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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. Solidsolid 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

HE 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.

Compound	Atmospheric crystal structure	Lattice parameters $a_0 c_0$ (Å)	Bond distance (Å)	Bandgap (eV)	Molecular volume (cc)	Density (g/cc)
BeO	Baa	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	$B_4^{\rm b}$	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	BA	5.65	2.45	2.820(4°K)	30.35	5.262
ZnTe	BA	6.07	2.63	2.39(4°K)	34.24	5.636
CdS	Ba	4.14-6.72	2.51, 2.53	2.50(R.T.)	29.94	4.825
CdSe	Ba	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

TABLE I. Pro	perties of	II-IV com	pounds
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^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 Gutsche¹ on CdS and Weir and Shastis² 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. Solidsolid 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 previously9; corrections were made for the expansion of

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¹ E. Gutsche, Naturwiss. 45, 486 (1958).

² C. E. Weir and L. Shastis, J. Am. Ceram. Soc. 39, 319 (1956).
 ³ A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys.

Rev. 130, 2277 (1963). ⁴ C. J. M. Rooymans, Phys. Letters 4, 186 (1963). ⁵ S. S. Kabalkina and Z. V. Troitskaya, Soviet Phys.—Doklady 8,800 (1964)

⁶ A. N. Mariano and E. P. Warekois, Science 142, 672 (1963) 7 G. A. Samara and H. G. Drickamer, J. Phys. Chem. Solids

¹⁶ G. A. Samara and H. G. Dickamer, J. Phys. Chem. Solids 23, 457 (1962).
 ⁸ A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, J. Phys. Chem. Solids 11, 140 (1959).
 ⁹ D. R. Stephens, J. Phys. Chem. Solids 25, 423 (1964).

the die.¹⁰ Most of the samples were run in a die of 0.500in. 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	 Harshaw Chemical Company Obtained as a boule from Dr. Norman Tallan WADC
β-ZnS	99.99 99.99	 Harshaw Chemical Company Obtained as a boule from Dr. Norman Tallan WADC Semi Elements Inc.
a-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	 Obtained as 6-in,-diam block from Dr. S. Carneglia of Atomics International
CdTe	99.99	(1) Obtained from Semi Elements as ¹ / ₂ -in. cubes

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).

Samples

All of the samples with the exception of BeO were single crystals. The polycrystalline BeO had a density of 3.006 g/cm³, which is 99.88% of theoretical. The sources of the samples are given in Table II.

III. RESULTS AND DISCUSSION

BeO

The BeO samples were right-circular cylinders approximately 0.5 in. in diameter by 1 in. high; they were core drilled out of a 6-in. hot pressured block. The hydrostatic results obtained on the samples are shown in Fig. 1. It is evident that there is considerable scatter in the data, due in part to the low compressibility of BeO. The scatter results in a $\pm 20\%$ error in the data.

Our isothermal compressibilities (at 1 atm) are shown in Table III. Adiabatic compressibilities as calculated

TABLE III. Isothermal and adiabatic compressibilities.

Compound	K _s (adiabatic) (×10 ³ kbar ⁻¹)	$\begin{array}{c} K_T \text{ (isothermal)} \\ (\times 10^3 \text{ kbar}^{-1}) \end{array}$
BeO	0.397	0.411
ZnO	0.697	2.22
ZnSa	1.275	1.30
CdS	1.626	2.62
CdSe	1.879	3.56
CdTea	2.360	3.96
ZnSe	1.680	2.469
ZnTe	1.962	2.427

* Sphalerite form, $K_s = 3(s_{11} + s_{12})$ (cubic), $K_s = 2(s_{11} + s_{12} + 2s_{13}) + s_{43}$ (hexagonal)

from elastic constant data¹²⁻¹⁸ are also listed. The agreement between the isothermal and adiabatic compressibilities for BeO is considered reasonable due to the scatter in the hydrostatic data. The isothermal compressibility should be larger than the adiabatic by a term



FIG. 1. Compression of BeO.

12 D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. 129, 1009 (1963)

¹³ H. Jaffe (private communication) 14 H. Dunegan, Lawrence Radiation Laboratory (private communication).

- T. B. Bateman, J. Appl. Phys. 33, 3309 (1962).
 D. I. Bolef, N. T. Melamed, and M. Menes, J. Phys. Chem.
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- 18 H. J. McSkimmin and D. G. Thomas, J. Appl. Phys. 33, 56 (1962).



