The Variation of the Adiabatic Elastic Constants of KCl, NaCl, CuZn, Cu, and Al with Pressure to 10,000 Bars*

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The adiabatic velocities of sound for longitudinal and transverse waves in single crystal specimens of five cubic solids have been measured as a function of pressure to 10,000 bars, using a pulse technique. The elastic constants calculated from these data in general agree well with previous measurements obtained for zero pressure elastic constants and compressibilities. With increasing pressure the anisotropy increases in crystals which are not closest-packed, but decreases in closest-packed structures. Consideration of the exchange force between nearest neighbors gives a qualitative explanation for this effect. Comparison of the present measurements with previous measurements of the variation of elastic constants with temperature indicates that the elastic moduli cannot be considered functions of volume alone but must also depend explicitly on the temperature.

INFORMATION derivable from a study of the variation of the elastic properties of solids as a function of hydrostatic pressure should be useful in the more general problem of formulating an equation of state for solids.[1] This paper presents results of measurements of the elastic constants of single crystal specimens of Cu, Al, CuZn, KCl, and NaCl subject to hydrostatic pressures to 10,000 bars.[2]

Previous measurements of the effects of pressure on the elastic properties of solids are limited to measurements of compressibility and shear modulus. Linear compressibilities have been determined for many solids by Bridgman and others using a dilatometric technique[3] based on measurement of the change in length of a specimen under pressure relative to the confining walls of the high pressure chamber. The observed data are plotted as a square-law curve, the first-order term giving the zero pressure compressibility, and the second-order term the change in compressibility with pressure. Since the compressibility of a solid is easily calculated from the elastic constants, measurements of the change of elastic constants with pressure give the *change* in compressibility as a *first-order* effect.

Birch[4] has measured the change in shear modulus with pressure to about 4000 bars for several polycrystalline metals, glasses, and minerals. His measurements were made by observing the resonant frequency of a cylindrical specimen excited in torsional oscillation. Viscosity effects were minimized in his measurements by use of nitrogen gas as a pressure fluid. This method and other techniques involving measurement of a set of resonant frequencies[5] are useful only for measurement of shear moduli over a somewhat limited pressure range. At high pressures measurement of compressional moduli would be impossible by such methods, since the large damping would preclude accurate determination of resonant frequencies.

The present investigation is made possible by the wartime development of pulsed circuits. Elastic constants are determined by a non-resonant method involving direct measurement of the transit time of a short pulse of ultrasonic energy through a solid. This technique, known as the pulsed ultrasonic method, or "reflectoscope" method, was first developed by Firestone[6] for detection of flaws in metals. More recently, the pulsed ultrasonic method has been employed by Huntington[7] and Galt[8] for measurement of the elastic constants of several cubic salts at atmospheric pressure.

For simplicity the present measurements are confined to cubic crystals, which have only three independent elastic constants. The specimens used represent the three principal groups of cubic crystals: simple cubic (NaCl, KCl), body-centered cubic (CuZn), and face-centered cubic (Cu, Al). These three designations, while not crystallographically correct, are useful in representing the lattice symmetry if differences between atoms are ignored. They represent extremes in packing of nearest neighbors, the simple cubic structure being least closely packed, and the face-centered cubic structure closest packed. In each of the extreme groups, two materials of considerably different degrees of anisotropy are investigated. By these choices it is hoped that some evaluation may be made of Zener's proposals[9] con-

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* The research described here was performed in the High Pressure Laboratory of the Institute for the Study of Metals, University of Chicago, and was supported in part by the ONR under Contract N-6-ori-20-XX.

[1] For discussions of equations of state for solids see: P. W. Bridgman, Rev. Mod. Phys. **7**, 1 (1935); F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940), Chap. X; N. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford University Press, London, 1936), Chap. I; K. Herzfeld and M. Goeppert-Mayer, Phys. Rev. **46**, 995 (1934); M. Born et al., Jour. Chem. Phys. **7**, 591 (1939); Proc. Camb. Phil. Soc. **36**, 160, 173, 454, 466 (1940); **37**, 34, 177 (1941); **38**, 61, 67, 82 (1942); **39**, 101, 104, 113 (1943); **40**, 151 (1944); R. Furth, Proc. Roy. Soc. **183**, 87 (1944).

[2] 1 bar $=10^6$ dynes/cm$^2=1.01972$ kg/cm^2.

[3] P. W. Bridgman, *Physics of High Pressure* (The Macmillan Company, New York, 1931), Chap. 4.

[4] F. Birch, J. App. Phys. **8**, 129 (1937).

[5] L. Balamuth, Phys. Rev. **45**, 715 (1934).

[6] F. A. Firestone, J. Acous. Soc. Am. **18**, 200 (1946).

[7] H. B. Huntington, Phys. Rev. **72**, 321 (1947).

[8] J. K. Galt, Phys. Rev. **73**, 1460 (1948).

[9] C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948), Chap. III; Phys. Rev. **71**, 846 (1947).

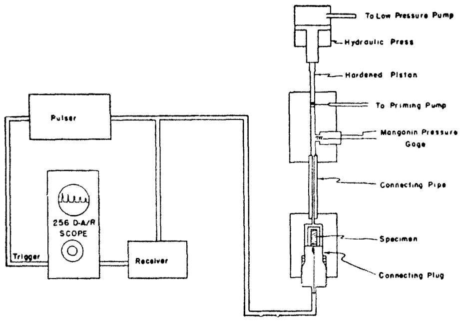

FIG. 1. Schematic arrangement of experimental apparatus.

cerning the effect of the short range exchange force between closed-shell ions on shear moduli. Zener pointed out that Fuchs' calculations[10] of the exchange contribution to the shear moduli of cubic crystals would indicate that in simple cubic lattices the shear modulus C_{44} might be expected to change much more slowly than the modulus $\frac{1}{2}(C_{11}-C_{12})$, or even in the opposite direction, with change in volume. According to this same viewpoint, the reverse effect might be expected in body-centered cubic lattices. In face-centered cubic lattices the modulus C_{44} would be expected to change slightly more slowly than $\frac{1}{2}(C_{11}-C_{12})$ with change in volume.

