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*Materials Research Laboratory, The Pennsylvania State University,
University Park, Pennsylvania***Pressure Dependence of Elastic Constants of Cesium Halides^{1),2)}**

By

Z. P. CHANG G. R. BARSCH, and D. L. MILLER

The single crystal elastic constants of CsCl, CsBr, and CsI have been measured at 13 °C as a function of hydrostatic pressure. The maximum pressure ranged from 2.3 to 6 kbar but was extended up to 10 kbar for two runs. The pressure dependence of the elastic constants was found to be linear within experimental error. The experimental results are compared with theoretical data by Nran'yan and Ghate. Also, the stability of the cesium chloride structure under pressure is discussed.

Die elastischen Konstanten von CsCl-, CsBr- und CsI-Einkristallen wurden bei 13 °C in Abhängigkeit vom hydrostatischen Druck gemessen. Der Höchstdruck lag zwischen 2,3 und 6 kbar und wurde für zwei Versuchsreihen auf 10 kbar erhöht. Innerhalb der Meßgenauigkeit wurde eine lineare Druckabhängigkeit der elastischen Konstanten gefunden. Die experimentellen Ergebnisse werden mit theoretischen Daten von Nran'yan und Ghate verglichen. Der Druckeinfluß auf die Stabilität der CsCl-Struktur wird diskutiert.

1. Introduction

Since the first paper on the pressure dependence of the elastic constants of cubic crystals was published by D. Lazarus in 1949 [1] a variety of experimental data representing different bond types and several simple crystal structures have been reported [2 to 16]. The crystal structures investigated so far are, in the standard crystallographic notation: A1 (Al, Cu, Ag, Au); A2 (Li, Na, K, Fe); A3 (Mg, Cd); A4 (Si, Ge); B1 (LiF, NaF, NaCl, KCl, KBr, KI, RbI, MgO); B2 (β' -CuZn); B3 (GaAs); C1 (CaF₂); C8 (α -SiO₂). In addition, a few isotropic materials have been measured also (polystyrene, pyrex glass, fused silica, and several polycrystalline materials). Strangely enough, the only representative of the B2 structure that has received attention until recently was brass (β' -CuZn), although several ionic substances occur in this structure also.

The B2 structure is of special interest because for CuZn the pressure coefficient of the shear modulus $c_s = \frac{1}{2}(c_{11} - c_{12})$ is negative [1]. From this one may infer that the B2 structure becomes unstable under pressure and that at sufficiently high pressure CuZn should transform into a different structure or decompose into two phases.³⁾ In order to decide whether this instability is due to the specific nature of the cohesive forces in CuZn, or whether it is a general feature of the B2 structure, we have measured the pressure dependence of the

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²⁾ Presented at the AIME meeting in Detroit, Michigan, October 1965.

³⁾ Attempts are being made at present in this laboratory to verify the occurrence of this transition and to determine its nature.

three elastic constants of single crystalline CsCl, CsBr and CsI at room temperature. The objective of this paper is to report the data obtained.

While this paper was being prepared other investigators have also reported about measurements on CsBr and CsI [17, 18]. These results will be compared below with the data presented here.

2. Experimental Details

2.1 Specimen and Transducers

Single crystals of CsI and CsBr were purchased from Harshaw Chemical Company, while a single crystal of CsCl was grown in this laboratory by O. D. Slagle by means of the Bridgman technique. All specimens were oriented to within 0.5° by means of the Laue back reflection technique and cut and ground to the shape of rectangular parallelepipeds with edges $8 \times 10 \times 12 \text{ mm}^3$ (CsCl), $10 \times 12 \times 12 \text{ mm}^3$ (CsBr) and $10 \times 9 \times 9 \text{ mm}^3$ (CsI). Due to the odd orientation and shape of the CsI crystal, a small tetrahedral-shaped corner of the size of about 8 mm^3 was missing in this case, but this irregularity was well outside the ultrasonic beam cross section. For the wave propagation the [100] and [110] directions were chosen for CsCl and CsBr, whereas for CsI, because of the less favorable orientation of the available crystal the [111] and [112] directions were selected. For the generation of longitudinal and transverse waves 20 MHz X-cut, and Y- or AC-cut disk-shaped quartz transducers of 8 mm diameter were used. Phenyl salicylate (salol) was used as bonding material for the determination of the second order elastic constants, and Dow Corning resin 276-V9 was used for measurements under hydrostatic pressure.

2.2 Ultrasonic Technique

In general, the velocity measurements were made by means of the pulse superposition method of McSkimin [19]; however, for CsCl and CsBr under hydrostatic pressure the phase comparison method [20] was used. The correction due to the phase shift occurring at the transducer-specimen interface was evaluated by means of the thin film approximation [21].

In the pulse superposition method, a pulse train of 2, 4, 8, or 16 pulses followed by the same period with no input pulses was sent into the crystals. The repetition rate of the driving ultrasonic pulses is adjusted until proper maximum echo peaks are introduced. An electronic automatic peak finder device was used for locking on this repetition rate. A frequency modulation is applied to the repetition frequency, sweeping the "correct" repetition rate, and producing amplitude modulation on the echo signal. The echo signal is then synchronously detected with respect to a frequency modulation, and an error correction signal is developed. This error signal is amplified and applied to the repetition oscillator to bring the repetition frequency to the "correct" value.

In the phase comparison method, pulse trains were sent into the crystals with the duration of the pulse longer than the transit time of the ultrasonic waves in the crystals so that part of the pulses overlap. By adjusting the frequency of the carrier wave such that constructive interference occurs, the velocities can be calculated.

