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The adiabatic elastic constants of single-crystal ammonium bromide have been measured as functions of temperature and pressure by a pulse-superposition technique. The values at 1 atm and 300°K are: $c_{11} = 3.414$, $C' = (c_{11}-c_{12})/2 = 1.316$, and $c_{44} = 0.722$, in units of 10^{11} dyn cm^{-2}. Measurements of c_{11} and C' were not made below the lambda transition at 234.5°K because of a sudden increase in attenuation; c_{44} was not attenuated in this manner and was measured from 105° to 320°K. The elastic constants were measured as functions of pressure between 0 and 12 kbar at constant temperatures which ranged from 255° to 315°K. In this region, which is far from the lambda line, disordered ammonium bromide behaves like a normal CsCl-type crystal.

INTRODUCTION

A LAMBDA transition at 234.5°K in crystalline ammonium bromide was first discovered from heat-capacity measurements.[1] This transition is now established as an order–disorder transition involving the relative orientations of adjacent ammonium ions. However, there are important differences between the ordering process in NH$_4$Br and that in NH$_4$Cl, which undergoes a cooperative order–disorder transition at about the same temperature (242.8°K). X-ray,[2] neutron-diffraction,[3] Raman,[4] and infrared[5] investigations show that above their critical temperatures both NH$_4$Br and NH$_4$Cl have a CsCl-type cubic structure with the tetrahedral ammonium ions oriented at random with respect to the two equivalent positions in the cubic cell (hydrogen atoms pointing toward nearest-neighbor halide ions). Hettich[6] observed that ammonium bromide does not become piezoelectric below the lambda point but does exhibit double refraction. This result and the low-temperature Raman spectrum led Menzies and Mills[4] to suggest that the ammonium ions in two adjacent unit cells were antiparallel (have opposite orientations relative to the crystallographic axes). Low-temperature x-ray studies[7] have shown that the crystal

structure of NH$_4$Br becomes tetragonal below the transition, and the neutron-diffraction work[3] establishes the location of the hydrogen atoms and confirms that this phase is ordered. The tetragonal unit cell, as shown in Fig. 1, contains two molecules of ammonium bromide.
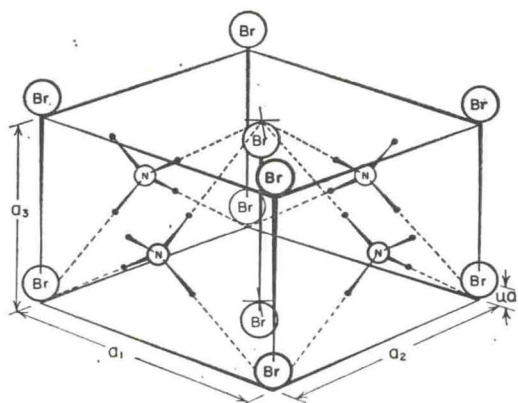

FIG. 1. Unit cell for γ-phase (ordered tetragonal) ammonium bromide. [From E. L. Wagner and D. F. Hornig, J. Chem. Phys. 18, 305 (1950).]

The ammonium ions are antiparallel ordered in the $a_1 - a_2$ plane and parallel ordered along the a_3 or tetragonal axis. The antiparallel ordering of ammonium ions is stabilized by the bromide ions which are displaced along the tetragonal axis alternately in positive and negative directions with respect to the $a_1 - a_2$ plane by ua_3 where $u = 0.02$. The tetragonal distortion is very slight, amounting to an extension of the a_3 axis by only 0.3% relative to the a_1 and a_2 axes.[7] In contrast, the low-temperature ordered phase in ammonium chloride is cubic (CsCl type), and all the ammonium ions are parallel (have same relative orientation with respect to crystallographic axes).

The thermal expansion data also show a marked difference between NH$_4$Br and NH$_4$Cl. In NH$_4$Cl, the lattice undergoes an anomalous contraction[8] when

[1] F. Simon, C. V. Simson, and M. Ruhemann, Z. Physik. Chem. 129, 344 (1927); A. G. Cole, Ph.D. thesis, MIT, 1952.

