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Optical absorption, resistivity, and phase transformation in CdS at high pressure

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Optical-absorption measurements to 100-kbar hydrostatic pressure have been performed on CdS in a diamond anvil cell. The results indicate that the energy gap is direct in the wurzite phase and indirect in the rock-salt phase, which becomes stable above ~28 kbar. The initial $dE_g/dP \approx 0$, followed by red shift above 60 kbar in the rock-salt phase, is interpreted in terms of a changeover from $\Sigma_v \rightarrow X_c$ to $L_v \rightarrow X_c$ gap. The measured gap of 1.7 eV and the above assignments would be consistent with the band-structure calculations for the rock-salt phase of CdS.

I. INTRODUCTION

Edwards and Drickamer[1] first investigated the effect of pressure on the optical-absorption edge of CdS and found an abrupt red shift (decrease in wavelength) of the absorption edge at about 27-kbar pressure, which they attributed to a first-order phase transition. In a subsequent resistivity study under pressure, Samara and Drickamer[2] found a sharp drop in resistivity of about 5 orders of magnitude, corresponding to the above transition. At higher pressures the resistivity gradually rose to almost the ambient pressure value, before saturating in the 150–200-kbar region. A high-pressure x-ray diffraction study by Owen *et al.*[3] in 1963 established the nature of the phase transition as wurtzite to rock-salt structure. More recently CdS has attracted much attention because of the unusual magnetic and electrical properties that have been claimed for rapidly quenched (Cl-doped) CdS[4–6] (with a few percent Cl as impurity) from 40–50-kbar pressure; an unusually large diamagnetism and possible superconductivity at 77 K are attributed to freshly quenched CdS.

Our interest in CdS was primarily stimulated by the desire to understand the optical absorption and the changes in the latter across the wurtzite to the rock-salt phase transition. Since band-structure calculations are available for CdS and the isoelectronic Cu and Ag halides in the rock-salt structure, we felt that this could provide us with a basis for understanding the optical-absorption data in CdS, especially in the rock-salt phase. Further, we felt that it is important to establish the optical behavior of pure CdS in a strictly hydrostatic pressure environment, to understand the unusual properties of the pressure-quenched CdS mentioned above. We have also performed four probe resistivity measurements on CdS under strictly hydrostatic conditions across the phase transition. The results of these studies will be presented and discussed in this paper.

II. EXPERIMENTS

Four probe resistivity measurements were carried out on undoped and Cu-doped single-crystal bar-shaped samples of CdS. For Ohmic contacts indium was cold pressed onto the bar and Cu leads were then embedded in them. Hydrostatic pressure was generated in a piston-cylinder device using the Teflon cell technique.[7] Resistance was measured with a high-impedance ohmmeter.

For optical experiments, thin undoped as-grown flakes of CdS were employed. The samples chosen were typically about 30 μm in thickness and the plane of the crystal included the *c* axis. Optical-absorption measurements were performed in a gasketed diamond anvil cell with a 4:1 mixture of methanol and ethanol for the pressure medium. The above mixture retains fluidity up to 100 kbar.[8] Pressure was determined using the ruby fluorescence technique.[9]

For optical-absorption studies, a micro-optic setup similar to the one described by Welber[10] was employed. The light from a Xe high-pressure arc source was focused to a fine spot (30 μm in diameter) and was adjusted to go either through the sample or the pressure medium. The transmitted light was collected by the microscope objective and fed to a monochromator via a quartz fiber-optic light pipe. At each pressure the intensity of the light transmitted through the sample, as well as the pressure medium, were measured and compared. Thus the final data obtained represent a truly differential measurement. Both mechanical vibration and scattering of light by the sample limited the maximum optical extinction that could be measured. The problems, however, were not serious in our case, for the optical density in a completely absorbing situation was still greater than 3. All measurements were carried out at room temperature (295 K).