2.3 Pressure System

The equipment used for the generation of hydrostatic pressure has been described before [16]. Argon gas was used as a pressure medium. The pressure was measured with a manganin cell in connection with a Foxboro recorder. The temperature of the sample was kept quite constant by water cooling the entire pressure chamber from outside. The temperature of a copper plate which was in direct contact with one of the side faces of the specimen was measured with a chromel-alumel thermocouple. By means of a second thermo-couple the temperature was measured also on the opposite side close to the specimen to check the presence of any thermal gradients within the sample. For each measurement the frequency was read 15 min after the pressure was changed, and even longer at lower pressure, to ascertain that the system had reached thermal equilibrium. In this way, most of the data were taken within a range of 0.5° C around 13° C.

3. Experimental Results

For CsCl four independent runs were made up to 3 to 4 kbar, and for CsBr and CsI three runs were made, each with maximum pressure attained ranging from 2.3 to 9.6 kbar. The experimental data were analyzed in terms of the "natural velocity" introduced by Thurston and Brugger [22]. Corrections for the temperature dependence of the thickness of the specimen and the velocities were made to convert all the velocities to 13° C. The plots of $\rho_0 W^2$ versus pressure p where ρ_0 is the initial density and W the natural velocity are shown in Fig. 1 to 3 for various modes in the three cesium-halides. As can be seen, within experimental accuracy the dependence on pressure is linear in the pressure range covered.

For waves propagating in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions the relationships between the slope of $\rho_0 W^2$ versus p were given in [22]. For pure waves in the $\langle 111 \rangle$ and $\langle 112 \rangle$ directions, they can be derived in the same manner and are given in Table I. As usual, $B_T^* = 1/3 (c_{11}^T + 2 c_{12}^T)$ denotes the isothermal bulk

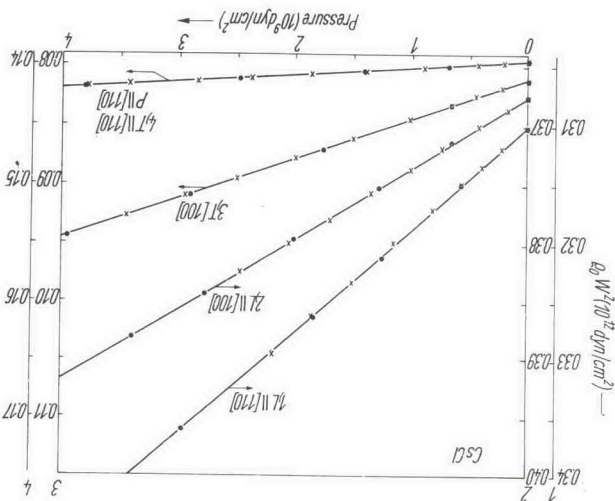
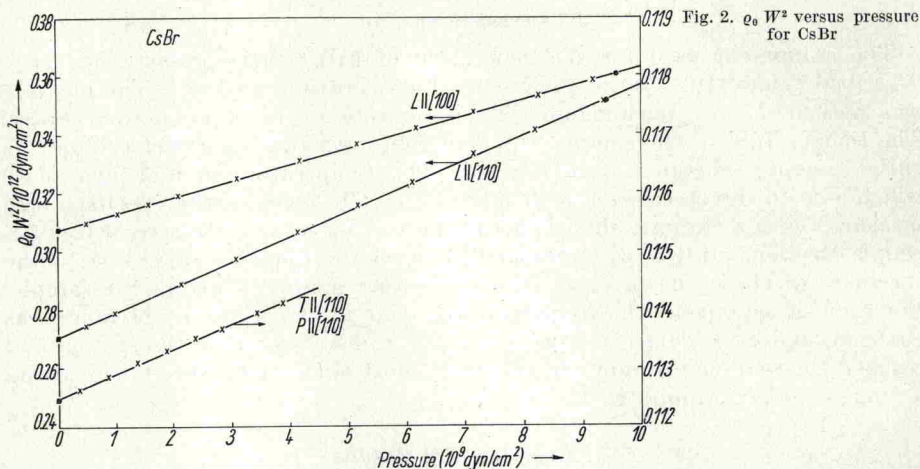
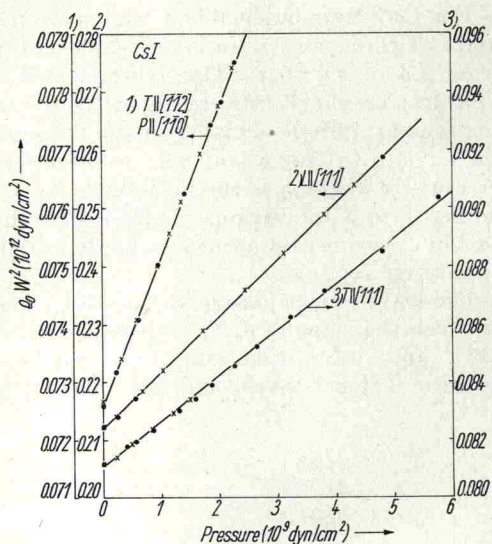


Fig. 1. $\rho_0 W^2$ versus pressure for CsCl. L and T denote longitudinal and transverse waves, respectively. P denotes the direction of particle motion. Dots were measured with increasing pressure and crosses with decreasing pressure.

Fig. 2. $\rho_0 W^2$ versus pressure for CsBrFig. 3. $\rho_0 W^2$ versus pressure for CsI

modulus at $p = 0$, and $c_a = c_{111} + 2c_{112}$, $c_b = 2c_{112} + c_{123}$, $c_c = c_{144} + 2c_{166}$ are three independent linear combinations of the intermediate third order elastic constants [23]. Obviously, the linear combinations of c_a , c_b , c_c occurring for each mode in the expression for $(\rho_0 W^2)'$ are of the same type as those of c_{11} , c_{12} and c_{12} occurring in the expression for $\rho_0 V^2$.

