PHYSICS

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Figure 1

Figure 1: Figure 1

Abstract

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STUDY OF THE STRUCTURE OF CADMIUM SULFIDE

AT HIGH PRESSURE UP TO 90 KBAR

(Presented by Academician N. V. Belov, April 4, 1963)

It is known that cadmium sulfide under ordinary conditions occurs in two modifications, one of which has the wurtzite lattice and the other the sphalerite lattice; the second phase can easily be obtained from the first by applying shear stresses, for example by grinding in a mortar[^1] (the substance changes color in the process, from yellow to red). The phase transition of cadmium sulfide at high pressure was first discovered by Drickamer and co-workers[^2][^3], who observed that under these conditions the edge of the CdS absorption spectrum shifts noticeably into the long-wavelength region. According to the optical data, the transition begins at 27.5 kbar and ends at 40 kbar. However, in the same work[^3] a value of 19 kbar is given for the transition pressure of CdS, obtained by measuring the intensity of light transmitted through the specimen.

Fig. 1. a —dependence of the electrical resistivity of bismuth R/R_0 on pressure; b —calibration curve of the x-ray chamber with respect to pressure. Designations: 1, 2, and 3 —results of the 1st, 2nd, and 3rd experiments, respectively, on measuring the electrical resistivity of Bi; 4 —results from the compressibility of AgC.

Explaining the results obtained, the authors suggested that at high pressure in CdS there occurs the usual transition from the wurtzite structure to the sphalerite structure. The basis for this explanation was the presence, on x-ray diffraction patterns of CdS specimens subjected to high pressure (after pressure release), of sphalerite lines along with the lines of the initial phase.

We have carried out an x-ray study of CdS in the pressure range 1–90 kbar at room temperature. The purpose of the work was to establish the structure of the new CdS phase directly in the region of its equilibrium. The exposures were made in a special high-pressure x-ray chamber, made after the model of the Jamieson and Lawson chamber[˜4]. Its main part is a pellet pressed from powdered boron with a channel for the specimen, d = 0.35 mm. The initial dimensions of the pellet were: outer diameter 2 mm, height 1 mm.

In the work, boron of the "amorphous" grade was used; however, it produced a considerable number of diffuse lines on the x-ray diffraction patterns. For the exposures an ordinary cassette 114 mm in diameter was used, making it possible to obtain up to five photographs on a single film at different pressures. The chamber was calibrated for pressure up to 100 kbar by recording the jumps in the electrical resistance of bismuth at three phase transitions. The pressure values were taken according to Kennedy' s scale[˜5].

See the article by S. S. Kabalkina and Z. V. Troitskaya, p. 1068.

Fig. 2. *a* –X-ray diffraction patterns of CdS at different pressures: **1** –p = 1 bar (before pressure was applied); **2** –p = 18 kbar; **3** –p = 32.5 kbar; **4** –p = 57.5 kbar (indices of the lines of the NaCl phase are indicated); *b* –X-ray diffraction pattern of CdS at p = 1 bar after release of pressure, recorded with Mo radiation without a filter.

See the article by P. P. Budnikov, S. M. Royak, and A. O. Kroichik, p. 1143.

Fig. 4. Microphotographs of clinker. Reflected light. Magnification 440×. *a* –raw mix based on MKTs; *b*, *v* –the same, based on belite sludge.

Figure 1 shows the dependence R/R_0 for a bismuth wire (0.2 mm in diameter), placed in the x-ray chamber, on the press load. The calibration curve for determining the pressure acting on the sample is also given there. In addition to the points obtained by measuring the electrical resistance of bismuth, it includes the results of determining the pressure from Bridgman' s data on the compressibility of silver chloride (^{6}); the latter was obtained x-rayographically in the chamber described above.

For the investigation, CdS of chemically pure grade, with the wurtzite structure, was taken. Debye patterns were obtained for it at high pressures up to 90 kbar; these confirmed the presence of a phase transition in CdS at these pressures. This is seen from Fig. 2, which presents five photographs of the substance under study at different pressures; in all photographs except the first and the last (p = 1 bar), the strong lines correspond to the high-pressure phase. The results of careful measurement of the x-ray patterns showed that the phase transition of CdS at high pressure is accompanied by a transition from the wurtzite structure to the NaCl structure.

