

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 δ - γ 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 structure⁹ and with recent infrared investigations²³ 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, Nagamiya²⁴ 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.

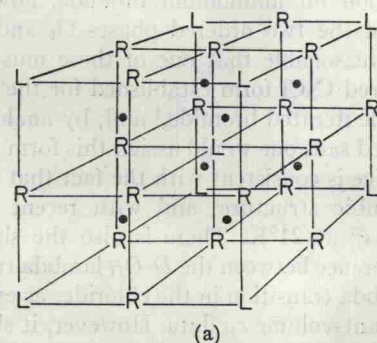
One of our two proposed structures for the O_{II} phase

²³ N. E. Schumaker, Ph.D. thesis, M.I.T., 1968.

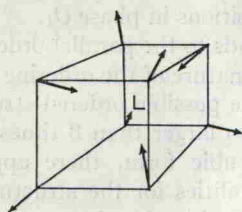
²⁴ T. Nagamiya, Proc. Phys. Math. Soc. Japan **25**, 540 (1943).

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.