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Behavior of PbS Photocells in the 20-25 kbar Phase Transition Region

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The resistance of commercial PbS photocells was measured in the 0-35 kbar pressure range and in the 200-300°K temperature range. The effective band gap decreased continuously at a declining rate with increasing pressures. The resistance decreased with increasing pressure up to ≃ 20 kbars, and then proceeds to increase at higher pressures. The phase transformation, commencing about 20 kbars, has little influence on carrier density, but reduces mobilities significantly.

A resistência de fotocélulas comerciais de PbS foi medida, no intervalo de pressão de 0-35 kbars e, de temperatura, de 200-300°K. A variação do intervalo efetivo entre as bandas de energia mostrou-se ser uma função inversa da temperatura. O comportamento da variação da resistência em função da pressão foi diferente em diferentes intervalos de pressão: até aproximadamente 20 kbars, um decréscimo da resistência ocorreu quando a pressão foi aumentada, enquanto que, na região acima de 20 kbars, houve um aumento da resistência com a pressão. A transformação de fase iniciada em 20 kbars teve pequena influência na densidade, mas produziu uma redução significativa nas mobilidades.

1. Introduction

Useful detectors of near-infrared radiation are lead sulfíde (PbS) photocells. The photosensitivity of PbS films at room temperature reaches a maximum near 2.3 microns. The photoconductive properties of this intrinsic semiconductor are determined in part by the energy gap between valence and conduction bands. It has been found that energy gaps (E_g) are very strongly influenced by matrix compression of the semiconductor at high pressures. Paul and Wauschauer' first suggested that the wavelength of maximum sensitivity may be tuneable by hydrostatic

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(or quasi-hydrostatic) pressure. Izvozchikov and Taksami[2] have recently reported $dE_g/dP = -8.5 \times 10^{-5}$ ev/kbar for the optical energy gap of PbS films, confirming measurements of Prakash, which were reported by Paul, DeMeis and Finegold[3]. This red shift of the absorption edge is mirrored by the decrease in resistance over the same pressure range[3,4].

Ultrahigh pressures have also been employed to study the resistivity of PbS crystals and films at room temperature[5,6]. The gross features of the pressure response, which were independent of crystal impurities, revealed a sharp increase in resistance around 23-25 kbars, followed by a decrease in resistance above 40-50 kbars (Refs. 5-6). The strong alteration in resistivity is presumably due to a phase transition in PbS, reported by Bridgrnan in this pressure region[7]. The aim of the present work is to explore the transition pressure region more carefully and to employ temperature as an additional variable for resistance studies of PbS semiconductors.

2. Experimental Procedure

The PbS films, deposited on glass substrates, were commercial photocells (Ektron) manufactured by Eastman Kodak. Most work was done on 2 x 2 mm^2 film and studied in the 213-283°K and the 0-35 kbar ranges of temperature and pressure. The estimated uncertainties in pressure and temperature measurements were 3% and 2%, respectively.

The experiments were carried out in a conventional piston and cylinder device[8]. The photocell and thermocouple were suspended in a pressure-transmitting medium of boron nitride powder in n-octadecane, as previously described[8]. An indication of the hydrostaticity of the pressure environment is the fact that the resistance measurements were reversible and the glass substrate remained unbroken by the pressures to which it was subjected. Temperature was varied by passing liquid nitrogen vapors through coils surrounding the steel plates. Resistance (R) measurements were made at successively higher isobars upon cooling and warming the sample. Temperature was more readily controlled during warm-up; hence, the values of R quoted below were determined with increasing temperatures. Resistance measurements, taken with an Electro Scientific Industries bridge, were accurate to 1% over the 0.1 to 100 MΩ range.

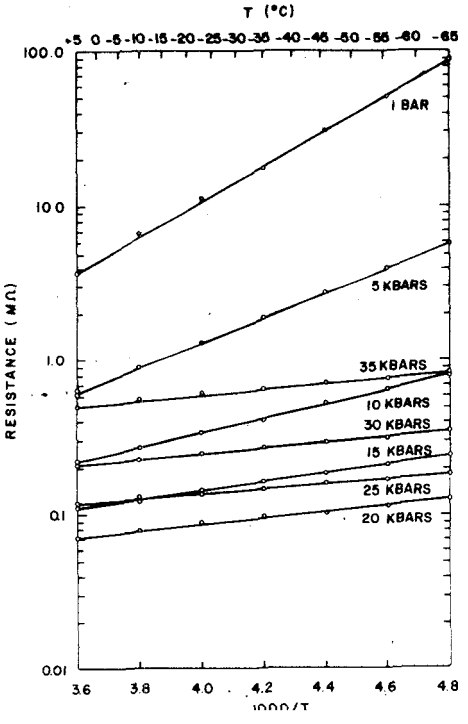

Figure 1. Temperature dependence of the PbS photocell resistance at several isobars.

