Reprinted from JOURNAL OF APPLIED PHYSICS, Vol. 38, No. 4, 1944–1948, 15 March 1967

Printed in U. S. A.

Elastic Constants of Hexagonal BeO, ZnS, and CdSe†

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(Received 29 September 1966; in final form 16 November 1966)

The elastic moduli of hexagonal beryllium oxide, zinc sulfide, and cadmium selenide at 25°C have been determined by measuring ultrasonic wave velocities in the 20- to 50-MHz frequency range. The data are compared with other literature data and discrepancies are discussed. The adiabatic bulk modulus, volume compressibility, and Debye temperatures are also computed.

INTRODUCTION

BERYLLIUM oxide, zinc sulfide, and cadmium selenide are three II–VI compounds that crystallize in the hexagonal wurtzite structure with space group $P6_3mc$. The latter two also crystallize in the cubic sphalerite structure. This study of the elastic moduli of the wurtzite forms has been an extension of a previous study[1] to obtain fundamental data for lattice dynamic calculations. At the time this study was initiated, there were no available data on the elastic moduli of BeO. In the period following, Austerman *et al.*[2] measured S_{11} by a resonance technique, and more recently Bentle[3] has published a paper on all the elastic moduli.

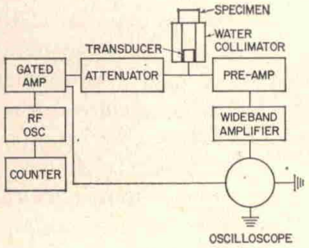

FIG. 1. Block diagram showing the electronic instrumentation and specimen configuration used for longitudinal velocity measurements.

The authors are not aware of any published data for the elastic moduli of the hexagonal modification of ZnS. There is, however, a paper by Einspruch[4] on the cubic modification.

A thorough study on CdSe has been published by Berlincourt *et al.*[5] who used a different technique.

Hexagonal crystal systems have five independent stiffness constants (C_{ij}). These constants can be calculated from the density and velocity measurements of a single crystal with three orientations—faces parallel to the c axis, a axis, and 45° to the a and c axes. The inverse of the C_{ij} matrix gives the compliances (S_{ij}). The bulk modulus and compressibility can be calculated from either of the above.[6]

Table I gives the relationship between the infinite medium velocities and the stiffness constants. The cross-coupling modulii C_{13} can be obtained by measuring either a longitudinal or shear velocity of the 45° cut crystal. Two internal checks that can be made on the results to indicate experimental accuracy are: comparison of C_{44} calculated from V_{s44a} (Table I) and V_{s44b}, and a comparison of C_{66} calculated from V_{s66} and V_{qs2}.

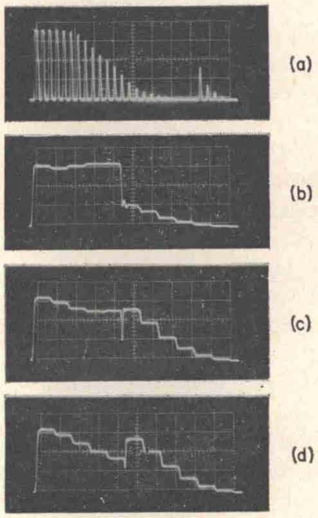

FIG. 2. (a) Echo train in a CdSe crystal at 20 MHz using water column. (b) (c) and (d) are the phase conditions of signals in (a) when the pulse length is increased and the frequency changed. The pattern in (d) is used for frequency measurements.

Table II gives the relationship between the compliances and stiffness constants obtained by taking the reciprocal of the C_{ij} matrix. The compressibilities calculated from these values are adiabatic and will differ from the isothermal compressibility theoretically by $(1+\alpha\gamma T)$, where α is the volume coefficient of thermal expansion, γ the Gruneisen constant, and T the absolute temperature.

CRYSTALS

The beryllium oxide crystals were grown from a lithium molybdate flux by a technique that is described in the literature.[7,8] Each side measured ap-

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[†] Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] C. F. Cline and D. Stephens, J. Appl. Phys. **36**, 2869 (1965).

[2] S. B. Austerman, D. Berlincourt, and H. H. Krueger, J. Appl. Phys. **34**, 339 (1963).

[3] G. G. Bentle, J. Am. Ceram. Soc. **49**, 125 (1966).

[4] N. G. Einspruch and R. J. Maning, J. Acoust. Soc. Am. **35**, 215 (1963).

