Elastic Constants of Ammonium Bromide. II. High-Pressure Ultrasonic Investigation of the Phase Transitions*

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The abiabatic elastic constants of single-crystal ammonium bromide have been measured at 20 MHz as functions of temperature and pressure in the region from 180°–240°K and from 0–6 kbar. A new high-pressure ordered phase, denoted as O_{II}, has been discovered in this temperature range. The acoustic properties of the new O_{II} phase were investigated with emphasis on the regions of the first-order phase transition from the O_{II} phase to the ordered tetragonal phase and the lambda transition from the O_{II} phase to the disordered cubic phase. The region of the lambda transition from the ordered tetragonal phase to the disordered cubic phase was also studied. A detailed comparison is made with the behavior of ammonium chloride near its order–disorder phase transition.

INTRODUCTION

Ammonium halide crystals undergo lambda transitions of the order–disorder type involving the relative orientations of the tetrahedral NH_4^+ ions. The most detailed investigations have been devoted to NH_4Cl and NH_4Br, and it is well established that both of these crystals at room temperature have a disordered CsCl-type cubic structure with the NH_4^+ ions distributed at random with respect to two equivalent orientations in the cubic cell.[1] However, there are major differences between the types of ordering observed in the chloride and in the bromide. In the case of NH_4Cl, there is a single lambda line marking the transition between the disordered cubic phase and a "parallel" ordered cubic phase. In NH_4Br, an ordered tetragonal phase is known to exist at low pressures in addition to a low-temperature ordered cubic phase.

An earlier paper[2] (to be called Paper I) has reported the results of ultrasonic velocity measurements on NH_4Br over a wide range of pressure (0–12 kbar) at temperatures between 255° and 315°K; a general review of other investigations of NH_4Br was given at that time and will not be repeated here. The high-pressure data in Paper I all pertain to the disordered phase away from any transition lines and provide a clear indication of the "normal" behavior of any CsCl-type ammonium halide free from the effects of ordering. In addition, Paper I includes some results of velocity measurements made at 1 atm near the order–disorder transition at 234.5°K; indeed, this lambda point has been the center of interest for most previous investigations of NH_4Br.

The present paper is closely related to an ultrasonic study of NH_4Cl which was made over a wide pressure–temperature region on both sides of the lambda line.[3] Special emphasis was given to the anomalous behavior in the NH_4Cl elastic constants due to the cooperative ordering process, and it was possible to interpret those results in terms of a compressible Ising model.[4] In view of the fact that no information was obtained in Paper I about high-pressure phase transitions, it was felt that new work on NH_4Br at lower temperatures would provide some interesting comparisons between cooperative phenomena in NH_4Cl and NH_4Br. This idea was confirmed by the fact that there were several puzzling aspects to the limited high-pressure data that were available on NH_4Br. Bridgman[5] found a phase change at 201°K and 1630 bar, which he assumed to be between the same two phases as that at 234.5°K and 1 bar. However, the volume change associated with this high-pressure transition was essentially discontinuous, as in a first-order change, and not the continuous rapid variation observed for NH_4Cl at 1 atm[6] and at high pressures[5] or for NH_4Br at 1 atm.[6] Furthermore, Stevenson[7] had obtained phase diagrams of several ammonium halides, but his high-pressure transition line for NH_4Br did not correlate well with the supposedly corresponding lambda line in NH_4Cl.

Therefore, we have made velocity measurements on both longitudinal and transverse accoustic waves in single-crystal ammonium bromide at pressures from 0 to 6 kbar and at temperatures between 180° and 240°K. These results are presented in terms of the variation of the three adiabatic elastic constants c_{11}, c_{44}, and $C' = (c_{11}-c_{12})/2$, which can all be obtained directly from experimental ultrasonic velocities (see Paper I for the relations between c_{ij} and the velocities). Third-order

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

[2] C. W. Garland and C. F. Yarnell, J. Chem. Phys. **44**, 1112 (1966).

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

[4] C. W. Garland and R. Renard, J. Chem. Phys. **44**, 1120 (1966); R. Renard and C. W. Garland, *ibid.* **44**, 1125 (1966).

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

[6] F. Simon and R. Bergmann, Z. Physik. Chem. (Leipzig) **B8**, 225 (1930).

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

elastic constants are not used, and for pressures above 1 atm the quantities c_{11}, c_{44}, and C' are "effective" elastic constants.[8]

To provide a framework for the subsequent presentation of quantitative data, the most important qualitative result of our work will be stated immediately: A new high-pressure ordered phase (to be denoted as O_{II}) has been discovered. The NH$_4$Br phase diagram, as largely determined by the present work, is shown in Fig. 1. Extensive measurements were made with both shear and longitudinal waves in the new high-pressure ordered phase O_{II} and in the disordered cubic phase D as well as along the new lambda line between these phases. Domain formation takes place in the ordered tetragonal phase O_T, and the resulting attenuation makes velocity measurements difficult. Various attempts were made to align the tetragonal axes and obtain a single-domain crystal, but these were unsuccessful. Pressure measurements were made, however, in this phase for the "average" c_{44} shear constant which results from a random orientation of the tetragonal axes of the domains along the directions of the three equivalent axes in the disordered cubic phase.[2] A few measurements were also made in the low-temperature ordered phase O_I. This was very difficult since single crystals crack upon undergoing the first-order phase change from O_{II} to O_I. The O_I phase definitely has a CsCl-type cubic structure,[9] and the ordering almost certainly corresponds to the parallel orientation of all NH$_4^+$ ions which is observed in the low-temperature phases of NH$_4$Cl and ND$_4$Br.[1] Although there are many simi-

larities in the acoustic behavior along the D–O_{II} lambda line and along the lambda line in NH$_4$Cl, it can be proved acoustically that the O_{II} phase is *not* analogous to the parallel-ordered cubic phase of NH$_4$Cl. Suggestions for possible O_{II} structures are given in the Discussion.

EXPERIMENTAL DETAILS

Ultrasonic velocity measurements were made by a pulse-superposition method at a frequency of 20 MHz. Since the experimental procedures were very similar to those used previously,[2,3] only a few changes in detail will be described here.

A new high-pressure cell, made from A-286 stainless steel and suitable for use at low temperatures, was obtained from the Harwood Engineering Company. Petroleum ether was used as the hydraulic pressure fluid, and the pressure cell was immersed in a large, sealed thermostat bath of petroleum ether. Down to about −40°C, this bath was cooled with a commercial Freon refrigerating unit; below that temperature, cold nitrogen gas (obtained by boiling liquid nitrogen) was circulated through the cooling coils. A proportional temperature controller, Bailey Instrument Model 87-8, was used to maintain any given temperature to within ±0.05°K. Pressures, as determined with a calibrated manganin resistance gauge, could be maintained constant to within ±3 bar. With this modified apparatus, it was possible to operate from 0 to 6 kbar over the temperature range from ∼180° to ∼260°K.

Almost all of the data were obtained with the pressure system described above since petroleum ether could be pressurized to 6 kbar at 180°K without freezing. However, the lubricating properties of petroleum ether are very poor, and its extended use as the hydraulic fluid led to serious leaks in the sliding seals of the pressure intensifier. Therefore, a system utilizing argon as the pressure-transmitting fluid was installed in place of the original liquid hydraulic system. The data obtained using this gas system (all in the 0–3-kbar range) were in complete agreement with the earlier data.

