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Acoustic Velocities in Polycrystalline NaCl at 300°K Measured at Static Pressures From 25 to 270 kbar

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The room temperature longitudinal and shear acoustic velocities in polycrystalline NaCl have been measured at static pressures in the range of 25–270 kbar (2.5–27.0 GPa). The measurements were made by ultrasonic interferometry in a variable lateral support Bridgeman anvil device. The velocity data are developed with the aid of the Decker equation of state. Previous measurements of acoustic velocities made in the range of 0–100 kbar are in agreement with the data. At higher pressures the shear mode velocity is approximately constant or slowly increasing with increasing pressure. This is in agreement with predictions made with next nearest neighbor interatomic force calculations. Nearest neighbor only and fourth-order finite strain theory calculations which use the assumption that the elastic parameter c_{44} goes to zero at the 292-kbar phase transition are determined to be inaccurate near the transition. It is suggested that the ratio of the acoustic velocities of polycrystalline NaCl can be used in the future as a parameter for calibration of ultrahigh-pressure devices.

INTRODUCTION

The equation of state of NaCl is used as a primary pressure calibration standard for X ray measurements [*Decker et al.*, 1972]. However, knowledge of the bulk modulus versus pressure for NaCl or any other material is often insufficient for the solution of problems in high-pressure physics. For example, the bulk modulus of rock materials may be insensitive to many phase changes occurring in the earth's interior. Knowledge of the acoustic velocities must be used, but predictions of the acoustic velocities, especially the shear velocities, are fraught with risk [*Anderson*, 1972].

In this paper, measurements of the acoustic velocities of polycrystalline NaCl to 270 kbar (27.0 GPa) are reported. The highest pressure to which the acoustic velocities of NaCl were previously reported is 100 kbar by *Voronov and Grigorèv* [1971] and *Voronov et al.* [1971]. The measurement of acoustic velocities in isotropic materials at very high pressures provides information for verifying the predictions of finite strain continuum and lattice dynamics theories. For example, *Anderson and Demarest* [1971] and *Thomsen* [1972] have predicted that the shear velocity of NaCl decreases or tends to zero near the 292-kbar phase transition.

In order to measure the acoustic velocities of any material under static pressures of more than 100 kbar, it is necessary to use a solid pressure device with a large specimen in comparison with the specimen size used in diamond anvil devices. In a solid system the question of whether the measured physical properties are affected by shear stresses always arises. This problem is minimized in this experiment by the use of a pressure device which balances lateral and horizontal forces actively.

DESCRIPTION OF THE EXPERIMENT

The pressure device used is a variable lateral support Bridgeman anvil device capable of exerting static pressures of up to 400 kbar and has been described by *Kendall et al.* [1975]. The advantage of this design is that an active lateral, as well as vertical, force is exerted upon the specimen. This should result in a much more uniform stress than is achieved when lateral support is provided only by a passive gasket.

The pressure device has been calibrated on the basis of the observation of resistometric changes at phase transitions such as those of bismuth at 25, 74, and 320 kbar [*Kendall et al.*, 1975; *Homan et al.*, 1975*a*] and those of GaP at 220 kbar [*Homan et al.*, 1975*b*] and NaCl near 290 kbar. From these observations a relationship between the specimen pressure and the hydraulic pressure upon the rams of the press (referred to as the 'load') has been developed. In general, the use of the load to specimen pressure relation has an error determined to be less than 15% of the pressure.

All data taken with this pressure device are referred to the 25-kbar pressure level. This is because both resistometric and ultrasonic observations indicate that the change in pressure with respect to the change in load is more erratic from run to run in the range of 0–25 kbar than the data at higher pressures.

The specimen is prepared from reagent grade NaCl. It is ground to a fine powder, baked at 100°C and 140×10^3 dyn/cm^2 air pressure for 3 hours, pressed into a pellet 1.2 mm in height and 4.35 mm in diameter, and stored in a desiccator. Prior to a run the specimen is placed in the pressure device, and a pressure of at least 35 kbar is exerted for several minutes. This insures that the specimen is fully compacted and that the gasket material is set. In addition, all data from the first run or two are disregarded. To check on specimen compaction, the density of a specimen after a series of runs was determined gravimetrically in absolute benzene. It was equal to the theoretical density within the accuracy of the measurement.