[5] D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. **129**, 1009 (1963).

[6] J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, New York, 1964), 2nd ed.

[7] H. J. Newkirk and D. K. Smith, Am. Mineral. **50**, 22, 44 (1965).

[8] S. B. Austerman, J. Am. Ceram. Soc. **46**, 6 (1963).

TABLE I. Velocity and C_{ij} relationship for hexagonal crystal system.

Velocity	Elastic constant	Propagation direction (axis)	Particle motion (axis)
V_{l33}	$[C_{33}/\rho]^{1/2}$	parallel c	parallel c
V_{s44a}	$[C_{44}/\rho]^{1/2}$	parallel c	normal c
V_{l11}	$[C_{11}/\rho]^{1/2}$	parallel a	parallel a
V_{s44b}	$[C_{44}/\rho]^{1/2}$	parallel a	parallel c
V_{s66}	$[C_{66}/\rho]^{1/2}=[\frac{1}{2}(C_{11}-C_{12})/\rho]^{1/2}$	parallel a	normal c
V_{ql}	$C_{13}=2[\frac{1}{2}(C_{11}+C_{44}-\rho V^2)\times\frac{1}{2}(C_{44}+C_{33}-\rho V^2)]^{1/2}-[C_{44}]$	45° a and c	45° a and c
V_{qs1}	$V=V_{ql}$ or V_{qs1}	45° a and c	45° a and c
V_{qs2}	$[\frac{1}{2}(C_{66}+C_{44})/\rho]^{1/2}$	45° a and c	normal a and c

proximately 1 cm. The impurity level was approximately 200 ppm, with aluminum and silicon being the major impurities. The crystals were oriented and then polished in a special chamber because of the hazard associated with beryllium oxide dust. The orientation was determined by back-reflection Laue techniques on both parallel faces for each of the three orientations. Two crystals were used to obtain the complete set of five independent measurements. The orientations were determined to ±1 deg.

The cadmium selenide and zinc sulfide were obtained as two oriented crystals of each from Harshaw Chemical Company. They had been oriented by light-figure techniques, but were checked by back-reflection Laue and where necessary were repolished to bring the two crystals within ±1 deg of the desired orientations.

The purity of the ZnS and CdSe was stated by the vendor to be at least 99.9%. The zinc sulfide crystals were examined under polarized light for evidence of stacking faults and appeared to be free of such defects and exhibited a uniaxial optical figure. The dimensions and flatness of the crystals were obtained by micrometer and interferometric techniques, respectively.

EXPERIMENTAL TECHNIQUE

The long-pulse technique developed by McSkimin[9] was used for making the velocity measurements. A different approach was used for making the longitudinal measurements which eliminated any corrections for phase changes of the signal due to coupling effects. This was accomplished by using a water collimator in place of a quartz-rod buffer for the longitudinal measurements. Figure 1 is a block diagram of the experimental setup. CW signals generated by the oscillator are gated and amplified by a pulser[10] modified for gated amplifier mode. The resulting pulses excite a lithium sulfate transducer[11] with a fundamental frequency of 20 MHz. The compressional waves generated by the transducer are propagated through the water column into the specimen where they undergo many reflections. The pulse length is increased until overlap of the pulses occur. The oscillator frequency is then changed and recorded from the counter for in-phase conditions of the pulses. This sequence is shown in Fig. 2. The advantages of the water column over the quartz rod are twofold: (1) Errors at the specimen buffer boundary due to coupling materials usually present are eliminated because a two-boundary as opposed to a three-boundary condition is met. (2) Mode conversions normally encountered in quartz rods at lower frequencies are eliminated by the water column. This has allowed resonance techniques[12] to be

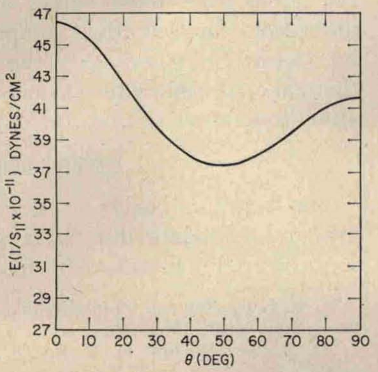

FIG. 3. Young's modulus of BeO as a function of angle from the "c" axis.