Dow Resin 276-V9 was used for bonding the quartz transducers to the NH$_4$Br crystals in almost all cases. This bonding material worked very well for transmitting both transverse and longitudinal waves at pressures up to 6 kbar and temperatures down to 180°K when the sample was immersed in petroleum ether. McSkimin[10] has made impedance measurements for this resin, so the seal correction due to the phase shift at the transducer-bond end of the sample could be calculated. When gas was used as the high-pressure fluid, seals made with Dow Resin 276-V9 broke quite often upon applying pressure. Therefore, Dow 200 fluid with a viscosity of 1000 centistoke was substituted for
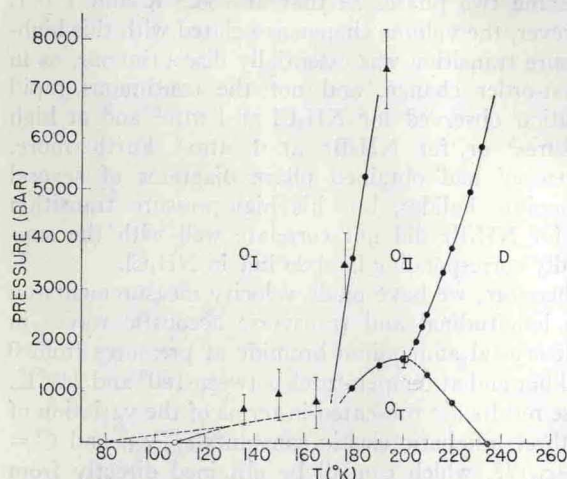

FIG. 1. Phase diagram for NH$_4$Br. Solid circles represent the present data, the open square point is from Bridgman (Ref. 5), the triangles are from Stevenson (Ref. 7), and the open circles at one atmosphere are from Stephenson and Adams (Ref. 14). The phases shown are the disordered cubic (D), ordered tetragonal (O_T), the new ordered phase (O_{II}), and the low-temperature ordered phase (O_I), which is thought to be the parallel-ordered CsCl-type cubic form.

[8] R. N. Thurston, J. Acoust. Soc. Am. **37**, 348 (1965).
[9] R. A. Young, Ph.D. thesis, M.I.T., 1968.

[10] H. J. McSkimin, IRE Trans. on Ultrasonics Eng. UE-5, 25 (1957).

the gas runs. In all cases, the bonds were very thin and the phase shifts were quite small.

A correction must be made to the ultrasonic velocity data in order to take into account this phase shift γ which occurs at the transducer-bond end of the sample. The correction is complicated by the fact that the resonance frequency f_r of the transducer varies with temperature and pressure, and therefore γ will also vary unless the exciting frequency f is changed to match the change in the resonance frequency. In practice it is easier to leave the exciting frequency fixed and calculate new values for γ since the change in the resonance frequency of quartz is well known as a function of temperature and pressure.[11] Luckily the change in the resonance frequency with temperature is small and can be neglected. For pressure measurements, the change is of the order of 1%–2% in f_r/f_{r_0} and a correction to the round-trip transit time must be calculated.

For the case of X-cut transducers, f_r/f_{r_0} increases with the pressure. If the exciting frequency is set at the 1-atm resonance value f_{r_0} for all the measurements, γ for measurements in the [100] direction will vary from $-7.6°$ at 1 bar to about $+7.0°$ at 6 kbar. Thus, the value of γ is small over the entire range of pressures. The maximum correction to the velocity due to phase shifts of this magnitude is only 0.02%. For Y-cut transducers, f_r/f_{r_0} decreases as the pressure increases. Since the change in γ with f/f_r is very much larger for $f/f_r>1$ than for $f/f_r<1$, the exciting frequency was set at about $0.98f_{r_0}$. In this way the variation of γ for C' measurements was kept between values of $+7.7°$ at 1 bar and $-5.0°$ at 6 kbar. In the same manner γ for c_{44} measurements was kept in the range from $+9.7°$ at 1 bar to $-6.5°$ at 6 kbar.

The single crystals used in this experiment were grown in the same manner as that described in Paper I. Quite large crystals, free from visible defects and with well-developed (100) faces, were obtained. These crystals had a very slight yellowish tinge, but chemical analysis showed that they were at least 99.9% NH_4Br with less than 0.05 wt% urea (the habit modifier used), 0.01% chloride, 0.5 ppm Cu, and 1 ppm free Br_2 as impurities. Various crystals were used to obtain the present data, and no significant differences in the velocities were observed between different crystals. The lengths of the crystals at 20°C used for velocity measurements in the [100] direction varied from 0.6444 ± 0.0001 to 1.2091 ± 0.0001 cm. One crystal was flycut for use in the [110] direction and had a measured length at 20°C of 0.6140 ± 0.0002 cm.

The elastic constants were obtained as functions of temperature and pressure from equations of the type

$$c=\rho U^2=\frac{\rho_{293}(2L_{293})^2(l_{293}/l_{p,T})}{\delta^2},\qquad(1)$$

where U is the appropriate velocity, δ is the true round-trip transit time associated with the sound wave, ρ_{293} is the density, $2L_{293}$ is the round-trip path length at 1 atm and 293°K (20°C), and $l_{293}/l_{p,T}$ is the ratio of the effective lattice parameter at 1 atm and 293°K to that at p and T. A ρ_{293} value of 2.4336 g cm^{-3} was obtained from a cubic lattice parameter l_{293} of 4.0580 Å; these values are the same as those used in Paper I and are based on several independent x-ray measurements. Finally, one needs to have values of the lattice parameter $l_{p,T}$ as a function of pressure and temperature. As used in Eq. (1), l represents an effective or average lattice parameter in the tetragonal phase. On the assumption that the tetragonal domains are randomly aligned along each of the three original cubic axes,[2] we have taken $l_{p,T}$ to be the cube root of the tetragonal unit-cell volume.

The determination of $l_{p,T}$ as a function of temperature at 1 atm and as a function of pressure at constant temperatures above 240°K has been discussed in Paper I, and the same procedures have been used here. The resulting variations of $l_{p,T}$ with pressure are shown in Fig. 2. The curves at 255°, 275°, and 295°K are based completely on data from Paper I, while the curve at 240°K was determined using ultrasonic data determined in this investigation. The 240°K result is in
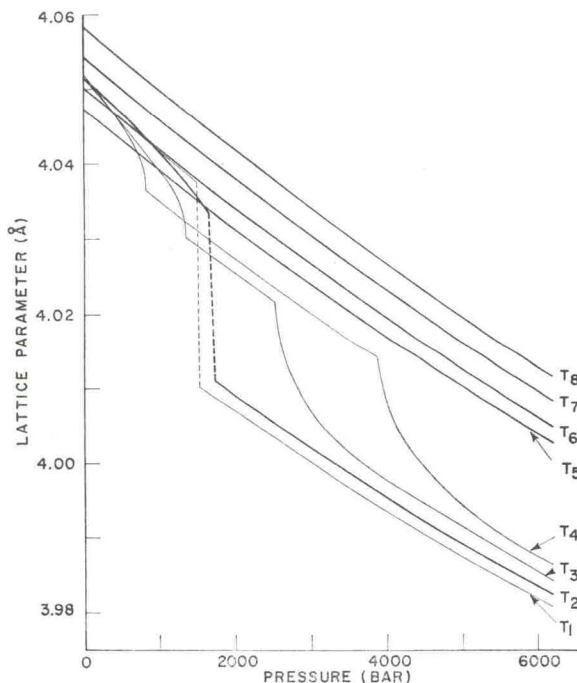

FIG. 2. Variation of the lattice parameter with pressure. Heavy curves at 200°, 240°, 255°, 275°, and 295°K are accurately known, whereas the three lighter curves are less well established (see text). Lattice parameters in the tetragonal phase (low-pressure portions of the 190° and 220°K curves) represent the cube root of the unit-cell volume. $T_1=190°K$, $T_2=200°K$, $T_3=210°K$, $T_4=220°K$, $T_5=240°K$, $T_6=255°K$, $T_7=275°K$, $T_8=295°K$.

[11] H. J. McSkimin and P. Andreatch, J. Acoust. Soc. Am. 34, 609 (1962).

excellent agreement with those at high temperatures. In addition, the change in the lattice parameter with pressure at 273°K when calculated in this manner agrees very well with the volume data obtained by Bridgman[5] at that temperature (the differences between the two values are never greater than 0.03%).

