

## Recovery of the High-Pressure Phase of Cadmium Sulfide\*

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The high-pressure phase of cadmium sulfide has been recovered to room pressure and room temperature. The recovered phase had the rocksalt structure with  $a_0 = 5.464 \pm 0.012 \text{ \AA}$ . The pressure dependence of the electrical resistance was found to vary significantly among the various cadmium sulfide phases.

THE large drop in electrical resistance of wurtzite single crystals of CdS at approximately 25 kbar was first reported by Samara and Drickamer.<sup>1</sup> The magnitude and abruptness of this change led to the suggestion of a phase transition to a more dense structure. Using high-pressure x-ray techniques, several investigators<sup>2-4</sup> have observed this phase transition and have identified the new phase as cubic with the rocksalt structure. Recently we have recovered this high-pressure phase of CdS to room pressure and room temperature and confirmed the rocksalt structure identification by standard x-ray powder analysis. The lattice constant was  $a_0 = 5.464 \pm 0.012 \text{ \AA}$ . The large uncertainty in the lattice constant is due to the inherent strain (hence fuzzy line pattern) in the recovered structure and the uncertainty quoted is the maximum deviation of measurements of four samples. Although the line pattern was not sharp enough to give accurate measurements of the line intensities, rough densitometer measurements were obtained and are compared with the intensities calculated by Owen *et al.*<sup>5</sup> in Table I.

All rocksalt x-ray patterns also contained three very weak superstructure lines of "d" spacing three times that of the three strongest lines, (111), (200), and (220).<sup>6</sup>

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<sup>1</sup> G. A. Samara and H. G. Drickamer, *J. Phys. Chem. Solids* **23**, 457 (1962).

<sup>2</sup> C. J. M. Rooymans, *Phys. Letters* **4**, 186 (1963).

<sup>3</sup> P. L. Smith and J. E. Martin, *Phys. Letters* **6**, 42 (1963).

<sup>4</sup> S. S. Kabalkina and Z. V. Troitskaya, *Dokl. Akad. Nauk SSSR* **151**, 1068 (1963) [English transl.: *Soviet Phys.—Doklady* **8**, 800 (1964)].

<sup>5</sup> N. B. Owen, P. L. Smith, J. E. Martin, and A. J. Wright, *J. Phys. Chem. Solids* **24**, 1519 (1963).

<sup>6</sup> Superstructure lines of various "d" spacing were observed on x-ray patterns of all recovered material regardless of starting material or final phase.

Several unsuccessful attempts were made to anneal the recovered material and obtain a better x-ray pattern. No improvement in line sharpness was obtained when the recovered material was annealed overnight at 100°C. An overnight anneal at 125°C causes reconversion of the structure, as will a short exposure (less than 1 min) to temperatures above 250°C. The rocksalt pellets are almost black and have a submetallic luster; therefore, they are easily distinguished from the other forms of CdS. When ground to powder, the rocksalt phase loses its luster and lightens but is still much darker than powders of the normal phases. Under microscopic examination the recovered material looks much like a piece of galena with many small orange specks, which are probably CdS in the normal structures. At this writing we have been unable to separate these phases.

The high-pressure experiments on the CdS transition were carried out in a ManLabs MIA-1 high-pressure belt<sup>7</sup> apparatus. The curves shown in Fig. 1 are representative of resistance measurements made in the belt apparatus on samples pelletized from various CdS powders. During these resistance measurements (at

TABLE I. Identification of the rocksalt phase of CdS by comparison of calculated and observed x-ray line intensities.

<i>hkl</i>	obs <i>I/I</i> <sub>0</sub>	calc <i>I/I</i> <sub>0</sub> (NaCl)	calc <i>I/I</i> <sub>0</sub> (ZnS)
111	37	55	100
200	100	100	22
220	95	77	57
311	27	32	46
222	24	28	7
400	14	13	10
420	40	35	5

<sup>7</sup> H. Tracy Hall, *Rev. Sci. Inst.* **31**, 125 (1960).

room temperature) the rocksalt phase was recovered in each case when the starting material was unannealed CdS powder.  $H_2S$  precipitated from CdCl. This precipitate is a very strained mixture of wurtzite and zinc-blende structures.

The powder used to make the pellets for resistance measurements labeled "rocksalt" was the recovered material and contained a small percentage ( $<10\%$ ) of normal CdS powder. By annealing CdS powder for several hours at  $700^\circ C$  the precipitate was completely converted to the wurtzite structure. The material recovered after pressure cycling the wurtzite powder was a mixture of zinc-blende and wurtzite structures as observed by other investigators.<sup>2-4</sup> The precipitate from  $CdSO_4$  was almost entirely of the zinc-blende structure and was used to make the pellets for the runs characterized by the curve labeled "zinc blende" in Fig. 1.

The fact that the rocksalt phase is consistently recovered when the starting material is an unannealed, badly strained precipitate leads one to conclude the existence of a memory mechanism in the material at high pressures. A possible mechanism is the degree of imperfection in the rocksalt structure as it is formed at high pressure. Experiments in our laboratory<sup>8</sup> have shown that when the rocksalt structure is formed from a wurtzite single crystal in a true hydrostatic environment, a hysteresis of more than 10 kbar is observed during release of pressure. This hysteresis could be caused by faults, dislocations, strains, and general imperfections introduced in the rocksalt structure of CdS due to the rather traumatic rearrangement of bonds during the change of phase. These imperfections could impede the reverse transformation in a manner similar to the way a pinning site impedes dislocation motion in metals. When the starting material is already in a very strained state, it is feasible that the transformed ma-

<sup>8</sup> In liquid medium, 30 kbar Harwood Press.

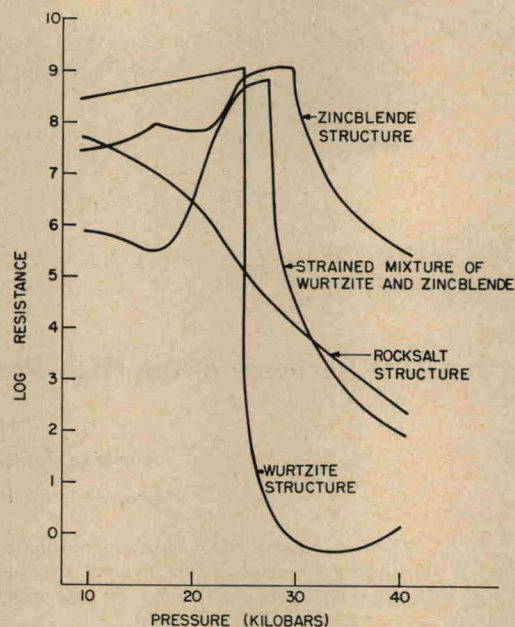


FIG. 1. Resistance characteristics of various CdS powders as a function of increasing pressure.

terial would be more severely strained than if one started with well annealed material. An experiment was carried out to test this hypothesis. Unannealed CdS powder (the CdCl precipitate) was pelletized, loaded in the belt, and the pressure raised to 40 kbar. Then the temperature inside the sample chamber was raised to  $\sim 1000^\circ C$  for 15 min, allowed to cool to room temperature, and the pressure released. The material recovered from this high-pressure annealing was of the normal zinc-blende structure. In this case, the reduction of imperfections by annealing permitted the return to the zero pressure structure.

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