III. RESULTS

For the given thickness the absorption coefficient α was investigated over a range of 2000 cm^{-1}. Visually, the crystal plates were clear and yellow in color. In the wurtzite phase the absorption edge is very steep (exponential) as shown in Fig. 1 and is due to the direct exciton absorption. This energy shifts blue with hydrostatic pressure at the rate of 4.55 ± 0.05 meV/kbar, indicating that the direct gap increases at this rate with pressure. Edwards and Drickamer,[1] and Grutsche[11] have obtained shifts of 3.3 and 4.4 meV/kbar, respectively, for the direct gap. Considering the possible uncertainties in the former measurement and the good agreement with the latter, our value for the dE_g/dP is quite reasonable. Near 27 kbar the crystal abruptly turns red. However the red transmission is not found to be uniform, for the sample has numerous fine-textured dark streaks in it. The sample dimensions show a visible reduction in size, indicating that the transition involves a large volume collapse, in agreement with $\Delta V/V \sim 20\%$ measured in high-pressure studies. The transition pressure varies somewhat from sample to sample and in our studies occurred anywhere between 23 to 30 kbar. The reverse transition exhibits considerable hysteresis up to ~ 15 kbar which is not unusual for a sluggish first-order phase transition.

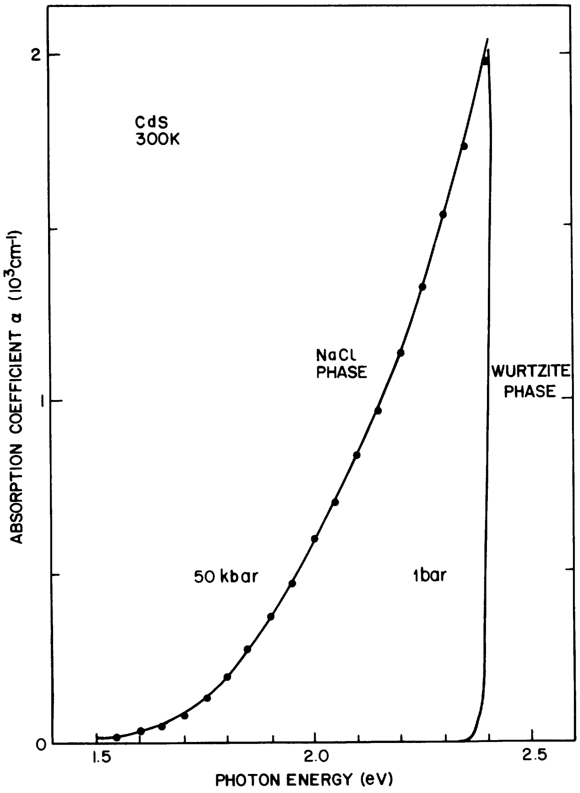

FIG. 1. The optical-absorption coefficient of CdS as a function of photon energy. The absorption edge is direct in the low-pressure wurtzite phase and indirect in the high-pressure NaCl phase.

The absorption edge of the rock-salt phase recorded at 50 kbar is shown in Fig. 1. The edge is strikingly different from that of the wurtzite phase and is clearly due to an indirect transition. The energy-gap values were obtained from a plot of $\alpha^{1/2}$ against $(E - E_0)$ and extrapolating the resultant straight line to $\alpha = 0$. However, the exact determination of E_0 is rendered difficult from the presence of scattering and dark streaks in the sample. Nevertheless the energy-gap changes can be estimated with reasonable accuracy. In the rock-salt phase the gap changes are quite small initially and then the gap decreases somewhat rapidly (> 70 kbar).

The shifts in the optical gap are plotted as a function of pressure up to 100 kbar in Fig. 2, which gives an overall picture of what happens across the transition. The general nature of the changes is quite similar to Edwards and Drickamer's[1] data, differing only slightly in quantitative terms. This may arise from the differences in the pressure environment used in

