

below  $T_\lambda$  only for transverse waves propagating along a [100] axis in the cubic phase, we shall give the appropriate equations in the tetragonal phase only for that type of wave. When an oriented cubic crystal becomes tetragonal, the transverse velocity  $U_t$  is still given by Eq. (2) if the tetragonal axis lies parallel to either the direction of wave propagation or the direction of polarization (particle motion). In case the tetragonal axis is oriented perpendicular to both the direction of propagation and the direction of polarization,  $U_t$  is then given by  $\rho U_t^2 = c_{66}$ . It is likely that a cubic  $\text{NH}_4\text{Br}$  single crystal is transformed below  $T_\lambda$  into a sample with small tetragonal domains, in which  $a_3$  is oriented parallel to the former  $x$ ,  $y$ , or  $z$  axes. If this is so, then the measured ultrasonic velocity will be some kind of mechanical average denoted by  $\bar{c}_{44}$ .

### EXPERIMENTAL WORK

Ultrasonic velocity measurements were made by a McSkimin pulse-superposition method<sup>14,15</sup> at a frequency of 20 Mc/sec. Although this method is experimentally and computationally more difficult than the pulse-echo method, it is capable of very high accuracy since the basic measurement involves a frequency value rather than a time delay and it is possible to evaluate quantitatively the effect of the phase shift  $\gamma$  associated with reflection of the sound wave at the transducer+seal end of the sample. A description of this method and of the necessary electronic apparatus has been given previously<sup>12</sup> and is not included here.

The hydraulic pressure equipment was of conventional design, but since the sample cell was fabricated from 4340 steel it was not considered safe to generate high pressure in it below 250°K. The temperature of this cell could be controlled to within  $\pm 0.05^\circ$  by a large thermostat bath. Further details of this pressure equipment and a description of the regulated temperature bath used for measurements at 1 atm are available elsewhere.<sup>12</sup>

The single crystals used in these experiments were grown by a modified Holden process.<sup>16</sup> To obtain a saturated solution at  $\sim 45^\circ\text{C}$ , 1200 g of ammonium bromide (analytical reagent grade) and 600 g of urea were added to one liter of distilled water. This large amount of urea was necessary as a habit modifier to prevent dendritic growth and to promote the growth of large cubic crystals with (100) faces. All of the single crystals obtained were pale yellow in color and had some imperfections. Fortunately, these imperfections were either near an edge or near the center of a single face and the transducer could always be located so that they would not lie in the path of the acoustic wave.

An analysis of the bromide-ion content indicated that these crystals were at least 99.9%  $\text{NH}_4\text{Br}$ . Three different crystals of ammonium bromide were used to obtain the present data. For Crystals I and II, a pair of natural (100) faces were used without any mechanical cutting or polishing. The lengths ( $L_{20}$ ) in the [100] direction as measured by a lightwave micrometer at 20°C were  $1.0905 \pm 0.0005$  cm for Crystal I and  $1.1935 \pm 0.0005$  cm for Crystal II. The third crystal (III) was fly cut to give a pair of parallel (110) faces, and the length  $L_{20}$  in the [110] direction was  $0.5641 \pm 0.0007$  cm at 20°C. As a result of handling, exposure to the atmosphere, and seal changes, the path lengths in all these crystals decreased slowly with time. Periodic length measurements were made and corrections were applied to eliminate any small systematic changes in the elastic constants due to path length changes.

A density  $\rho_{20}$  of  $2.4336 \text{ g cm}^{-3}$  was calculated from a lattice constant of  $4.0580 \text{ \AA}$  at 20°C; this unit cell constant is based on several different x-ray investigations around room temperature.<sup>7,17</sup> The elastic constants at 1 atm were obtained as a function of temperature from equations of the type