For temperatures below 240°K, the problem of determining $l_{p,T}$ was complicated by the various phase transitions. Fortunately, good volume data can be obtained at 200°K from the compressibility measurements of Bridgman[5] at 201°K. Above about 2 kbar, the lattice parameter at 200°K behaves as one would expect for a crystal which is not influenced by any phase changes. This region was thus taken to determine the "normal" behavior of the new O_{II} phase. From the behavior of the shear elastic constant c_{44} (see Fig. 3), it appears that the high-pressure variation of the lattice parameter at 190°K is also essentially "normal." Thus, the compressibility above 2 kbar at 190°K should be comparable to that observed above 2 kbar at 200°K. To obtain the O_{II} lattice parameters at 190°K, a thermal expansion coefficient comparable to that observed at high pressures in the disordered phase was used to extrapolate the 200°K data above 2 kbar. A similar extrapolation was performed to get the values for the lattice parameter in the disordered cubic phase at 210° and 220°K. In the tetragonal phase at 190°K (which is quite far from the lambda line), a straight line was drawn for the variation of the lattice parameter with pressure having a slope equal to the initial slope of Bridgman's data at 201°K. The only remaining parts of the phase diagram for which the lattice parameters were unknown were in the ordered phases near the lambda transition lines. In these regions (one in the new O_{II} phase and one in the tegragonal phase), we have assumed that it is a good approximation to use the relation

$$\Delta c_{44} \propto \Delta V/V_{dl}, \qquad (2)$$

where V_{dl} is the extrapolated volume of the disordered lattice, and Δc_{44} and ΔV are the differences between the actual values and the extrapolations of the disordered values of c_{44} and the volume, respectively. This procedure required an iterative method whereby the zero-order elastic constant c_{44} was calculated using an estimated value of the lattice parameter. The use of Eq. (2) is based on the demonstrated correspondence[12] between the behavior of c_{44} and V in the vicinity of the order–disorder transition in NH_4Cl and seems plausible for the closely related lambda transitions in NH_4Br. The resulting plots of the lattice parameter $l_{p,T}$ as a function of pressure at four constant temperatures below 240°K are also shown in Fig. 2. From this figure it can be seen that there is an anomalous decrease in the molar volume when NH_4Br transforms at high

pressure from the disordered cubic phase to the new O_{II} phase. This is in contrast to the expansion observed when NH_4Br transforms at low pressure from the disordered cubic phase to the ordered tetragonal phase. Thus, there is a large volume contraction associated with the first-order transition from the ordered tetragonal phase to the new O_{II} phase.

All the above extrapolations and approximations for $l_{p,T}$, even if slightly incorrect, do not introduce any serious errors into the calculated variations of the elastic constants since the directly observed transit times are much more sensitive than the lattice parameter to changes in temperature and pressure. If the high-pressure values of $l_{p,T}$ were in error by as much as 0.01 Å, the resulting systematic error in the high-pressure values of c_{ij} would only amount to 0.25%.

RESULTS

As stated previously, the most interesting general result of the present work was the discovery of a new high-pressure ordered phase of ammonium bromide. The positions of the various phase boundaries were easily determined from the anomalous behavior of the elastic constants (especially c_{44}) as functions of pressure and temperature. First-order phase changes were distinguished from lambda transitions due to the essentially discontinuous change in the elastic constants at first-order transition points as opposed to the very rapid but continuous variations over a considerable range near a lambda point. All of the information which is currently known about the phase diagram at temperatures between 70° and 315°K is shown in Fig. 1.[13] The new ordered phase, denoted here as O_{II}, was extensively studied with special emphasis on the region near its lambda transition to the disordered cubic form, D. The lambda transition from the disordered cubic to the ordered tetragonal form, O_T, was also studied. From these studies the positions of the two lambda lines have been determined quite accurately. (The error associated with the data points is indicated by the size of the solid circles plotted in Fig. 1.) The three data points on the first-order transition line between the new high-pressure O_{II} phase and the ordered tetragonal phase, O_T, likewise determine the position of this line quite well, and there is very good agreement with the square data point at 201°K obtained from Bridgman's compressibility work on a polycrystalline sample.[5] The ultrasonic data points on the first-order phase line between O_I and O_{II} are not as precisely known as the others, but they are still much more reliable than any previous values. The triangles with large error bars represent points obtained by Stevenson[7] with a piston-

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[12] C. W. Garland and R. A. Young, J. Chem. Phys. 48, 146 (1968).

[13] At 1 atm and 411°K there is a first-order transition between the disordered CsCl-type structure and a disordered NaCl-type structure; see Ref. 7 for more details about this high-temperature phase change.
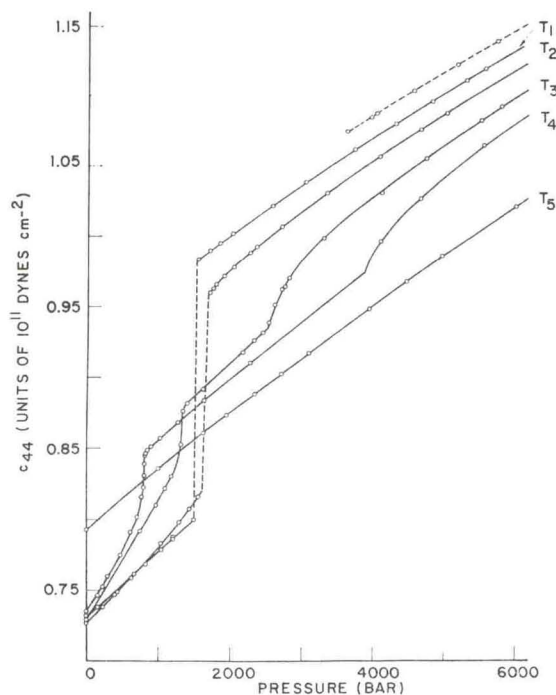
FIG. 3. Variation of c_{44} with pressure. The dashed curve near the top represents data taken in phase O_I at 180°K, where the lattice parameter is not well known. The vertical dashed lines at 190° and 200°K represent first-order phase changes from the ordered tetragonal phase to the O_{II} phase. $T_1 = 190°K$, $T_2 = 200°K$, $T_3 = 210°K$, $T_4 = 220°K$, $T_5 = 240°K$.
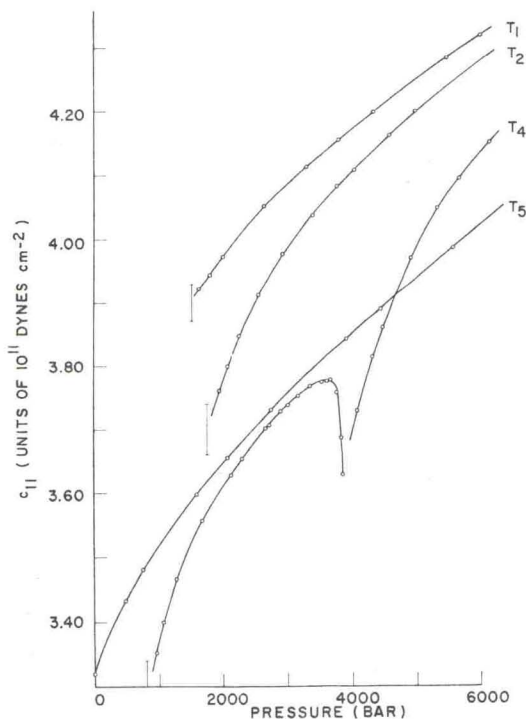

FIG. 4. Variation of c_{11} with pressure. No data could be obtained in the ordered tetragonal phase. The transition pressures for the first-order O_T–O_{II} phase change at T_1 and T_2 and for the O_T–D lambda transition at T_4 were obtained from c_{44} data; these pressures are indicated by vertical bars. $T_1 = 190°K$, $T_2 = 200°K$, $T_4 = 220°K$, $T_5 = 240°K$.

displacement method which was subject to considerable hysteresis. It is a curious accident that both Bridgman and Stevenson failed to make any observations in the region of the O_{II}-D lambda line.