[2] F. Simon and C. V. Simson, Naturwiss. 14, 880 (1926); G. Bartlett and I. Langmuir, J. Am. Chem. Soc. 43, 84 (1921).

[3] H. A. Levy and S. W. Peterson, Phys. Rev. 83, 1270 (1951); 86, 766 (1952); J. Am. Chem. Soc. 75, 1536 (1952).

[4] A. C. Menzies and H. R. Mills, Proc. Roy. Soc. (London) A148, 407 (1935); R. S. Krishnan, Proc. Indian Acad. Sci. 26A, 432 (1947); 27A, 321 (1948).

[5] E. L. Wagner and D. F. Hornig, J. Chem. Phys. 18, 296 (1950); J. Chem. Phys. 18, 305 (1950).

[6] A. Hettich and A. Schleede, Z. Physik 50, 249 (1928); A. Hettich, Z. Physik. Chem. A168, 353 (1934).

[7] J. A. A. Ketelaar, Nature 134, 250 (1934); J. Weigle and H. Saini, Helv. Phys. Acta 9, 515 (1936); V. Hovi, K. Heiskanen, and M. Varteva, Ann. Acad. Sci. Fenn. Ser. A. VI, No. 144, 1–12 (1964).

[8] Y. Sakamoto, J. Sci. Hiroshima Univ. A18, 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[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

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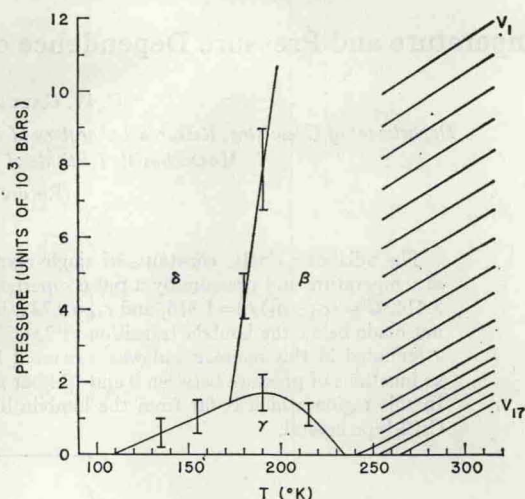
FIG. 2. Phase diagram for NH_4Br. The β phase corresponds to a disordered, CsCl-type cubic phase; the γ phase to an (antiparallel) ordered tetragonal phase; the δ phase to a (parallel) ordered, CsCl-type cubic phase. The vertical bars represent transition points as determined by the static volume measurements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

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:

Propagation in the [100] *direction*

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

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

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*

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

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

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 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).

below T_λ 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 NH$_4$Br single crystal is transformed below T_λ 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[14,15] 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 γ 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[12] 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 ±0.05° 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.[12]

The single crystals used in these experiments were grown by a modified Holden process.[16] To obtain a saturated solution at ~45°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% NH$_4$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±0.0005 cm for Crystal I and 1.1935±0.0005 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±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 ρ_{20} of 2.4336 g cm^{-3} was calculated from a lattice constant of 4.0580 Å at 20°C; this unit cell constant is based on several different x-ray investigations around room temperature.[7,17] The elastic constants at 1 atm were obtained as a function of temperature from equations of the type

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

where U is the appropriate velocity, δ 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[9] and from the low-temperature x-ray data of Hovi, Heiskanen, and Varteva.[7] Obviously, the x-ray measurements give the tetragonal cell dimensions $(a_3 \neq a_1 = a_2)$ below T_λ. 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_λ. 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[18] 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

[14] H. J. McSkimin, J. Acoust. Soc. Am. **33**, 12 (1961).
[15] H. J. McSkimin and P. Andreatch, J. Acoust. Soc. Am. **34**, 609 (1962); **37**, 864 (1965).
[16] A. N. Holden, Discussions Faraday Soc. **5**, 312 (1949).

[17] 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).
[18] R. K. Cook, J. Acoust. Soc. Am. **29**, 445 (1957).