TABLE II. Compliance conversions for hexagonal system.

$$S_{11}=S_{22}=\frac{C_{11}C_{33}-C_{13}^2}{(C_{12}-C_{11})\{2C_{13}^2-C_{33}(C_{12}+C_{11})\}}$$

$$S_{12}=S_{21}=\frac{C_{13}^2-C_{12}C_{33}}{(C_{12}-C_{11})\{2C_{13}^2-C_{33}(C_{12}+C_{11})\}}$$

$$S_{13}=S_{31}=S_{23}=S_{32}=\frac{C_{13}}{2C_{13}^2-C_{33}(C_{12}+C_{11})}$$

$$S_{13}=S_{24}=S_{34}=S_{41}=S_{42}=S_{43}=0$$

$$S_{33}=\frac{C_{11}+C_{12}}{C_{33}(C_{11}+C_{12})-2C_{13}^2}$$

$$S_{44}=1/C_{44}$$

$$S_{66}=1/C_{66}$$

$$\text{Compressibility } \beta=\frac{2C_{33}+(C_{11}+C_{12})-4C_{13}}{(C_{11}+C_{12})(C_{33})-2(C_{13})^2}$$

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[9] H. J. McSkimin, J. Acoust. Soc. Am. **31**, 287 (1959).

[10] Arenberg Ultrasonics Laboratory, Model PG-650-C.

[11] Fabricated for the Lawrence Radiation Laboratory by Automation Industries, Boulder, Colorado.

[12] Not published.

TABLE III. Experimental data and calculation of V_{ql} in a CdSe crystal obtained with water column. $L=0.66446$ cm; average velocity $=3.576\times10^5$ cm/sec.

N	f_n (MHz)	Δf (MHz)	Δf_{avg} (MHz)	$f_n/\Delta f_{\text{avg}}$	n	$V=2Lf_n/n$ (10^5 cm/sec)
1	22.338510	0.268458	0.269285	82.9549	83	3.5767
2	22.070052	0.269854		81.9580	82	3.5768
3	21.800198	0.269532		80.9558	81	3.5766
4	21.530666	0.268967		79.9549	80	3.5766
5	21.261699	0.269299		78.9561	79	3.5766
6	20.992400	0.269963		77.9561	78	3.5766
7	20.722435	0.268466		76.9535	77	3.5764
8	20.453969	0.269059		75.9566	76	3.5766
9	20.184910	0.271199		74.9574	75	3.5766
10	19.913711	0.269398		73.9503	74	3.5753
11	19.644313	0.268712		72.9499	73	3.5762
12	19.375601	0.269031		71.9520	72	3.5762
13	19.106568	0.269571		70.9530	71	3.5762
14	18.836997	0.269477		69.9519	70	3.5761
15	18.567520	0.269030		68.9512	69	3.5761
16	18.298490	0.268829		67.9521	68	3.5761
17	18.029661	0.268787		66.9538	67	3.5761
18	17.760874	0.269720		65.9557	66	3.5762
19	17.491154	0.268955		64.9540	65	3.5761
20	17.222199	0.269386		63.9553	64	3.5761
21	16.952813	···		62.9549	63	3.5760

used on specimens too thin to be measured by other means. Disadvantages of using water are obvious if the materials tested are affected by humidity differences. Also, attenuation of sound in the water limits the frequency of measurements to approximately 20 MHz.

The shear-velocity measurements reported here were made by using a fused-silica buffer rod and Y-cut quartz crystals at an upper frequency of 46 MHz. No coupling corrections were applied to the data.

Table III gives the results of measurements on a CdSe crystal obtained with the water column. Note that the integer is not truly an integer but very nearly so. Since no coupling corrections were necessary, this difference was assumed to be due to the averaging in

TABLE IV. Velocities and elastic constants for BeO, ZnS, and CdSe.

