UCRL 7706

DEC 3 1965

Reprinted from JOURNAL OF APPLIED PHYSICS, Vol. 36, No. 9, 2869–2873, September 1965
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CLIN CF65 0125

Volume Compressibility of BeO and Other II–VI Compounds*

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(Received 7 April 1965)

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

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* 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.

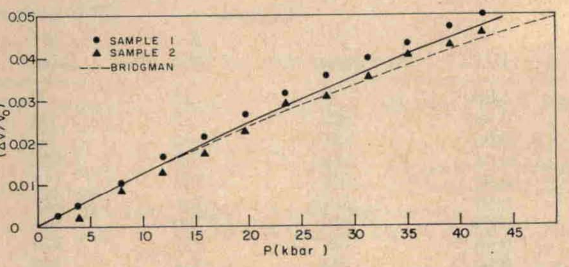

FIG. 3. Compression of ZnS, sphalerite structure.

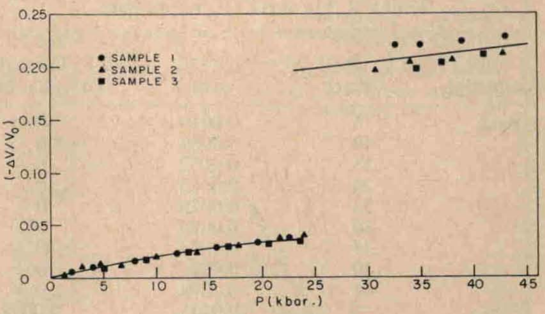

FIG. 4. Compression of CdS.

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.

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

TABLE XI. Transformation volume changes in II–VI Cd compounds.

Element	Investigator	$(\Delta V/V_0)$ trans.
CdS	Mariano and Warekois	0.199
	Rooymans	0.218
	Cline and Stephens	0.160
	Jayaraman *et al.*	~0.100
CdSe	Mariano and Warekois	0.206
	Rooymans	0.188
	Cline and Stephens	0.164
	Jayaraman *et al.*	0.090
CdTe	Mariano and Warekois	0.190
	Cline and Stephens	0.164
	Jayaraman *et al.*	0.100

The isothermal value of Gutsche[1] is in good agreement with the adiabatic value; the reason for the disagreement of the two sets of isothermal measurements is unknown.

CdSe

The CdSe was available in large crystals; we feel that the data are good. The transformation pressure is compared with other data in Table X. The compressibility plot is given in Fig. 5. In all cases the CdSe returned to the wurtzite form on release of pressure to 1 atm. There was no trace of the sphalerite form from powder x-ray data.

The lack of agreement between the adiabatic and isothermal compressibility is of concern to us as we would not have expected the $(1+\alpha\gamma T)$ correction to be so large; however, the same behavior is observed when Bridgman's[20] data on ZnSe are compared with adiabatic results.[12] The data for γ and α are not known for ZnSe, but data on CdSe[13] do not explain the disagreement.

CdTe

The cadmium telluride was in the form of 0.5-in. cubes; two runs were made. The plot of $-\Delta V/V_0$ vs pressure is presented in Fig. 6; the transformation pressure data is compared with other data in Table X.

The compressibility runs indicated a possible second transformation on the reverse cycle, which was reproducible. This transformation may be from the rocksalt to the cinnabar structure, since the cinnabar structure is a distorted rocksalt structure. However, our preliminary high-pressure x-ray studies using a diamond cell have indicated no structural change below the rocksalt → sphalerite change. The x-ray apparatus is, however, a high-shear device since the sample is contained between two diamond flats, while the compressibility studies are essentially hydrostatic. The CdTe returned to the sphalerite form in both runs.

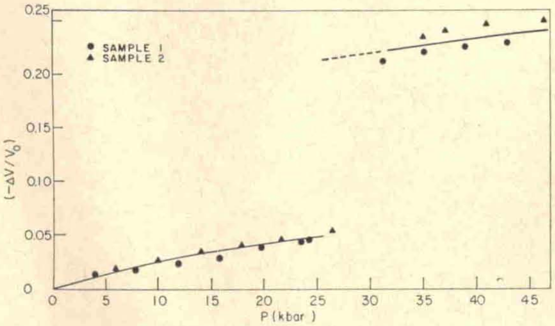

FIG. 5. Compression of CdSe.

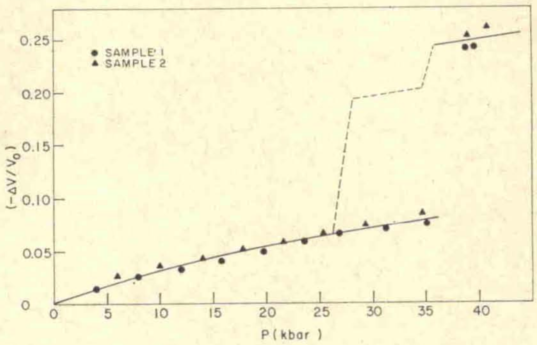

FIG. 6. Compression of CdTe.

CONCLUSIONS

The volume compressibilities of BeO and other II–VI compounds follow expected trends based on available elastic data. The trend in a given homologous series, for example the Cd series, is that compressibility increases with increasing polarizability of the anion. It appears that for other series, i.e., Zn, Cd, H, etc., the smaller the average Z (atomic number), the lower the compressibility.

The solid–solid transformations observed in CdS, CdSe, and CdTe by previous investigators were verified in this work. We feel that the trend of the increasing transformation pressure as one proceeds down a series is due to the increased energy required for the electronic rearrangement necessary to exist in the rocksalt structure.

The indication that a second transformation may exist on the reverse cycle for CdTe (perhaps the cinnabar structure) has not been previously mentioned.

The disagreement between the isothermal and adiabatic compressibility seems to be real for the Cd series; however, the $(1+\alpha\gamma T)$ correction does not seem to explain the observed differences.