Since the elastic constants of all the above materials have been measured at zero pressure by a different method, a check is afforded on the accuracy of the present measurements. In addition, the elastic constants of three of these substances, KCl, NaCl,[11] and CuZn[12] have been measured as functions of temperature, so that some correlation may be obtained between the variation of elastic constants with temperature and with pressure.

The present measurements may also prove useful in comparison of the theories of finite strain proposed by several authors.[13] These theories all contain undetermined third-order constants. Unfortunately, all the third-order constants cannot be uniquely determined from pressure data alone. However, it may be possible to derive certain useful relationships between these quantities which will be helpful in evaluating the various theories.

EXPERIMENTAL METHODS

Measurement of elastic constants by the pulsed ultrasonic method involves determination of a set of velocities of sound in various directions in a crystal: By use of two crystals of a material with principal axes in the [100] and [110] directions, five velocities can be measured and the elastic constants computed with two

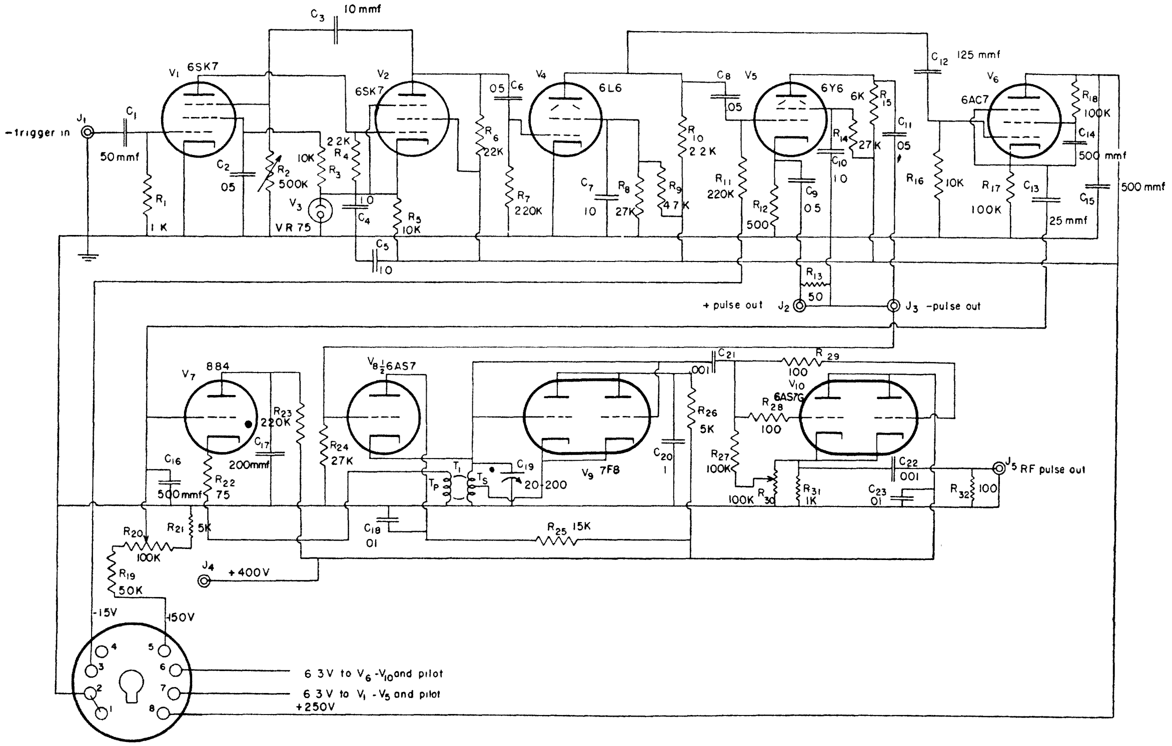

FIG. 2. Circuit diagram of pulser

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[10] K. Fuchs, Proc. Roy. Soc. **151**, 585 (1935); **153**, 622 (1936); **157**, 444 (1936).

[11] M. A. Durand, Phys. Rev. **50**, 449 (1936); F. C. Rose, Phys. Rev. **49**, 50 (1936).

[12] W. A. Good, Phys. Rev. **60**, 605 (1941); J. S. Rinehart, Phys. Rev. **58**, 365 (1940).

[13] F. D. Murnaghan, Am. J. Math. **49**, 235 (1937); L. Brillouin, *Les Tenseurs* (Masson et Cie., Paris, 1938), Chap. X, XI; M. A. Biot, Phil. Mag. **27**, 468 (1939); F. Birch, Phys. Rev. **71**, 809 (1947).

internal checks. The velocities are expressible in terms of the elastic constants and the density ρ as shown below:[14]

$$\left.\begin{array}{l}
V_1=(C_{11}/\rho)^{\frac{1}{2}}=\text{velocity of longitudinal wave in (100) crystal in [100] direction.}\\
V_2=[(C_{11}+C_{12}+2C_{44})/2\rho]^{\frac{1}{2}}=\text{velocity of longitudinal wave in (110) crystal in [110] direction.}\\
V_3=(C_{44}/\rho)^{\frac{1}{2}}=\text{velocity of transverse wave in (100) crystal in [100] direction.}\\
V_4=[\frac{1}{2}(C_{11}-C_{12})/\rho]^{\frac{1}{2}}=\text{velocity of transverse wave in (110) crystal in [1}\bar{1}\text{0] direction.}\\
V_5=(C_{44}/\rho)^{\frac{1}{2}}=\text{velocity of transverse wave in (110) crystal in [100] direction.}
\end{array}\right\} \quad (1)$$

A schematic diagram indicating the arrangement of the various components involved in the present measurements is shown in Fig. 1. The apparatus consists of an electro-mechanical system for production of ultrasonic pulses and measurement of transit times, and a system for generation of high pressures.