The parts of the phase diagram which are shown with dashed lines are not at all well known, and these dashed lines should be viewed as rough approximations to the actual phase lines. However, the O_I–O_T transition temperatures at atmospheric pressure are well established to be 78°K on cooling and 108°K on warming.[14] The initial slope at 108°K can be estimated from the thermodynamic data of Cole[15] and the Clapeyron equation. The value of $\Delta S = 0.29$ cal deg^{-1}·mole^{-1} combined with a value of $\Delta V = 0.78$ cm^3 mole^{-1} taken from recent x-ray work[9] gives a slope of 15 bar deg^{-1}. This initial slope is shown as a short solid line in Fig. 1.
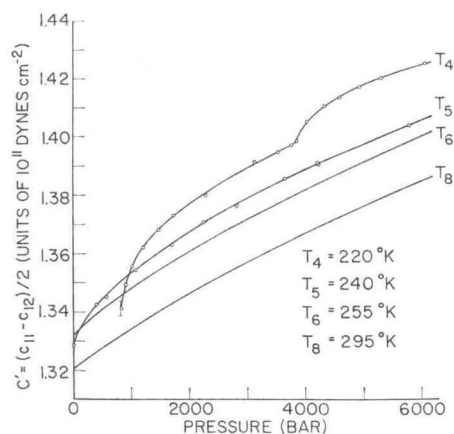

FIG. 5. Variation of $C' = (c_{11} - c_{12})/2$ with pressure. The curves at 255° and 295°K are taken from Paper I. No data could be obtained in the ordered tetragonal phase. The O_T–D lambda transition pressure at T_4 is indicated by a vertical bar.

The transition from O_I to the ordered tetragonal phase was not studied in the present work because single crystals frequently cracked on going through this first-order phase change. This region may be difficult to study with any method if the extreme hysteresis and sluggishness observed in the O_I–O_T phase transition at one atmosphere persist up to the triple point with the O_{II} phase.

Constant-Temperature Data

The experimental values of c_{44}, c_{11}, and C' are shown as functions of pressure at various constant temperatures in Figs. 3–5. In most runs, pressure measurements were made for both increasing and decreasing pressures. The time necessary for equilibrium upon changing the pressure could easily be monitored by observing the in-phase frequency change with time. Generally, 20 min

[14] C. C. Stephenson and H. E. Adams, J. Chem. Phys. **20**, 1658 (1952).

[15] A. G. Cole, Ph.D. thesis, M.I.T., 1952.

was ample time for equilibrium except for points very close to the transition lines. In these cases 30 min was usually long enough. In no case was hysteresis observed. In Fig. 3 the lower portions of the curves at 190°, 200°, 210° and 220°K represent data in the tetragonal phase and should be considered as "average" shear constants $\bar{c}_{44}$; see Paper I for further details. As seen from Figs. 4 and 5, it was not possible to get any data in the tetragonal phase for c_{11} and C' due to the very large attenuation in that phase for the acoustic waves yielding these constants.[16] In Fig. 5 the solid curves shown at 255° and 295°K are taken from Paper I and are included for comparison. These curves have been shifted up by 0.18% to make them internally consistent with the present data. Smooth-curve values of the effective elastic constants as a function of pressure are given in Table I.

Let us now make an estimate of the errors associated with the measurements of the various quantities needed to calculate the elastic constants. The uncertainty in the path length is about 0.02% at 1 atm, and the error due to changes in length with pressure or temperature is probably less than 0.05% even in the regions close to the transitions. The frequency of pulse generation can be measured to within 0.01% consistently. Before this frequency can be used to obtain the round-trip transit time, a correction must be made for the phase shift γ. Since this seal correction never exceeded 0.02% of the measured frequency, even a large error in estimating γ should not cause more than a 0.01% error in the transit time. Variations in temperature during a pressure run could produce an error in c_{ij} of 0.02%, but uncertainties in the pressure determination would not cause a noticeable error. The *random* error in c_{ij} from the above causes is less than 0.2%. All data collected from several different crystals agree to within this limit of error.

A known source of systematic error is the increase in the velocity due to diffraction effects.[17] The velocities were corrected for this effect, and the magnitude of the correction was 0.035% for c_{11}, 0.016% for c_{44}, and 0.01% for C'. An unknown systematic error may occur in calculating the phase shifts since the seal corrections were based on the properties of the bonding material

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[16] This is presumably due to scattering from small tetragonal domains. An attempt was made to obtain a single-domain crystal by exerting a lateral (biaxial) compression perpendicular to one of the original cubic axes. Spring-loaded or screw-tightened plates on the crystal faces did not work; and in order to apply larger and more uniform pressures, the crystal was "potted" in a disk of methylmethacrylate and ethylene glycol dimethacrylate polymer. This polymer has a larger thermal expansion coefficient than ammonium bromide and upon cooling applied a considerable lateral pressure to the sample. This method did not align the tetragonal domains along the unstressed direction but did apply enough pressure to the sample to cause a slight increase in the value of the average shear constant. Thus, it does not appear feasible to align the domains with a modest biaxial pressure on the sides of the crystal.

[17] H. J. McSkimin, J. Acoust. Soc. Am. **32**, 1401 (1960); **33**, 539 (1961).

TABLE I. Smooth-curve values of the effective adiabatic elastic constants as functions of pressure at various temperatures. All entries are given in units of 10^{11} dyn cm^{-2}. Values of the adiabatic bulk modulus $1/\beta^S = (c_{11} - 4C'/3)$ are also given at two temperatures. At 190° and 200°K, the transition pressure p_t is indicated for the first-order phase change from the ordered tetragonal phase to the O_{II} phase. At 210° and 220°K, the critical pressure p_λ is indicated for the O_T–D lambda transition (lower p_λ value) and the D–O_{II} lambda transition (higher p_λ value). At 240°K, no transitions are observed below 6 kbar. The values reported for c_{44} in the ordered tetragonal phase should be interpreted as average shear constants for that phase.

p(kbar)	c_{11}	c_{44}	p(kbar)	c_{11}	c_{44}
			$T_1 = 190°$K		
0	...	0.7315	1.8	3.946	0.993
0.5	...	0.754	2.0	3.974	1.001
1.0	...	0.777	3.0	4.087	1.037
1.5	...	0.7995	4.0	4.173	1.070
$1.53 = p_t(O_T$–$O_{II})$			5.0	4.253	1.1025
1.6	3.917	0.986	6.0	4.323	1.134
			$T_2 = 200°$K		
0	...	0.727	1.8	~3.71	0.9655
0.5	...	0.752	2.0	3.778	0.976
1.0	...	0.780	3.0	3.987	1.018
1.6	...	0.819	4.0	4.107	1.054
$1.65 = p_t(O_T$–$O_{II})$			5.0	4.202	1.087
1.7	...	0.9595	6.0	4.280	1.1195

p(kbar)	c_{44}	p(kbar)	c_{44}	p(kbar)	c_{44}
		$T_3 = 210°$K			
0	0.729	1.5	0.887	3.0	0.982
0.7	0.788	2.0	0.911	3.5	1.0075
1.0	0.813	2.4	0.929	4.0	1.028
1.2	0.832	$2.523 = p_\lambda$	0.935	5.0	1.065
1.3	0.849	2.6	0.947	6.0	1.100
$1.339 = p_\lambda$	0.876	2.8	0.9675		