From the expressions of $(\rho_0 W^2)'_{p=0}$ for waves propagating in the [100] and [110] directions as shown in Table 1 of [22], one obtains a linear relation which permits an internal check among the four measurements on the CsCl specimen. The agreement was good to 0.1% of the smallest quantity involved, indicating good self-consistency of the measurements.

The data shown in Fig. 1 to 3 were analyzed in terms of a least square fit to a straight line. The results for the adiabatic elastic constants $c_{\mu\nu}^S$ are listed in Table 2, those for the linear combinations c_a , c_b , c_c of the T.O.E. constants

Table 1
Expressions for $\rho_0 V^2$ and $(\rho_0 W^2)'$ at zero pressure for wave propagation
in two directions of cubic crystals under hydrostatic pressure

Propagation direction	Displacement direction	$w = (\rho_0 V^2)_{p=0}$	$(\rho_0 W^2)'_{p=0}$
[111]	[111]	$\frac{1}{3}(c_{11}^s + 2c_{12}^s + 4c_{44})$	$-1 - \frac{2w}{3B^T} - \frac{1}{3B^T} \frac{c_a + 2c_b + 4c_c}{3}$
[111]	[111]	$\frac{1}{3}(c_{11}^s - c_{12}^s + c_{44})$	$-1 - \frac{2w}{3B^T} - \frac{1}{3B^T} \frac{c_a - c_b + c_c}{3}$
[112]	[110]	$\frac{1}{6}(c_{11}^s - c_{12}^s + 4c_{44})$	$-1 - \frac{2w}{3B^T} - \frac{1}{3B^T} \frac{c_a - c_b + 4c_c}{6}$

Table 2
Adiabatic elastic constants $c_{\mu\nu}^S$, and isothermal elastic constants $c_{\mu\nu}^T$, at 13°C (in 10^{12} dyn cm⁻²)

	$\mu\nu$	11	12	44	s	B
CsCl	$c_{\mu\nu}^S$	0.3683 ± 0.0018	0.0893 ± 0.0015	0.0817 ± 0.0009	0.1395 ± 0.0008	0.1822 ± 0.0016
	$c_{\mu\nu}^T$	0.355	0.0756	0.0817	0.1395	0.168
CsBr	$c_{\mu\nu}^S$	0.3077 ± 0.0015	0.0827 ± 0.0013	0.0760 ± 0.0008	0.1125 ± 0.0007	0.1577 ± 0.0014
	$c_{\mu\nu}^T$	0.2951	0.0702	0.0760	0.1125	0.145
CsI	$c_{\mu\nu}^S$	0.2462 ± 0.0032	0.0659 ± 0.0012	0.0644 ± 0.0012	0.0902 ± 0.0016	0.1260 ± 0.0019
	$c_{\mu\nu}^T$	0.239	0.0589	0.0644	0.0902	0.119

as calculated from the equations in [22] and Table 1 are given in Table 3, and those for the intermediate pressure derivatives of the elastic constants in Table 4. In Tables 2 and 4 the indices s and B are used to denote the shear modulus $c_s = 1/2(c_{11} - c_{12})$ and the bulk modulus $c_B = 1/3(c_{11} + 2c_{12})$, respectively. For all directly measured quantities the probable errors are indicated which were determined from the mean square deviation of the experimental data and from estimates of the errors in the measurement of specimen density, ultrasonic path length and hydrostatic pressure. The main error arises from the pressure measurement for which an estimate of 2% has been used.

In Table 2 the isothermal elastic constants $c_{\mu\nu}^T$ have been included, and in Table 3 the purely adiabatic and the purely isothermal linear combinations c_{α}^S and c_{α}^T ($\alpha = a, b, c$) are presented also.⁴ These data were calculated by using the standard formulae as discussed in [23] and from the numerical values of the required thermomechanical constants compiled in [24]. The purely adiabatic

⁴ The data of Tables 3 and 4 have been reported in a previous publication [24]. Due to a revision of the numerical analysis slight changes have been made for all values referring to CsI, so that the data in Tables 3 and 4 supersede those given in [24].

Table 3

The three linear combinations c_α ($\alpha = a, b, c$) of the third order elastic constants at 13 °C (in 10^{12} dyn cm^{-2}) for the three thermodynamic boundary conditions

		c_a	c_b	c_c
CsCl	c_α^S	-4.36	-2.15	-2.39
	c_α	-4.31 ± 0.07	-2.13 ± 0.14	-2.38 ± 0.07
	c_α^T	-4.42	-2.24	-2.38
CsBr	c_α^S	-3.57	-1.76	-2.13
	c_α	-3.48 ± 0.08	-1.79 ± 0.08	-2.11 ± 0.15
	c_α^T	-3.61	-1.92	-2.11
CsI	c_α^S	-2.95	-1.46	-1.73
	c_α	-2.95 ± 0.24	-1.46 ± 0.13	-1.75 ± 0.08
	c_α^T	-3.06	-1.57	-1.75

and purely isothermal pressure derivatives of the elastic constants given in Table 4 were calculated from the second order elastic constants and the linear combinations c_α^S , c_α , c_α^T of the T.O.E. constants by using the formulae of Birch [25] listed in Table 1 of [23].

4. Discussion

As can be seen from Table 3 the differences between the adiabatic and the intermediate linear combinations, $c_\alpha^S - c_\alpha$, are smaller than the experimental error, except in one case. The difference between the isothermal and the intermediate linear combinations, $c_\alpha^T - c_\alpha$, is seen to be larger than the probable error in many cases.

