

## Neutron-diffraction measurements on the $P$ - $T$ phase diagram of ammonium bromide

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The  $P$ - $T$  phase diagram of  $\text{ND}_4\text{Br}$  and  $\text{NH}_4\text{Br}$  has been investigated by neutron-diffraction techniques. Although many of the features previously reported have been confirmed, a new high-pressure phase could not be found. Measurements of the hysteresis of the II-III transition as a function of pressure indicate that the transition is discontinuous at all pressures and that no tricritical point exists along this phase line. The lattice constant of  $\text{ND}_4\text{Br}$  has been measured as a function of temperature by x-ray diffraction.

### I. INTRODUCTION

At high temperatures the ammonium halides crystallize within the rocksalt structure<sup>1</sup> (space group  $Fm\bar{3}m$ ) in which the ammonium group is orientationally disordered. Near 100°C the center-of-mass arrangement transforms to the CsCl structure. Various modifications<sup>1</sup> of the latter exist: Phase II is orientationally disordered (space group  $Pm\bar{3}m$ ) with the  $\text{NH}_4^+$  tetrahedra randomly distributed over two equivalent orientations. Phase III is slightly distorted with respect to the ideal CsCl structure (space group  $P4/nmm$ ). The  $\text{NH}_4^+$  tetrahedra are antiorordered within the  $a$ - $b$  plane, and stacked parallel along the  $c$  axis. The transition to this phase is not entirely orientational in character, because simultaneously with the orientational ordering of the  $\text{NH}_4^+$  groups the  $\text{Br}^-$  ion shifts away from the high-symmetry position of the CsCl structure. Phase IV, finally, is ordered parallel (space group  $P\bar{4}3m$ ).

The phase diagram of  $\text{NH}_4\text{Br}$  in temperature-pressure space<sup>2,3</sup> is shown in Fig. 1(a). In contrast to  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{Cl}$  does not exhibit an antiorordered phase III. Stevenson showed, however, that the phase diagram of  $\text{NH}_4\text{Cl}$  has the same features as that of  $\text{NH}_4\text{Br}$ , the essential difference being the origin of the pressure axis.<sup>2</sup> Two approaches<sup>4-7</sup> have been used to explain the existence of the various modifications of CsCl-type  $\text{NH}_4\text{Br}$ . Both are based on the concept of competing interactions, which can either give rise to parallel or antiparallel order. A direct octupole-octupole interaction between nearest-neighbor  $\text{NH}_4^+$  ions favors a parallel ordering. The stabilization of antiparallel order is due to an indirect interaction, which is introduced in terms of a (pseudo) spin-phonon coupling by Yamada *et al.*<sup>4</sup> On the other hand, in Hüller's<sup>5-7</sup> approach the indirect interaction is provided by an electrostatic interaction be-

tween tetrahedra via the polarizable halide ions. At least a qualitative understanding of the ammonium halides has been achieved in both of these approaches. However, some puzzling features appear to remain—in particular, the case of the ammonium bromides. A measurement of the ultrasonic propagation in  $\text{NH}_4\text{Br}$  as a function of both pressure and temperature by Garland and Young<sup>3</sup> confirmed the phase lines first reported by Stevenson.<sup>2</sup> In addition a new high-pressure phase line was observed at somewhat higher temperatures, indicating the presence of a new phase V in a narrow region between the disordered phase II and the parallel-ordered phase IV. It was proposed that this new phase could have an intermediate type of order, with three tetrahedra having one orientation and the fourth having the other (space group  $I\bar{4}3m$ ). A neutron-diffraction study is an obvious choice to clarify these questions, and in this paper we report experiments carried out with both  $\text{ND}_4\text{Br}$  powder and  $\text{NH}_4\text{Br}$  single crystals, using a cryostat with a high-pressure cell.

Another interesting question is whether there is a tricritical point (TCP) on the phase line separating the tetragonal antiparallel-ordered phase

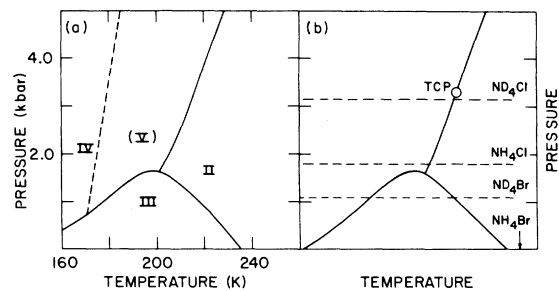


FIG. 1. (a) Phase diagram for  $\text{NH}_4\text{Br}$  reported in Refs. 2 and 3. (b) Modified generalized phase diagram for the ammonium halides.

