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Volume Compressibility of BeO and Other II–VI Compounds*

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The volume compressibilities of BeO, ZnS, CdS, CdSe, and CdTe have been measured to 45 kbar. Solid–solid transitions were observed in CdS, CdSe, and CdTe at 17.5, 21.3, and 31.8 kbar, respectively, with corresponding volume changes of 16.0%, 16.4%, and 16.4%.

I. INTRODUCTION

THE room-temperature volume compressibilities of BeO, CdS, CdSe, ZnO, CdTe, and ZnS have been measured to 45 kbar as part of a continuing program on the fundamental properties of II–VI compounds. The first four compounds have a wurtzite structure while the latter two have a zinc-blende structure. Table I lists some of the properties of the compounds of interest.

TABLE I. Properties of II–IV compounds.

Compound	Atmospheric crystal structure	Lattice parameters a_0, c_0 (Å)	Bond distance (Å)	Bandgap (eV)	Molecular volume (cc)	Density (g/cc)
BeO	B_9[a]	2.695–4.39	1.64, 1.65	~11.6 (R.T.)	8.31	3.010
ZnO	B_9	3.243–5.195	1.95, 1.98	3.14 (R.T.)	14.31	5.676
ZnS	B_4[b]	5.412	2.36	3.91 (14°K)		4.096
	B_9	3.811–6.234	2.33, 2.33	3.84 (14°K)	23.83	4.089
ZnSe	B_4	5.65	2.45	2.820 (4°K)	30.35	5.262
ZnTe	B_4	6.07	2.63	2.39 (4°K)	34.24	5.636
CdS	B_9	4.14–6.72	2.51, 2.53	2.50 (R.T.)	29.94	4.825
CdSe	B_9	4.30–7.01	2.63, 2.64	1.840 (1.8°K)	41.00	5.854
CdTe	B_4	6.46	2.78	1.705 (2.1°K)	41.00	5.854

[a] B_9 = wurtzite structure.
[b] B_4 = sphalerite structure.

A search of the literature revealed only two studies of isothermal compressibility of II–VI compounds. They are the work of Gutsche[1] on CdS and Weir and Shastis[2] on BeO. The CdS was done using an optical technique. The BeO data were scattered and only extended to 10 kbar.

The results are compared with the adiabatic compressibility calculated from elastic constants. Solid–solid transformations were observed for CdS, CdSe, and CdTe and are compared with previous work.[3–8]

II. EXPERIMENTAL

Method

A die with a tungsten carbide inner core and with steel support rings was used. The method has been described previously[9]; corrections were made for the expansion of the die.[10] Most of the samples were run in a die of 0.500-in. bore; some of the smaller samples, such as ZnO, were run in a 0.312-in. die.

In addition, shock-wave data were obtained for BeO to 1.1 mbar. Techniques for these measurements are described by Rice *et al.*[11]

TABLE II. Source of samples.

Samples	Purity (%)	Sources
CdS	99.99	(1) Harshaw Chemical Company
		(2) Obtained as a boule from Dr. Norman Tallan WADC
β-ZnS	99.99	(1) Harshaw Chemical Company
	99.99	(2) Obtained as a boule from Dr. Norman Tallan WADC
	99.98	(3) Semi Elements, Inc.
α-ZnS	99.99	(1) Harshaw Chemical Company
CdSe	99.98	(1) Semi Elements, Inc.
		(2) Harshaw Chemical Company
ZnO	99.99	(1) Obtained as pure crystals from Minneapolis Honeywell
BeO	99.95	(1) Obtained as 6-in.-diam block from Dr. S. Carneglia of Atomics International
CdTe	99.99	(1) Obtained from Semi Elements as ½-in. cubes

* Work done under the auspices of the U. S. Atomic Energy Commission.

[1] E. Gutsche, Naturwiss. **45**, 486 (1958).
[2] C. E. Weir and L. Shastis, J. Am. Ceram. Soc. **39**, 319 (1956).
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[9] D. R. Stephens, J. Phys. Chem. Solids **25**, 423 (1964).
[10] D. R. Stephens, J. Appl. Phys. (to be published).
[11] M. H. Rice, J. M. Walsh, R. G. McQueen, and F. L. Yarger, Phys. Rev. **108**, 196 (1957).

in poor agreement. This is probably due to the scatter in the hydrostatic data. Thus, we believe the Hugoniot measurements to be superior to the hydrostatic work in this case.

The phase transformation predicted by Jaryaraman *et al.*[3] for BeO was not observed.