It is observed that the zero-pressure thickness of a specimen decreases from one run to the next by a few percent. This is due to extrusion of a small amount of specimen material. Most of this extrusion has been determined to occur between the 0- and 25-kbar pressure levels on the increasing pressure stroke of a run. Thus the assumption of constant specimen mass can be made from 25 kbar to any higher pressure.

For the results of this paper, nine runs are utilized. Only the data obtained on the increasing pressure portion of a run are used. Most runs were terminated at pressures of 130 kbar or less to establish a reliable base line for higher-pressure runs. Of the two highest maximum pressure runs, one run reached a pressure of more than 300 kbar, and the 292-kbar phase change was observed with simultaneous resistance measurements at approximately 290 kbar. The reported ultrasonic data are terminated at 270 kbar because of the onset of a noticeable degradation of the ultrasonic signal at this pressure level. The

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degradation could be interpreted as dispersion in the sample material, perhaps due to individual grains transforming prior to the specimen as a whole.

The apparatus for making the acoustic velocity measurements is shown in Figure 1. A transducer is attached to the force-free surface of the anvil. The anvil acts as a buffer rod between the transducer and the specimen. The ultrasonic signal can be continuously varied from 4 to 16 MHz for data collection. By switching between the longitudinal transducer on one anvil and the shear transducer on the other, effectively simultaneous measurements of both acoustic modes can be made as the load is continuously increased.

Since the specimen thickness is of the order of magnitude of the acoustic wavelength, the most practical method of measuring the acoustic velocities is the technique of ultrasonic interferometry [*Ahrens and Katz*, 1962; *Papadakis*, 1971]. It consists of observing minima in the echoes returning from the specimen-anvil interfaces. Because the acoustic impedance of the anvil material is greater than the impedance in the specimen, acoustic waves traveling in the anvil and reflected off the specimen receive a phase shift of π. Destructive interference in the echo returning to the transducer occurs when there are an integral number of acoustic wavelengths in the specimen. This condition is given as

$$F_n = nv/2d \tag{1}$$

where n is an integer, d is the specimen thickness, v is the acoustic velocity of the specimen material, and F_n is the frequency at which the destructive interference minimum is observed. For an isotropic material there are two acoustic velocities, the longitudinal velocity v_p and the isotropic shear velocity v_s. For each mode there is a set of destructive interference minima. For a nondispersive medium the frequency interval $\Delta f = F_{n+1} - F_n$ is independent of n in each set. The result is a measurable frequency interval for each acoustic mode:

$$\Delta f_p = v_p/2d \qquad \Delta f_s = v_s/2d \tag{2}$$

Use of (2) assumes that the anvil faces are flat and parallel. The lack of 'dishing' or plastic deformation of the anvil faces of less than 2.5×10^{-3} mm after ultrahigh-pressure runs and the clear minima that we obtained indicated that those conditions were adequately maintained.

Method of Data Analysis

In (2) there are three unknowns in the two equations: the velocities v_p and v_s and the specimen thickness d. To solve this system of equations, a third equation relating the bulk modulus to the velocities is used. The relationship for any isotropic material under hydrostatic conditions is [*Truesdell and Noll*, 1965]

$$(1 + \Delta)B_T = B_S = \rho(\partial P/\partial \rho)_S = \rho(v_p^2 - 4v_s^2/3) \tag{3}$$

where B_T and B_S are the isothermal and adiabatic bulk moduli, respectively, and $\Delta = 9\alpha^2 TB_S/\rho C_P$ [*Zemansky*, 1957], where ρ is the density, α is the linear thermal expansion coefficient, T is the temperature (in degrees Kelvin), and C_P is the specific heat at constant pressure.

It is necessary to be concerned with both the isothermal and the adiabatic bulk modulus because static compression is approximately isothermal and the acoustic velocities are the result of infinitesimal adiabatic compressions. The ratio of the bulk moduli is pressure dependent. *Gilmore* [1968] has derived an approximate relationship for the pressure variation of Δ:

$$\Delta/\Delta_0 \simeq (B_S\rho)_0/(B_S\rho) \tag{4}$$

where the subscript 0 denotes evaluation at zero pressure. For NaCl, Δ_0 equals 0.054.