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

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

where δ_1 and δ_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[18] 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 δ_1/δ_p).
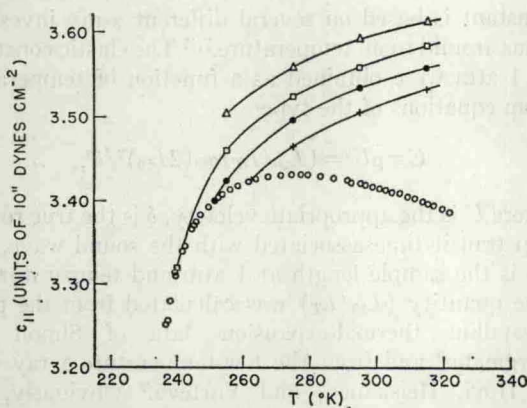

FIG. 3. Variation of c_{11} with temperature. Open circles represent data at 1 atm; for a definition of the symbols used for values at various constant volumes, see the legend of Fig. 5.

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[12] and was used for all the pressure runs.

The Dow resin and Nonaq seals were all very thin. Thus the phase shifts γ were small (between $-5°$ and $-8°$) at all temperatures, and the corrections to the transit times[12] 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 γ as a function of pressure. This effect of pressure on the behavior of
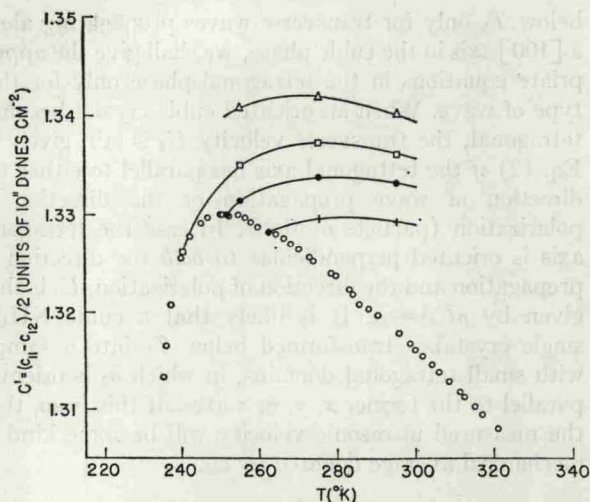

FIG. 4. Variation of C' with temperature. Open circles represent data at 1 atm; for a definition of the symbols used for values at various constant volumes, see the legend of Fig. 5.

the transducers is known[14] 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

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

Since the temperatures in Table I are all above the lambda point, all entries pertain to the disordered cubic phase of NH_4Br.
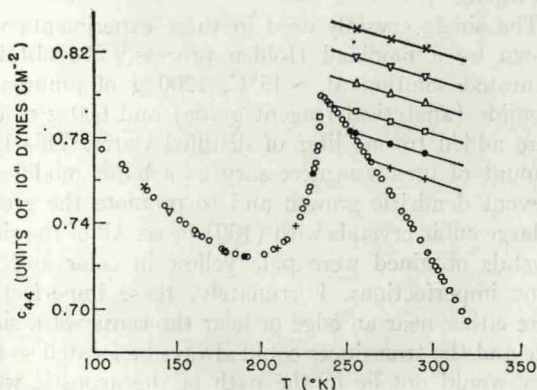

FIG. 5. Variation of c_{44} with temperature. Open circles represent data at 1 atm. Values at various constant volumes are distinguished by the symbols: $X \cdots V_{12}$ ($a_{12}=4.040$ Å); $\nabla \cdots V_{13}$ ($a_{13}=4.0425$ Å); $\triangle \cdots V_{14}$ ($a_{14}=4.045$ Å); $\square \cdots V_{15}$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

$T(°K)$	c_{11}	c_{44}	C'	$1/\beta^S$
235	...	0.7992	1.3110	...
236	...	0.7987	1.3171	...
237	3.2640	0.7977	1.3205	1.5033
238	3.2860	0.7968	1.3231	1.5219
240	3.3190	0.7948	1.3260	1.5510
245	3.3694	0.7897	1.3292	1.5971
250	3.3942	0.7842	1.3300	1.6209
260	3.4205	0.7726	1.3289	1.6486
270	3.4293	0.7605	1.3264	1.6608
280	3.4293	0.7478	1.3232	1.6650
290	3.4236	0.7349	1.3197	1.6640
300	3.4144	0.7218	1.3160	1.6597
310	3.4028	0.7083	1.3122	1.6532
320	3.3885	0.6944	1.3083	1.6441