FIG. 2. Pressure vs V/V_0 for BeO.

 $(1+\alpha\gamma T)$, where α is the volume coefficient of thermal expansion, γ the Gruneisen constant, and T the absolute temperature (°K). In the case of BeO this term is very small, so the two compressibilities should be about the same.

TABLE IV. Evaluated constants.

Compound	$\frac{10^{3}a}{({\rm kbar})^{-1}}$	$-10^{5}b$ (kbar) ⁻²	10 ⁶ c (kbar) ⁻³
BeO	0.413	0.43	
CdSa	2.63	8.0	1.43
CdSeª	3.58	1.39	2.98
CdTes	3.98	8.8	1.09
ZnO	2.22	0.37	
ZnS	1.31	0.410	

a Low-pressure fit only.

Table IV tabulates the calculated coefficients a, b, band c which were obtained by a least-squares fit to an equation of state of the form $-\Delta V/V_0 = ap + bp^2 + cp^3$. The compressibility at P=0 is the *a* in the preceding equation. Table V is a comparison of the experimental data with values calculated from the equation of state.

In addition to the hydrostatic experiments, dynamic data were also obtained for BeO. The methods have been described in the literature.^{11,19} These data are presented in Table VI. Unfortunately the samples were not at theoretical density ($\rho_0 = 3.0096 \text{ cm}^3$).

The data were corrected for density and temperature effects as follows: First, the Mie-Gruneisen and Dugdale-McDonald equations were used to obtain a fit of the Gruneisen γ with volume. The method is described in Ref. 11. The constants used are shown in Table VII. Then the Mie-Gruneisen and Hugoniot equations were

¹⁹ J. M. Walsh and R. H. Christian, Phys. Rev. 97, 1544 (1955).

TABLE V. Fit of $\Delta V/V_0$ vs pressure.				
und	P (kbar)	$\frac{\Delta V/V_0}{(\exp)}$	$(\Delta V/V_0)$ expt'l- $(\Delta V/V_0)$ calc	

Compound	(kbar)	(exp)	$(\Delta V/V_0)$ calc
BeO	5	0.0019	0
	10	0.0037	0
	15	0.0052	0
	20	0.0065	0
	25	0.0076	0
	30	0.0086	Ō
	35	0.0093	0
	40	0.0097	0
	41	0.0098	0
CdS	5	0.0115	0.0002
	10	0.0200	0.0003
	- 15	0.0265	-0.0002
	20	0.0325	0
	23.4	0.0370	-0.0003
	30	0.2045	
	35	0.2100	
	40	0.2155	· · · · ·
	43	0.2195	
CdSe	5	0.0140	-0.0007
	10	0.0250	0.0003
	15	0.0340	0.0017
	20	0.0415	0.0020
	25.2	0.0480	-0.0013
	30	0.220	
	35	0.227	
	40	0.2340	Contract in
	44	0.2385	
CdTe	5	0.0175	-0.0002
	10	0.0315	-0.0004
	15	0.0435	0.0002
	20	0.0535	0.0007
	25	0.0620	0.0008
	30	0.0710	0.0013
	36	0.0805	0.0001
	40	0.2500	
	43	0.2550	10 M 1 DT
ZnS	5	0.0064	0
(sphalerite)	10	0.0127	0.0000
	15	0.0188	0.0000
	20	0.0247	-0.0001
	25	0.0303	0
	30	0.0358	0.0002
	35	0.0413	0.0005
	40	0.0464	0.0005
	42	0.0483	0.0005
	1 2	A CONTRACTOR	

used to calculate the shock Hugoniot locus for BeO of theoretical density. The pertinent equations are:

 $P_H - P_0 = (\gamma/V_H)(E_H - E_0),$ (Mie-Gruneisen)

where P_H , E_H = pressure and specific internal energy

TABLE VI. Dynamic data for BeO.

Initial density ρ_0 (g/cm ³)	Shock velocity U_s (cm/ μ sec)	Particle velocity U_p (cm/ μ sec)	P (kbar)	V Experi- mental	/V ₀ Normal- ized to theoretical density
2.908	0.865	0.78	197	0.912	0.942
2.905	0.929	1.25	338	0.866	0.895
2.909	0.962	1.56	437	0.838	0.866
2.919	1.015	1.91	566	0.812	0.839
2.914	1.022	2.06	613	0.798	0.824
2.910	1.085	2.42	765	0.777	0.803
2.926	1.126	2.74	905	0.765	0.782
2.914 (Av.)	0.760	0	0	1.000	1.033

TABLE VII. Assumed constants for BeO.