| p(kbar)	c_{11}	c_{44}	C'	$1/\beta^S$
		$T_4 = 220°$K		
0	...	0.735	...	...
0.4	...	0.7675	...	...
0.6	...	0.7875	...	...
0.7	...	0.801	...	...
0.8	...	0.829	...	...
$0.817 = p_\lambda$	...	0.845	~1.34	...
0.9	3.326	0.851	1.351	1.525
1.0	3.368	0.856	1.357	1.559
1.4	3.496	0.874	1.369	1.671
2.0	3.609	0.899	1.379	1.770
2.5	3.680	0.919	1.386	1.832
3.0	3.736	0.939	1.392	1.880
3.4	3.770	0.955	1.396	1.909
3.6	3.778	0.963	1.398	1.914
3.7	3.774	0.967	1.399	1.909
3.8	3.735	0.971	1.400	1.869
$3.870 = p_\lambda$	>3.6	0.9735	1.401	...
3.9	...	0.977	1.402	...
4.0	~3.68	0.987	1.406	...
4.1	3.732	0.995	1.408	1.854
4.5	3.864	1.019	1.414	1.978
5.0	3.986	1.042	1.419	2.093
5.5	4.072	1.062	1.423	2.174
6.0	4.137	1.081	1.427	2.235
		$T_5 = 240°$K		
0	3.321	0.793	1.328	1.550
0.5	3.434	0.815	1.344	1.642
1.0	3.515	0.836	1.353	1.710
2.0	3.646	0.875	1.367	1.823
3.0	3.755	0.913	1.379	1.917
4.0	3.850	0.950	1.388	1.999
5.0	3.938	0.987	1.397	2.075
6.0	4.024	1.022	1.405	2.151
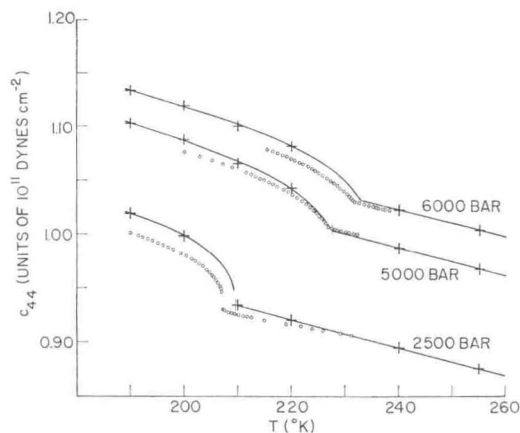
FIG. 6. Variation of c_{44} with temperature: Detail of transition from disordered cubic to O_{II} phase. Crosses represent points take from the smoothed curves in Fig. 3. The circles indicate data points taken on cooling runs during which the pressure varied slightly (see text).

at 1 atm and room temperature and these properties might be different at low temperatures and high pressures. A significant phase shift may also occur at the free end of the sample as the pressure fluid is cooled and compressed.

The $n=0$ condition[3] for c_{11} was independently determined for our crystal, and the present c_{11} value at 240°K and 1 atm differs by 0.05% from the value reported in Paper I, which is well within the experimental error. For C' it was decided to use the values reported in Paper I to get the correct n. In this case the difference between the two C' measurements at 240°K and 1 atm was 0.18%, whereas a change by ±1 in n would give C' values differing by ±2%. The determination of the correct n value is not as easy for c_{44} as for the other two constants. Thus it was felt to be necessary to make another independent check on the previous values. With data on two crystals with different path lengths, the correct n was unambiguously determined, and the present c_{44} value at 240°K and 1 atm was found to differ by 0.25% from the value reported in Paper I. Thus the present data tie in very well indeed with those reported previously.

Constant-Pressure c_{44} Data

Several isobaric plots of c_{44} versus temperature are shown in Fig. 6, where the crosses represent points read from smooth curves of c_{44} as a function of pressure at various constant temperatures. Values of c_{44} at 255°K were taken from Paper I; values at 240°K and below are from the present work. Associated with each curve is a series of open circles. These circles are directly determined data points taken in the closed pressure cell with the temperature slowly varying. Because the system was closed, the pressure naturally decreased as

the cell was cooled. However, the pressure variation is small (about a 400 bar difference between lowest and highest temperature for a given run), and the circles provide a direct indication of the behavior of c_{44} through the lambda transition from disordered cubic to O_{II} as a function of temperature at several almost constant pressures. The lambda point, indicated on each curve by a light vertical line, was determined from the phase diagram given in Fig. 1.

Figure 7 is similar to Fig. 6, with the solid curves representing the temperature dependence of c_{44} at constant pressures of 1300 and 1 bar. At both these pressures the crystal undergoes a lambda transition from disordered cubic to O_T. The curve at 1 bar is taken from Paper I as is the point at 255°K and 1300 bar. The crosses are taken from smooth curves of c_{44} as a function of pressure at various temperatures, and the solid circles are data points taken on a cooling run with the pressure cell closed (again, the pressure changed slightly with the temperature).

As can be seen from Figs. 6 and 7, c_{44} at constant pressure varies in the normally expected way with temperature in the disordered cubic phase. Indeed, when all the data from Paper I and the present investigation are combined, it becomes clear that c_{44} varies in a very regular way with both p and T throughout the entire disordered phase. Over the range 220°–320°K and 0–8000 bar, one can represent c_{44} *in the disordered phase* by

$$c_{44}(p, T) = c_{44}(1 \text{ bar}, 295°K) + 3.85(p-1)$$
$$-2.5 \times 10^{-11}(p-1)^2 - 1.31 \times 10^8(T-295), \quad (3)$$

where c_{44} (1 bar, 295°K) $= 0.728 \times 10^{11}$ dyn cm^{-2} and p is also expressed in dyn cm^{-2} units. The only region for which Eq. (3) is not quite valid is close to the
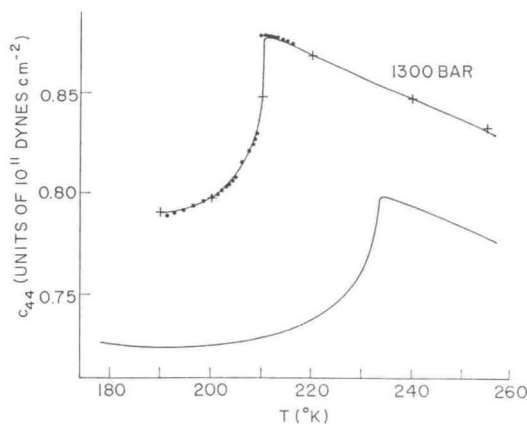

FIG. 7. Variation of c_{44} with temperature: Detail of transition from disordered cubic to O_T phase. The symbols on the upper curve have the same significance as in Fig. 6. The lower curve, taken from Paper I for comparison, represents the directly observed variation at 1 bar.

$D-O_T$ lambda line. There is a very small anomalous variation in c_{44} at temperatures just above this transition line; for example, c_{44} observed at 235°K and 1 bar is 0.005×10^{11} smaller than the value calculated with Eq. (3).

Constant-Volume Data

It is possible to combine the results presented above and those from Paper I to obtain the variation of the effective adiabatic elastic constants with temperature at constant volume. From Fig. 2, one can determine the hydrostatic pressure which must be applied to the crystal at any given temperature in order to maintain its volume at a specified constant value. The value of the constant-volume elastic constant is then obtained by interpolation from the smoothed isothermal plots of c_{ij} as a function of pressure (Figs. 3–5 of this paper together with Figs. 6–8 of Paper I).