As the temperature was lowered toward the transition temperature, an increase in attenuation was observed. For longitudinal waves in the [100] and [110] direction and for the transverse wave which yields C', the attenuation increased rapidly at the transition temperature and the echoes completely disappeared. As the temperature was lowered below 210°K, echoes slowly began to reappear. The shape of these echoes was very poor, and there was still a great deal of attenuation. Thus it was not possible to make meaningful velocity measurements for c_{11} and C' below the transition.

For the transverse waves associated with c_{44} there was only slight attenuation in the critical region, and data could be obtained over the entire temperature range 100°–320°K including the immediate vicinity of T_λ. Values of c_{44} were determined between 215° and 235°K on all three crystals (using both [100] and [110] propagation directions) and good agreement was obtained. This lends support to the idea that there are small domains with their tetragonal axes randomly oriented along the x, y, or z axes of the original cubic crystal. In that case, the measured ρU_t^2 values below the transition point correspond to an average shear

$T(°K)$	c_{44}	$T(°K)$	c_{44}
110	0.7713	205	0.7273
120	0.7639	210	0.7297
130	0.7567	215	0.7331
140	0.7496	220	0.7386
150	0.7427	225	0.7481
160	0.7364	230	0.7627
170	0.7307	231	0.7680
180	0.7265	232	0.7725
190	0.7244	233	~0.778
200	0.7258	234	~0.79

constant $\bar{c}_{44}$ which is related to the single-crystal tetragonal constants by $\bar{c}_{44} = \frac{1}{3}(2c_{44}+c_{66})$. Values of $\rho U_t^2 = \bar{c}_{44}$ obtained from measurements along a [100] direction (in the original cubic crystal) are given in Table II and shown in Fig. 4.

Although it is not shown in Fig. 4, hysteresis was observed in the temperature behavior of c_{44}. On cooling the sample a sharp drop in c_{44} occurred at 234.2°K, whereas the most rapid jump in the c_{44} value on warming the sample occurred at 234.8°K. This temperature hysteresis of 0.6°K is quite comparable to the hysteresis of 0.9°K observed for both c_{44} and C' in ammonium chloride.[12]

The greatest sources of error in these elastic constants at 1 atm are due to uncertainties in the path lengths at 20°C ($\pm 0.1\%$) and ambiguities in the choice of the $n=0$ condition[12] for shear waves (especially for c_{44}). Therefore, to check the possibility that a wrong $n=0$ value had been chosen and also to check the internal consistency of our data, the velocity of the longitudinal

Obs.	$T(°K)$	c_{11}	c_{44}	C'	c_{12}	$1/\beta^S$
P	300	3.414	0.722	1.316	0.782	1.66
H	293	3.38	0.685	1.24	0.91	1.73
S and B	298	2.96	0.53	1.19	0.59	1.38
B	298	...	...	...	...	1.63

wave in the [110] direction was measured as a function of temperature. The experimental value of $\rho U_{l'}^2$ for this wave and that calculated from Eq. (4) using the tabulated values of c_{11}, c_{44}, and C' were within 0.1 percent of each other over the entire temperature range 250°–300°K. This eliminates the possibility of a systematic error in the choice of the $n=0$ value for C'. For c_{44} there is still a possibility that the reported values may be systematically in error by $\pm 0.9\%$. A propagation-of-errors treatment indicates that the random error in all three elastic constants is about $\pm 0.2\%$ at all temperatures.

