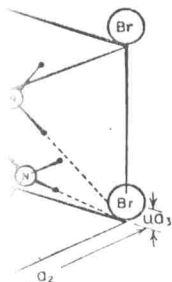


Ammonium Bromide\*

Engineering

actions  
 $c_{11} =$   
 were  
 as not  
 asured  
 115°K.  
 normal

onal below the  
 work<sup>3</sup> establishes  
 and confirms that  
 unit cell, as shown  
 ammonium bromide.



(cubic) ammonium  
 bromide, J. Chem. Phys.

ordered in the  
 the  $a_3$  or tetrag-  
 ammonium ions  
 are displaced  
 in positive and  
 the  $a_1$ - $a_2$  plane by  
 distortion is very  
 the  $a_3$  axis by only  
 In contrast, the  
 ammonium chloride  
 ammonium ions are  
 with respect to

show a marked  
 In  $NH_4Cl$ , the  
 attraction<sup>8</sup> when  
 95 (1954).

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<sup>9</sup> 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<sup>10</sup> 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  $\beta$ ,  $\gamma$ , and  $\delta$  phases correspond to the structures disordered cubic (CsCl), antiparallel ordered tetragonal and parallel ordered cubic (CsCl), respectively. An  $\alpha$  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  $\gamma$ - $\delta$  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<sup>11,12</sup> 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

<sup>9</sup> F. Simon and R. Bergmann, Z. Physik. Chem. **8B**, 255 (1930).  
<sup>10</sup> R. Stevenson, J. Chem. Phys. **34**, 1757 (1961).  
<sup>11</sup> C. W. Garland and J. S. Jones, J. Chem. Phys. **39**, 2874 (1963).  
<sup>12</sup> C. W. Garland and R. Renard, J. Chem. Phys. **44**, 1130 (1966).

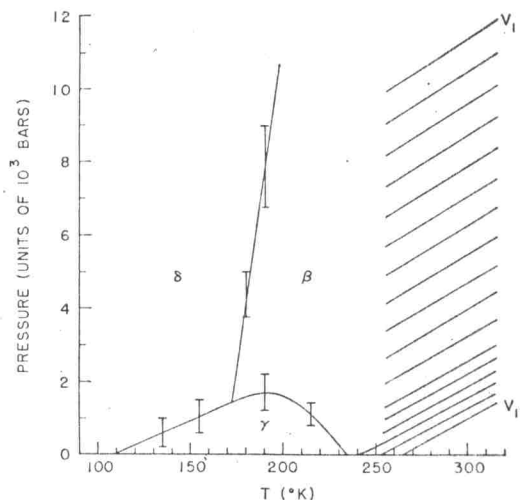


FIG. 2. Phase diagram for  $NH_4Br$ . The  $\beta$  phase corresponds to a disordered, CsCl-type cubic phase; the  $\gamma$  phase to an (antiparallel) ordered tetragonal phase; the  $\delta$  phase to a (parallel) ordered, CsCl-type cubic phase. The vertical bars represent transition points as determined 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.

are not used, and for pressures above 1 atm the quantities  $c_{11}$ ,  $c_{44}$ , and  $C'$  are "effective" elastic constants.<sup>13</sup> The relations between the ultrasonic velocities and the elastic constants of a cubic crystal are well known:

Propagation in the [100] direction

$$c_{11} = \rho U_l^2, \tag{1}$$

$$c_{44} = \rho U_t^2, \tag{2}$$

where  $\rho$  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

$$C' = (c_{11} - c_{12})/2 = \rho U_{l'}^2, \tag{3}$$

$$c_{11} + c_{44} - C' = \rho U_{t'}^2, \tag{4}$$

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  $\beta$ - $\gamma$  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

<sup>13</sup> R. N. Thurston, J. Acoust. Soc. Am. **37**, 348 (1965).