$$C = \rho U^2 = (L_{20}/L_T) \rho_{20} (2L_{20})^2 / \delta^2, \quad (5)$$

where  $U$  is the appropriate velocity,  $\delta$  is the true round-trip transit time associated with the sound wave, and  $L_T$  is the sample length at 1 atm and temperature  $T$ . The quantity  $(L_{20}/L_T)$  was calculated from the polycrystalline thermal-expansion data of Simon and Bergmann<sup>9</sup> and from the low-temperature x-ray data of Hovi, Heiskanen, and Varteva.<sup>7</sup> Obviously, the x-ray measurements give the tetragonal cell dimensions ( $a_3 \neq a_1 = a_2$ ) below  $T_\lambda$ . On the assumption that a large cubic single crystal is transformed into small domains with the tetragonal axes of these domains lying at random along any one of the original [100] directions, we have taken  $L_T$  to be the cube root of the volume below  $T_\lambda$ . The two sets of data are in very good agreement except in the region 230°–235°K, where the x-ray data indicate an almost discontinuous change in  $L_T$  with temperature. The rapid but continuous variation obtained from Simon and Bergmann's data was used in this region. However, this choice has a negligible effect (0.05%) on the values of the elastic constants at 1 atm.

To calculate the elastic constants as a function of pressure, it is convenient<sup>18</sup> to introduce another path-length ratio  $s(p) = L_1/L_p$ , where  $L_1$  is the sample length at a given temperature and 1 atm and  $L_p$  is the length at the same temperature under an external applied pressure  $p$ . The elastic constants at a given temperature can

<sup>14</sup> H. J. McSkimin, J. Acoust. Soc. Am. **33**, 12 (1961).

<sup>15</sup> H. J. McSkimin and P. Andreatch, J. Acoust. Soc. Am. **34**, 609 (1962); **37**, 864 (1965).

<sup>16</sup> A. N. Holden, Discussions Faraday Soc. **5**, 312 (1949).

<sup>17</sup> V. T. Deshpande and D. B. Sirdesmukh, Acta Cryst. **14**, 353 (1961); V. C. Anselmo and N. O. Smith, J. Phys. Chem. **63**, 1344 (1959).

<sup>18</sup> R. K. Cook, J. Acoust. Soc. Am. **29**, 445 (1957).

then be obtained as a function of pressure from equations of the type

$$C(p) = C(1 \text{ atm}) (\delta_1/\delta_p)^2 s(p), \quad (6)$$

where  $\delta_1$  and  $\delta_p$  are the transit times corresponding to 1 atm and to a pressure  $p$ . In general, the calculation of  $s(p)$  requires a knowledge of the isothermal compressibility as a function of pressure. However, an excellent approximation to  $s(p)$  can be calculated directly from our present adiabatic velocity data<sup>18</sup> since the difference between the isothermal and adiabatic compressibilities is very small except in the immediate vicinity of the lambda point. [At 300°K and 1 atm,  $(\beta^T - \beta^S)/\beta^S$  is only 0.007.] Since  $s(p)$  values vary only between 1.00 and 1.02 for the pressure range 0 to 12 kbar, small uncertainties in the  $s(p)$  variation do not cause significant errors in the elastic constant values (which depend mostly on  $\delta_1/\delta_p$ ).

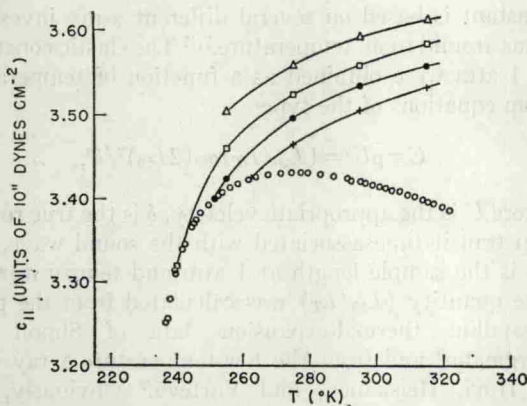


FIG. 3. Variation of  $c_{11}$  with temperature. Open circles represent data at 1 atm; for a definition of the symbols used for values at various constant volumes, see the legend of Fig. 5.

For measurements made at 1 atm, the quartz transducers were cemented to the sample with Dow resin 276-V9 as the seal material for all runs between 215° and 320°K. Below 215°K, these seals broke and Nonaq stopcock grease was used in a few runs despite the fact that it seemed to dissolve the sample slowly. Since the Dow resin was soluble in the hydraulic pressure fluid, it was necessary to find a new seal material for the high-pressure work. A polymer of phthalic anhydride and glycerin was found suitable<sup>12</sup> and was used for all the pressure runs.

