltage at room temperature as a function of incident light intensity for unfiltered radiation from a high pressure Hg lamp. The line represents $V = n(kT/e)\ \ell n\ (1 + L)$, where $n = 160$ and L is proportional to the incident light intensity. Electrode distance is 8 mm.

the magnitude of the photovoltaic response.

At $\lambda = 250$ mμ a photon flux density of 2×10^{13}/sec cm^2 caused an open circuit photovoltage of 20 volts to appear across a 1 cm electrode separation. Using an absorption coefficient 8×10^4 cm^{-1} [5], we obtain a pair generation rate of 1.6×10^{18} / sec cm^3.

The spectral response of the short circuit photocurrent, which is approximately proportional to light intensity, was measured at various temperatures and is given in Fig. 3. The onset of photocurrent occurs near the energy found by Spear and Adams [5] for simultaneous generation of holes and electrons in their photoconductivity experiments. This is to be expected inasmuch as the extremely high dark resistivity ($>10^{19}$ Ω cm) [6] of orthorhombic sulfur indicates a low concentration of majority carriers in which case the photovoltaic effect will not occur unless both carrier types are created by the incident light. Thus, the photovoltaic effect provides a way of finding the band gap energy (defined as that minimum energy for the creation of unbound hole-electron pairs) of substances in which the dark majority carrier concentration is low. This is particularly convenient in the case of molecular crystals such as orthorhombic sulfur where the energy of the absorption edge does not necessarily correspond to the band gap because of the excitation of molecular states at energies less than the band gap. As the sample temperature is reduced, the magnitude of the short circuit photocurrent decreases and the peak at 4.7 eV sharpens. When

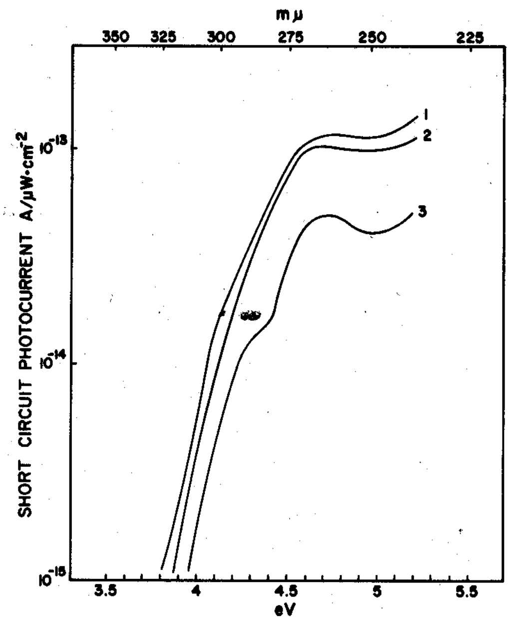

FIG. 3

Dependence of short circuit photocurrent per incident light intensity on photon energy at various sample temperatures. (1) 298° K; (2) 208° K; (3) 169°K. Electrode distance is 8 mm.

the data of Fig. 3 are normalized, one can see that the photocurrent edge is shifted to slightly lower energies and that the temperature coefficient is very small ($\approx -1 \times 10^{-4}$ eV/° K).

The anomalous photovoltages in films and single crystals of ZnS have been attributed to the intermixing of hexagonal and cubic phases.[2,4] However, the samples of sulfur crystals reported on herein were, as far as we could determine from polariscopic and X-ray analyses, uniformly orthorhombic (space group Fddd, which contains a center of symmetry). In addition, the sign, direction and magnitude of the photovoltage did not change significantly with grinding, polishing or etching of the surface nor with the composition of the ambient atmosphere as long as it was kept dry. On the other hand, if the bulk of the crystal underlying a {111} face was ground away, thus leaving a platelet 1-2 mm in thickness, the photovoltage was greatly diminished. This result suggests that the photovoltage may arise from a series of strain areas built in during growth which become relieved when the sample is ground thin enough. Further evidence for this picture is suggested by the strong hydrostatic pressure dependence of the photovoltage. It was found that the open circuit signal increased by an order of magnitude upon bringing the sample from vacuum to about 2 bars of pressure regardless whether dry air, N_2, O_2 or argon was used as the pressure fluid, and the effect was reversible.

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