Substitution of (2) into (3) yields a useful form of the bulk modulus velocity relationship:

$$(1 + \Delta)B_T/\rho = 4d^2(\Delta f_p^2 - 4\Delta f_s^2/3) \tag{5}$$

Since the equation of state of NaCl is considered to be well determined [*Decker et al.*, 1972], known values for B_T/ρ can be used in (5) to determine the specimen thickness and the acoustic velocities. Such an analysis of the ultrasonic data has been done, and the results are given in Table 1 and shown in Figures 3 and 4.

For a material whose equation of state is unknown, *Katz and Ahrens* [1963] showed that an equation of state can be solved for by assuming that the geometry of the specimen changes under pressure such that

$$\rho = \rho_0 X^n \tag{6}$$

where

$$X = d_0/d \tag{7}$$

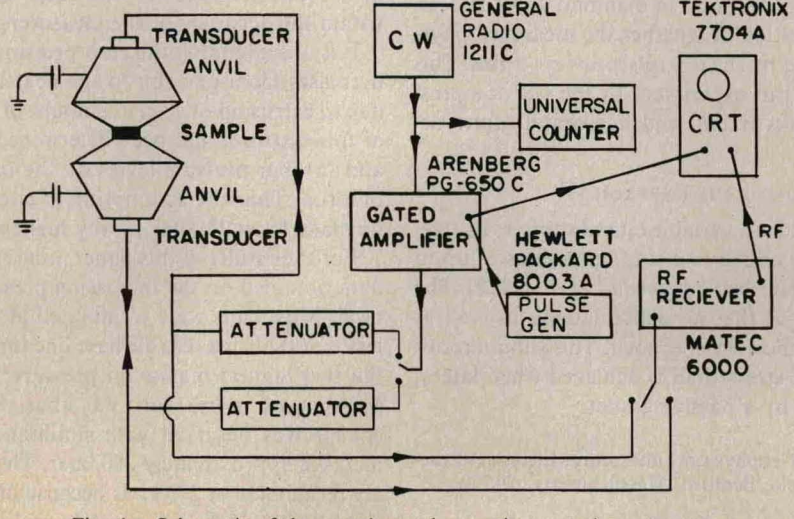

Fig. 1. Schematic of the experimental acoustic measuring apparatus.

TABLE 1. Measured Values and Uncertainties for Polycrystalline Longitudinal and Shear Velocities in NaCl

Pressure, kbar	v_p, m/s	$\sigma(v_p)$, m/s	v_s, m/s	$\sigma(v_s)$, m/s	No. of Runs
25	5007	49	2679	48	9
30	5088	53	2696	53	9
35	5165	59	2710	64	9
40	5238	65	2722	74	9
45	5307	73	2732	85	9
50	5380	74	2750	86	9
55	5450	76	2768	88	9
60	5518	77	2785	90	9
65	5585	75	2804	86	9
70	5648	73	2820	82	9
75	5710	71	2835	79	9
80	5769	71	2849	79	9
90	5877	69	2867	76	8
100	5986	75	2894	84	7
110	6092	78	2923	90	7
120	6193	83	2950	98	7
130	6290	54	2976	51	2
150	6478	80	3033	91	2
170	6647	56	3076	52	2
190	6785	51	3083	44	2
210	6915	55	3088	58	2
230	7056	48	3123	38	2
250	7188	45	3154	21	2
270	7304	...	3169	...	1

The parameter n is any positive number and is assumed to be independent of pressure. The change in the specimen density and thickness can be determined from the data as follows:

$$X^{n-2} = 1 + \left(\frac{n-2}{n}\right)\frac{1}{4d_0^2\rho_0}\int_0^P Y\,dP \qquad (8a)$$

for $n \neq 2$, and

$$X = \exp\left[\frac{1}{8d_0^2\rho_0}\int_0^P Y\,dP\right] \qquad (8b)$$

for $n = 2$, where

$$Y = \frac{1+\Delta}{\Delta f_p^2 - 4\Delta f_s^2/3}$$

If the forces acting upon a specimen are perfectly balanced, such as they are in a liquid pressure transmitting device, the parameter n in (6) is equal to 3.0. All strains are due to hydrostatic stresses. The assumption of hydrostatic compression led *Ahrens and Katz* [1962] to use an expression identical to (8*a*) with $n = 3$. If the deformation of the specimen is pistonlike, i.e., the side walls are rigid and only the thickness changes, then the value of n is 1.0. If the side walls either are rigid or move outward as the thickness decreases, $n \leq 1.0$.