ZnO

The ZnO was in the form of a small crystal about 0.0625 in. in diameter by 1 in. long. The sample was too small for the 0.5-in. die so that a 0.132-in.-diam die was used. The measured isothermal compressibility is listed in Table III, but the adiabatic compressibility calculated from the elastic constants is considered more reliable. This is mainly due to the large friction corrections associated with compression of the small crystal.

The ZnO did not convert to the sphalerite under these conditions. This was verified by x-ray studies after pressurization.

ZnS

The ZnS samples were obtained from a number of sources of which Harshaw provided the only hexagonal crystals. This fact was relatively unimportant because the hexagonal form always converted to the sphalerite form under pressure. This fact, combined with knowledge of the scarcity of hexagonal crystals in nature, as well as the problem in growing a wurtzite crystal, lead us to the conclusion that the wurtzite form of ZnS is metastable under normal conditions. The data on compressibility in Fig. 3 are therefore compared with Bridgman's[20] data; it may be seen that the agreement is good. The agreement between the adiabatic and isothermal compressibilities is also good.

CdS

The CdS samples were obtained from various sources and were all essentially equivalent. The compressibility data are plotted in Fig. 4. The solid-state transformation to the rocksalt form has been identified by others using x-ray techniques.[4–6] We believe that the transformation pressures obtained in this work are quite accurate.

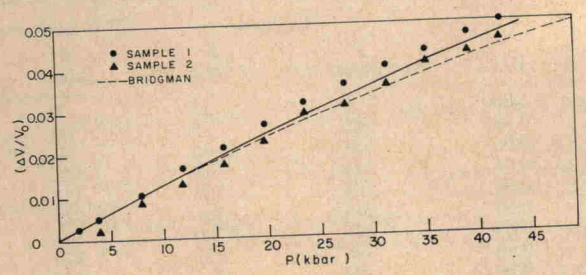

FIG. 3. Compression of ZnS, sphalerite structure.

[20] P. W. Bridgman, Am. Acad. Arts Sci. 74, 21 (1940).

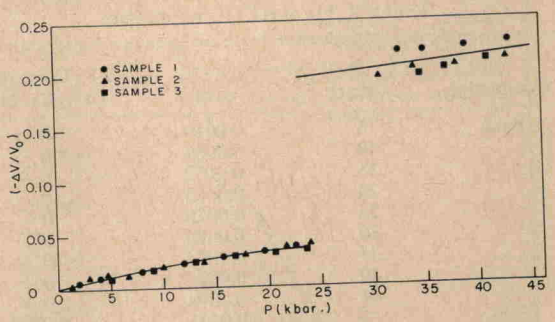

FIG. 4. Compression of CdS.

There is hysteresis in the transition on the increasing and decreasing pressure cycles; the pressures were averaged in Table IX. These data are compared with the data of Jayaraman[3] and others in Table X. Table XI tabulates the volume changes observed in this work and that of previous investigators.

TABLE IX. Transformation pressures in II–VI Cd compounds.

Compound	Transformation pressure (kbar)	
CdSe	Increased pressure	25.2±1
	Decreased pressure	17.2±0.7
	Average pressure	21.3±0.8
CdS	Increased pressure	23.4±0.6
	Decreased pressure	11.4±1.0
	Average pressure	17.5±0.8
CdTe	Increased pressure	34.9±0.2
	Decreased pressure	28.6±0.8
	Average pressure	31.8±0.5

The compressed CdS samples returned to 1 atm pressure as a mixture of the sphalerite and wurtzite forms, with the sphalerite form predominant. This is consistent with the reverse structural sequence[5] rocksalt → sphalerite → wurtzite. The agreement between the adiabatic and isothermal compressibility is poor (see Table III).

TABLE X. Transformation pressures in II–VI Cd compounds.

Compound	Investigator	P_T(kbar)
CdS	Cline and Stephens	17.5±0.8
	Jayaraman *et al.*	20
	Mariano and Warekois	33[a]
	Rooymans	20[a]
	Samara and Drickamer	~20–30
	Edwards *et al.*	27.5
CdSe	Cline and Stephens	21.3±0.8
	Jayaraman *et al.*	~19
	Mariano and Warekois	32[a]
	Rooymans	30[a]
CdTe	Cline and Stephens	31.8±0.5
	Jayaraman *et al.*	33
	Mariano and Warekois	36[a]
	Samara and Drickamer	30–35

[a] Pressure applied is not necessarily the transformation pressure.