III and the cubic disordered phase II. TCP's have been observed on the phase line separating phases II and IV in<sup>8,9</sup>  $\text{NH}_4\text{Cl}$  ( $P_{\text{TCP}} = 1.5$  kbar) and<sup>10</sup>  $\text{ND}_4\text{Cl}$  ( $P_{\text{TCP}} = 128$  bar), respectively. While the corresponding TCP's exist in<sup>3</sup>  $\text{NH}_4\text{Br}$  ( $2.5 \leq P_{\text{TCP}} \leq 5$  kbar) and  $\text{ND}_4\text{Br}$ —although their location on the phase line has not been accurately determined so far—the question of an additional TCP on the phase line between phases II and III remains. Since the fields conjugate to the order parameters in phases III and IV, respectively, cannot be realized experimentally, variation of pressure or composition seems to be the only practical means to change the relative magnitude of the competing interactions other than by temperature. We have investigated the nature of the II-III transition in  $\text{NH}_4\text{Br}$  as a function of pressure, in contrast to recent investigations at atmospheric pressure in which composition was varied ( $\text{NH}_4\text{Cl}_x\text{Br}_{1-x}$ ).<sup>11,12</sup>

As mentioned above, it is useful to construct a  $P$ - $T$  phase diagram common to  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ .<sup>2</sup> There is, however, a sizable isotope effect upon deuteration as well. At atmospheric pressure the transition temperature  $T_{\text{II} \rightarrow \text{III}}$  decreases from 235 to 215 K, in contrast to the usual situation. In general, orientational order-disorder transitions tend to shift toward higher temperatures as a result of deuteration. This feature will be considered in Sec. V.

## II. EXPERIMENTAL

Most of the neutron-diffraction measurements were carried out on a triple-axis spectrometer at the Brookhaven High Flux Beam Reactor. Measurements were performed at an incoming energy  $E_i = 13.7$  meV ( $\lambda = 2.46$  Å) with pyrolytic graphite as monochromator and analyzer and with all collimators having 20 min horizontal divergence. The use of an analyzer set for the same energy as the monochromator significantly improved the signal-to-noise ratio, which was particularly useful in the case of the hydrogenous sample.  $\text{ND}_4\text{Br}$  powder was obtained from the J. T. Baker Chemical Co. with a quoted deuteration of >99%. The powder was passed through a 200-mesh sieve in a glove box containing  $\text{P}_2\text{O}_5$  as desiccant, in order to minimize the exchange reaction with atmospheric  $\text{H}_2\text{O}$ . The powder was finally compressed into cylindrical pellets (outside the dry box) about 2.5 cm long and 1 cm in diameter.

The  $\text{NH}_4\text{Br}$  single crystal was a slice from a larger crystal cut with a diamond saw. The slice had dimensions  $12 \times 1.5 \times 1.2$  mm<sup>3</sup>, with the long axis parallel to  $[1\bar{1}0]$ . The mosaic distribution was essentially Gaussian, with a full width at half-maximum of  $1.3^\circ$ . The large mosaic is probably

related to a large visible defect in the center of the original crystal. All neutron-diffraction measurements were made in a Cryogenic Associates CT-14 cryostat with a pressure cell which has been described in more detail elsewhere.<sup>13</sup> The pellet essentially filled the entire cell volume, but for the single crystal an aluminum holder was machined to fill the empty volume and hold the sample in place. Pressures were measured with a manganin gauge (precision  $\pm 5$  bar); below 1.5 kbar, a Heise gauge was used as an additional check. Temperatures were controlled to within 0.003 K, with an absolute accuracy of about  $\pm 0.02$  K. No obvious gradient in the sample was observed.

## III. NONEXISTENCE OF AN ADDITIONAL HIGH-PRESSURE PHASE (V)

As mentioned in Sec. I the ultrasound measurements of Garland and Young indicated the presence of a new phase V in  $\text{NH}_4\text{Br}$ . Since there was no evidence of any departure from cubic symmetry, either the intermediate structure<sup>3</sup> (space group  $I\bar{4}3m$ ) previously mentioned, which is analogous to a ferrimagnet, or a cubic ordered structure analogous to a  $G$ -type antiferromagnet (space group  $F\bar{4}3m$ ) seemed to be plausible. Both of these give rise to characteristic superlattice reflections.