The value of n to be used with the present device in future investigations of materials for which the equation of state is unknown is determined from the present NaCl data set. A plot of the log of the ratio of the specimen thickness at zero pressure to the thickness at pressure versus the log of the density ratio should yield a straight line whose slope is equivalent to the parameter n in (6). The results of this analysis for the NaCl runs are shown in Figure 2. Since all data start at 25 kbar, the initial thickness d_0 has been calculated with the assumption of $n = 1$. Use of other values of n would only require the y axis to be shifted left or right.

The straight line which best fits the specimen thickness data has a slope of 1.5, as is shown in Figure 2. The error bars represent the maximum run-to-run variation in the data. Thus a value of $n = 1.5$ may be used in (6) for the present device, with the large uncertainty indicated by the error bars.

The lines shown in Figure 2 for $n = 3.0$ and $n = 1.0$ represent the locations of the ratios if the compression in the pressure cell were hydrostatic or pistonlike. It should be noted that while the run-to-run variation in the compression of a specimen is large, in all cases the specimen diameter is decreasing during increasing pressure. This is in contrast to most solid pressure transmitting devices in which the diameter would be stationary or increasing.

DISCUSSION

In order to analyze the data it has been assumed that shear stresses in the sample and heating of the sample during pressurization can be neglected and that the effect of dislocations on the velocity is small. These assumptions will be considered first. Finally, the velocity data will be compared with previous experimental data and theoretical predictions, and their use for pressure calibration will be discussed.

Analysis of Assumptions

Neglect of shear stresses. The pressurization with the variable lateral support Bridgeman anvil device is not purely hydrostatic. Thus shear stresses must exist within the specimen, probably not greater than the shear strength of NaCl. If the shear stress is large, two problems arise. First, use of (3) may be invalid. Second, use of a resistance-based pressure calibration may be inappropriate for ultrasonics because the average specimen pressure, important in ultrasonics, is significantly different from the highest pressure in the specimen, which is measured in resistance-based calibrations.

Previous work [*Piermarini et al.*, 1973; *Block and Piermarini*, 1975] has shown that large pressure gradients can exist across a specimen of NaCl. The largest gradients occur in ungasketed specimens. More pressure uniformity occurs with gasketed specimens. *Block and Piermarini* [1975] report pressure varia-

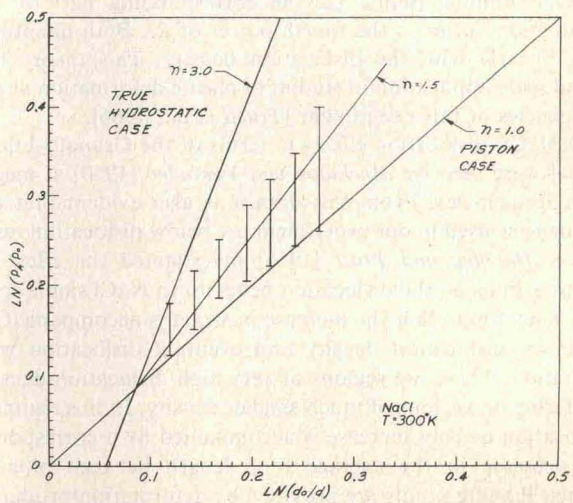

Fig. 2. Specimen thickness ratio versus the density ratio as determined for the nine data sets used in this paper. The figure has been normalized for the piston ($n = 1.0$) case. The straight lines representing the expected ratio for the piston and the purely hydrostatic ($n = 3.0$) cases are shown for comparison.

tions of 11 kbar at an average pressure of 100 kbar in a gasketed NaCl specimen in a diamond anvil device. More uniformity than that is expected in the present device because the gasket support is increased as the force upon the anvil is increased. In addition, the larger specimen thickness in our device should minimize surface effects on the average stress distribution.

