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]

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

$$c_{44}{}^T = c_{44}{}^S = c_{44} \qquad (9b)$$

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,

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

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:

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

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

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

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

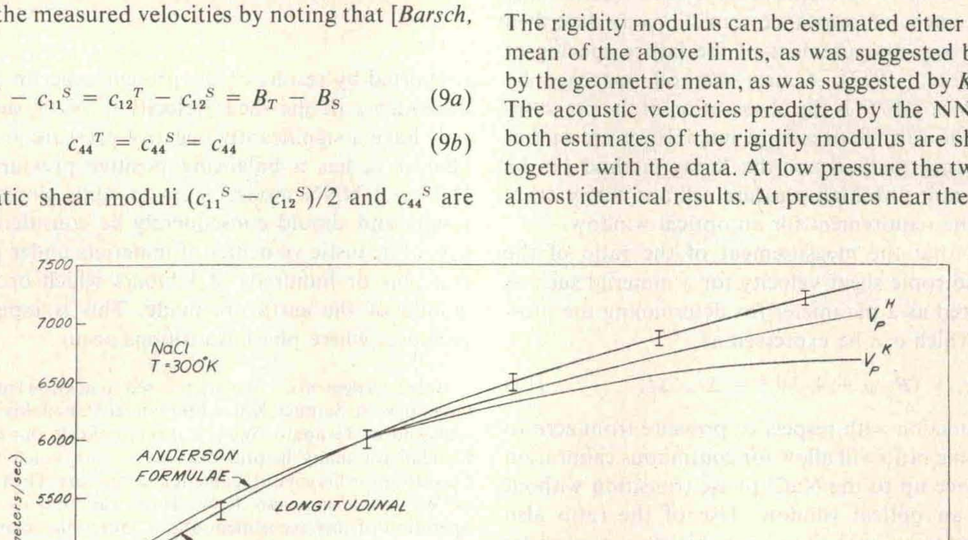

Fig. 4. Acoustic velocities (longitudinal and shear) at static pressures to 270 kbar. The measured values v_p and v_s are shown together with the predicted values of *Anderson and Demarest* [1971] with both the arithmetic average for the rigidity modulus [*Hill*, 1952], indicated by a superscript H,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

	v_p/v_s			
Pressure, kbar	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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