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

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

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

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
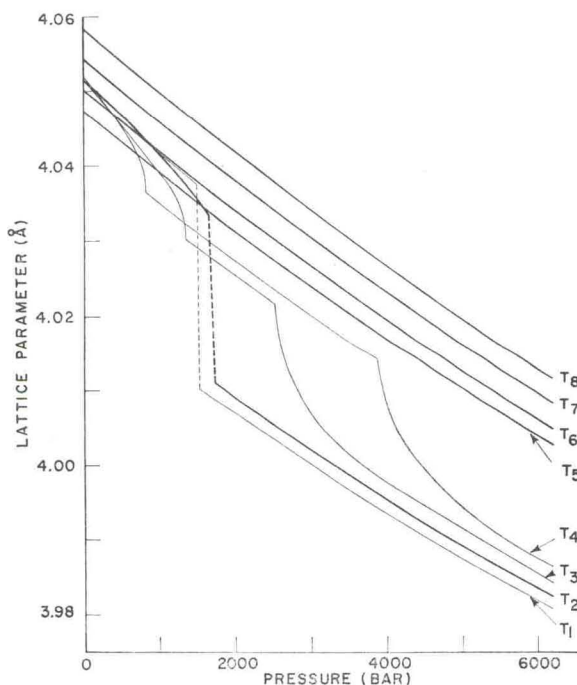

FIG. 2. Variation of the lattice parameter with pressure. Heavy curves at 200°, 240°, 255°, 275°, and 295°K are accurately known, whereas the three lighter curves are less well established (see text). Lattice parameters in the tetragonal phase (low-pressure portions of the 190° and 220°K curves) represent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

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 tetragonal 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.