While no direct measurements of the pressure variations are available, there are observations that indicate a small pressure gradient. Resistometric transitions are spread out on resistance versus load plots by pressure gradients. Full-sized bismuth specimens were observed in the present device to have resistometric phase changes spread out over a few kilobars [*Homan*, 1975]. A thin strip of bismuth embedded in NaCl showed almost no spread in pressure for the resistance changes. In addition, the ratio between the Bi resistance peaks due to the I-II transition and the II-III transition was 3.31, compared to 3.35 previously measured in a hydrostatic medium (discussed by *Gilmore* [1968]). Another indication is the observation of ultrasonic interference patterns at distinct frequencies. If the acoustic velocity were significantly different in different regions of the specimen, because of pressure gradients the minima in the echoes would be smeared out over a range of frequencies.

Neglect of heating effects. The analysis assumes isothermal compression. To insure the validity of this assumption, the temperature effects on the velocities due to pressurization at different rates were looked for in two runs. None were found. To insure maximum heat dissipation, all other runs were done at the slowest possible pressurization rate (approximately 3 kbar/min), and runs were made at intervals of 3 hours or more. Since the changes of the elastic constants with temperature at zero pressure are 0.02%/°K for c_{44} and 0.03%/°K for c_s [*Demarest*, 1972*a*], the effect of heating upon the measurements is deemed negligible.

Effects of dislocations on the sound velocity. The theory of the effect of dislocations on the mechanical properties of crystalline solids at megacycle frequencies is based on the dislocation strain model of *Granato and Lücke* [1956]. This model predicts that at frequencies below the dislocation resonance the decrease in the velocity of sound due to dislocations is proportional to the square of the average effective loop length between pinning points L_e; the corresponding part of the attenuation varies as the fourth power of L_e. Both quantities vary linearly with the dislocation density. This theory has found wide application in studies of plastic deformation at the frequencies of this experiment [*Truell et al.*, 1966].

In NaCl, dislocation effects in terms of the Granato-Lücke model were seen by *Merkulov and Yakovlev* [1960] at megacycle frequencies. From this data it is also evident that the frequencies used in our experiment are below dislocation resonance. *Davidge and Pratt* [1964] investigated the effect of plastic strains on the dislocation behavior in NaCl single crystals. They found that the increase in strain is accompanied by increased dislocation density and eventual dislocation wall formation. These are regions of very high dislocation density bordering on regions of much smaller density. In this regime a dislocation density increase is accompanied by a corresponding decrease in the average loop length between pinning points. Pinning points are provided by deformation-produced defects [*Frankel and Meisel*, 1967] and by other dislocations. This effect has been seen in attenuation measurements during deformation accompanying a sharp yield point in magnesium single crystals which had been solution-treated with a small amount of nitrogen [*Chiao and Gordon*, 1963] and for repeated fatigue-type deformation in pure aluminum crystals and polycrystalline aluminum alloys [*Chick et al.*, 1963; J. Frankel, unpublished data, 1970]. In these experiments a decrease in attenuation develops after a certain amount of deformation, so that the increase in dislocation density must be accompanied by a decrease in L_e. The velocity change should also show evidence of this behavior with sufficient deformation because of its second-order dependence on L_e. *Merkulov and Yakovlev* [1960] found that the velocity decreased linearly up to values of 0.43% and 0.16% for the maximum 2.5% strain of their experiment for two similar NaCl single crystals with different thermal histories. Their data suggest that this level of strain is associated with a relatively small increase in dislocation density (and hence no drastic drop in L_e); this finding is supported by the direct dislocation density measurements of *Davidge and Pratt* [1964].

Our samples, which were deformed during powdering and compaction by an unknown amount, were subjected to an additional plastic strain of about 6% at the 270-kbar pressurization. Thus our samples should be considered severely cold-worked into the region of wall formation and decreasing L_e. If we extrapolate the larger of the velocity changes in the Merkulov and Yakovlev experiment to our 6% plastic deformation, we obtain a 1% drop in the velocity at 270 kbar and certainly not more than 2% if we include the cold work performed during fabrication. Thus the maximum estimated error due to dislocations is well within the total experimental error. A systematic change in the velocity with succeeding runs in one specimen as the cold work increased was looked for, and none was found. An in situ irradiation technique to pin the dislocations completely and evaluate the dislocation effect directly is not possible with the present equipment.

Velocity Results

The isotropic acoustic velocities of NaCl are contained in Table 1. The uncertainties given do not include the uncertainty due to the pressure calibration or that in the Decker equation of state. In Figure 3 the data are seen to agree within the uncertainty of the measurement with available velocities up to 80.5 kbar [*Voronov et al.*, 1971; *Voronov and Grigorèv*, 1971].

