

## RECOVERY OF ROCKSALT STRUCTURE CdS TO ROOM PRESSURE

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**Abstract**—The high pressure phase of CdS has been recovered to room pressure at 77°K. The starting material was single crystal CdS, and the recovered material varied from powder to single crystal NaCl structure CdS. The annealing temperature of the reverse transformation of the NaCl phase was measured as was the annealing temperature of the zincblende to wurtzite phase transformation.  $E_g$  of the high pressure phase is  $2.04 \pm 0.02$  eV.

### 1. INTRODUCTION

A CRYSTAL structure transformation in CdS with pressure was first reported by EDWARDS, SLYKHOUSE and DRICKAMER<sup>(1)</sup> in the range 20–30 kb. A shift in the fundamental absorption edge was measured optically. The band gap of the high pressure phase was reported to be 1.7 eV. A value of  $E_g = 2.50$  eV for normal CdS at atmospheric pressure was the reference. The structure of the high pressure phase was investigated by KALBALIKINA and TROITSKAYA<sup>(2)</sup> using a high pressure X-ray camera. They reported a transformation of the original wurtzite structure to a NaCl phase in the pressure range 18–35 kb. Upon release of the pressure, the NaCl structure transforms to a cubic zincblende structure with a small admixture of the wurtzite structure. CORLL<sup>(3)</sup> reported the recovery of the high pressure phase to room pressure at room temperature. His starting material was CdS powder, precipitated from CdCl with H<sub>2</sub>S. The powder was a strained mixture of the zincblende and wurtzite phases. X-ray diffraction patterns showed that the crystals were heavily strained. The recovered NaCl structure transformed to the zincblende phase when annealed at 125°K over night or at 250°C for less than a minute. The wurtzite structure was obtained on further annealing at 700° for several hours. SAMARA and GIARDINI,<sup>(4)</sup> using electrical measurements, have determined values of 2.3 eV and 1.3 eV,

respectively, for the band gaps of the wurtzite and NaCl phases.

In this paper, we report the recovery of the high pressure phase of CdS to room pressure at 77°K using single crystal CdS as the starting material. The recovered material contains relatively large single crystal regions along with regions of relatively unstrained powder. We also report results on the annealing temperature of the NaCl and zincblende phases and on the absorption edge of the NaCl phase.

### 2. EXPERIMENTAL

The starting materials were Li-doped single crystals grown in this laboratory by vapor phase deposition. Li-doped CdS crystals can be subjected to uniaxial stresses up to three times greater than pure crystals without being crushed, and were used in this work for their higher strength characteristics. The samples were cut into plates perpendicular to the *c*-axis and lapped to thicknesses varying from 2.5 to 36 mil.

The high pressure bomb was modeled after Drickamer's high pressure optical bomb except that it had no optical windows. The high pressure chamber was  $\frac{3}{16}$  in. dia. by  $\frac{1}{8}$  in., and the working fluid was single crystal NaCl. A standard Sheffer HH Series 2000 hydraulic cylinder was used to pressurize the bomb.

The CdS sample was placed in the bomb between two NaCl wafers. The bomb was pressurized to approximately 38 kb, and lowered into liquid N<sub>2</sub> in a large styrofoam dewar. After the bomb temperature reached 77°K the pressure was released. The bomb was disassembled under liquid nitrogen and the resulting sample pellet removed. The pellet could be cleaved apart in the nitrogen bath and the CdS specimen removed.

The recovered sample was black in color with a shiny metallic-like luster similar to that reported by CORLL.<sup>(3)</sup> When observed with transmitted light, the thinnest samples were quite transparent and red in color.

The absorption edge of the NaCl structure was measured with a Cary model 14 photospectrometer, and is compared with that of pure CdS wurtzite structure platelet in Fig. 1. The NaCl

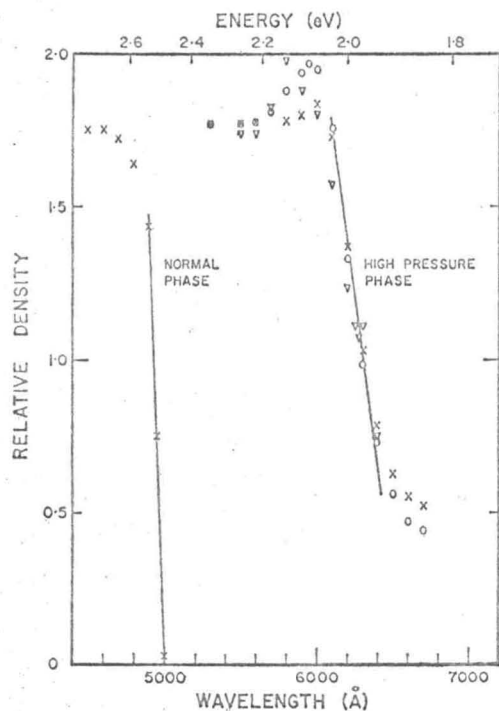


FIG. 1. Absorption edge of wurtzite and NaCl structures in CdS at 77°K.

structure is labeled "high pressure phase". Visual inspection of the NaCl structure showed relatively large regions which were transparent, indicating

single crystal structure, while other areas were translucent to the transmitted light.