I. The Electro-Mechanical System

The basic unit of the electrical system is a DuMont 256D-A/R oscilloscope. This instrument provides triggering pulses to an external pulser and means for accurate measurement of the time of travel of the ultrasonic pulse through the specimen. In operation the cycle is initiated by application of a triggering pulse to the pulser by the oscilloscope. The pulser then generates a short group of 12-mc waves. This signal is applied to a thin quartz crystal. The quartz crystal is in turn cemented to the specimen crystal, so that a short pulse of 12-mc acoustical waves is generated, and travels back and forth through the specimen several times before being completely damped. Each time the sound pulse passes through the quartz crystal an electrical pulse is generated which is applied to the receiver. After amplification and detection, the received set of pulses is displayed on the linear time base sweep of the oscilloscope. This cycle is repeated at a rate of about 2000 cps.

A. Oscilloscope—The oscilloscope contains precision delay circuits whereby the sweep may be initiated a measurable time after the triggering pulse. This delay circuit is set by means of a helical potentiometer, and can be calibrated to better than 0.1 percent by means of internal 10 microsecond crystal controlled range markers. These range markers have been checked by beating against station WWV, and found to be accurate to one part in 10^5. With adjustment of the delay time, the echoes can be made to move across the face of the oscilloscope and the 10 to 40 microsecond interval between echoes can be measured with considerable accuracy. The ultimate precision is largely limited by pulse distortion which makes accurate location of the leading edge of a pulse difficult.

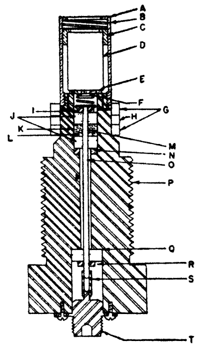

FIG. 3. Plug and specimen holder. *A*—screw cap; *B*—spring; *C*—retaining washer; *D*—specimen crystal; *E*—quartz crystal; *F*—spring contact; *G*—steel packing washers; *H*—lead washer; *I*—steel washer; *J*—bakelite washers; *K*—rubber washer; *L*—steel washer; *M*—steel ring; *N*—hardened steel washer; *O*—piano wire; *P*—body of plug; *Q*—bakelite spacer; *R*—nut; *S*—finger contact; *T*—type *N* connector.

B. Pulser—To minimize the effects of pulse distortion, some pains are taken in the design of the pulser circuit, shown in Fig. 2, to provide a steeply rising leading edge on the transmitted pulse. This is achieved first by the formation of a well-defined video rectangular pulse in the direct-coupled one-cycle multivibrator circuit of V_1 and V_2. This pulse is variable in width from 0.5 to 20 microseconds by setting rheostat R_2. After amplification, the negative rectangular pulse is applied to the grid of the clamp tube V_8, permitting oscillations to build up in the Hartley circuit of V_9. Simultaneously with the application of the negative pulse to V_8, a positive pulse is applied to the grid of thyratron V_7, which is normally biased beyond cut-off. Discharge of the thyratron sends a large surge of current through the close-coupled primary of the transformer T_1, causing oscillations to build up rapidly in the circuit $C_{19}T_S$. When the negative pulse is removed from the grid of clamp tube V_8 the oscillation decays rapidly because of the very low plate resistance of V_8. The resulting radio-frequency pulse is fed directly to the cathode-follower circuit of V_{10}, so that no high-Q tuned circuits are required between the oscillator and output. Use of two halves of a 6AS7G in parallel in the output cathode-follower results in an extremely small output impedance, so that the pulse shape is not distorted by the use of a

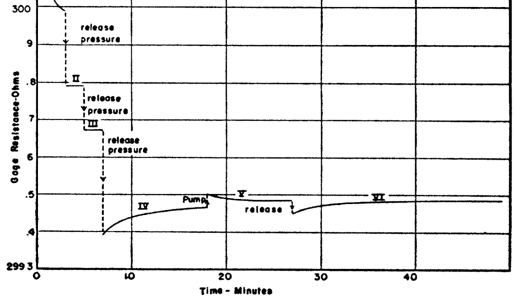

FIG. 4. Calibration of manganin pressure gage by determination of the freezing point of Hg at 0°C.

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[14] W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, New York, 1946), Chap. IV.

TABLE I. Densities and adiabatic velocities of sound for various hydrostatic pressures. (Densities in gm/cm^3.)

Material	Pressure (bars) Velocity (km/sec.)	0	2000	4000	6000	8000	10,000
KCl	V_1	4.541	4.646	4.752	4.845	4.914	5.044
	V_2	3.896	3.926	4.002	4.079	4.116	4.169
$\rho_0=1.986$	V_3	1.781	1.759	1.734	1.715	1.694	1.671
	V_4	2.921	2.990	3.069	3.135	3.201	3.282
	V_5	1.784	1.761	1.736	1.713	1.693	1.672
NaCl	V_1	4.766	4.875	4.947	5.041	5.140	5.230
	V_2	4.513	4.558	4.598	4.647	4.690	4.778
$\rho_0=2.162$	V_3	2.434	2.430	2.426	2.422	2.417	2.414
	V_4	2.920	2.987	3.039	3.099	3.156	3.208
	V_5	2.440	2.435	2.431			
CuZn	V_1	3.942	3.953	3.962	3.975	3.985	4.004
	V_2	4.931	4.945	4.954	4.971	4.985	5.011
$\rho_0=8.304$	V_3	3.151	3.164	3.171	3.180	3.187	3.192
	V_4	1.083	1.084	1.087	1.089	1.090	1.091
	V_5	3.152	3.162	3.170	3.179	3.180	3.187
Cu	V_1	4.373	4.383	4.393	4.403	4.405	4.415
	V_2	4.982	4.995	4.992	4.995	5.012	5.035
$\rho_0=8.941$	V_3	2.905	2.907	2.909	2.908	2.909	2.910
	V_4	1.621	1.623	1.626	1.629	1.633	1.637
	V_5	2.913	2.915	2.916			
Al	V_1	6.257	6.288	6.326	6.376	6.411	6.495
	V_2	6.409	6.468	6.479	6.487	6.520	6.562
$\rho_0=2.699$	V_3	3.252	3.269	3.286	3.306	3.334	3.357

relatively long 50-ohm coaxial lead between the pulser and the specimen.