For the pressure derivatives Table 4 shows that the differences between the purely adiabatic and the intermediate values are in general larger than the experimental error. The same holds also for the differences between the purely isothermal and the intermediate ones.

Included in Table 4 are also the intermediate pressure derivatives for CsBr and CsI measured by Koliwad and Ruoff [18].⁵⁾ Although for CsI the two sets of data agree reasonably well, the differences for CsBr seem to be larger than the estimated error of the present data.

Another check of the experimental data reported here can be made by comparing the isothermal bulk modulus and its isothermal pressure coefficient calculated from the ultrasonic data with the results of Bridgman's static equation of state measurements. Such a comparison was made first by Overton [26].

⁵⁾ The values quoted in Table 4 are corrected values as reported in the talk; therefore they supersede the values given in the abstract quoted as reference [18].

Writing the isothermal equation of state in the form

$$-\frac{\Delta V}{V_0} = a p - b p^2 + c p^3 + \dots \quad (1)$$

the first two expansion coefficients are related to the bulk modulus and its pressure derivative by

$$a = \frac{1}{B^T}, \quad (2a)$$

$$b = \frac{1}{2(B^T)^2} \left[\left(\frac{\partial B^T}{\partial p} \right)_T + 1 \right]. \quad (2b)$$

Equation of state measurements for Cs halides have been made by Bridgman in the pressure ranges up to 12, 50, and 100 kbar [27 to 29]. Leastsquare quadratic fits of $\Delta V/V_0 p$ versus p from these data were made to obtain the coefficients a and b . The bulk modulus and its pressure derivative were

Table 4
Adiabatic, intermediate, and isothermal pressure
derivatives of the elastic constants at 13 °C

	$\mu \nu$	11	12	44	s	B
CsCl	$\left(\frac{\partial c_{\mu \nu}^S}{\partial p} \right)_S$	6.31	4.76	3.22	0.77	5.28
	$\left(\frac{\partial c_{\mu \nu}^S}{\partial p} \right)_T$	6.82 ± 0.2	5.05 ± 0.3	3.56 ± 0.2	0.89	5.64
	$\left(\frac{\partial c_{\mu \nu}^T}{\partial p} \right)_T$	7.07	5.30	3.56	0.89	5.89
CsBr	$\left(\frac{\partial c_{\mu \nu}^S}{\partial p} \right)_S$	5.89	4.54	3.34	0.68	4.99
	$\left(\frac{\partial c_{\mu \nu}^S}{\partial p} \right)_T$	6.30 ± 0.2 $5.81^*)$	4.93 ± 0.2 $4.37^*)$	3.68 ± 0.4 $3.20^*)$	0.68 $0.72^*)$	5.38 $4.85^*)$
	$\left(\frac{\partial c_{\mu \nu}^T}{\partial p} \right)_T$	6.63	5.26	3.68	0.68	5.71
CsI	$\left(\frac{\partial c_{\mu \nu}^S}{\partial p} \right)_S$	6.14	4.67	3.40	0.74	5.16
	$\left(\frac{\partial c_{\mu \nu}^S}{\partial p} \right)_T$	6.57 ± 0.7 $6.68^*)$	4.90 ± 0.4 $5.11^*)$	3.72 ± 0.2 $3.88^*)$	0.84 $0.78^*)$	5.46 $5.63^*)$
	$\left(\frac{\partial c_{\mu \nu}^T}{\partial p} \right)_T$	6.90	5.23	3.72	0.84	5.79

*) Experimental values by Koliwad and Ruoff [18].

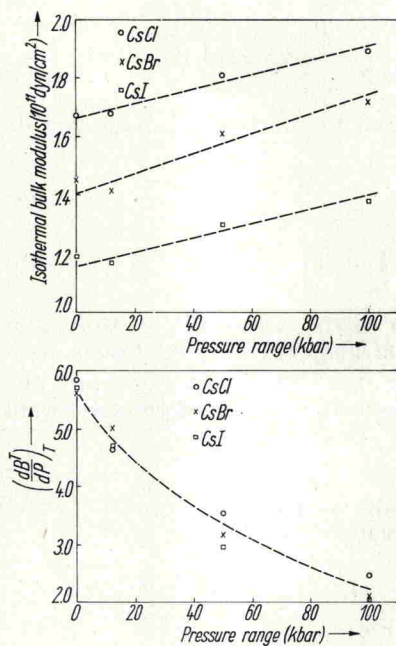


Fig. 4. Comparison of ultrasonically determined isothermal bulk modulus and its isothermal pressure derivative (representing the zero pressure values) with Bridgman's data [27 to 29] (plotted versus the pressure range covered in a particular run)

then calculated according to (2). The values so obtained differ considerably for the three runs. However, if these values are plotted against the pressure range of the run as in Fig. 4 with the isothermal values calculated from the ultrasonic data plotted on the vertical axis, it can be seen that the agreement between the ultrasonic and the static volumetric data is improved if the latter are extrapolated to zero pressure range. Although the scattering of the static data is too large to permit an exact extrapolation, the trend is obvious.

The dependence of Bridgman's data on the pressure range seems to indicate the influence of the fourth and higher order expansion coefficients in (1) which were neglected in the calculation of B^T and $(\partial B^T/\partial p)_T$. These higher order terms would become more pronounced at higher pressure, leading to an apparent pressure dependence of the expansion coefficients a and b . In addition, or alternatively, any systematic error can also cause such an apparent pressure dependence.