Compound	Velocity (10^5 cm/sec)	C_{ij} (10^{11})[a]	S_{ij} (10^{-12})	β (10^{-12})	θ (°K)
BeO $\rho=3.010$ g/cc	$V_{11}=12.37$	$C_{11}=46.06$	$S_{11}=0.2397$	0.4456	1280
	$V_{33}=12.78$	$C_{33}=49.16$	$S_{33}=0.2151$		
	$V_{s66}=7.449$	$C_{66}=16.70$	$S_{66}=0.5988$		
	$V_{s44a}=7.005$	$C_{44}=14.77$	$S_{44}=0.6770$		
	$V_{s44b}=7.026$	$C_{12}=12.65$	$S_{12}=-0.05964$		
	$V_{ql}=11.93$	$C_{13}=8.848$	$S_{13}=-0.03241$		
	$V_{qs1}=8.019$				
	$V_{qs2}=7.206$				
ZnS $\rho=4.089$ g/cc	$V_{11}=5.512$	$C_{11}=12.42$	$S_{11}=1.103$	1.303	351
	$V_{33}=5.852$	$C_{33}=14.00$	$S_{33}=0.8507$		
	$V_{s66}=2.799$	$C_{66}=3.203$	$S_{66}=3.122$		
	$V_{s44a}=2.647$	$C_{44}=2.864$	$S_{44}=3.419$		
	$V_{s44b}=2.652$	$C_{12}=6.015$	$S_{12}=-0.4573$		
	$V_{ql}=5.362$	$C_{13}=4.554$	$S_{13}=-0.2101$		
	$V_{qs1}=3.246$				
	$V_{qs2}=2.728$				
CdSe $\rho=5.684$ g/cc	$V_{11}=3.630$	$C_{11}=7.490$	$S_{11}=2.327$	1.862	181
	$V_{33}=3.856$	$C_{33}=8.451$	$S_{33}=1.694$		
	$V_{s66}=1.592$	$C_{66}=1.441$	$S_{66}=6.939$		
	$V_{s44a}=1.521$	$C_{44}=1.315$	$S_{44}=7.605$		
	$V_{s44b}=1.520$	$C_{12}=4.609$	$S_{12}=-1.144$		
	$V_{ql}=3.572$	$C_{13}=3.926$	$S_{13}=-0.5498$	(3.393)	using negative C_{13}
	$V_{qs1}=1.881$				
	$V_{qs2}=1.556$				

[a] Elastic constants given in cgs units.

Δf, so it was rounded off to an integer before the velocity was calculated.

RESULTS AND DISCUSSION

Table IV is a summary of the elastic-moduli data obtained in this study. The data were programmed and computed on the IBM 7094 computer, along with the Debye-temperature calculations. The Debye temperatures were calculated by a method proposed by Anderson.[13] Debye temperatures were also calculated for ZnO,[14] CdS, and CdTe,[15] and are tabulated in Table V. The Poisson's ratio $(-S_{12}/S_{11})$ and another elastic constant C, which corresponds to a strain which changes the c/a ratio at constant volume, are also included in Table V for completeness. Figures 3–5 illustrate the values of Young's modulus $E=(1/S_{11})$ for BeO, CdSe, and ZnS as a function of orientation. The data for BeO indicate a minimum at 50° to the c axis, which agrees with the earlier data of Bentle[3] and Sjodhal and Chandler.[16]

TABLE V. Elastic properties of II–VI compounds.

Compound	Debye temperature θ (°K)	$C^{a}\times10^{12}$	Poisson's ratio $(-S_{12}/S_{11})$
BeO	1280	12.16	0.249
ZnO[b]	416	3.32	0.437
ZnS	351	2.82	0.415
CdS[c]	216	0.132	0.483
CdSe	181	0.128	0.492
CdTe[d]	160	···	···

[a] $C=C_{11}+C_{12}+2C_{33}-4C_{13}$.
[b] Data from Bateman.[14]
[c] Data from Berlincourt.[5]
[d] Data from McSkimin.[15]

Tables VI and VII compare our data with the work of Bentle[3] on BeO and Berlincourt *et al.*[5] on CdSe. The greatest difference between Berlincourt's most accurate values, i.e., C_{33}, C_{44}, and C_{66}, and ours amounts to less than 0.5%. The agreement with Bentle's work on BeO is not so good. The agreement between C_{11}, C_{33}, and C_{44} falls well into the estimated error of 5% quoted by Bentle, but differences of 32% and 35% for C_{12} and C_{13}, respectively, do not fall into the 10% error bracket quoted by Bentle. This discrepancy can be partially resolved for the difference in C_{66} and C_{12} by use of a value of 1.63×10^{12} for C_{66} which Bentle reported but considered in error. Use of this value gives agreement with our value of C_{66} to 2.4% and change his value of C_{12} so that the agreement is within 12% instead of 32%, which is much more reasonable. The positive value of C_{13} was used in each case for the compressibility calculations. There is no physical reason