C. Receiver—The pulse receiver is constructed by modification of an APS-15A 30 megacycle intermediate frequency amplifier. An additional radio-frequency stage was added and new coils wound to provide a tuned 12-mc receiver, with an over-all band width of about 3 cm between half-power points. The video amplifier stages of the receiver were unaltered and connected directly to the video amplifier of the oscilloscope. In practice, some increase in the accuracy of location of the leading edge of a pulse is obtained by deliberately overloading the receiver.

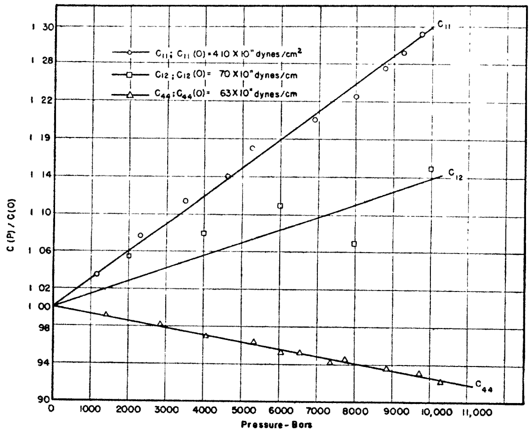

FIG. 5. Variation of the adiabatic elastic constants of KCl with pressure.

D. Transducer—The thin quartz transducer crystals[15] are gold sputtered for single-ended connection in the manner described by Huntington,[7] with an active area of about 1 cm^2. Longitudinal or transverse acoustical waves are excited in the specimen by use of X or Y cut quartz crystals, respectively. The quartz crystal must be fixed to the specimen with a binder permitting transmission of the sound pulse to the specimen.

An annoying problem was encountered in finding a satisfactory cement which would transmit shear waves through the specimen in the high pressure system. Phenyl salicylate, which was used by Huntington and Galt, is satisfactory for mounting the X-cut crystals, but dissolves rapidly in the pressure fluid at pressures above 500 bars and is thus unsuitable for mounting the Y-cut crystals. Similarly, all glues and resins soluble in hydrocarbons are unsatisfactory. Water-glass cements cannot be sufficiently dried even with appreciable baking to give adequate pulse transmission. DeKhotinsky wax proves satisfactory to about 5000 bars, but cracks at higher pressures. A satisfactory solution has been achieved by the use of red sealing wax. This wax is applied by heating the quartz crystal and specimen to about 150°C in a furnace. The surfaces of the specimen and quartz to be joined are then coated liberally with wax and placed together under a 500-gm weight. At this temperature the wax flows freely and uniform coats as thin as 0.001 in. can be obtained. This binder is usable over a pressure range of 12,000 bars. Unfortunately, the large difference in compressibilities between the quartz and the wax almost invariably results in shattering the quartz crystal during a high pressure measurement. Since the wax does not crack, this shattering does not in any way inhibit taking data, but does make it impossible to use the quartz crystal for a second run.

Since the acoustic pulse travels through the combined length of the specimen, transducer crystal, and cement film, the observed velocity is subject to a small correction for the thickness of the quartz and cement. This correction has been determined by measuring velocities

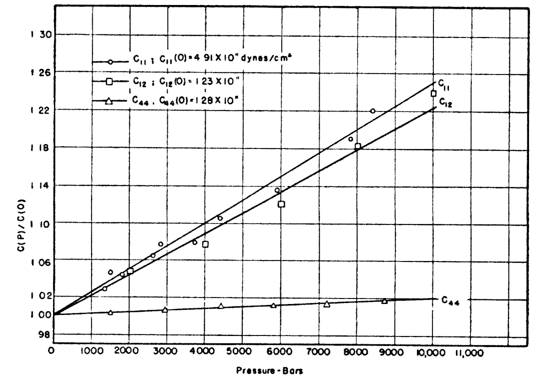

FIG. 6. Variation of the adiabatic elastic constants of NaCl with pressure.

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[15] Purchased from James Knights Co., Sandwich, Illinois.

for longitudinal and transverse waves in specimens of different lengths, and is found to be 0.10–0.15 microseconds, depending on the thickness of the cement film and the quartz crystal used.

II. The High Pressure System

The specimen crystal, with quartz transducer attached, is mounted in a lower chamber by means of a special connecting plug, shown in detail in Fig. 3. This plug is designed to serve the dual purpose of providing a mount for the specimen and furnishing means for transmitting the electrical pulse to the quartz crystal. The cylindrical specimen, *D*, with quartz crystal, *E*, fixed at one end, is supported by means of the screw cap *A* and retaining washer *C*. Connection to the center of the quartz crystal is effected by the spring contact *F*. The outer conducting area of the crystal connects to ground through the outer shell of the plug.

The lower chamber is connected to the upper high pressure generating system by means of a pipe, the pressure being transmitted by the hydraulic fluid. The hydraulic fluid employed in the present measurements is petroleum ether, consisting principally of normal hexane, with a boiling point of 60°C. This fluid does not freeze at room temperature within the pressure range investigated.

The high pressure generating system is similar to that employed by Bridgman[16] and need not be separately described here. Pressure is determined by measurement of the change in resistance of a manganin resistance gage which is immersed in the pressure fluid.