The independent adiabatic elastic constants of single-crystal ammonium bromide at room temperature have been measured by Sundara Roa and Balakrishnan[19] and by Haussuhl,[20] who also measured the temperature dependence down to the transition. Table III gives a comparison of the elastic constants and the bulk modulus obtained by these investigators with the results

[19] R. V. G. Sundara Rao and T. S. Balakrishnan, Proc. Ind. Acad. Sci. **28A,** 480 (1948).
[20] S. Haussuhl, Acta Cryst. **13,** 685 (1960).

of the present experiments. Also included is the adiabatic bulk modulus of a polycrystalline sample calculated from Bridgman's isothermal value.[21] The large difference between the present results and those of Sundara Roa and Balakrishnan should not be taken too seriously since the latter were reported to be accurate only to within 10%. The agreement with Haussuhl's elastic constants is not very good, although the slopes of his elastic constants versus temperature agree quite well with those of the present measurements.

Constant-Temperature Data

The experimental values of c_{11}, c_{44}, and C' as functions of pressure at various constant temperatures are shown
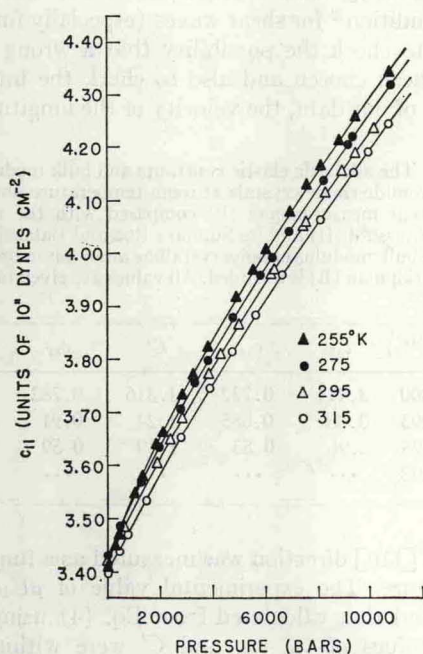

FIG. 6. Dependence of c_{11} on pressure at various temperatures.

in Figs. 6–8. Data on the shear constants were obtained with 20-Mc/sec transducers, but these showed a bad tendency to break after several high-pressure runs. Measurements of c_{11} were made at 30 Mc/sec by using a 10-Mc/sec transducer, and this did not break on repeated runs at various temperatures. A tabulation of the smooth-curve values of these elastic constants as a function of pressure is given in Table IV. The limits of error in these elastic constant values at high pressures is somewhat greater than that at 1 atm due to greater uncertainty in the phase-shift correction term. (There is an appreciable increase in γ with an increase in the pressure.)

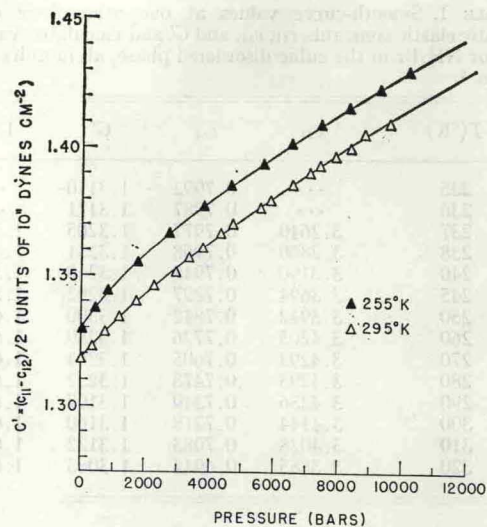---

[21] P. W. Bridgman, Phys. Rev. **38**, 182 (1931).

FIG. 7. Dependence of C' on pressure at two temperatures.

Bridgman[21] has measured $\Delta V/V_0$ as a function of pressure for ammonium bromide at 0° and 75°C. A comparison of his values with the values calculated from our present data shows that his values are about 6% high. Bridgman's difference between $\Delta V/V_0$ for a given pressure interval at the two temperatures is about 3 to 4 times greater than that observed in these experiments. The explanation for this difference seems to be that Bridgman's data were taken on a pressed polycrystalline sample, which one would expect to be more
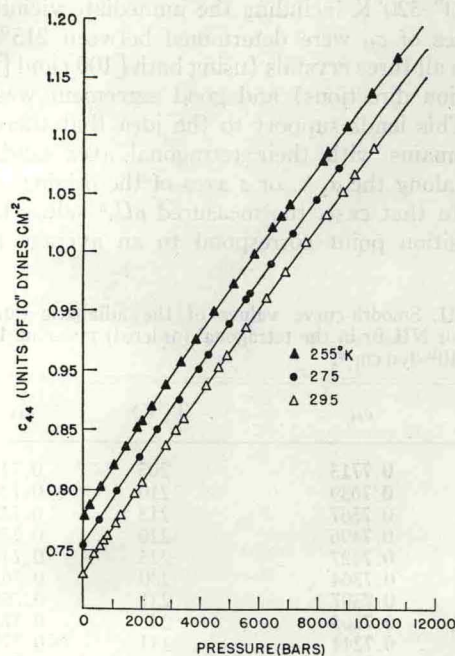