The Dow resin and Nonaq seals were all very thin. Thus the phase shifts  $\gamma$  were small (between  $-5^\circ$  and  $-8^\circ$ ) at all temperatures, and the corrections to the transit times<sup>12</sup> due to phase shifts amounted to only 0.01% at 1 atm. Since all high-pressure measurements were carried out at a frequency equal to the resonance frequency of the transducer at 1 atm, there were appreciable changes in the phase shifts  $\gamma$  as a function of pressure. This effect of pressure on the behavior of

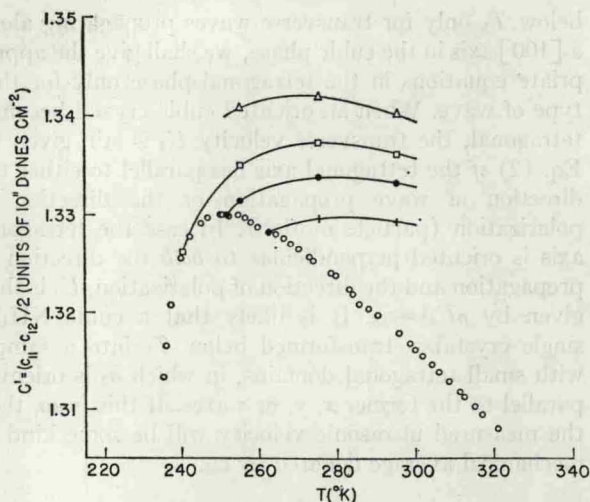


FIG. 4. Variation of  $C'$  with temperature. Open circles represent data at 1 atm; for a definition of the symbols used for values at various constant volumes, see the legend of Fig. 5.

the transducers is known<sup>14</sup> and was corrected for. The effect of pressure on the seal is not known and has been neglected.

## RESULTS

### Constant-Pressure Data

The open-circle points shown in Figs. 3-5 are experimental data points for the elastic constants  $c_{11}$ ,  $c_{44}$ , and  $C'$  as functions of temperature at 1 atm. Smooth-curve values of these directly measured quantities are presented in Table I together with the adiabatic bulk modulus  $1/\beta^S$ , which can be calculated from

$$1/\beta^S = c_{11} - 4C'/3. \quad (7)$$

Since the temperatures in Table I are all above the lambda point, all entries pertain to the disordered cubic phase of  $\text{NH}_4\text{Br}$ .

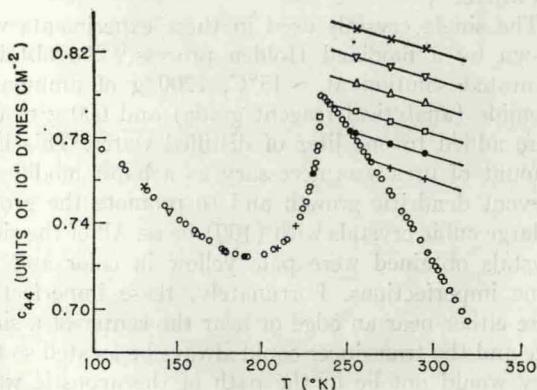


FIG. 5. Variation of  $c_{44}$  with temperature. Open circles represent data at 1 atm. Values at various constant volumes are distinguished by the symbols:  $X \cdots V_{12}$  ( $a_{12} = 4.040 \text{ \AA}$ );  $\nabla \cdots V_{13}$  ( $a_{13} = 4.0425 \text{ \AA}$ );  $\Delta \cdots V_{14}$  ( $a_{14} = 4.045 \text{ \AA}$ );  $\square \cdots V_{15}$  ( $a_{15} = 4.0476 \text{ \AA}$ );  $\bullet \cdots V_{16}$  ( $a_{16} = 4.0496 \text{ \AA}$ );  $+ \cdots V_{17}$  ( $a_{17} = 4.0517 \text{ \AA}$ ).