The pressure gage used in the present measurements is a ten-foot length of No. 40 manganin wire, of about 300-ohms resistance, wound in a circular helix about $\frac{1}{2}$ in. in diameter and 1 in. long. The resistance of the coil is stabilized by heating to 150°C for about four hours. Before calibration the gage is "seasoned" by repeated cycling through a pressure range of at least 10,000 bars. After perhaps six such cycles, the zero pressure resistance is reproducible to better than one part in 10^5. The pressure gage is calibrated by determination of the freezing pressure of mercury at 0°C, using Bridgman's value of 7640 kg/cm^2, determined by a free piston gage, as a standard. For this measurement, hexane, which freezes at about 6000 bars at 0°C, is not a suitable pressure fluid. Normal pentane, which has a freezing point above 10,000 bars at 0°C, is employed. A typical calibration curve is shown in Fig. 4. The freezing point is found by approach from both sides, and can be located with a precision of 0.1 percent. As shown by Adams, Goranson, and Gibson,[17] the manganin pressure gage is sufficiently linear so that only a single calibration point is required for a 0.1 percent accuracy in determination of pressure.

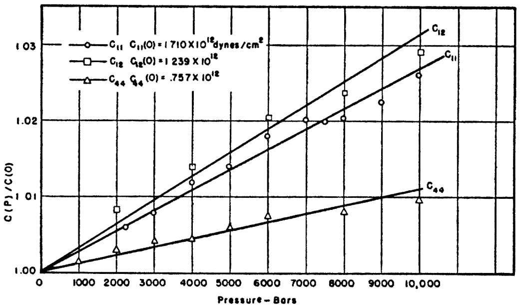

FIG. 8. Variation of the adiabatic elastic constants of Cu with pressure.

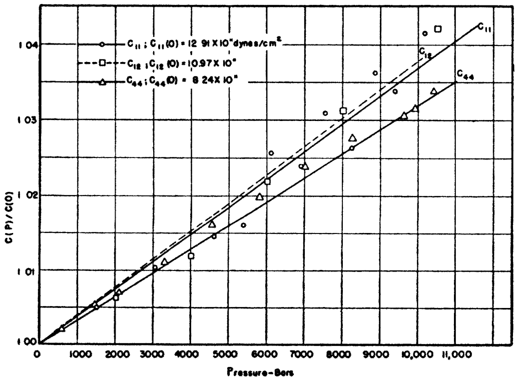

FIG. 7. Variation of the adiabatic elastic constants of CuZn with pressure.

III. Preparation of Specimens

The single crystal specimens have been prepared in the shape of right circular cylinders of about 2-cm diameter and 2 to 3-cm length. A diameter large compared to the acoustical wave-length is used to insure that the sound pulse is transmitted as a plane wave, so that infinite-medium moduli are measured. This outer diameter is always at least twice the diameter of the active area of the quartz crystal. Measurements taken with polycrystalline samples of successively smaller diameters indicate no change in measured velocity as long as

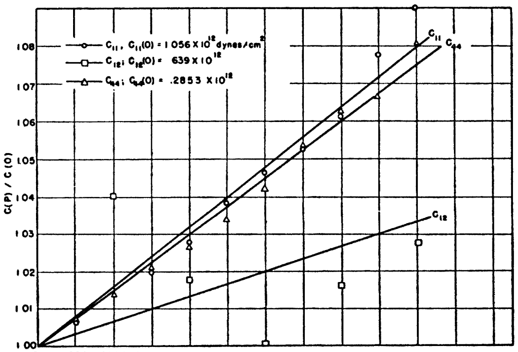

FIG. 9. Variation of the adiabatic elastic constants of Al with pressure.

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[16] P. W. Bridgman, *Physics of High Pressure*, Chap. 2.

[17] Adams, Goranson, Gibson, Rev. Sci. Inst. 8, 230 (1937).

TABLE II. Variation of $(C_{12}-2P)/C_{44}$ with pressure for KCl and NaCl.

Pressure (bars)	0	10,000
Material		
KCl	1.119	1.05
NaCl	0.954	1.01

the specimen diameter is greater than that of the wave front, taken as equal to the diameter of the active area of the quartz crystal.

Single crystal specimens of beta-brass, copper, and aluminum have been prepared in this laboratory. The crystals were grown from the melts in graphite crucibles by lowering at a rate of about 1.5 cm per hour through a vertical tube furnace.

In preparation of the beta-brass melt, a considerable reduction in zinc loss is achieved by heating proper amounts of pure copper and zinc together with a small amount of fused borax. With increasing temperature the borax melts and forms a protective coating over the surface of the molten metal. Loss of zinc by oxidation is thus reduced to about five grams per kilogram.

The metal single crystals are grown about 3 cm in diameter and 10 cm in length so that sufficiently large sections of proper orientation can be cut from the large crystal. The orientations of the crystals are determined by means of back-reflection diffraction pictures. All crystals are cut with a water-cooled carborundum cut-off wheel. This method of cutting introduces very little strain in the crystal, judging from the sharpness of the Laue spots diffracted from such cut surfaces. After one face of a crystal has been properly oriented to within one or two degrees, the opposite face of the specimen is made accurately parallel to the first by mounting the crystal in a surface grinder. Successive 0.0005-inch cuts are taken with a water-cooled wheel until a flat parallel surface is obtained. After working, the finished specimens are annealed for 24 hours at about 400°C. No residual surface strains are detected by x-ray analysis after this treatment.

The metal specimens have been analyzed chemically and show the following compositions in weight percent:

Beta-brass crystals: Cu: 51.06; Zn: 48.94; Ag, B, Si, Pb, Al, Ca, Mg, Fe<0.01
Copper crystals: Cu: 99.99; Ca, Mg, Ag, Al, Si, Fe<0.01
Aluminum crystals: Al: 99.991; Mg: 0.003; Si, Fe, Cu, Ca<0.002.

The single crystal specimens of NaCl and KCl were purchased from the Harshaw Chemical Company. These crystals are oriented by Harshaw by cleaving along (100) planes. The orientations have been checked by back-reflections pictures and found to be accurate to within about a tenth degree. The alkali-halide crystals are also annealed before use.

