

probably no major change in crystal structure from phase *D* to phase *O*_{II} apart from the NH₄⁺ 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 3.1₆ 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

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

where *p*_λ is expressed in bar and $\Delta T = T - 234.5^\circ\text{K}$. 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

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

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 *Vα* gave $(dp/dT)_\lambda = -51.8$ bar deg⁻¹ and $(\partial S/\partial T)_t = 3.77 \times 10^6$ erg deg⁻¹·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 NH₄Cl, 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 817₄ bar, and it is probably gone even at 400 bar as in the case of NH₄Cl³.

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

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

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 $\Delta T = T - 204^\circ\text{K}$. 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 Stevenson⁷ through his much less accurate data on ND₄Br. A slope of ~ 110 bar deg⁻¹ can be estimated for the ND₄Br 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 ND₄Br which is analogous to the *O*_I-*O*_{II} line in NH₄Br. 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 warming²²).

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 $\sim 202^\circ\text{K}$, 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_4Br and NH_4Cl . All c_{44} values are in units of 10^{11} dyn cm^{-2} , and volumes are in cm^3 mole $^{-1}$. The NH_4Br values correspond to a completely ordered crystal in the O_{II} phase; the NH_4Cl values were taken from Ref. 12.

	$T(^{\circ}\text{K}), p(\text{bar})$	$(\partial c_{44,dl}/\partial V)_T$	ΔV	$(\partial c_{44,dl}/\partial V)_T \Delta V$	$c_{44,I}$	Δc_{44}
NH_4Br	190°, 5000	-0.193	-0.42	0.081	-0.03	0.051
NH_4Cl	265°, 4500	-0.243	-0.085	0.021	0.027	0.048

NH_4Br 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_4Cl .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_4Br is perhaps identical to the ordered phase of NH_4Cl . 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_4Cl , 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_4Br can be proved acoustically to be different from that in the parallel-ordered cubic phase of NH_4Cl .

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 has¹²

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

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_4Br and NH_4Cl 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_4Br is completely offset and Δc_{44} is positive. The $c_{44,I}$ value for NH_4Cl 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_4Br 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