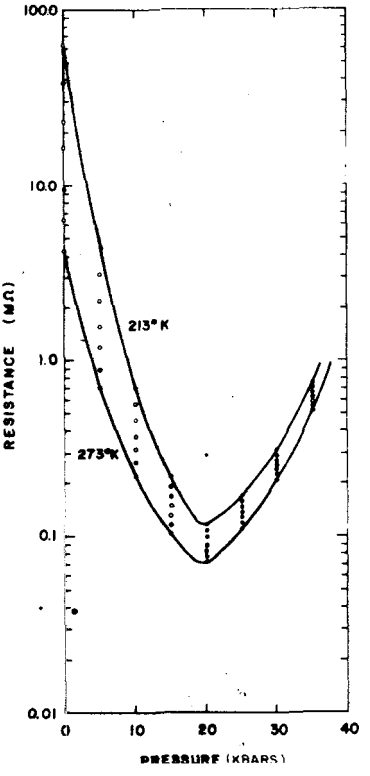

Figure 2. Pressure dependence of the resistance of PbS photocells.

3. Results and Discussion

The results of the pressure-temperature measurements are summarized in Figures 1-3. The log R *vs.* $1/T$ plots in Fig. 1 are linear over the temperature and pressure range investigated. It is seen that the band gap, as determined by the slope in Fig. 1, continues to decrease in the phase transition region, while the resistance increases above *20* kbars. Fig. *2* shows the reversal in resistance around 20 kbars for two isotherms. The nonlinear pressure dependence of the resistance is far more sensitive to temperature in the low-pressure phase than in the high-pressure phase of PbS films. The empirical band gap at one atmosphere $E_g(0)$, and the initial pressure dependence dE_g/dP differed somewhat for the various photocells studied, but the band gap at 30 kbars was the same

for all commercial films investigated. Fig. 3 shows a typical change in E_n, dropping from the value of 13 x 10^{-3} ev/kbar to 0.4 x 10^{-3} ev/kbar at the higher pressures. There is no discontinuous change in $E_g(P)$ as the films pass through the phase transition region.

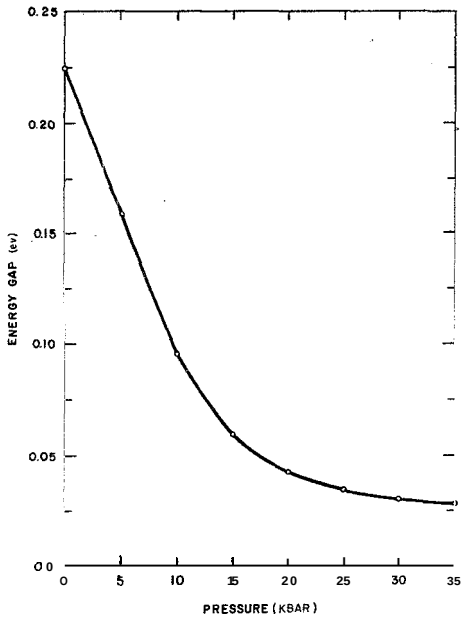

Figure 3. The influence of pressure on the effective band gap in PbS photocells.

An interesting observation in this work is the difference in the pressure dependence of R and E_n when the crystal structure is transformed under pressure. The transition pressure of PbS has been reported to be about 23-25 kbars (Refs. 5-7), although the commercial photocells used in the experiments give evidence for the onset of the transformation around 20 kbars. Paul *et al.*[3], found no evidence for a phase transition below 30 kbars in their studies of PbS crystals. The influence of phase transitions on transport properties in solids is difficult to quantify, on the basis of present observations, because the purity and microscopic state of these photocells is unknown; it is hoped that some of our presently planned experiments will clarify this point. The results indicate that the band gap and carrier density actually change in a continuous manner for the two pressure phases. In contrast, the mobilities appear to be greatly reduced by the presence of the second phase. It is postulated that this reduction reflects a predominant increase in lattice scattering.

The extent to which the changes in the band structure and scattering mechanism contribute to the observed pressure effects cannot be determined from present results. The data demonstrate that the infrared response of PbS photocells can be shifted toward longer wavelengths and that the extent of the shift is not influenced by pressure-induced crystal transformations.

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