RESULTS

I. Variation of Adiabatic Elastic Constants with Pressure

The observed velocities of sound for the various materials studied are indicated in Table I, together with the measured zero-pressure densities. Density values are obtained by hydrostatic weighing. The values V_1-V_5 refer to velocities of waves in various crystallographic directions as indicated in Eqs. (1). The velocities are computed from the relation

$$V_i=d_{0i}(1+\chi_TP)^{-\frac{1}{3}}t_i^{-1} \tag{2}$$

where d_{0i} is the zero-pressure path length as measured by a calibrated micrometer, χ_T is the isothermal cubic compressibility and t_i the observed transit time, corrected for the thickness of the cement and quartz crystal.

The elastic moduli of Eqs. (1) are calculated by the equation

$$m_i=\rho_0(1+\chi_TP)V_i^2 \tag{3}$$

where ρ_0 is the zero-pressure density. From Eqs. (2) and (3) it is evident that the compressibility enters explicitly in the computation of the elastic constants only through the factor $(1+\chi_TP)^{\frac{1}{3}}$. The value for χ_T used in the above relations can be easily calculated, in the absence of previous data, by a self-consistent solution since

$$\begin{aligned}\chi_T&=\chi_s+(TV\alpha^2/C_P)\\&=[3/(C_{11_s}+2C_{12_s})]+TV\alpha^2/C_P\end{aligned} \tag{4}$$

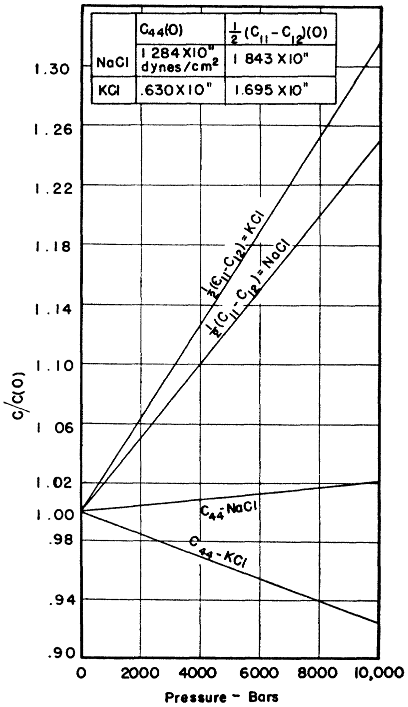

FIG. 10. Variation of the shear moduli of KCl and NaCl with pressure.

where T is the absolute temperature, V the molal volume, α the cubic thermal expansion coefficient and C_P the molal specific heat at constant pressure. The subscript s refers to adiabatic moduli. For most solids, χ_T is small, and a fairly large error in the assumed value for the compressibility introduces only a small error in the calculated value for the elastic constants.

In the case of aluminum, data are not given in Table I for the (110) shear velocities V_4 and V_5. For this specimen it has not been possible to resolve the two normal modes of vibration by positioning of the Y-cut quartz crystal. This anomaly presumably arises as a result of the very small anisotropy of aluminum, previous measurements[18] indicating that the velocities V_4 and V_5 should differ by only a few percent. With inevitable imperfections present in the metal crystal, some cross-coupling between normal modes must be anticipated. In anisotropic materials the cross-coupling is small if the transducer crystal is properly oriented. However, in aluminum the effect is evidently sufficiently large so that only a single average shear velocity is observed for a (110) crystal.

The adiabatic elastic constants calculated by Eqs. (1) and (3) are plotted as functions of pressure in Figs. 5–9.

All measurements are taken at room temperature, nominally 25°C. Changes in pressure are made sufficiently slowly so that temperature equilibrium is maintained. The change in viscosity of the pressure fluid with temperature may be presumed to have no observable effect. At 10,000 bars hexane has a viscosity of about 3 poises,[19] roughly the same as that of glycerin at zero pressure. Measurements taken for both compressional and shear waves in specimens immersed in air, hexane, and glycerin at atmospheric pressure have shown no detectable differences in velocities for the various media.

As can be seen from the graphs, the precision in the measurements for transverse waves is somewhat better than that for longitudinal waves. This difference results from the rather large radiation damping encountered at high pressures with longitudinal waves which limits the number of distinct echoes observable. This source of error is most serious for the alkali-halides, since the amount of energy radiated to the pressure fluid is proportional to the ratio of the compressibility of the solid to that of the liquid. Although the zero pressure constants, measured in air, are accurate to about ±0.2 percent, the accuracy in the high pressure values for C_{11} is probably no greater than ±1.0 percent for the alkali-halides, ±0.6 percent for Al and ±0.4 percent for Cu and CuZn. The accuracy of the shear measurements is about the same as at zero pressure. Since the constant C_{12} is obtained by difference, the precision of this value at high pressures is about ±4 percent for NaCl, ±6 percent for KCl, ±0.5 percent for CuZn, and ±1 percent for Cu.

TABLE III. Comparison of zero-pressure adiabatic elastic constants with previous values (units—10^{11} dynes/cm^2).

	Present			Previous			
Material	C_{11}	C_{12}	C_{44}	C_{11}	C_{12}	C_{44}	Reference
KCl	4.095	0.705	0.630	4.00	0.6	0.625	*
NaCl	4.911	1.225	1.284	4.99	1.31	1.26	*
CuZn	12.91	10.97	8.24	5.20	3.35	17.3	**
Cu	17.10	12.39	7.56	16.98	12.26	7.53	***
Al	10.56	6.39	2.853	10.82	6.22	2.84	****

* M. A. Durand, Phys. Rev. **50**, 449 (1936).
** W. A. Good, Phys. Rev. **60**, 605 (1941).
*** E. Goens, Ann. Phys. **17**, 233 (1933).
**** E. Goens and J. Weerts, Physik. Zeits. **37**, 321 (1936).

For Al, the value of C_{12} must be obtained by taking a double difference, owing to the impossibility of measuring the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ directly. The high pressure values for C_{12} are thus subject to an error of about ±3 percent for this material.