In Table 5 the linear combinations c_x^T of the isothermal T.O.E. constants are compared with theoretical room temperature data⁶) calculated by Ghate [30] and Nran'yan [32] on the basis of a central force model including Coulomb forces and exponential Born-Mayer repulsion. In Ghate's paper repulsion between first and second nearest neighbors is taken into account, whereas Nran'yan considers only first nearest neighbor interaction. Although the theoretical data give the correct sign and order of magnitude the discrepancies are larger than 100% in some cases. For the first choice of the repulsive parameter Ghate's theoretical value of c^T is quite close to the experimental value, but c_b^T and c_c^T are too small. For the second choice of the repulsive parameter the agreement is improved for c_a^T and c_c^T , but deteriorated for c_b^T . The values by Nran'yan are all too small. The discrepancy between any of the theoretical and the experimental data must certainly be attributed to the crudeness of the force model used. The primary deficiency seems to be the omission of van der Waals interaction. Although many-body forces may contribute to the discrepancy their influence cannot be expected to be very large because the Cauchy relation $c_b = c_c$ is approximately fulfilled for the experimental data. It should be noted, however, that the difference $c_b - c_c$ is positive for the experimental

⁶) The theoretical data of Ghate are referred to 25 °C, whereas the experimental data are taken at 13 °C. Taking this temperature difference into account will change the last digit by at most 4 units and therefore does not improve the agreement.

Table 5

Comparison of experimental and theoretical values of the linear combinations c_a^T , c_b^T , c_c^T of the isothermal third order elastic constants (at 13°C in 10^{12} dyn cm^{-2})

		$-c_a^T$	$-c_b^T$	$-c_c^T$
CsCl	Exp.	4.42	2.24	2.38
	Th. (a)	4.18	1.17	1.02
	Th. (b)	5.44	2.43	2.03
	Th. (c)	3.37	1.31	1.11
CsBr	Exp.	3.61	1.92	2.11
	Th. (a)	3.68	1.11	0.96
	Th. (b)	4.58	2.03	1.68
	Th. (c)	3.10	1.32	1.15
CsI	Exp.	3.06	1.57	1.77
	Th. (a)	3.02	1.02	0.86
	Th. (b)	3.83	1.88	1.49
	Th. (c)	2.68	1.28	1.13

(a) P. B. Ghatge [30] (Hardness parameter $b = 0.3333$)

(b) P. B. Ghatge [30] (Hardness parameter b from [31])

(c) A. A. Nran'yan [32]

data, whereas it should be negative according to all three theoretical estimates. Thus assuming that the effect of temperature is properly taken into account in the theoretical data one must conclude that many-body contributions should cause deviations from the Cauchy relations opposite in sign to those caused by the thermal effects.

The question of the stability of the cesium halides under pressure that was raised in the introduction can be discussed on the basis of the data in Table 4. As the pressure derivatives of both shear moduli c_{44} and c_s (and of the bulk modulus) are positive for all three cesium halides, it appears that they remain stable under pressure. Thus on the basis of the pressure derivatives of the elastic constants there is no evidence for a high pressure phase transition in the cesium halides. On the other hand the instability of β' -CuZn that may be predicted from the negative sign of $\partial c_s / \partial p$ should be due to the specific features of the metallic bond rather than a property of the B2 structure.

The above conclusions are based on a linear extrapolation of the pressure dependence of the elastic constants. However, according to theoretical calculations that are to be published the shear modulus c_s may have a maximum and decrease with pressure at sufficiently high pressures. Thus it appears that the B2 structure may become unstable at high pressure for ionic bonding also, and that the differences between ionic and metallic bonding affect the stability of the B2 structure only quantitatively, but not qualitatively.

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NONLINEAR PRESSURE DEPENDENCE OF ELASTIC CONSTANTS AND FOURTH-ORDER ELASTIC CONSTANTS OF CESIUM HALIDES

Z. P. Chang and G. R. Barsch

Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania

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The pressure dependence of the elastic constants of CsCl, CsBr, and CsI was measured up to 10 kbar by an ultrasonic technique and found to be nonlinear. The second pressure derivatives of the elastic constants and three linear combinations of the fourth-order elastic constants were determined.

The complete set of the single-crystalline, third-order elastic (TOE) constants or some of their linear combinations have been measured up to the present for about ten or 30 materials, respectively. No data, however, are as yet available on fourth-order elastic (FOE) constants, although their contribution to anharmonic effects may be comparable with that arising from the TOE constants.

The elastic constants of CsCl, CsBr, and CsI were measured at 298°K as a function of hydrostatic pressure up to 10 kbar by using the ultrasonic-pulse superposition technique. This extends previous measurements¹ on these materials to a higher pressure range and increased accuracy. Four independent runs referring to different propagation and polarization directions were made to determine the three elastic constants as a function of pressure and to obtain one internal check which indicated good self-consistency of all measurements. Figure 1 shows typical results for the square of the reciprocal transit time versus pressure. The change of the path length contributes at most one-half of this curvature in the case of c_{12} , and much less for c_{11} and c_{44} . It was taken into account by Cook's method,²