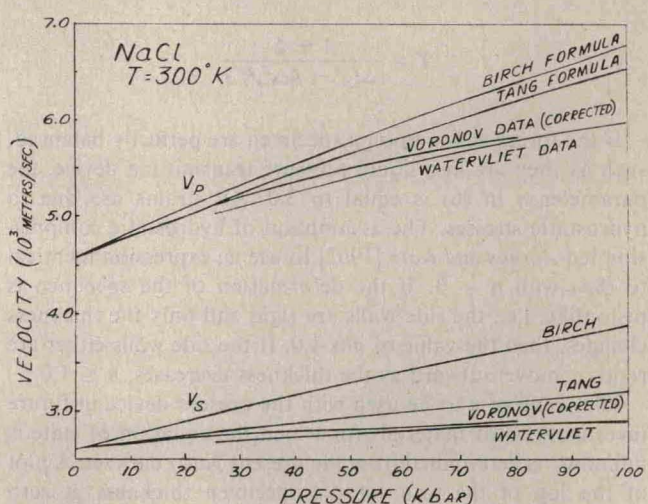

Fig. 3. Acoustic velocities (longitudinal and shear) at static pressures to 100 kbar for polycrystalline NaCl at room temperature. The measurements made by the present authors and the measurements of *Voronov et al.* [1971] and *Voronov and Grigorèv* [1971] are shown together with the estimates of *Birch* [1938] and *Tang* [1966].

Voronov et al. and Voronov and Grigorèv reported their data to 100 kbar, but we changed their pressure calibration [*Voronov and Grigorèv*, 1969] from 89.3, 27.2, and 58.5 to 74, 25, and 55 kbar for the upper and lower bismuth and barium transitions, respectively. There are no previously reported values for velocities beyond 100 kbar.

Comparison With Theory

Attempts have been made, by using continuum mechanics, to calculate isotropic velocities to high pressures. A well-known velocity-pressure relation is the linear formula of *Birch* [1938, 1939], based on his Eulerian finite strain theory and the work of *Murnaghan* [1937]. A similar relation is the formula of *Tang* [1966], based on the nonlinear elasticity theory of *Bolotin* [1963]. These authors do not claim validity above 10 kbar, and indeed a comparison of these formulae with the data in Figure 3 shows that while these formulae were useful to pressures of a few kilobars, neither these nor any other linear velocity-pressure relations are adequate at pressures much above 10 kbar.

For cubic crystals, equations for the elastic constants based on interatomic forces [*Anderson*, 1970; *Anderson and Demarest*, 1971; *Demarest*, 1972*a*, *b*] and on fourth-order finite strain theory [*Thomsen*, 1972] are available.

The elastic constants for single crystals (c_{11}, c_{12}, c_{44} or B_S, c_s, c_{44}) were formulated as a function of pressure at zero temperature [*Anderson*, 1970]. The differences between adiabatic and isothermal elastic constants were not taken into account by Anderson because of the approximate nature of the formulation. The results of the elastic constants formulae can still be compared with the measured velocities by noting that [*Barsch*, 1967]

$$c_{11}^T - c_{11}^S = c_{12}^T - c_{12}^S = B_T - B_S \tag{9a}$$

$$c_{44}^T = c_{44}^S = c_{44} \tag{9b}$$

The two adiabatic shear moduli $(c_{11}^S - c_{12}^S)/2$ and c_{44}^S are equal to the isothermal moduli $(c_{11}^T - c_{12}^T)/2$ and c_{44}^T, respectively. It is necessary only to choose the bulk modulus B properly. The transformation from single-crystal to polycrystalline elastic parameters is done in a standard manner [*Anderson and Demarest*, 1971].

The interatomic force model using only nearest neighbor (NN) terms adopts the assumption that c_{44} goes to zero at the NaCl phase transition. If the elastic parameters and their derivatives at zero pressure are the only input data for the model, the model falls seriously in error [*Anderson and Demarest*, 1971]. *Anderson* [1970] has suggested that the knowledge of the phase transition be used to calculate an effective value for the atomic screening parameter α in the NN model. According to this suggestion,

$$B_{S_0}/\alpha = (5P_T/2)(\rho_0/\rho_T)^{4/3} = 410.5 \text{ kbar} \tag{10}$$

where the subscripts 0 and T denote evaluation at zero pressure and the transition. The parameter α is used in the NN model by assuming it to be independent of pressure.