Such constant-volume plots of c_{44} and c_{11} in the vicinity of the $D-O_{II}$ lambda line are shown in Figs. 8 and 9. The variation of c_{44} has been evaluated at six values of the volume: $V_1 = 38.12$ cm³ mole⁻¹ corresponds to a cubic lattice parameter $a_1 = 3.985$ Å, and volumes V_2-V_6 correspond to successive increases of 0.005 Å in the lattice parameter; thus a_6 equals 4.010 Å and $V_6 = 38.84$ cm³ mole⁻¹. From Fig. 8 it is evident that the anomalous behavior of the constant-volume c_{44} is essentially the same for every volume. This is in contrast to the isobaric variations shown in Fig. 6, where the anomalous effect diminishes in magnitude and abruptness with increasing pressure. Note also that the anomalous changes in c_{44} at constant volume are opposite in sign to those observed at constant pressure. The variation of c_{11} is only given at a single volume (V_5) in Fig. 9. Unfortunately, there were not sufficient data points near the lambda temperature at other volumes to make a significant comparison between the shape of this V_5 curve and any other.
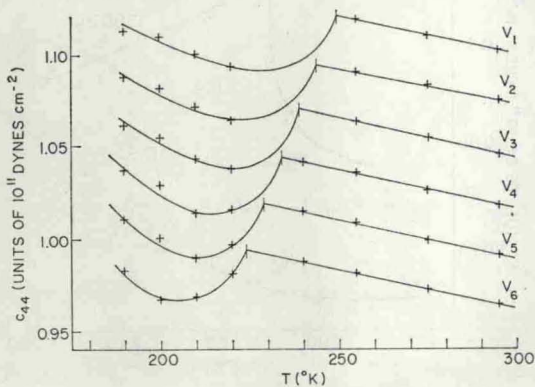
FIG. 8. Variation of c_{44} with temperature at various constant volumes: Region of lambda transition from disordered cubic to O_{II} phase. Crosses represent points taken from smooth-curve plots of c_{44} and V (see text).
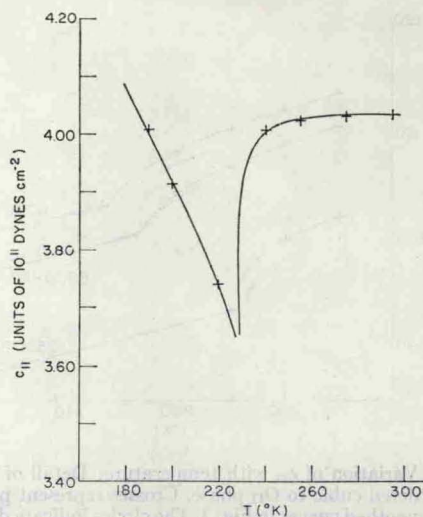
FIG. 9. Variation of c_{11} with temperature at constant volume. Points are shown for $V_5 (a = 4.005$ Å), at which volume the $D-O_{II}$ lambda temperature is 229°K.

DISCUSSION

Behavior far from Any Phase Transition

The temperature and pressure dependence of the elastic constants of ammonium bromide in the disordered cubic phase far from any phase transitions were discussed in Paper I. Our new data in the disordered phase agree very well with those results and will not be discussed further here. It is now possible, however, to compare the "normal" behavior (meaning behavior unaffected by phase transitions) of the disordered phase with that of the O_{II} phase and, to a limited extent, with that of the O_I phase. Significant comparison with the O_T phase is not possible due to the presence of domains and the small $p-T$ range of that phase.

Over-all, the pressure variations of all three elastic constants are very similar in the O_{II} and D phases. As indicated by Eq. (3), $(\partial c_{ij}/\partial p)_T$ values vary somewhat with pressure but little with temperature. Thus, comparison will be made at a given molar volume (i.e., lattice parameter) although the temperatures at which the respective values are evaluated will, of course, differ. For $(\partial c_{11}/\partial p)_T$, one finds 6.9 for the disordered phase at 255°K, 9.3 kbar (3.985 Å) and 7.0 for the O_{II} phase at 190°K, 5.4 kbar (3.985 Å). For $(\partial c_{44}/\partial p)_T$, the corresponding values are 3.3 for the D phase and 3.1_5 for the O_{II} phase. For the other shear constant, $(\partial C'/\partial p)_T = 0.75$ for the D phase at 255°K, 8.5 kbar (3.990 Å) and 0.73 for the O_{II} phase at 220°K, 5.5 kbar (3.990 Å). Also the inequality $P_{44} > P_{11} > P'$, where $P_{ij} = (\partial \ln c_{ij}/\partial p)_T$, holds for the O_{II} phase as it does in the disordered phase. This is what would be expected for a CsCl-type structure[2] and indicates that there is

probably no major change in crystal structure from phase D to phase O_{II} apart from the NH_4^+ ordering and perhaps very small shifts in the Br^- positions.

It is obvious from Fig. 3 that the behavior of c_{44} in the O_I phase is very similar to that in O_{II}: $(\partial c_{44}/\partial p)_T = 3.0$ for O_I at 180°K and 5.5 kbar as compared to 3.1_5 for O_{II} at 190°K and 5.5 kbar. Since the volume in the O_I phase is not well established, one cannot make this comparison at a specified value of the lattice parameter.

Phase Transition Lines

The D–O_T lambda line can be very well represented by the empirical equation

$$p_\lambda = -57.6\Delta T + 0.12(\Delta T)^2, \qquad (4)$$

where p_λ is expressed in bar and $\Delta T = T - 234.5°K$. Thus, the slope of the lambda line varies from -57.6 bar deg^{-1} at 1 atm to approximately -50 bar deg^{-1} near the triple point. It is interesting to compare this observed slope with that which would be predicted on the basis of available thermodynamic data and the Pippard equations.[18] The pertinent equation for our purpose, given in the form derived by Buckingham and Fairbank,[19] is

$$C_p/T = (dp/dT)_\lambda V\alpha + (\partial S/\partial T)_t, \qquad (5)$$

where C_p is the heat capacity at constant pressure, α is the isobaric volume coefficient of thermal expansion, $(dp/dT)_\lambda$ is the slope of the lambda line, and $(\partial S/\partial T)_t$ is essentially a constant. Values for α and V were obtained from Simon and Bergmann,[6] and the values for C_p were taken from Cole.[15] A plot of C_p/T versus $V\alpha$ gave $(dp/dT)_\lambda = -51.8$ bar deg^{-1} and $(\partial S/\partial T)_t = 3.77\times10^6$ erg deg$^{-1}\cdot$mole^{-1}. Although the plot was quite linear near T_λ, it was noticed that the linearity extends over a much greater temperature range below T_λ (perhaps 10°K) than above T_λ (less than 3°K). This is in accord with observations on NH_4Cl, to which the Pippard equations have been successfully applied.[20] Thus, the agreement between the direct experimental and the Pippard values of the slope is fairly good, although a hysteresis of 0.6°K observed in T_λ at 1 atm may complicate the situation at low pressures. This hysteresis is completely absent on crossing the lambda line at 220°K and 817 bar, and it is probably gone even at 400 bar as in the case of NH_4Cl^3.

For the transition line between phases D and O_{II}, the lambda pressure can be quite well represented by the empirical expression

$$p_\lambda = 1870 + 103\Delta T + 1.4(\Delta T)^2, \qquad (6)$$

[18] A. B. Pippard, Phil. Mag. 1, 473 (1956).
[19] M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, C. J. Gorter, Ed. (North-Holland Publ. Co., Amsterdam, 1961), Vol. 3, Chap. 3.
[20] C. W. Garland and J. S. Jones, J. Chem. Phys. 39, 2874 (1963).

where p_λ is expressed in bar and $\Delta T = T - 204°K$. The slope of the lambda line is about 10% larger than that of the lambda line in ammonium chloride and the curvature is about 60% greater.[21] The average slope, however, compares well with a straight line drawn by Stevenson[7] through his much less accurate data on ND_4Br. A slope of ~110 bar deg^{-1} can be estimated for the ND_4Br phase line which Stevenson calls the β–δ transition line. This line and our D–O_{II} lambda line lie very close to one another in pressure–temperature coordinates and almost certainly represent the same phase change for both the deuterated and the normal bromide. It is difficult to determine exactly how close together the two lines are because of the scatter in Stevenson's data, but they are within a few degrees of each other all the way from 2 to 6 kbar. Thus, we predict that a high-pressure transition line should be observed in ND_4Br which is analogous to the O_I–O_{II} line in NH_4Br. If this line exists and lies very close to the position observed in the normal bromide, the O_I–O_{II}–O_T triple point should be located quite near the well-established 1 atm transition temperature between O_I and O_T (which is 166.7°K on warming[22]).