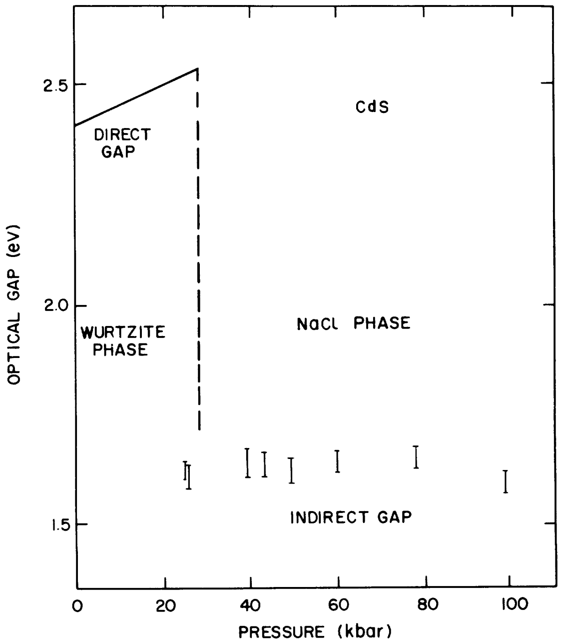

FIG. 2. Pressure dependence of the energy gap in CdS. The energy gap decrease by ~ 0.9 eV at the structural transformation.

the two studies, truly hydrostatic medium in our case and a soft solid pressure transmitting medium in the studies of Edwards and Drickamer.[1]

Resistivity measurements. The results of resistivity measurements on three of our samples are shown in Fig. 3. Although the starting resistivities are quite different, the resistivities in the high-pressure phase are comparable. High-resistivity samples show a drop in resistivity of 8 or 9 orders of magnitude [see Fig. 3 curve (a)]. In some samples, ρ increases with pressure after the transition, whereas for others it remains essentially unchanged with pressure. The resistivity behavior of CdS under pressure has been reported in two earlier studies[12,13] and results for hydrostatic pressure[13] are in reasonable agreement.

In the wurtzite phase, ρ exhibits an exponential increase with pressure in the Cu-doped samples and from the straight line portion the activation energy change with pressure for the donor state involved can be estimated as ~7 meV/kbar, assuming ρ changes due to the carrier concentration. In the high-pressure phase an exponential increase was observed by Samara and Drickamer[2] in the very-high-pressure range. Our own results of sample (a) are not inconsistent with this behavior. The resistance of (b), however, is pressure independent and increases by 15% on heating from room temperature to 170 °C, as if it were of metallic type.

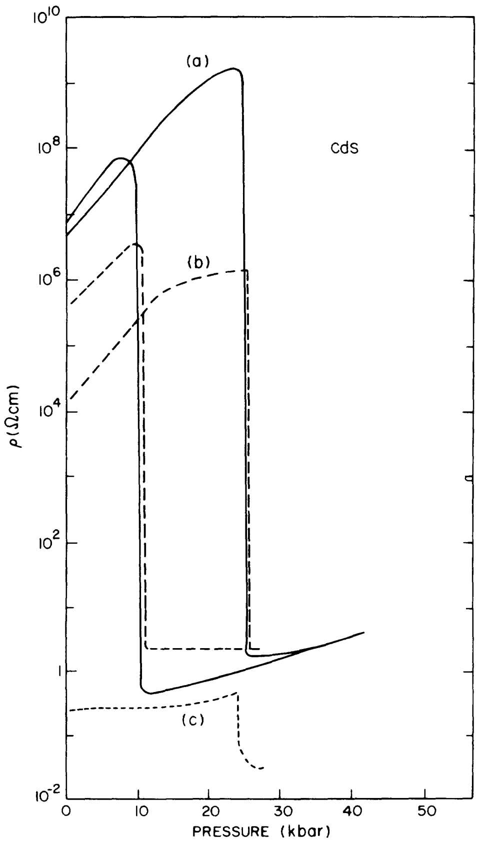

FIG. 3. Pressure dependence of the electrical resistivity for three different Cs samples. Sample (c) is Cu doped, whereas (a) and (b) are undoped.

From our optical-absorption studies and resistivity measurements across the phase transition we conclude that CdS in the rock-salt phase is not metallic but a semiconductor with a gap of about ~1.7 eV. We believe that the lower electrical resistivity in the high-pressure phase is due to imperfections and defects generated during the first-order phase transition from wurtzite to the rock-salt structure. We have to bear in mind the drastic change in the coordination from tetrahedral to octahedral. It is also likely that during the transition some segregation of Cd occurs at the grain boundaries, as was suggested by Hutson.[14] On release of pressure all the samples which went through the phase transition appear orange in color. In a high-power optical microscope, a mixture of yellow and orange microcrystallites can be identified. This must be due to the defects in the material, or perhaps due to the presence of a zinc-blende form of CdS.