The isotropic acoustic velocities can be calculated from the bulk modulus and the rigidity modulus μ:

$$v_p = [(B_S + 4\mu/3)/\rho]^{1/2} \qquad v_s = (\mu/\rho)^{1/2} \tag{11}$$

The NN model gives values for the elastic parameters c_s and c_{44} which are used to estimate the rigidity modulus. An upper and a lower bound, known as the Voigt and the Reuss limit, respectively, for the rigidity modulus are

$$\mu^V = (1/5)(2c_s + 3c_{44}) \quad \mu^R = (10c_s c_{44})/(4c_{44} + 6c_s) \tag{12}$$

The rigidity modulus can be estimated either by the arithmetic mean of the above limits, as was suggested by *Hill* [1952], or by the geometric mean, as was suggested by *Kumazawa* [1969]. The acoustic velocities predicted by the NN model by using both estimates of the rigidity modulus are shown in Figure 4 together with the data. At low pressure the two estimates yield almost identical results. At pressures near the transition, as the

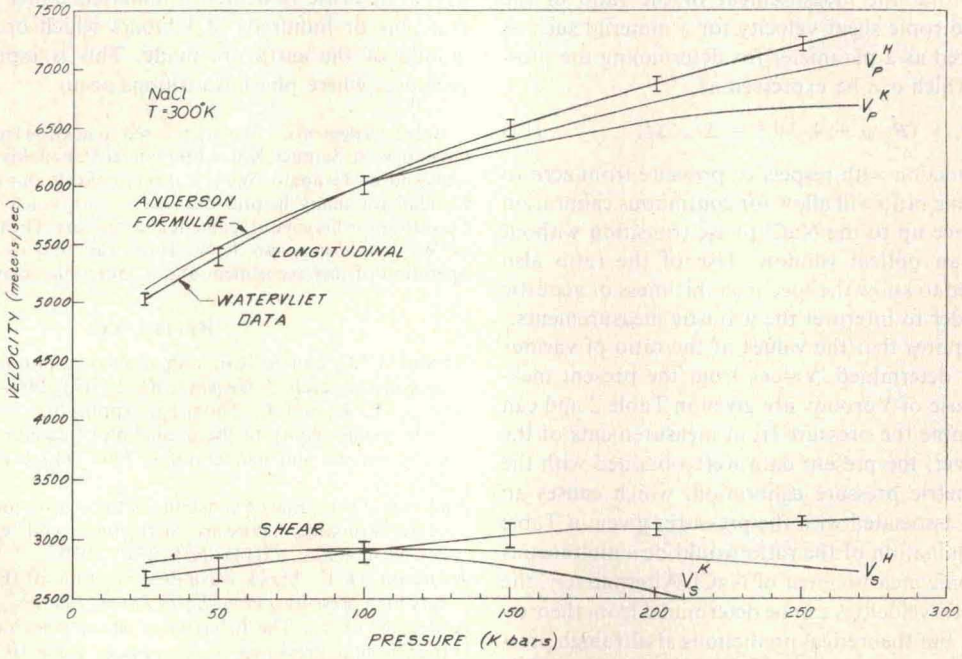

Fig. 4. Acoustic velocities (longitudinal and shear) at static pressures to 270 kbar. The measured values v_p and v_s are shown together with the predicted values of *Anderson and Demarest* [1971] with both the arithmetic average for the rigidity modulus [*Hill*, 1952], indicated by a superscript H, and the geometric average for the rigidity modulus [*Kumazawa*, 1969], indicated by a superscript K.

predicted c_{44} goes to zero, the predicted value of μ decreases either to a small positive value or to zero.

The comparison of the measured acoustic velocities to the prediction of *Anderson and Demarest* [1971] is good up to approximately 130 kbar. At higher pressures the predicted acoustic velocities are less than the measured ones. *Thomsen* [1972] concluded tentatively that c_{44} goes to zero at the NaCl phase transition, predicting velocities smaller than those measured. However, *Ahrens and Thomsen* [1972] concluded later that the formulation was not accurate above 200 kbar.

