PREDICTION OF HIGH-PRESSURE PHASE TRANSITIONS

 $(P_{th}, K_{th}, \text{etc.})$ approach negative infinity. While a negative value of the bulk modulus is forbidden by the Born stability criterion, it is possible that there will be a sudden decrease in the bulk modulus and some of the other elastic constants as an immediate precursor to a phase transition. This sort of precursor has been observed in calcite [Matsushima et al., 1975], but in most cases we expect that the phase transition will take place before this sort of thermal precursor can occur.

III. EXPERIMENTAL ELASTIC CONSTANTS OF KC1 AT THE PHASE TRANSITION

We wanted to test our theories about the behavior of the elastic constants in the vicinity of a phase transition. KCl is an ideal candidate for this type of test since it has the wellstudied NaCl structure and undergoes a phase transition to the CsCl structure at 19.3 kbar [Vaidya and Kennedy, 1971]. This is within the range of our experiment for the measurement of sound velocities under high hydrostatic pressures.

A. Experimental Technique

A technique similar to that described by Jayaraman and Maines [1971] was used to generate a hydrostatic environment. This involved a conventional piston cylinder device with a Teflon cell, which contains the sample and the pressure transmitting fluid (a 50/50 mixture of isoamylalcohol and isopentane). The sample was held in a special holder, and the wires from the transducer went out through alumina thermocouple tubing. Further details of the experimental method will be given in a forthcoming paper by Ota and Anderson.

Since we were unable to fit a manganin coil and our sample holder into the teflon cell at the same time and still allow enough room for the compression of the pressure fluid, we determined the pressure in the cell from the oil pressure driving the piston. The relationship between oil pressure and cell pressure was calibrated by placing a manganin coil and a Bismuth wire in the Teflon cell and by assuming that the resistance change in the manganin coil was linear up to the Bi I+II transition at 25.4 kbar. The effect of friction was about 5% of the total pressure.

A large KCl single crystal was purchased from the Harshaw Chemical Company, and from it were obtained two cubic samples, about 4 mm on a side, with faces oriented to within 0.6 degrees of the (100) and (110) directions. 20 Mhz P- or S- transducers were mounted to the samples with silver paint, and the travel times for P and S waves were measured by the method of pulse superposition, with a single transducer being used both to transmit and to receive the reflected pulse.

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B. Results

The pulse repetition frequency was measured at zero pressure and as a function of pressure from 0 to 20 kbar for the two longitudinal and two shear waves described in Table 1. This provided enough information for the determination of the three independent elastic constants, with one redundant measurement for a check on our accuracy. Over the entire range, the consistency of our data was excellent.

TABLE 1. Velocities Used for Elastic Constant Determination

| Mode | Р | S | enge zun pol sister | S |
|-----------------|------------------------|-----------------|--------------------------------------|--------------------------------|
| Propagation | CT CLESMAN | A CALL SO | nest succession and an | State State |
| direction | (100) | (100) | (110) | (110) |
| Polarization | | | | |
| direction | (100) | (010) | (110) | (110) |
| pv ² | <i>c</i> ₁₁ | C ₄₄ | $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ | $\frac{1}{2}(C_{11} - C_{12})$ |
| | | | | |

In Table 2, we compare our zero pressure elastic constants with those of other experimenters. The agreement with Dobretsov and Peresada [1969] is extremely good, while the agreement with the less recent work [Lazarus, 1949; Haussuhl, 1960; Bartels and Schuele, 1965; Drabble and Strathen, 1967] is only modestly good, with a two percent disagreement in the bulk modulus.

Our data for pulse repetition frequency as a function of pressure were converted to elastic constants as a function of pressure by *Cook's* method [1957]. In this analysis, we assumed $\beta = 110.4 \cdot 10^{-6} \text{ deg}^{-1}$, and $C_p = 12.23 \text{ cal mol}^{-1} \text{ deg}^{-1}$. The normalized elastic constants C(P)/C(0) are plotted in Figures 3 and 4 from zero to 20 kbar, and are tabulated in Table 3. Our results are remarkably linear. There is no indication of any strange behavior for either C_{44} or K in the neighborhood of the transition. The value of C_{44}/K at the transition is 0.205, a value in good agreement with the modified Born criterion.

There is no evidence of a slight decrease of a K at the transition, which might be expected if one of the normal mode frequencies were approaching zero at or very near to the transition pressure. We can calculate the mode Grüneisen parameter, γ_i , for the mode associated with any elastic modulus C_i by the formula $\gamma_i = -\frac{1}{6} + \frac{1}{2} \frac{K_T}{C_i} \frac{dC_i}{dP}$ [Schuele and Smith, 1964].