ordering occurs on cooling the crystal below the lambda temperature. In NH_4Br the situation is reversed; on cooling there is an anomalous lattice expansion[9] as the bromide crystal undergoes the transition to the ordered tetragonal form. These volume changes associated with changes in ordering make it easy to follow the transition temperatures as a function of applied pressure. Stevenson[10] has obtained the phase diagrams of ammonium chloride, bromide and iodide. His phase diagram for ammonium bromide is reproduced in Fig. 2. (The region encompassed by the sloping lines labeled V_1 to V_{17} in this figure indicates the region of the phase diagram studied in the present investigation.) The β, γ, and δ phases correspond to the structures disordered cubic (CsCl), antiparallel ordered tetragonal and parallel ordered cubic (CsCl), respectively. An α phase corresponding to a disordered NaCl-type cubic structure occurs at high temperatures but is not shown here. There is also a very pronounced hysteresis associated with the γ–δ order–order transition at 1 atm, which is not shown in this figure.

The present paper reports on a variety of ultrasonic velocity measurements which have been made on single-crystal ammonium bromide. Both longitudinal and transverse waves were studied over a wide range of pressure (0 to 12 kbar) at several constant temperatures in the range 255°–315°K. These data all pertain to the disordered phase away from any transition line, and should provide a clear example of the "normal" behavior of a CsCl-type ammonium halide free from any effects due to ordering. Velocity measurements have also been made as a function of temperature at 1 atm, although data could be obtained below the lambda temperature (234.5°K) only for the transverse wave associated with c_{44}.

This investigation is closely related to previous studies[11,12] of the elastic constants of ammonium chloride as functions of temperature and pressure. These studies show that the shear elastic constants for ammonium chloride (especially c_{44}) varied almost linearly with the volume. Since the volumes of ammonium chloride and bromide vary in an opposite manner at the lambda temperature, we would expect that c_{44} should also vary in an opposite manner. For ammonium chloride, c_{44} increases markedly as the temperature is lowered through the transition; therefore c_{44} for the bromide would be expected to decrease.

The results presented below are given in terms of the variation of the three adiabatic elastic constants c_{11}, c_{44}, C', which can be obtained directly from the experimental sound velocities. Third-order elastic constants are not used, and for pressures above 1 atm the quantities c_{11}, c_{44}, and C' are "effective" elastic constants.[13] The relations between the ultrasonic velocities and the elastic constants of a cubic crystal are well known:

[9] F. Simon and R. Bergmann, Z. Physik. Chem. **8B**, 255 (1930).

[10] R. Stevenson, J. Chem. Phys. **34**, 1757 (1961).

[11] C. W. Garland and J. S. Jones, J. Chem. Phys. **39**, 2874 (1963).

[12] C. W. Garland and R. Renard, J. Chem. Phys. **44**, 1130 (1966).

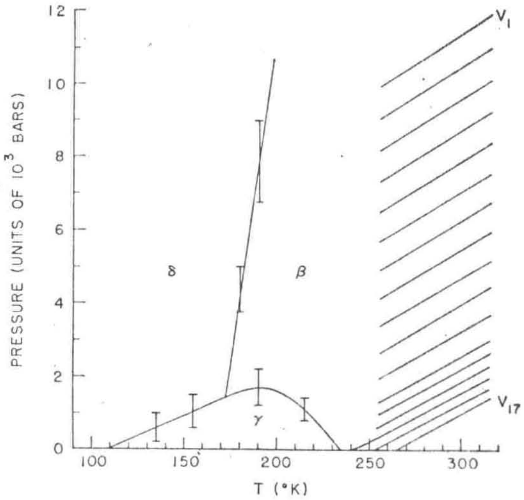

FIG. 2. Phase diagram for NH_4Br. The β phase corresponds to a disordered, CsCl-type cubic phase; the γ phase to an (antiparallel) ordered tetragonal phase; the δ phase to a (parallel) ordered, CsCl-type cubic phase. The vertical bars represent transition points as determined by the static volume measurements of Stevenson (Ref. 10). The set of sloping lines labeled V_1 through V_{17} represent isochores at various volumes.

Propagation in the [100] *direction*

$$c_{11}=\rho U_l^2, \qquad (1)$$

$$c_{44}=\rho U_t^2, \qquad (2)$$

where ρ is the mass density of the crystal, U_l is the velocity of the longitudinal sound wave, and U_t is the velocity of a transverse wave polarized in any direction perpendicular to the [100] axis.

Propagation in the [110] *direction*

$$C'=(c_{11}-c_{12})/2=\rho U_{t'}^2, \qquad (3)$$

$$c_{11}+c_{44}-C'=\rho U_{l'}^2, \qquad (4)$$

where $U_{l'}$ is the velocity of the longitudinal wave and $U_{t'}$ is the velocity of a transverse wave polarized perpendicular to the [001] axis. Values of $U_{l'}$ were measured only at 1 atm from 250° to 300°K as a check on the internal consistency of the data.

Since the crystal structure of ammonium bromide changes from cubic to tetragonal below the β–γ lambda transition, one must consider the effect of this symmetry change on the elastic constants of a crystalline sample. The tetragonal axis a_3 is now not equivalent to the other axes, and therefore $c_{33}\neq c_{11}$, $c_{13}\neq c_{12}$, and $c_{66}\neq c_{44}$ in the low-temperature phase. Since data were obtained

[13] R. N. Thurston, J. Acoust. Soc. Am. **37**, 348 (1965).