Since a considerable number of independent readings were taken for each curve, and no systematic error was noted, the slopes of the lines for C_{11} and C_{44} should be accurate to within ±0.5 percent. In no case is there apparent justification for assuming a relation other than linear between the elastic constants and pressure.

II. Variation of Anisotropy with Pressure

Several interesting effects can be noted by comparison of the rates of change of the two independent shear moduli C_{44} and $\frac{1}{2}(C_{11}-C_{12})$, as shown in Figs. 10 and 11. For the materials whose crystal structures are not closest-packed, the anisotropy increases with increasing pressure. The originally larger shear modulus, $\frac{1}{2}(C_{11}-C_{12})$ for the alkali-halides, C_{44} for beta-brass, increases with pressure at about the same rate as C_{11}, while the smaller modulus increases more slowly, or in the case of KCl, actually decreases. Face-centered-cubic copper, which has a closest-packed structure shows the reverse effect, the anisotropy decreasing with pressure.

The effects noted for the alkali-halides are in excellent agreement with Zener's predictions regarding the effects of exchange forces on the shear moduli. The supposition

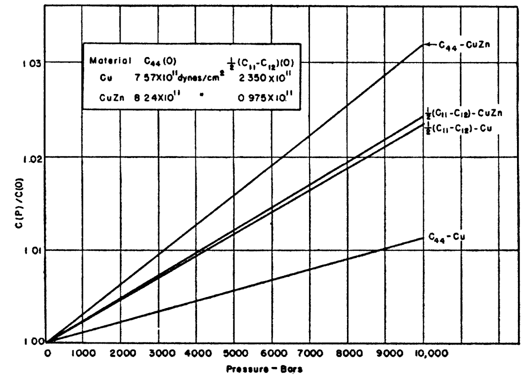

FIG. 11. Variation of the shear moduli of CuZn and Cu with pressure.

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[18] E. Goens, Ann. Phys. 17, 233 (1933).
[19] P. W. Bridgman, *Physics of High Pressure*, Appendix.

TABLE IV. Comparison of present computed isothermal compressibilities with previous values. (Units of a are 10^{-7} bar^{-1}, b—10^{-12} bar^{-2}.)

Material	Present a	Present b	Previous a	Previous b	Reference
KCl	56.8	72.4	56.3	74.4	*
NaCl	43.1	49.6	42.6	51	**
CuZn	9.06	2.30	9.11	0.99	***
Cu	7.38	1.36	7.29	1.6	***
Al	13.49	4.6	13.65	4.9	***

* J. C. Slater, Proc. Am. Acad. **61**, 135 (1926).
** P. W. Bridgman, Proc. Am. Acad. **64**, 33 (1929).
*** P. W. Bridgman, Proc. Am. Acad. **70**, 285 (1935).

that the difference in rates of change of the two moduli results from the exchange repulsion is further verified by the marked decrease in C_{44} for KCl. Since the potassium ion is somewhat larger than the sodium ion, the exchange force would be expected to be larger for KCl than for NaCl, and thus the effect on C_{44} of decreasing the inter-atomic distance larger for KCl.

The difference in rates of change of C_{44} and $\frac{1}{2}(C_{11}-C_{12})$ for copper are also qualitatively explained by consideration of exchange forces. According to Fuchs' results for this material, the exchange contribution is about 90 percent of the modulus $\frac{1}{2}(C_{11}-C_{12})$ and 75 percent of C_{44}. On this basis the former would be expected to change more rapidly with pressure than the latter, in agreement with the observed result.

In the case of beta-brass, the difference in rates of change of the two moduli, while significant, is much smaller than that anticipated on the basis of consideration of exchange forces alone. According to Zener's calculations a marked decrease in $\frac{1}{2}(C_{11}-C_{12})$ with pressure would be expected, rather than a small increase in this modulus.

At zero pressure the Cauchy relation[20] $C_{12}=C_{44}$, derived from the assumption of central forces between ions, is approximately realized for the alkali-halides. Love[21] has shown that under an external pressure P, the Cauchy relation is given by $C_{44}=C_{12}-2P$. The ratio $(C_{12}-2P)/C_{44}$ for KCl and NaCl is given in Table II.

The Cauchy relation is evidently satisfied somewhat better at high pressures than at zero pressure for both materials.

III. Comparison with Previous Data

A. Zero-pressure constants

As a general indication of the precision of the pulse method, it is worth while to compare the present zero-pressure adiabatic constants with those measured by other methods. This comparison is made in Table III.

With the exception of the constants for beta-brass the correlation is good. The large discrepancies between Good's values and the present values of the elastic constants of beta-brass were noted in a recent paper.[22] The differences probably result from a gross error in Good's measurement of C_{44}, resulting from the presence of impure modes in his resonant sample. Good's values for C_{11} and C_{12} were computed from Rinehart's[12] values for Young's modulus using this value for C_{44}. Values for Young's modulus computed from the present elastic constants correlate well with Rinehart's data.

TABLE V. Comparison of present value for change of shear modulus with pressure with previous values.

Material	Present $\left(\frac{\partial \ln C_{44}}{\partial P}\right)_T$	Present $\left(\frac{\partial \ln \frac{1}{2}(C_{11}-C_{12})}{\partial P}\right)_T$	Previous $\left(\frac{\partial \ln G}{\partial P}\right)_T$
Cu	1.13×10^{-5} bars^{-1}	2.45×10^{-5}	2.76×10^{-5}
Al	7.49×10^{-5}		7.76×10^{-5}

B. Compressibility

In Table IV the values for isothermal compressibility computed from the present data by Eq. (4) are compared with those previously reported by Bridgman and Slater. The coefficients a and b in the table refer to Bridgman's usual expression for the change in volume with pressure,

$$-[(V(P)-V_0)/V_0]=aP-bP^2 \tag{5}$$

where V (P) is the volume at pressure P and V_0 the zero-pressure volume.