The slope of the phase transition line between O_{II} and O_T varies from 55 bar deg^{-1} at 180°K to essentially zero at $\sim202°K$, where the line terminates in an O_{II}–O_T–D triple point. Since this O_{II}–O_T transition definitely appears to be a first-order phase change, the Clapeyron equation is applicable and the problem arises of justifying either a considerable decrease in ΔS or increase in ΔV as the temperature changes from 180° to 200°K. From the behavior of c_{44} one would certainly conclude that ΔV does not change appreciably over the temperature range considered. It is, however, very possible that the change in entropy on going from phase O_{II} to O_T becomes very small as the triple point is approached. If there is substantial disorder present in both ordered phases for points close to the lambda lines (as suggested by the c_{11} data at 200°K), then the entropy change in going from one "ordered" phase to the other may even approach zero near the triple point. In contrast to the behavior of the O_{II}–O_T line, the O_I–O_{II} transition line has an essentially constant slope of 320 bar deg^{-1}, which suggests a very small volume difference between O_I and O_{II}.

Behavior near the Transition Lines

Very little can be said about the variation of the elastic constants near the O_{II}–O_T phase line, but the behavior of the c_{44} shear wave in Fig. 3 strongly indicates that this is a first-order transition. In contrast to this, the behavior near the D–O_{II} lambda transition is well established and will be discussed in some detail.

First of all, the anomalous behavior of the three

[21] R. Renard and C. W. Garland, J. Chem. Phys. 45, 763 (1966).
[22] C. C. Stephenson and A. Karo, J. Chem. Phys. 48, 104 (1968).

TABLE II. A comparison between the contributions to Δc_{44} in NH$_4$Br and NH$_4$Cl. All c_{44} values are in units of 10^{11} dyn cm^{-2}, and volumes are in cm^3 mole^{-1}. The NH$_4$Br values correspond to a completely ordered crystal in the O_{II} phase; the NH$_4$Cl values were taken from Ref. 12.

	$T(°K), p(\text{bar})$	$(\partial c_{44,dl}/\partial V)_T$	ΔV	$(\partial c_{44,dl}/\partial V)_T \Delta V$	$c_{44,I}$	Δc_{44}
NH$_4$Br	190°, 5000	−0.193	−0.42	0.081	−0.03	0.051
NH$_4$Cl	265°, 4500	−0.243	−0.085	0.021	0.027	0.048

NH$_4$Br elastic constants in the vicinity of the D–O_{II} lambda line, as shown in Figs. 3–6, is very similar to the type of behavior observed near the lambda line in NH$_4$Cl.[3] Neither c_{44} nor C' show any appreciable anomaly in the disordered phase. On crossing the lambda line, both shear constants undergo an anomalously rapid increase over a fairly wide p–T range and then eventually revert to a "normal" behavior. This effect is much smaller in the case of C' than for c_{44}; thus, the best detailed information near the transition point comes from c_{44} data. As shown clearly in Fig. 6, the detailed behavior in the transition region varies with pressure and the most abrupt increases in c_{44} take place at the lowest pressures. The change in c_{44} is so sudden that it may be discontinuous in this lower pressure range (1850–2500 bar). This behavior is also analogous to that observed in ammonium chloride.[3] For c_{11}, the extent of the anomalous behavior is even greater than for c_{44}, as indicated by the 220°K data in Fig. 4. In this case there is a rapid variation in the ordered *and* in the disordered phase (extending perhaps 2 kbar below p_λ). It is difficult to determine the extent of the effect of the D–O_{II} lambda transition because of the overlapping effect of the D–O_T lambda transition. The effect that one does see, however, is a substantial decrease in the value of c_{11} as the D–O_{II} transition line is approached from the disordered phase, with a very sharp dip accompanied by high attenuation right at the transition. In phase O_{II}, c_{11} rises very rapidly and goes far higher than one might expect on the basis of an extrapolation of c_{11} from the disordered phase far from the influence of phase transitions. The c_{11} curve at 200°K, and even at 190°K, shows a considerable droop although these isotherms do not actually cross any lambda line; such an effect can be explained by the considerable p–T range of anomalous c_{11} behavior.

In view of all the above similarities between the elastic behavior in the bromide and the chloride, one might be led to believe that the corresponding lambda transitions are acoustically indistinguishable, which would suggest that the O_{II} phase of NH$_4$Br is perhaps identical to the ordered phase of NH$_4$Cl. This conclusion can be shown to be false by examining the constant-volume variation of c_{44}. As shown in Fig. 8, the c_{44} anomaly at constant volume is opposite in sign to that observed in isothermal or isobaric plots. The marked *decrease* in c_{44} on ordering at constant volume is in striking contrast

with the behavior in NH$_4$Cl, where there is an anomalous increase in c_{44} on ordering even after the volume effect has been eliminated.[3] Thus, the ordering in the O_{II} phase of NH$_4$Br can be proved acoustically to be different from that in the parallel-ordered cubic phase of NH$_4$Cl.

A more quantitative comparison of the c_{44} variation in ammonium bromide and chloride can be made by appealing to some of the results of the compressible Ising model which has been successfully applied to the chloride. It has been shown that the anomalous changes in c_{44} contain contributions from two distinct effects: the primary effect of ordering at constant volume and the secondary effect of the volume change which occurs as a result of ordering. At a given p and T, one has[12]

$$\Delta c_{44} = c_{44,I} + (\partial c_{44,dl}/\partial V)_T \Delta V, \qquad (7)$$

where $\Delta c_{44} = (c_{44} - c_{44,dl})$ and $\Delta V = V - V_{dl}$; c_{44} and V are the actual values of the shear stiffness and molar volume, while $c_{44,dl}$ and V_{dl} are the values in a hypothetical reference state which is completely disordered at that p and T (see Ref. 12 for further details). The quantity $c_{44,I}$ is the constant-volume Ising (configurational) contribution. We shall not be concerned here with a detailed analysis of the behavior of Δc_{44} as a function of temperature or pressure, but will apply Eq. (7) to a limiting case where the crystal is completely ordered. Under these conditions the experimental values of Δc_{44} and $-\Delta V$ will assume their maximum values and the resulting $c_{44,I}$ value should represent a limiting value also. A comparison of the various quantities in Eq. (7) for NH$_4$Br and NH$_4$Cl is given in Table II, and one can see immediately why the over-all effect of ordering is almost the same for both salts in spite of the marked difference in the effect at constant volume. The anomalous volume change in the bromide is so much larger than the volume change in the chloride that the negative $c_{44,I}$ contribution in NH$_4$Br is completely offset and Δc_{44} is positive. The $c_{44,I}$ value for NH$_4$Cl is very close to the maximum value of 0.03×10^{11} dyn cm^{-2} reported previously,[12] and the $c_{44,I}$ value for NH$_4$Br compares reasonably with the limiting values of $-0.035 \pm 0.005 \times 10^{11}$ dyn cm^{-2} which can be inferred directly from the constant-volume curves in Fig. 8.

As a final comment on the D–O_{II} transition, it should be noted that the constant-volume c_{11} variation shown

in Fig. 9 is very similar to that observed in NH_4Cl (see Fig. 4 of Ref. 3). It has been shown[3,4] that the dominant configurational contribution to c_{11} near a lambda line is a negative term which varies like the configurational heat capacity. Hence, one expects that c_{11} should display a very pronounced minimum at the lambda point, as it does. It would be of interest to make high-pressure thermal measurements in the vicinity of this new lambda transition since there would certainly be a large excess heat capacity related to the $D-O_{II}$ ordering process.