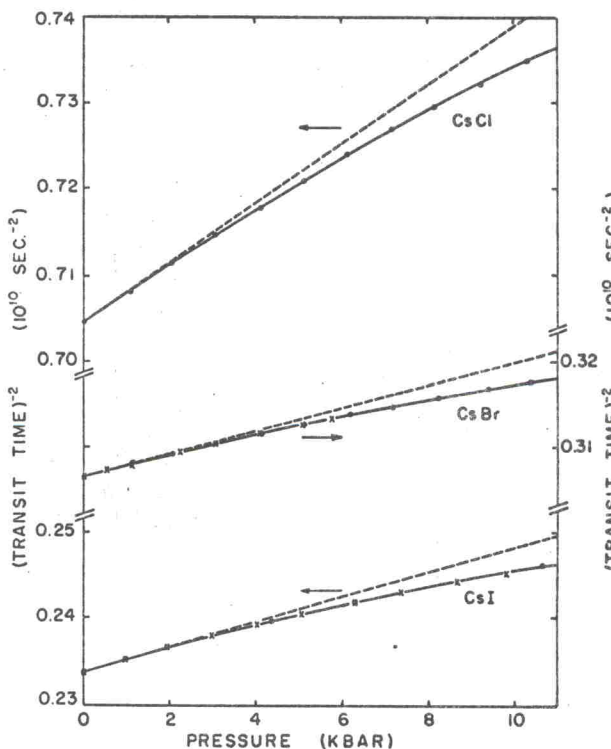


FIG. 1. Square of reciprocal transit time of transverse waves (propagating in $[110]$ and polarized in $[11\bar{0}]$) versus pressure for CsCl, CsBr, and CsI. The solid lines represent a least-squares fit to a parabola.

using the isothermal values for the bulk modulus and its first pressure derivative calculated according to Overton.³ The adiabatic elastic constants can be represented as a quadratic function of the pressure. The elastic constants and their first and second derivatives obtained from a least-squares fit to the experimental data are compiled in Table I. The error shown arises from the standard deviation of the least-squares fit and, predominantly, from the uncertainty in the pressure reading, which was taken from a Foxboro recorder in connection with a Manganin cell and estimated at 1.5%. The quantities C_{ijkl}' and C_{ijkl}'' are the isothermal pressure derivatives of the adiabatic elastic constants.

From them the mixed adiabatic-isothermal partial contractions $\Gamma_{ijkl}^{(3)} = C_{ijklmm}$ and $\Gamma_{ijkl}^{(4)} = C_{ijklmmp}$ of the tensors of the TOE and FOE

$$C_{ijkl}' = \left(\frac{\partial C_{ijkl}^S}{\partial p} \right)_T = -\frac{1}{3B^T} (C_{ijkl}^S + \Gamma_{ijkl}^{(3)}) + (\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}), \quad (1)$$

and its extension to the zero-pressure value of the second pressure derivative,⁶

$$C_{ijkl}'' = \left(\frac{\partial^2 C_{ijkl}^S}{\partial p^2} \right)_T = \frac{1}{9(B^T)^2} [(1+3B')C_{ijkl}^S + (4+3B')\Gamma_{ijkl}^{(3)} + \Gamma_{ijkl}^{(4)}]. \quad (2)$$

Here $B^T = \frac{1}{3}C_{ijij}T$ is the isothermal bulk modulus, $B' = \frac{1}{3}C_{ijij}'$ its isothermal pressure derivative, both at zero pressure, and δ the Kronecker symbol. The numerical data are listed in Table II. It is apparent that the partial contractions of the TOE constants are about 10 to 25 times, and the partial contractions of the FOE constants about 200 to 500 times larger than

Table II. Partial contractions $\Gamma_{ijkl}^{(3)} = C_{ijklmm}$ and $\Gamma_{ijkl}^{(4)} = C_{ijklmmp}$ of intermediate adiabatic-isothermal TOE and FOE elastic constants (in 10^{11} dyn cm⁻²).

	CsCl	CsBr	CsI
$\Gamma_{1111}^{(3)}$	-43.9 ± 2.9	-36.2 ± 2.7	-30.0 ± 1.9
$\Gamma_{1122}^{(3)}$	-21.7 ± 2.0	-18.9 ± 2.2	-15.4 ± 1.6
$\Gamma_{1212}^{(3)}$	-24.4 ± 1.8	-21.4 ± 1.8	-17.9 ± 1.3
$\Gamma_{1111}^{(4)}$	730 ± 130	600 ± 130	490 ± 100
$\Gamma_{1122}^{(4)}$	410 ± 90	360 ± 100	290 ± 70
$\Gamma_{1212}^{(4)}$	460 ± 80	420 ± 80	350 ± 60

Table I. Adiabatic elastic constants C_{ijkl}^S (in 10^{11} dyn cm⁻²), their first isothermal pressure derivatives C_{ijkl}' (dimensionless), and their second isothermal pressure derivatives C_{ijkl}'' (in 10^{-11} dyn⁻¹ cm²) for three cesium halides.

	CsCl	CsBr	CsI
C_{1111}^S	3.670 ± 0.017	3.063 ± 0.017	2.452 ± 0.015
C_{1122}^S	0.889 ± 0.013	0.809 ± 0.018	0.667 ± 0.016
C_{1212}^S	0.808 ± 0.009	0.753 ± 0.010	0.628 ± 0.010
C_{1111}'	7.01 ± 0.23	6.71 ± 0.26	6.72 ± 0.25
C_{1122}'	5.14 ± 0.22	5.21 ± 0.31	5.12 ± 0.30
C_{1212}'	3.69 ± 0.15	3.81 ± 0.19	3.84 ± 0.18
C_{1111}''	-6.8 ± 1.2	-7.5 ± 1.5	-9.2 ± 1.6
C_{1122}''	-1.8 ± 1.1	-2.4 ± 1.7	-3.0 ± 1.7
C_{1212}''	-2.5 ± 0.7	-2.2 ± 1.0	-2.5 ± 1.0

constants can be determined by means of Birch's formula for the zero-pressure value of the first pressure derivative,^{4,5}

the corresponding second-order elastic constants. This illustrates the slow convergence of the Taylor expansion of the internal energy with respect to the Lagrangian strains. All partial contractions are negative for the TOE constants, but positive for the FOE constants. Validity of the Cauchy relations for the TOE and FOE constants would require that $\Gamma_{1122}^{(3)} = \Gamma_{1212}^{(3)}$ and $\Gamma_{1122}^{(4)} = \Gamma_{1212}^{(4)}$. Obviously these relations are approximately fulfilled both for the TOE and for the FOE constants with the deviation increasing from about 10% for CsCl to about 20% for CsI.