Bridgman's and Slater's values for a and b are corrected for Bridgman's most recent value for the compressibility of iron.[23]

The agreement is generally good for both first and second-order coefficients. Because of the low precision in the present high-pressure value of C_{12} for Al, the agreement in b coefficients for this material, while fortuitous, is probably not very significant. In the case of beta-brass, the present b coefficient is appreciably larger than that reported by Bridgman. The discrepancy is well beyond the experimental error of the present measurements. Bridgman's low value of b may have resulted from the use of rapidly quenched polycrystalline specimens in his measurement, or possibly from differences in composition between his specimens and those used in the present investigation.

C. Shear modulus

Values of the pressure variation of the shear moduli C_{44} and $\frac{1}{2}(C_{11}-C_{12})$ of Cu and Al are compared in Table V with those observed by Birch[4] for polycrystalline specimens.

Birch's somewhat larger value for copper may be due to grain boundary effects.

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[20] A. E. H. Love, *Mathematical Theory of Elasticity* (Cambridge University Press, Cambridge, 1934), p. 100.

[21] See Reference 20, p. 619.

[22] D. Lazarus, Phys. Rev. **74**, 1726 (1948).

[23] P. W. Bridgman, Rev. Mod. Phys. **18**, 1 (1946).

D. Correlation with temperature data

The elastic modulus M of a crystal may be regarded as both an implicit function of temperature, through its volume V, and as an explicit function. Thus

$$M=M(V,T),$$

and

$$d\ln M=(\partial\ln M/\partial V)_T dV+(\partial\ln M/\partial T)_V dT.$$

The measured variation of M with temperature is evidently given by

$$\frac{d\ln M}{dT}=\left(\frac{\partial\ln M}{\partial P}\right)_T\left(\frac{\partial V}{\partial P}\right)_T^{-1}\frac{dV}{dT}+\left(\frac{\partial\ln M}{\partial T}\right)_V=-\frac{\alpha}{\chi_T}\left(\frac{\partial\ln M}{\partial P}\right)_T+\left(\frac{\partial\ln M}{\partial T}\right)_V.$$

Solving for $(\partial\ln M/\partial T)_V$, one obtains

$$(\partial\ln M/\partial T)_V=\alpha/\chi_T(\partial\ln M/\partial P)_T+(d\ln M/dT). \quad (6)$$

The value of $(\partial\ln M/\partial T)_V$ compared with the observed $(d\ln M/dT)$ gives a measure of the explicit dependence of the modulus on temperature, since evidently the left-hand term of Eq. (6) vanishes if $M=M(V)$.

The previous measurements of the temperature variation of the adiabatic elastic moduli are compared with the present pressure measurements in Table VI. Comparison is made for the bulk modulus $\frac{1}{3}(C_{11}+2C_{12})$ using Bridgman's values for $(d\ln M/dT)$. For the alkali-halides the comparison is also made for the moduli C_{11}, $\frac{1}{2}(C_{11}-C_{12})$, and C_{44}, using Rose's and Durand's values for $(d\ln M/dT)$. For beta-brass, the present results are compared with those of Rinehart for the Young's moduli $E_{[100]}$, $E_{[110]}$, and $E_{[111]}$ rather than with Good's values for the elastic constants, for reasons noted above. The Young's moduli are calculated from the elastic constants by the relations[24]

$$\begin{aligned}E_{[100]}^{-1}&=\frac{\chi_s}{9}+\left[3\frac{(C_{11}-C_{12})}{2}\right]^{-1},\\E_{[110]}^{-1}&=\frac{\chi_s}{9}+(4C_{44})^{-1}+\left[12\frac{(C_{11}-C_{12})}{2}\right]^{-1},\\E_{[111]}^{-1}&=\frac{\chi_s}{9}+(3C_{44})^{-1}.\end{aligned}\quad (7)$$

TABLE VI. Comparison of present data with previous measured changes in adiabatic elastic constants with temperature.

Material	Modulus (M)	$(\partial\ln M/\partial P)_T$	$(d\ln M/dT)$	$(\partial\ln M/\partial T)_V$
KCl	$\frac{1}{3}(C_{11}-2C_{12})$	2.609×10^{-5} bar^{-1}	-5.10×10^{-4} deg. C^{-1}	-0.45×10^{-4} deg. C^{-1}
	C_{11}	2.99	−9.80	−4.47
	$\frac{1}{2}(C_{11}-C_{12})$	3.16	−11.49	−5.85
	C_{44}	−0.74	−2.68	−4.00
NaCl	$\frac{1}{3}(C_{11}+2C_{12})$	2.46	−8.51	−1.66
	C_{11}	2.49	−7.60	−0.67
	$\frac{1}{2}(C_{11}-C_{12})$	2.53	−11.70	−4.66
	C_{44}	0.21	−2.50	−1.92
CuZn	$\frac{1}{3}(C_{11}+2C_{12})$	0.382	−5.37	−2.49
	$E_{[100]}$	0.249	+2.23	+4.41
	$E_{[110]}$	0.282	+0.93	+3.06
	$E_{[111]}$	0.384	−4.34	−1.44
Cu	$\frac{1}{3}(C_{11}+2C_{12})$	0.280	−4.17	−2.15
Al	$\frac{1}{3}(C_{11}+2C_{12})$	0.507	−4.69	−1.99

It appears from Table VI that any assumptions that elastic moduli are unique functions of volume are evidently invalid, especially in the case of shear moduli.

In this connection it was thought advisable to ascertain whether compositional differences between the beta-brass crystals used in the present measurements and those employed by Rinehart might not be involved in the large positive values for $(\partial\ln M/\partial T)_V$ for $E_{[100]}$ and $E_{[110]}$. Since the predominant terms in these moduli arise from the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ the latter value has been checked roughly between room temperature and −100°C. The measured shear modulus is found to decrease with decreasing temperature in essential agreement with Rinehart's observation.

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[24] C. Zener, Phys. Rev. **71**, 846 (1947).