FIG. 8. Dependence of c_{44} on pressure at various temperatures.

TABLE IV. Smooth-curve values of the effective adiabatic elastic constants c_{11}, c_{44}, and C', in units of 10^{11} dyn cm^{-2}, as a function of pressure at various temperatures. Calculated values of $1/\beta^S$ are also given at two temperatures.

$T = 315°K$

p(kbar)	c_{11}	p(kbar)	c_{11}	p(kbar)	c_{11}
0	3.396	4	3.757	8	4.063
2	3.583	6	3.914	10	4.205

$T = 295°K$

p(kbar)	c_{11}	c_{44}	C'	$1/\beta^S$
0	3.419	0.792	1.318	1.662
2	3.615	0.805	1.343	1.824
4	3.789	0.879	1.363	1.972
6	3.949	0.951	1.3815	2.107
8	4.097	1.020	1.398	2.233
10	4.236	1.091	1.4145	2.350

$T = 275°K$

p(kbar)	c_{11}	c_{44}	p(kbar)	c_{11}	c_{44}
0	3.430	0.754	6	3.978	0.975
2	3.639	0.830	8	4.129	1.046
4	3.819	0.903	10	4.272	1.114

$T = 255°K$

p(kbar)	c_{11}	c_{44}	C'	$1/\beta^S$
0	3.411	0.778	1.330	1.638
2	3.654	0.856	1.358	1.843
4	3.843	0.931	1.379	2.004
6	4.010	1.003	1.397	2.147
8	4.162	1.073	1.4135	2.277
10	4.302	1.140	1.4285	2.397

compressible than a single crystal. Indeed, the same kind of discrepancy between single crystal and Bridgman's polycrystalline value is also observed in ammonium chloride.[12]

Constant-Volume Data

In the temperature region above the lambda point, it is possible to combine the results presented above to obtain the variation of the elastic constants with temperature at constant volume. From the known temperature dependence of the cubic cell parameter at 1 atm and the pressure dependence of $s(p)$, one can compute the hydrostatic pressure which must be applied to the crystal at any given temperature in order to maintain its volume at a constant value. This has been done for the 17 different values of the volume: V_1 corresponds to a unit cell dimension of $a_1 = 3.985$ Å; V_2 through V_{12} correspond to a values which are each 0.005 Å greater than the previous value (up to $a_{12} = 4.040$ Å); V_{13} through V_{17} correspond to $a_{13} = 4.0425$, $a_{14} = 4.045$, $a_{15} = 4.0476$, $a_{16} = 4.0496$, and $a_{17} = 4.0517$ Å. The corresponding p-T isochores are plotted in Fig. 2. With these isochores, one can easily evaluate the effective adiabatic elastic constants at constant volume. Such constants have been plotted in Figs. 3–5 for a few high-volume values as a comparison with the variation at constant pressure. Constant-volume elastic con-

stants are shown in Fig. 9 as a function of temperature for all 17 values of V.

DISCUSSION

Far from the Lambda Transition

As shown in Fig. 2, the principal region of this investigation is the disordered β phase of ammonium bromide. At pressures up to about 3000 bar the elastic constants show a nonlinear variation with pressure due to the fact that the crystal is still in the vicinity of the β–γ lambda line. At higher pressures, farther from the lambda line, the variation is linear as expected for a normal solid having no transition. This is clearly illustrated by the temperature variation of the constant-volume elastic constants shown in Fig. 9. Presented in Table V is a comparison of our data on ammonium bromide with recent data on ammonium chloride[12]; these results are discussed below in the general context of the behavior which is known for alkali halide crystals. The NH$_4$Cl elastic constants have been measured in a region of the phase diagram which contains the lambda line[12]; therefore the behavior of these constants will be somewhat influenced by the proximity of the order–disorder transition. On the other hand, NH$_4$Br should be typical of a "normal" CsCl-type crystal (at least above 3000 bar).