TABLE VI. Results of measurements on CdSe. Density = 5.684 g/cc.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
	(in units of 10^{11} dyn/cm^2)					
Present work	7.490	4.609	3.926	8.451	1.315	1.441
Berlincourt *et al.* (Ref. 5)	7.42	4.53	3.93	8.477	1.317	1.445

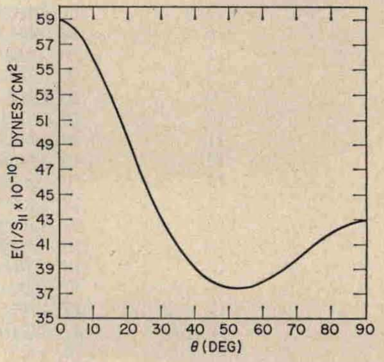

FIG. 4. Young's modulus of CdSe as a function of angle from the "c" axis.

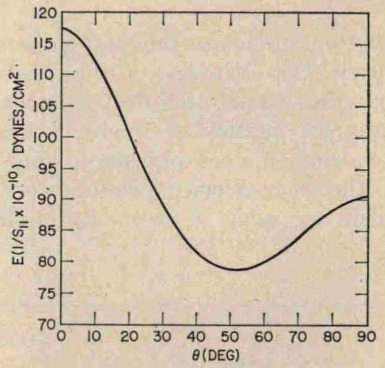

FIG. 5. Young's modulus of ZnS as a function of angle from the "c" axis.

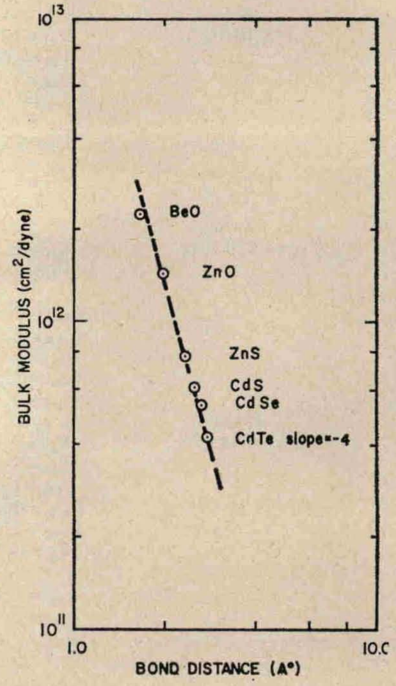

FIG. 6. Bulk modulus vs bond distance for II–VI compounds.

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[13] O. L. Anderson, J. Phys. Chem. Solids **24**, 909 (1963).

[14] T. B. Bateman, J. Appl. Phys. **33**, 3309 (1962).

[15] H. J. McSkimin and D. G. Thomas, J. Appl. Phys. **33**, 56 (1962).

[16] L. H. Sjodahl and B. A. Chandler, J. Am. Ceram. Soc. **46**, 351 (1963).

TABLE VII. Results of measurements on BeO. Density = 3.01 g/cc.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
			(in units of 10^{12} dyn/cm^2)			
Present work	4.606	1.265	0.8848	4.916	1.477	1.670
Bentle (Ref. 3)	4.70	1.68	1.19	4.94	1.53	1.52(1.63)[a]

[a] Reported but considered in error. Estimated errors in $C_{ij} \pm 1\%$; $C_{ii} \pm 0.2\%$.

for the choice of the positive value, although a plausibility agreement has been discussed in the literature.[17]

There is very little anisotropy in these compounds as evidenced from the ratios of C_{66}/C_{44} and $C_{33}/_{11}$; however, the value of Bentle for $C_{66}/C_{44} = 1.00$ is not reasonable for a hexagonal crystal.

Figure 6 is a log–log plot of bulk modulus vs bond distance for the compounds of interest and a slope of -4 fits the data. Gilman[18] has related the slope of -4 to the relationship of electrostatic forces between atomic particles and bond distance, which should reflect in the same way for the elastic moduli and bond distance.

ACKNOWLEDGMENTS

The authors would like to acknowledge the help of Herbert Newkirk for providing the BeO crystals. Deane Smith and Neal Houlding provided invaluable assistance in orienting and grinding the samples. Our appreciation is also extended to Tom Freeman and Ernie Lorbeer for their help in the computer programming.

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[17] E. S. Fisher and H. J. McSkimin, J. Appl. Phys. **29**, 1473 (1958).

[18] J. J. Gilman, *Mechanical Behavior of Crystalline Solids* (NBS Monograph 59, 1963), p. 79.