The isotropic shear velocity, which depends on both c_s and c_{44}, does not decrease with increasing pressure. Since c_s has a positive pressure dependence [*Anderson*, 1975], c_{44} cannot have a significantly greater negative pressure gradient up to 270 kbar. Also, measurements on a NaCl specimen through the phase transition did not indicate a drop in the shear velocity near the transition.

Demarest [1972*a*, *b*] has developed a next nearest neighbor (NNN) model which does not assume that c_{44} is zero at the NaCl transition. He has predicted that c_{44}/B should decrease to approximately 0.17 at the NaCl transition. The rigidity modulus predicted from the values of c_{44} given by *Demarest* [1972*a*] is 25–40% larger than the measured value of 329 kbar at 270 kbar of pressure.

Ratio of the NaCl Velocities as a Pressure Calibration Parameter

With any ultrahigh-pressure experiment, calibrating the system is the first priority. Two methods have been traditionally used: the measurement of resistance transitions as described above and the X ray measurement of the lattice spacing of NaCl [*Decker et al.*, 1972]. A new method proposed by *Piermarini and Block* [1975] is the observation of the pressure-induced shift in the ruby fluorescence line. However, neither the ruby fluorescence method nor the X ray method can be used with the present ultrahigh-pressure cell and many other cells because of the requirement for an optical window.

It is proposed that the measurement of the ratio of the longitudinal to isotropic shear velocity for a material such as NaCl be considered as a parameter for determining the pressure. The ratio, which can be expressed as

$$v_p/v_s = (B_S/\mu + 4/3)^{1/2} = \Delta f_p/\Delta f_s \qquad (13)$$

is a monotonic function with respect to pressure from zero to 292 kbar. Use of the ratio will allow for continuous calibration of a pressure device up to the NaCl phase transition without the presence of an optical window. Use of the ratio also eliminates the need to know the specimen thickness or acoustic path length in order to interpret the acoustic measurements.

Use of (13) requires that the values of the ratio of various pressures be well determined. Values from the present measurements and those of Voronov are given in Table 2 and can be used to determine the pressure from measurements of the ratio (13). However, the present data were obtained with the aid of a resistometric pressure calibration, which causes an uncertainty to be associated with the pressures given in Table 2. The best determination of the ratio would be simultaneous X ray and ultrasonic measurement of NaCl. Alternatively, the ratio of the acoustic velocities can be determined from theoretical formulations, but theoretical predictions at ultrahigh pressures are presently too unreliable to be quantitatively useful.

TABLE 2. Ratio of Longitudinal to Shear Velocity in Polycrystalline NaCl

Pressure, kbar	v_p/v_s This Paper	Voronov	Anderson and Hill	Anderson and Kumazawa
25	1.869	1.874	1.816	1.816
30	1.887	1.889	1.833	1.833
35	1.906	1.905	1.850	1.850
40	1.917	1.922	1.866	1.867
45	1.943	1.937	1.883	1.884
50	1.956	1.955	1.899	1.901
55	1.969	1.972	1.916	1.917
60	1.981	1.986	1.932	1.935
65	1.992	1.998	1.948	1.952
70	2.003	2.007	1.964	1.969
75	2.014	2.012	1.980	1.987
80	2.025	2.012	1.996	2.005
90	2.050	···	2.027	2.040
100	2.068	···	2.058	2.078
110	2.084	···	2.089	2.115
120	2.099	···	2.121	2.154
130	2.114	···	2.151	2.196
150	2.136	···	2.212	2.284
170	2.161	···	2.273	2.385
190	2.201	···	2.335	2.505
210	2.239	···	2.398	2.652
230	2.259	···	2.461	2.846
250	2.279	···	2.525	3.132
270	2.304	···	2.590	3.658

CONCLUSIONS

The general concept that c_{44} goes to zero near high-pressure-induced phase transitions in ionic-cubic materials cannot be supported by results of the present experiment. The pressure dependence of the shear velocity of NaCl shows that c_{44} can only have a significantly negative pressure gradient up to 270 kbar if c_s has a balancing positive pressure gradient. The Demarest NNN models seem to come closest to the present results and should consequently be considered when prediction of acoustic velocities of materials under pressures of several tens or hundreds of kilobars which occur in the lower mantle of the earth are made. This is especially true near pressures where phase transitions occur.

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