

## Elastic Constants of Hexagonal BeO, ZnS, and CdSe†

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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

**B**ERYLLIUM 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<sup>1</sup> to obtain fundamental data for lattice dynamic calculations. At the time this study was initiated, there were no available data on the elastic

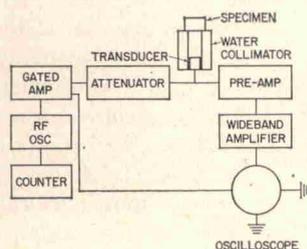


FIG. 1. Block diagram showing the electronic instrumentation and specimen configuration used for longitudinal velocity measurements.

moduli of BeO. In the period following, Austerman *et al.*<sup>2</sup> measured  $S_{11}$  by a resonance technique, and more recently Bentle<sup>3</sup> has published a paper on all the elastic moduli.

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<sup>4</sup> on the cubic modification.

A thorough study on CdSe has been published by Berlincourt *et al.*<sup>5</sup> 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 ( $S_{ij}$ ).

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<sup>1</sup> C. F. Cline and D. Stephens, *J. Appl. Phys.* **36**, 2869 (1965).

<sup>2</sup> S. B. Austerman, D. Berlincourt, and H. H. Krueger, *J. Appl. Phys.* **34**, 339 (1963).

<sup>3</sup> G. G. Bentle, *J. Am. Ceram. Soc.* **49**, 125 (1966).

<sup>4</sup> N. G. Einspruch and R. J. Maning, *J. Acoust. Soc. Am.* **35**, 215 (1963).

<sup>5</sup> D. Berlincourt, H. Jaffe, and L. R. Shiozawa, *Phys. Rev.* **129**, 1009 (1963).

The bulk modulus and compressibility can be calculated from either of the above.<sup>6</sup>

Table I gives the relationship between the infinite medium velocities and the stiffness constants. The cross-coupling moduli  $C_{13}$  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: com-

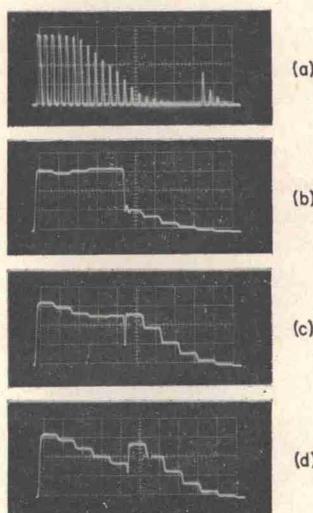


FIG. 2. (a) Echo train in a CdSe crystal at 20 MHz using water column. (b) (c) and (d) are the phase conditions of signals in (a) when the pulse length is increased and the frequency changed. The pattern in (d) is used for frequency measurements.

parison of  $C_{44}$  calculated from  $V_{s44a}$  (Table I) and  $V_{s44b}$ , and a comparison of  $C_{66}$  calculated from  $V_{s66}$  and  $V_{qs2}$ .

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  $\alpha$  is the volume coefficient of thermal expansion,  $\gamma$  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.<sup>7,8</sup> Each side measured ap-

<sup>6</sup> J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, New York, 1964), 2nd ed.

<sup>7</sup> H. J. Newkirk and D. K. Smith, *Am. Mineral.* **50**, 22, 44 (1965).

<sup>8</sup> 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)
$V_{133}$	$[C_{33}/\rho]^{1/2}$	parallel $c$	parallel $c$
$V_{s44a}$	$[C_{44}/\rho]^{1/2}$	parallel $c$	normal $c$
$V_{111}$	$[C_{11}/\rho]^{1/2}$	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 $c$
$V_{q1}$	$C_{13} = 2[\frac{1}{2}(C_{11} + C_{44} - \rho V^2) \times \frac{1}{2}(C_{44} + C_{33} - \rho V^2)]^{1/2} - [C_{44}]$	45° $a$ and $c$	45° $a$ and $c$
$V_{qs1}$		$V = V_{q1}$ or $V_{qs1}$	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  $\pm 1$  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  $\pm 1$  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<sup>9</sup> was used for making the velocity measurements. A different approach was used for making the longitudinal measurements which eliminated any corrections for

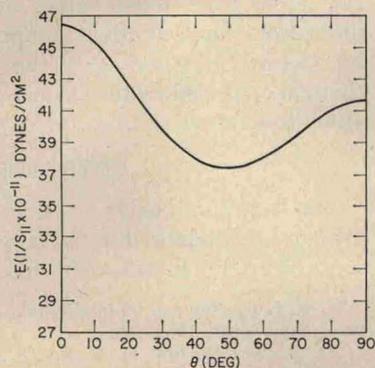


FIG. 3. Young's modulus of BeO as a function of angle from the "c" axis.

<sup>9</sup> H. J. McSkimin, J. Acoust. Soc. Am. **31**, 287 (1959).

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<sup>10</sup> modified for gated amplifier mode. The resulting pulses excite a lithium sulfate transducer<sup>11</sup> 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<sup>12</sup> to be

TABLE II. Compliance conversions for hexagonal system.

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

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

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

$$S_{14} = S_{24} = S_{34} = S_{41} = S_{42} = S_{43} = 0$$

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

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

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

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

<sup>10</sup> Arenberg Ultrasonics Laboratory, Model PG-650-C.

<sup>11</sup> Fabricated for the Lawrence Radiation Laboratory by Automation Industries, Boulder, Colorado.

<sup>12</sup> Not published.