Haussuhl[22] has found that all alkali halides of the NaCl type obey the inequality $T' < T_{11} < T_{44}$, where T_{ij} represents $(\partial \ln c_{ij}/\partial T)_p$ at atmospheric pressure and is a negative quantity. For several alkali halides of the CsCl type the inequality has been found[20] to be

$$T_{44} < T_{11} < T'. \qquad (8)$$

As shown in Table V, the slopes at 320°K of the elastic constants of ammonium bromide obey this CsCl in-
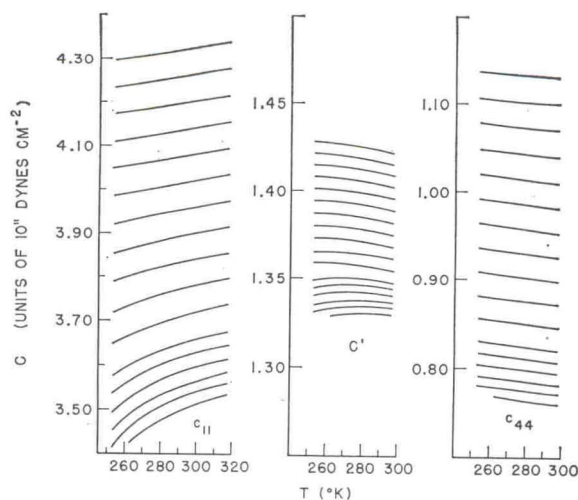

FIG. 9. Adiabatic elastic constants versus temperature at various constant volumes from V_1 to V_{17} (see text). The highest curves correspond to V_1.

[22] S. Haussuhl, Z. Physik **159**, 223 (1960).

TABLE V. The adiabatic elastic constants of ammonium bromide and their temperature and pressure derivatives compared with the results of Garland and Renard (Ref. 12) for ammonium chloride. The value of $\partial \ln c_{11}/\partial T$ at 350°K was measured by Weintraub (Ref. 23); the other $\partial \ln c/\partial T$ values were determined at 320°K. The elastic constants are in units of 10^{11} dyn cm^{-2}; the temperature derivatives are in units of 10^{-4} deg^{-1}, and the pressure derivatives are in units of 10^{-12} cm^2 dyn^{-1}.

	NH$_4$Cl			NH$_4$Br		
	c_{11}	C'	c_{44}	c_{11}	C'	c_{44}
c(295°K)	3.814	1.466	0.8753	3.419	1.318	0.7285
$(\partial \ln c/\partial T)_{p=0}$	-1.5 -5.3(350°K)	-2.83	-17.1	-4.32	-2.93	-19.8
$(\partial \ln c/\partial T)_V$	4.0	-0.78	-2.66	3.60	-0.05	-5.86
$(\partial \ln c/\partial p)_{T=295°K}$	4.63	0.81	5.12	3.17	1.03	5.30

equality. At 320°K the slope of c_{11} for ammonium chloride does not seem to fit the pattern; however, if one assumes that c_{11} hasn't reached its limiting "normal" behavior (i.e., that it is still being influenced by the nearby lambda transition), the slopes for the elastic constants would obey the inequality. Indeed, the unpublished results of Weintraub[23] on the variation of c_{11} with temperature between 300° and 375°K indicate that c_{11} becomes linear with respect to T only above 335°K, where $T_{11} = -5.27 \times 10^{-4}$ deg^{-1}. This value would satisfy the CsCl inequality very well.