The annealing temperature of the NaCl structure to zincblende phase was measured optically with the Cary photospectrometer. The sample was placed in a copper holder which had a Rosemont type 118G platinum resistance thermometer soldered to it. The holder was placed in a quartz dewar and the sample was warmed at a slow rate. 6600 Å light was shone through the crystal and the optical density vs. temperature was recorded. The sample in the zincblende phase is a fine powder due to the large volume expansion associated with the transformation,<sup>(2,4)</sup> and is optically dense. The transformation was evident by the increase in density. The results for 2.5 and 4.0 mil samples are shown in Fig. 2. A 36 mil-thick sample was transformed at a temperature of  $150 \pm 5^\circ\text{K}$ .

The annealing of the zincblende to wurtzite phase took place in less than  $\frac{1}{2}$  hour at 375°. At higher temperatures, the transformation takes place in seconds.

Laue back reflection X-ray studies on the high pressure phase showed that when the starting crystal was 36 mil thick, the recovered sample was a powder. Crystal thicknesses of 4.0 to 10.0 mil yielded poly-crystalline samples, and crystal thicknesses of 4.0 mil or less yielded large regions of single crystal NaCl structure.

### 3. DISCUSSION

In the absorption edge measurements (Fig. 1) the NaCl structure crystal was so thin, i.e. approximately 2.5 mil thick, that it was necessary to leave the crystal on one-half of the salt pellet. The scattering of the data points at the high density end of the edge is due to the crystal-salt interface. Using the previously reported value of 4850 Å at 77°K for the absorption edge of the CdS wurtzite structure platelet, the corresponding density on the NaCl structure crystal gives  $E_g = 2.04 \pm 0.02$  eV. This value is not in agreement with previously reported values of 1.3 eV by SAMARA and GIARDINI<sup>(4)</sup> and of 1.7 eV by EDWARDS, SLYKHOUSE and DRICKAMER.<sup>(1)</sup> Edwards, Slykhouse and Drickamer measured the shift of the absorption edge to determine  $E_g = 1.7$  eV for the band gap. They stated that the transformation at approximately 27.5 kb "resulted in a loss of most of the light available, and in only two runs" were

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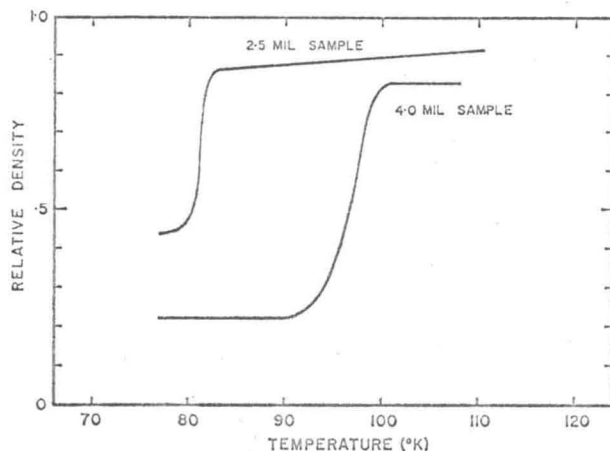


FIG. 2. Relative optical density vs. temperature showing NaCl to zincblende phase transformation.

they able to measure the absorption edge beyond the transition. We experienced the same difficulty with our thicker samples, and found that the loss of light was due to the NaCl phase being in a powder form. In some of the 6.0 mil samples, the edge was very broad. The short wavelength end of the edge would remain the same regardless of whether the samples were powdered or single crystal, but the long wavelength end of the edge would shift to longer wavelengths as the crystal progressed from a pure single crystal to a powder. Their edge was measured at an attenuation coefficient of  $64 \text{ cm}^{-1}$  so the reported edge would be shifted to a longer wavelength and thus the value of  $E_g$  would be low. The error of  $E_g$  determined at an attenuation coefficient of  $64 \text{ cm}^{-1}$  would be progressively worse as the absorption edge was broadened.

Samara and Giardini's determination of  $E_g = 1.3 \text{ eV}$  is based on the assumption that the crystal is in the intrinsic conductivity range ( $550\text{--}800^\circ\text{C}$ ) and that the mobility is constant. There is a question whether the crystal is really in the intrinsic region at this temperature. If it is not, the

measured value of  $E_g$  would be the activation energy of one of the donor levels and would be less than the true  $E_g$ . We feel that their value of  $E_g$  is not the fundamental band gap but of some deep trapping level.

The annealing temperature of the NaCl to zincblende phase is directly proportional to the amount of strain in the recovered samples, as would be expected. This is also in agreement with CORLL's work<sup>(3)</sup> in which the recovered NaCl structure was heavily strained and annealed at  $150^\circ$  or higher temperatures.

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