7 0	(cal/mole °K)	$(\partial P/\partial T)_V$ (bar/°K)	E_1 (cal/mole)	
1.97	2.91	28	690	

along the Hugoniot and P_0 , E_0 =pressure and specific internal energy along a reference curve.

$$E_H - E_1 = \frac{1}{2} P_H (V_1 - V_H),$$
 (Hugoniot)

where E_1 , V_1 = specific internal energy and volume at P=0. Here $V_1=1/\rho_0$, where ρ_0 is the theoretical density. In this case the reference curve employed was the

experimental Hugoniot curve (see Table VIII). The final equation in terms of P_H and V_H is

$$P_{H} = \frac{(E_{1} - E_{0}) + (V_{H}/\gamma)P_{0}}{V_{H}/\gamma - (1/2)(V_{1} - V_{H})}.$$

Therefore the Hugoniot for theoretical density was calculated and the temperatures along the Hugoniot were also determined.¹¹ The corresponding 25°C isotherm was calculated by assuming $(\partial P/\partial T)_V$ was constant. Thus at constant volume, the pressure correction was

$\Delta P = (\partial P / \partial T)_V \Delta T.$

These results are shown in Table VIII and in Fig. 2.

In the codes used to calculate temperatures C_V is assumed constant. Unfortunately, the value for C_V is about one-half the Dulong and Petit limit. The maximum temperatures calculated along the Hugoniot are over 1000°C and at these temperatures C_V has probably reached the Dulong and Petit value. The effect of C_V increasing in this manner is that the calculated temperatures are too high, and the corresponding pressure corrections are too large. The true 25°C isotherm is then somewhere between the two dotted curves in Fig. 2. However, the error is negligible at lower pressure and the comparison between the hydrostatic data and the 25°C isotherms should be valid. However, the data are

TABLE VIII. Calculated Hugoniot and 25°C isotherm. BeO at theoretical density.

	Huge	Hugoniot		
	P	T	Р	
V/Vo	(kbar)	(°C)	(kbar)	
1.000	0	25	0	
0.980	40	33	40	
0.96	83	46	83	
0.94	129	69	128	
0.92	184	105	182	
0.90	244	156	240	
0.88	311	240	305	
0.86	388	359	379	
0.84	474	544	460	
0.82	569	776	548	
0.80	678	1110	648	
0.78	800	1512	758	

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's²⁰ 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.





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 Jayaraman³ and others in Table X. Table XI

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

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

tabulates the volume changes observed in this work and that of previous investigators.

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 sequence⁵ rocksalt \rightarrow sphalerite \rightarrow 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	$P_T(\text{kbar})$
CdS	Cline and Stephens Jayaraman <i>et al.</i> Mariano and Warekois Rooymans Samara and Drickamer Edwards <i>et al.</i>	$17.5 \pm 0.8 \\ 20 \\ 33^{a} \\ 20^{a} \\ \sim 20-30 \\ 27.5$
CdSe	Cline and Stephens Jayaraman <i>et al.</i> Mariano and Warekois Rooymans	$21.3 \pm 0.8 \\ \sim 19 \\ 32^{a} \\ 30^{a}$
CdTe	Cline and Stephens Jayaraman <i>et al.</i> Mariano and Warekois Samara and Drickamer	31.8±0.5 33 36 ^a 30-35

^a Pressure applied is not necessarily the transformation pressure.

Element	Investigator	$(\Delta V/V_0)$ trans.
CdS	Mariano and Warekois Rooymans Cline and Stephens Jayaraman <i>et al.</i>	0.199 0.218 0.160 ~0.100
CdSe	Mariano and Warekois Rooymans Cline and Stephens Jayaraman <i>et al</i> .	0.206 0.188 0.164 0.090
CdTe	Mariano and Warekois Cline and Stephens Jayaraman <i>et al.</i>	$\begin{array}{c} 0.190 \\ 0.164 \\ 0.100 \end{array}$
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TABLE XI. Transformation volume changes in II–VI Cd compounds.

The isothermal value of Gutsche¹ 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's²⁰ data on ZnSe are compared with adiabatic results.¹² The data for γ and α are not known for ZnSe, but data on CdSe¹³ 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



FIG. 5. Compression of CdSe.



FIG. 6. Compression of CdTe.

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 \rightarrow 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.

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.

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