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Pressure Dependence of the Elastic Constants of Single-Crystalline Magnesium Oxide

Z. P. CHIANG AND G. R. BARSCH

*Materials Research Laboratory and Department of Physics
Pennsylvania State University, University Park, Pennsylvania 16802*

New precision measurements have been made of the pressure dependence of the elastic constants of MgO single crystals by using the ultrasonic pulse superposition method in connection with an automatic peak finder. The results for the first pressure derivatives of the elastic constants lie mostly between the earlier data of Bogardus and the data of Anderson and Andreatch and essentially agree, within the joint experimental error, with both sets of values.

The pressure dependence of the elastic constants of single-crystalline magnesium oxide (MgO) has been measured by several authors [Susse, 1961; Bogardus, 1965; Anderson and Andreatch, 1966]; however, there are some discrepancies among these values. Because of the importance of magnesium oxide as a major constituent of the mantle, it is highly desirable to obtain more accurate values of the elastic constants and their pressure dependences. In addition, magnesium oxide is of interest because of many high-temperature applications and because of its chemical stability in the atmosphere, which makes MgO useful as a standard for the elastic constants and their pressure derivatives.

For these reasons, new measurements were made with an improved experimental technique and increased experimental accuracy by using one of the six specimens of Bogardus [1965]. The purpose of this note is to report the results and to present a careful evaluation of the total experimental error.

The elastic constants of magnesium oxide were determined from ultrasonic velocity measurements as a function of hydrostatic pressure up to 10 kb. The pulse-superposition method of McSkimin [1961] was used with an automatic peak finder constructed by Miller [1969] according to the principles put forth by McSkimin [1965] and McSkimin and Andreatch [1967]. Ultrasonic wave pulses were generated and received with X-cut and ac-cut quartz transducers of 0.35-inch diameter with a resonance frequency of 20 MHz. The pressure was deter-

mined by measuring the resistance change of a manganin cell with a Carey-Foster type bridge obtained from the Harwood Engineering Co., Walpole, Massachusetts. The temperature of the specimen was monitored with a thermocouple, and the measured values of the repetition rate frequency were converted to 25°C by using values for the temperature coefficients of the elastic constants that had been determined with the same ultrasonic interferometer.

The specimen was identical with one of the crystals used by Bogardus [1965]. It was prepared from a larger single-crystalline specimen (purchased from the Norton Co.), which had been obtained by cooling from the melt. Only minor traces of Si, Al, Ca, and Fe could be found by qualitative spectrochemical analysis. The density was measured as 3.579 g/cm³ and agrees well with the X-ray density of 3.581 calculated from the lattice constant of 4.213 Å reported by Swanson and Tatge [1953]. The faces of the specimen were oriented to within 15 min in the directions [110], [1 $\bar{1}$ 0], and [001], and the respective dimensions are 11.5 × 11.2 × 14.2 mm.

Measurements were made for four wave modes, the three pure modes with propagation in the [110] direction and the longitudinal mode propagating in the [001] direction. This procedure permits one internal check among the data. The relation between $\rho_0 W^2$ (where ρ_0 denotes the initial density and W the natural velocity introduced by Thurston and Brugger [1964]) and pressure, shown in Figure 1, can be seen to be linear. A least-squares method was used to determine the three second-order adia-

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batic elastic constants and their isothermal pressure derivatives by using the formulas given by *Thurston and Brugger* [1964]. The standard error was calculated from the mean-square deviation, and the total error was determined by including an estimated error of 0.1 and 1.0% for the density and pressure, respectively. The elastic constants and their pressure derivatives were also converted to purely isothermal and purely adiabatic conditions by using the standard formulas [*Voigt*, 1910; *Barsch*, 1967] and the thermal and thermoelastic data tabulated by *Barsch and Chang* [1967]. The results are listed in Table 1 together with the values for the shear modulus $c_s = \frac{1}{2}(c_{11} - c_{12})$ and for the bulk modulus K . The second-order elastic constant data are in good agreement with the values of *Bogardus* [1965] and *Anderson and Andreatch* [1966]. Also included in Table 1 are the results reported by these investigators for

the isothermal pressure derivatives of the adiabatic elastic constants.

The data reported as the values of *Bogardus* were calculated from the measurements under hydrostatic pressure, which are given in Table IV of *Bogardus* [1965] and have been published before [*Barsch and Chang*, 1967]. The value for the pressure coefficient of the bulk modulus given here differs from the value reported by *Bogardus* [1965] because of a numerical error in that paper and because *Bogardus* used the measurements under uniaxial stress in addition to the values under hydrostatic pressure. The values for the pressure coefficient of the bulk modulus listed in Table IX of *Bogardus* [1965] were calculated from the equation $(\partial K^*/\partial p) = -(1/9K)(c_{111} + 6c_{112} + 2c_{123}) + 1$, where $K^* = V_0(\partial p/\partial V)$ is the bulk modulus with reference to the initial volume V_0 , and c_{111} , c_{112} , and c_{123} are third-order elastic constants. Since