Table 1

hkl	*d*, Å	*a*, Å
111	3.02	5.23
200	2.64	5.28
220	1.85	5.25

Fig. 3. Parameters a and c of the low-pressure phase of CdS as a function of pressure

Figure 2: Fig. 3. Parameters a and c of the low-pressure phase of CdS as a function of pressure

hkl	d, Å	a, Å
311	1.59	5.27
222	1.52	5.27
400	1.32	5.28
420	1.18	5.28
422	1.08	5.29

$$a_{\text{av}} = 5.27 \pm 0.01 \text{ Å}$$

Table 1 presents data for the new phase of CdS at $p = 88.5$ kbar. According to the data obtained by us, the phase transition in most cases begins at $p = 18$ kbar and ends at approximately 35 kbar; a small amount of the old phase persists up to 60 kbar.

Figure 3 graphically shows the parameters of the low-pressure phase of CdS at different pressures. Figure 4 presents the values of the unit-cell volume of the low-pressure phase and the high-pressure phase as a function of pressure.

Fig. 3. Parameters a and c of the low-pressure phase of CdS as a function of pressure

On the basis of the data obtained, the following values of the compressibility of CdS were calculated: in the pressure interval from 0 to 27 kbar for the old phase

$$\chi_{\perp} = \frac{1}{p}\frac{\Delta a}{a} = 5.9 \cdot 10^{-7} \text{ bar}^{-1};$$

$$\chi_{\parallel} = \frac{1}{p}\frac{\Delta c}{c} = 3.5 \cdot 10^{-7} \text{ bar}^{-1}; \qquad \chi = \frac{1}{p}\frac{\Delta v}{v} = 15.3 \cdot 10^{-7} \text{ bar}^{-1};$$

for the new phase, from 20 to 90 kbar,

$$\chi = \frac{1}{p}\frac{\Delta v}{v} = 9.2 \cdot 10^{-7} \text{ bar}^{-1}.$$

Thus, the compressibility of the high-pressure phase, as should have been expected, is less than the compressibility of the low-pressure phase. It is interesting to compare our data on the compressibility of the low-pressure phase of

Fig. 4. Volume of the unit cell of the low-pressure phase (I) and of the high-pressure phase (II) as a function of pressure

Figure 3: Fig. 4. Volume of the unit cell of the low-pressure phase (I) and of the high-pressure phase (II) as a function of pressure

CdS with the results of measurements by the optical method up to 4 kbar (7), according to which

$$\chi_{\perp} = 5.4 \cdot 10^{-7}\ \text{bar}^{-1}, \quad \chi_{\parallel} = 5.8 \cdot 10^{-7}\ \text{bar}^{-1} \quad \text{and} \quad \chi = 1.66 \cdot 10^{-6}\ \text{bar}^{-1}.$$

The presence of x-ray patterns in which lines of both modifications are simultaneously present made it possible to determine the pure volume jump at the phase transition in CdS. It proved to be $29.6 \pm 0.6\%$. The result was obtained from three x-ray patterns taken at pressures of 18, 27, and 57.5 kbar. Further, using this value of the jump, we determined the volume of the new phase of CdS at $p = 1$ bar, whence we calculated the value of the parameter at atmospheric pressure:

$$a_0 = 5.56 \pm 0.01\ \text{Å}$$

and, correspondingly, the sum of the ionic radii:

$$r_{\text{S}^{2-}} + r_{\text{Cd}^{2+}} = 2.78\ \text{Å};$$

the latter, within the limits of experimental error, agrees with tabulated data.

Figure 2b shows the X-ray diffraction pattern at $p = 1$ bar after the pressure was released, from which it is evident that the reverse phase transition in CdS is accompanied by a transition from the NaCl-type structure to the sphalerite structure with a small admixture of wurtzite. The latter makes understandable the misconception of the authors (2,3) concerning the structure of the high-pressure phase of CdS. In fact, it is precisely the transition from the wurtzite structure to the NaCl structure, with a change in coordination number, that is the cause of the sharp shift of the absorption edge of CdS at high pressure.

Fig. 4. Volume of the unit cell of the low-pressure phase (I) and of the high-pressure phase (II) as a function of pressure

The transition of CdS at high pressure to the NaCl-type structure is not unexpected. A similar picture is observed for the cadmium analogue—mercury (8). One of the modifications of mercury sulfide at ordinary pressure, and mercury selenide at $p = 7.5$ kbar, have a distorted NaCl-type structure, where the distortion is a consequence of mercury' s tendency to form two strong bonds.

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