Despite the fact that the above phase diagram was established in the hydrogenous materials, the initial experiments were performed with  $\text{ND}_4\text{Br}$  powder—because of the better signal-to-noise ratio from deuterium as compared to hydrogen. At a pressure  $P = 2.07$  kbar a number of reflections which increase considerably in intensity from the disordered phase II to the parallel-ordered phase IV were scanned as a function of temperature down to 185 K [Fig. 2(a)]. Only one transition was observed at  $T = 214$  K, there being no other anomalous changes in either the Bragg intensities or the lattice constants. Subsequently, powder patterns were recorded just above and below the observed phase transition temperature ( $T_1 = 220$ ,  $T_2 = 208$  K) and, additionally, at  $T = 255$  K. The two measurements at higher temperatures yield a powder pattern typical for the disordered phase II, while at  $T_2 = 208$  K the pattern indicates the presence of the parallel-ordered phase IV. No superlattice reflections have been observed at any temperature. The conclusion is that there is no additional phase V in  $\text{ND}_4\text{Br}$ . To confirm this conclusion, temperature scans were extended to pressures  $P = 3.04$  and 4.16 kbar [Figs. 2(b), 2(c)]. Again just one phase transition is observed. The sensitivity of these powder measurements is

rather low, which is why transition temperatures can be given only to within about  $\pm 1$  K. We may note, however, that the temperatures quoted by Stevenson<sup>2</sup> are systematically too low by about 10–12 K. Furthermore, the data indicate that the phase transition is discontinuous at  $P=2$  kbar, while it is continuous at high pressures. This suggests the presence of a tricritical point—equivalent to the ones observed in  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$  at a pressure of about 2.5–3 kbar. Single-crystal measurements are required to locate this point more accurately.

Despite the fact that the existence of a phase V in  $\text{NH}_4\text{Br}$  but not in  $\text{ND}_4\text{Br}$  seemed rather unlikely, further measurements were carried out with an  $\text{NH}_4\text{Br}$  single crystal. A single-crystal measurement has the disadvantage that it is impractical to search more than a small fraction of reciprocal space, but on the other hand  $\text{NH}_4\text{Br}$  powder gives a rather low signal-to-noise ratio for the Bragg peaks. Analogous to the procedure adopted with  $\text{ND}_4\text{Br}$ , a Bragg peak which strongly increases in

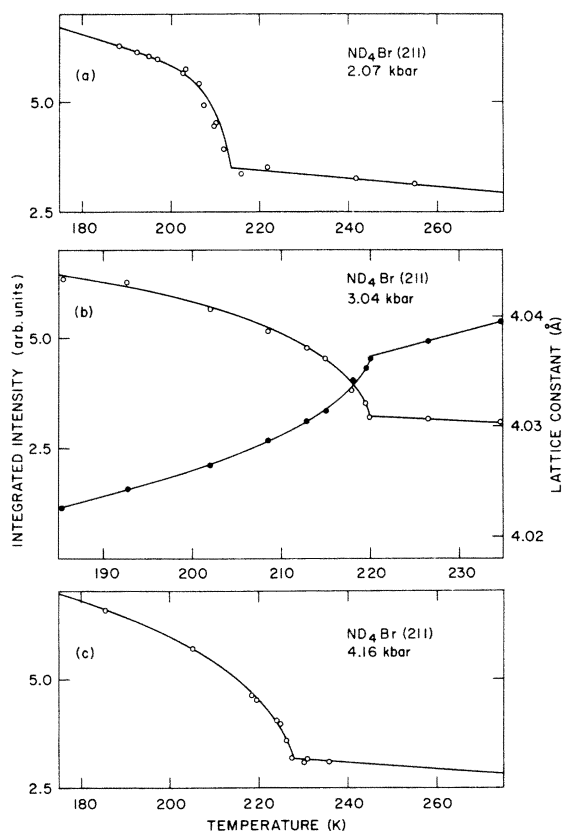


FIG. 2. Integrated intensity of the (211) reflection from polycrystalline  $\text{ND}_4\text{Br}$  as a function of temperature at three different pressures; (a) 2.07 kbar; (b) 3.04 kbar (note also the dependence of the lattice parameter on temperature); (c) 4.16 kbar.

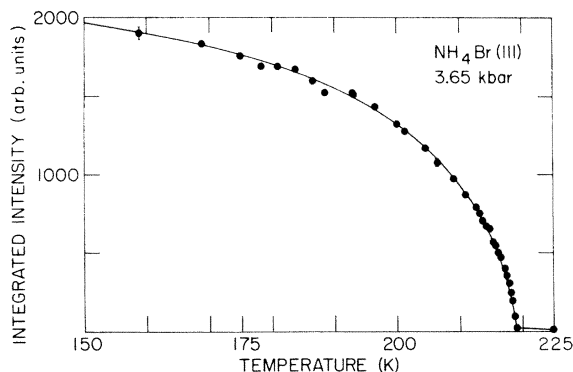


FIG. 3. Integrated intensity of the (111) reflection from single-crystal  $\text{NH}_4\text{Br}$  as a function of temperature at 3.65 kbar. The line is only a guide to the eye. The integrated intensity of the Al powder peak is approximately 80 units on this scale.