Homan *et al.*[4] claim that the pressure-quenched CdS has a black metallic luster and consists of platelets embedded in a powder compact matrix. Apparently this mixture consists of (Brown *et al.*[6]) zincblende and rock-salt phases, presumably stablized by the presence of 1 or 2 at. % Cl impurity in the starting material.

IV. DISCUSSION

The energy-band structure of CdS in the rock-salt modification has been calculated at one lattice constant, namely 5.32 Å, using a fully symmetrized augmented-plane-wave method by Liu and Rabii.[15] The results shown in Fig. 4 indicate that it is an indirect-gap semiconductor with a band gap of 1.5 eV. Our measurements on the rock-salt phase are in agreement with the indirect gap obtained in the above calculation and the value of 1.7 eV for the gap obtained by us is close to the calculated value.

The band calculation of Liu and Rabii clearly indicates that the valence band has two nearly degenerate maxima at the L and Σ directions and likewise the conduction band has a minimum at the Γ and a set of minima at the X point with almost the same energy. Therefore, four types of indirect gaps, namely $L_v \rightarrow X_c$, $L_v - \Gamma_c$, $\Sigma_v \rightarrow X_c$, and $\Sigma_v \rightarrow \Gamma_c$, with nearly the same gap energy are possible for the rock-salt CdS. We can rule out the Γ_c conduction-band minimum, because it would result in a pronouned blue-shift of the absorption gap. From our results and Edwards and Drickamer's,[1] it is also clear that there are two pressure coefficients for rock-salt CdS,

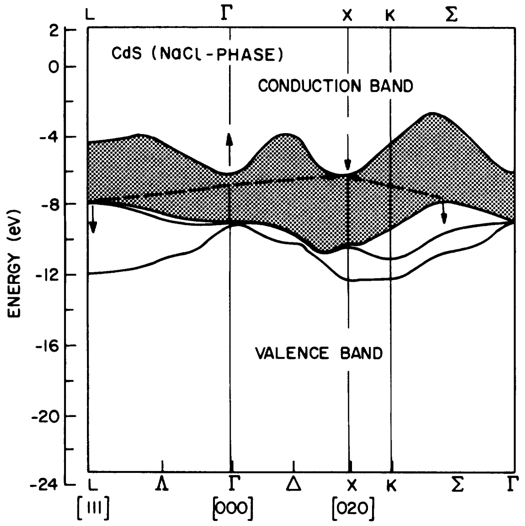

FIG. 4. Part of the band-structure diagram as calculated by Liu and Rabii (Ref. 13). Shown are only the highest occupied and the lowest unoccupied bands. The shaded area is the forbidden-gap region. The arrows indicate the directions of the pressure shift at selected symmetry points. We assign the optical-absorption edge to transitions $\Sigma_v \rightarrow X_c$ for pressures up to 70 ±10 kbar and to $L_v \rightarrow X_c$ above (broken lines).

in the pressure region investigated. A negligible shift with pressure from 30 to about 80 kbar and a distinct red shift at higher pressure are observed in the rock-salt phase of CdS. Edwards and Drickamer[1] found no shift from 30 to about 60 kbar and a red shift of −0.7 meV/kbar between ~60 to ~160 kbar. From the behavior of Cu halides,[16] we attribute the indirect gap in rock-salt CdS to $\Sigma_v \rightarrow X_c$ at low pressure and to $L_v \rightarrow X_c$ at pressures above 60 kbar.

V. CONCLUDING REMARKS

From this study we conclude that the pressure-induced structural phase transformation in CdS to the rock-salt phase can be understood within the same framework as other II–VI compounds and related III–V and I–VII compounds. Particularly, the magnitude of the optical gap and its pressure shift are in agreement with available band-structure calculations. On these grounds, CdS is a "well-behaved" semiconductor at least to 100 kbar. It appears, therefore, that the reported magnetic anomalies in pressure-quenched CdS cannot be an intrinsic property of CdS. We observe dark streaks in the high-pressure phase and nonhomogeneous coloration in pressure-released CdS. Whether these optical inhomogenities are due to defects or chemical disproportionation in CdS is a question that we cannot answer at present.

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