The pressure derivatives of the elastic constants, $P_{ij} = (\partial \ln c_{ij}/\partial p)_T$, will obey similar inequalities. Data as a function of pressure are available for several alkali halides of the NaCl type[24] for which the inequality is $P' > P_{11} > P_{44}$. This is reasonable since a decrease in temperature corresponds to an increase in pressure in terms of its effect on the molar volume (and thus the elastic constants). Although no data appear to be available on the pressure dependence of the elastic constants of alkali halides of the CsCl type, the expected inequality would be

$$P_{44} > P_{11} > P'. \qquad (9)$$

Both the ammonium bromide and chloride data obey this inequality over the entire range of temperatures for which pressure measurements have been made; the values of P_{ij} at 295°K, as given in Table V, are typical.

At *constant volume* the inequalities for the temperature derivatives of the alkali halides of the NaCl type which have been studied is $T' < T_{44} < T_{11}$ (constant volume). For the ammonium halides at constant volume the corresponding inequality is

$$T_{44} < T' < T_{11} \qquad \text{(constant volume)}. \qquad (10)$$

This comparison of the behavior of the ammonium halides with that of NaCl-type alkali halides imme-

[23] A. Weintraub, senior thesis, MIT, 1963.
[24] D. Lazarus, Phys. Rev. **76**, 545 (1949); R. A. Miller and C. S. Smith, J. Phys. Chem. Solids **25**, 1279 (1964).

diately reveals a significant difference: the slope of c_{11} versus temperature at constant volume for ammonium bromide and chloride is *positive* while it is always negative for the NaCl-type salts.[24] This behavior cannot be due to an influence of the lambda transition since for NH$_4$Br at the lowest volumes (far from the transition) anomalous temperature variations in c_{11} are absent and c_{11} varies linearly with temperature (as a normal crystal should).

Comparison of the elastic constant values in Table V shows that those of ammonium chloride are greater than the corresponding ones for the bromide. This is in general what is observed for all of the alkali halides. As the molar volume (and mass) increases, the stiffness (and thus the elastic constants) decreases. The temperature and pressure derivatives of the elastic constants of ammonium bromide are very similar to those of ammonium chloride, although the pattern is not regular enough to permit scaling. If these derivatives are taken as measures of the anharmonicity of the crystal, then ammonium chloride and ammonium bromide have quite similar anharmonicity.

Near the Lambda Transition

Our information concerning the β–γ transition is limited to data obtained at 1 atm, especially on c_{44} for which measurements could be made below the lambda point.

As the temperature is lowered, c_{44} for ammonium bromide increases linearly with temperature down to the lambda point where it abruptly *decreases* and then at a lower temperature (about 40°K below the lambda point) resumes its normal increase with decreasing temperature (see Fig. 5). The temperature behavior of c_{44} for ammonium bromide is qualitatively compatible with that for ammonium chloride where there is an anomalous increase in c_{44}. This is expected since c_{44} is a sensitive function of the volume, and ammonium chloride contracts on ordering while ammonium bromide expands. A quantitative analysis of the effect of ordering at constant unit-cell dimension is complicated by the

tetragonal distortion of the lattice and the displacements of the bromide ions which occur in the γ phase on ordering. Nor is the Ising model theory[25] applied to the NH$_4$Cl data valid in the case of the β–γ transition in NH$_4$Br.

The behavior of c_{11} just above the lambda point in ammonium bromide is very similar to that observed in ammonium chloride, whereas the behavior of C' is different in the two cases. Unlike the data for the chloride, C' values for the bromide show a marked anomalous decrease which is apparent as much as 15°K above the lambda point (see Fig. 4). Attenuation of the ultrasonic waves associated with both c_{11} and C'

was very high over a considerable range of temperatures below the lambda point. This is presumably due to the presence of domains consisting of tetragonal crystallites with their unique axes lying at random along one of the three original cubic axes. The presence of domains is common in antiferromagnetic crystals and γ-phase ammonium bromide is analogous to an antiferromagnet.

A more extended discussion of the properties of the ordered phase and of the lambda transition region is difficult and inappropriate at this time. New experimental work is now in progress on ammonium bromide in the region 100° to 250°K and 0 to 6 kbar. This will provide information on both the γ and δ phases, as well as new data in the regions of the various transition lines.

[25] R. Renard and C. W. Garland, J. Chem. Phys. **44**, 1125 (1966).