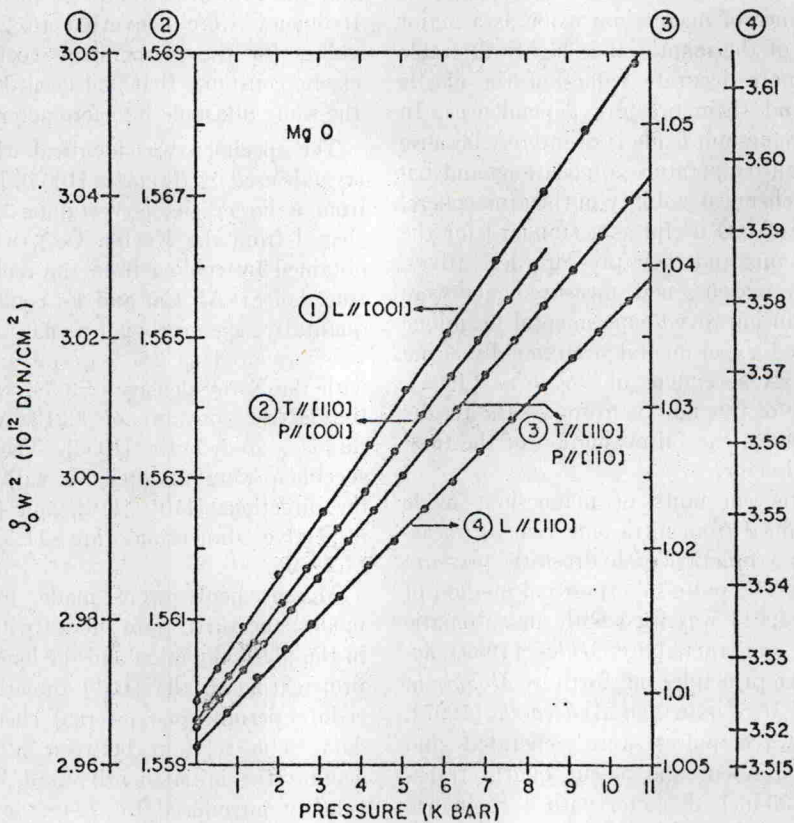


Fig. 1. $\rho_0 V^2$ versus pressure for MgO. L and T denote longitudinal and transverse waves, respectively; P denotes the direction of particle motion.

TABLE 1. Second-Order Elastic Constants (in 10^{11} dynes/cm²) of MgO and Their Pressure Derivatives (Dimensionless) at Zero Pressure

$c_s = \frac{1}{2}(c_{11} - c_{12})$; K = bulk modulus; S and T denote adiabatic and isothermal conditions, respectively ($\rho_0 = 3.579$ g/cm³, $T = 25^\circ\text{C}$).

M	c_{11}	c_{12}	c_{44}	c_s	K	Reference
M^S	29.664 ± 0.030	9.508 ± 0.011	15.581 ± 0.016	10.078 ± 0.010	16.226 ± 0.017	Present work
M^T	29.404	9.248	15.581	10.078	15.967	Present work
$(\partial M^S/\partial p)_S$	8.98	1.84	1.09	3.57	4.22	Present work
$(\partial M^S/\partial p)_T$	1.03	3.34	...	Susse [1961]
	8.93	1.76	1.20	3.59	4.16	Calculated from Bogardus [1965]
	9.477	1.992	1.160	3.743	4.497	Anderson and Andreatch [1966] (at 23°C)
	9.16	1.82	1.12	3.67	4.27	Present work
	± 0.10	± 0.09	± 0.06	± 0.06	± 0.08	
$(\partial M^T/\partial p)_T$	9.18	1.84	1.12	3.67	4.29	Present work

the pressure derivative of the bulk modulus $K = -V(\partial p/\partial V)$, with reference to the instantaneous volume V , is given by $(\partial K/\partial p) = (\partial K^*/\partial p) - 1$, the values reported in Table IX of the Bogardus paper should be decreased by 1, giving, for example, $(\partial K/\partial p) = 3.8$ for MgO.

For $(\partial c_{32}/\partial p)$, $(\partial c_{44}/\partial p)$, and $(\partial c_s/\partial p)$, the results of the present work agree within the combined experimental error with both the data calculated from the measurements of Bogardus [1965] and the results of Anderson and Andreatch [1966], if it is assumed that all three sets of data are subject to the same experimental error that is reported for the results of the present work. For $(\partial c_{11}/\partial p)$ and $(\partial K/\partial p)$ the discrepancy is larger than this combined experimental error. With the exception of

$(\partial c_{44}/\partial p)$, all results of the present work lie between those of Bogardus [1965] and those of Anderson and Andreatch [1966]. The values reported by Susse [1961] for $(\partial c_{44}/\partial p)$ and $(\partial c_s/\partial p)$ are considerably smaller than any of the other values.

The three linear combinations of the intermediate third-order elastic constants, which can be determined from the isothermal pressure derivatives of the adiabatic elastic constants, are given in Table 2. Again, the values calculated from the measurements of Bogardus [1965] are based on his hydrostatic data only. The data given in the first line are based on the individual third-order elastic constants listed in Table V of Bogardus [1965], which were calculated by neglecting the difference between the adiabatic and isothermal bulk moduli. It is apparent that the effect of this approximation together with the inclusion of the measurements under uniaxial stress is especially pronounced for c_6 .

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TABLE 2. Linear Combinations of the Adiabatic-Isothermal Third-Order Elastic Constants (in 10^{11} dynes/cm²) of MgO

$c_a = c_{111} + 2c_{112}$, $c_b = 2c_{122} + c_{123}$, and $c_c = c_{441} + 2c_{442}$ ($T = 25^\circ\text{C}$).

c_a	c_b	c_c	Reference
-508.5	-25.9	-120.5	Bogardus [1965]
-506.0	-46.0	-121.1	Calculated from Bogardus [1965]
-532.0	-57.1	-119.1	Anderson and Andreatch [1966] (at 23°C)
-516.2	-48.8	-117.3	Present work
± 4.8	± 4.5	± 2.7	

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