Near the phase transition from the disordered cubic to the ordered tetragonal phase, the behavior of the elastic constants is quite different from that discussed above. Upon approaching the $D-O_T$ lambda line, the C' values in the disordered phase exhibit a marked dip whereas there is no anomalous effect near the $D-O_{II}$ lambda line until the transition is reached. This C' dip is quite pronounced with the C' values 2% lower than would normally be expected, which is about twice the maximum change in C' caused by ordering in the O_{II} phase. This precursor effect occurs over a rather wide p-T range since the anomalous variation can be observed at least 20 deg above the lambda point at 1 atm and at least 2000 bar above the lambda point at 220°K and 817 bar. (It is somewhat difficult to determine if the C' variation has become "normal" even at 3000 bar due to the high-pressure phase change to O_{II}.) Unfortunately, the acoustic shear wave from which C' is obtained was so highly attenuated in the O_T phase that no data were obtained there. In the case of c_{11}, the effect is quite similar to that observed at the $D-O_{II}$ transition, although once again it is difficult to get a complete picture near the transition since data could not be obtained in the tetragonal phase.

Figures 6 and 7 show that the c_{44} anomaly associated with the $D-O_T$ phase change is similar in shape but opposite in sign to that observed for the $D-O_{II}$ phase change. Since the molar volume *increases* upon ordering in the O_T phase, this alone would cause a substantial decrease in the value of c_{44}. The anomalous change in c_{44} at constant volume has also been found to be negative making the total isobaric effect larger than just the volume effect alone. The effect of the $D-O_T$ phase change on c_{44} has been compared at two different pressures in Fig. 7, and it appears that the anomalous effect gets slightly more pronounced at higher pressures. This is in contrast to the results obtained along the $D-O_{II}$ phase line and along the lambda line in ammonium chloride. The absolute magnitude of Δc_{44}, evaluated at a temperature 20°K below T_λ, is 0.113×10^{11} dyn cm^{-2} for the transition occurring at 1300 bar as compared to 0.090×10^{11} dyn cm^{-2} at 1 bar. Constant-volume c_{44} curves in this region do not show such an effect; thus it seems almost certain that the variation of Δc_{44} with pressure is primarily a volume effect (see Fig. 2). It would be interesting to make a direct measurement of

the anomalous volume variations along the $D-O_T$ lambda line to confirm this prediction that the volume anomalies become larger as the pressure is increased.

Ordering in Ammonium Bromide

The ordering of the ammonium ions in ammonium bromide is obviously much more complex than in the case of ammonium chloride since three ordered phases are now known to exist in the bromide as compared to only one in the chloride. Thus, a generalized phase diagram for all the ammonium halides, such as proposed by Stevenson,[7] does not exist. However, it does seem possible that a phase corresponding to the O_{II} phase may exist in ammonium iodide. If there were such a phase for the iodide, it would explain the fact that the slope of the first-order $\delta-\gamma$ transition line given by Stevenson appears to undergo a change in sign.

The question for ammonium bromide, however, is the nature of the two ordered phases O_I and O_{II}. It seems most reasonable that one of these must be the parallel-ordered CsCl form established for the chloride and for the deuterated bromide,[1] and, by analogy with the deuterated salt, one would assign this form to phase O_I. This choice is consistent with the fact that O_I has a CsCl-type cubic structure[9] and with recent infrared investigations[23] at 21°K. There is also the significant acoustic difference between the $D-O_{II}$ lambda transition and the lambda transition in the chloride, as evidenced by the constant-volume c_{44} data. However, it should be noted that there has been no direct determination of the hydrogen positions in phase O_I.

If O_I corresponds to the parallel-ordered cubic phase, then what is the nature of the ordering in O_{II}? From an analysis of all the possible ordered structures in which the unit cell is no larger than 8 times the unit cell of the disordered cubic form, there appear to be two reasonable possibilities for the structure of phase O_{II}. In such a consideration of various structures, one would like to be able to show that one phase is energetically more favorable than another. The difficulty is that one of the *least* energetically favorable phases in terms of the repulsive forces between neighboring ammonium ions is the antiparallel O_T phase, which, of course, is known to exist. In addition, Nagamiya[24] has shown that a sufficiently polarizable anion could stabilize even a completely antiparallel configuration. If the bromide ion is allowed to move, then there are still further possibilities for lowering the energy of an ordered phase.[24] The two structures discussed below both have a lower energy due to the repulsive forces between hydrogens than the ordered tetragonal phase, and thus are certainly possible from an energy standpoint.

One of our two proposed structures for the O_{II} phase

[23] N. E. Schumaker, Ph.D. thesis, M.I.T., 1968.
[24] T. Nagamiya, Proc. Phys. Math. Soc. Japan 25, 540 (1943).

is shown in Fig. 10. In part A of this figure, L and R stand for left-handed and right-handed, which denote the two possible orientations of the ammonium ions. In this structure one-quarter of the NH_4^+ ions are L, and each L has six R's as nearest neighbors. To visualize the positions of the hydrogens, consider the eight ammonium ions (two L's and six R's) surrounding a given bromide ion. One of the L ammonium ions and the three R's nearest to that L will have a hydrogen pointing directly at the bromide. No other hydrogens are pointing toward that bromide from the other four ammonium ions. By analogy with the O_T structure, the bromide ion might be able to stabilize this configuration by moving in the direction of that L ammonium ion. This postulated bromide ion motion around each L is indicated by the arrows in part B of Fig. 10.

The unit cell for this proposed structure is 8 times
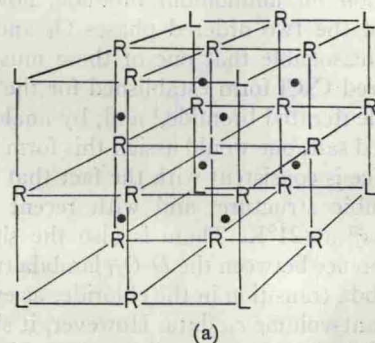
(a)
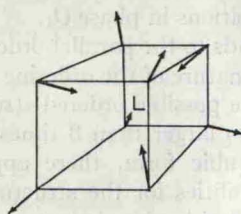
(b)

FIG. 10 Proposed crystal structure of O_{II} phase of NH_4Br. (a) Solid circles represent the bromide ions, and L or R represent ammonium ions with left-handed or right-handed orientations. (a) The arrows represent the direction of the displacement of the bromide ions around each left-handed ammonium ion. The four arrows inside the elementary cube point toward the hydrogens on the ammonium ion at the center.

larger than the disordered cubic unit cell. The number of nearest-neighbor pairs of ammonium ions which have an antiparallel orientation (i.e., R next to a L) is one-half the total number of such pairs. This is the same fraction as in the disordered cubic form and is less than the two-thirds antiparallel pairs in the ordered tetragonal phase. Obviously, to get a transformation from the disordered cubic phase to an ordered phase such as that shown in Fig. 10, the bromide ions would have to lower the energy through polarization or displacement but not as much as for the tetragonal phase. It is the possibility of a displacement of the bromide in a manner very similar to that which is known to occur in the tetragonal phase of ammonium bromide which makes this structure particularly appealing. In addition, this structure is cubic and the ultrasonic data strongly suggest that the elastic properties in O_{II} are the same along all the original cubic axes (nor is attenuation due to domain scattering observed).

The other possible structure for O_{II} involves alternating planes of all L ammonium ions and all R ammonium ions. In this structure, each bromide ion would be surrounded by four coplanar hydrogens. These hydrogens would lie in a (110) plane (with respect to the original disordered cubic axes) passing through the bromide. There is no possibility for a stabilizing displacement of the bromide ion with respect to the hydrogens other than a uniform contraction of the entire lattice. However, the polarizability of the bromide ion might be large enough to stabilize the structure without a Br^- displacement. This structure has the advantage of not needing as much stabilization from bromide contributions anyway, because only one-third of the nearest-neighbor NH_4^+ pairs are antiparallel. Thus this configuration has a lower energy than the disordered cubic structure without the Br^- ions playing any special role. On the other hand, this structure is formally tetragonal and there is no ultrasonic evidence of a unique axis.

An x-ray investigation at around 190°K and 2 kbar should settle whether the O_{II} phase is cubic or not and might also indicate whether there are systematic displacements in the Br^- positions, but a high-pressure neutron-diffraction study of NH_4Br or ND_4Br would be of even greater interest.