intensity from phase II to phase IV was investigated as a function of temperature. In the case of  $\text{NH}_4\text{Br}$  the (111) reflection is more suitable for this purpose. There is, however, an aluminum powder peak (sample cell) nearby. This was accounted for by fitting the peaks obtained with  $\theta$ - $2\theta$  scans with two Gaussians. Integrated intensities so obtained at 3.65 kbar for  $\text{NH}_4\text{Br}$  (111) are shown in Fig. 3 and the lattice constant as extracted from the peak positions in Fig. 4. Again only one phase transition is observed at 219.16 K. This agrees well with the “new” phase line observed by Garland and Young. An extensive search for superlattice peaks of the alternate structures described above and along principal symmetry directions at various temperatures below  $T=219.16$  K was performed. The sensitivity of these single-crystal measurements is rather high: the stronger Bragg peaks yield counting rates more than three orders of magnitude above the noise level. Again there was no indication of a superstructure in this phase.

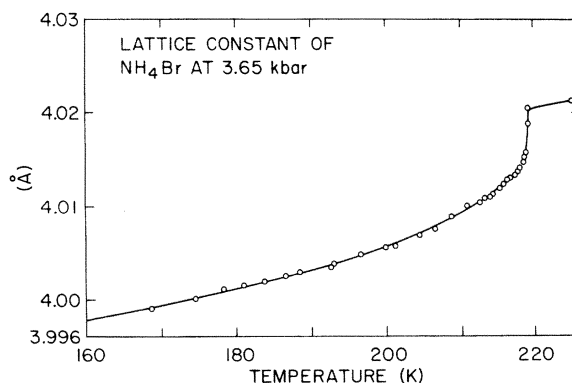


FIG. 4. Lattice constant of single-crystal  $\text{NH}_4\text{Br}$  as a function of temperature at 3.65 kbar.

We have to conclude, therefore, that the ammonium bromides do not possess an additional phase V and that there is only one phase line separating disordered and ordered cubic phases II and IV. This finding agrees with a recent measurement by Couzi *et al.*<sup>14</sup> Prompted by the equivalence of the phase diagrams of  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$  these authors looked for an additional phase line in  $\text{NH}_4\text{Cl}$  under pressure.

Some measurements were carried out on a double-axis spectrometer at the High Flux Isotope Reactor at Oak Ridge, using a neutron wavelength  $\lambda = 1.27 \text{ \AA}$  and a high-pressure cell that has been described elsewhere.<sup>10</sup> The shorter wavelength used here permitted the scanning of relatively high-order reflections, allowing for the possibility that the structural changes associated with a phase V are small displacements which are evident only at large wave-vector transfers. Powder patterns for  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$  were obtained in regions of  $(P, T)$  corresponding to phases II, III, and IV (Fig. 1), with results clearly characteristic of each phase. Scans in the reported phase-V region were virtually identical to phase-IV scans. As expected, the undeuterated powder gave rise to a rather high level of incoherent scattering background. However, this background was completely flat and the scans for  $\text{NH}_4\text{Br}$  were almost equal in quality to those for  $\text{ND}_4\text{Br}$ . Additional scans in which the (211) intensity of  $\text{NH}_4\text{Br}$  was monitored as  $T$  was varied at constant  $P$  were also obtained, at  $P = 2.7$  and  $2.4$  kbar. These scans showed no indication of a phase boundary separating phase IV from a new phase V.

As in the case of  $\text{ND}_4\text{Br}$  one may proceed to ask whether the II-IV transition in  $\text{NH}_4\text{Br}$  changes from a continuous to a discontinuous one. Garland and Young's measurement shows the II-IV transition to change from first to second order between 2.5 and 5 kbar. According to the present measurements, the transition still appears to be continuous at 3.65 kbar (Fig. 3), i.e., no difference between heating and cooling runs is observed within experimental accuracy, which suggests that the TCP along the II-IV phase line is located between 2.5 and 3.65 kbar. An accurate determination of the TCP following the method used by Yelon *et al.*<sup>10</sup> was attempted but was not successful. The critical scattering from the small  $\text{NH}_4\text{Br}$  sample was not sufficiently strong to allow measurements similar to the ones performed in  $\text{ND}_4\text{Cl}$ . A fit of the (111) intensity over the reduced temperature range  $\epsilon = (T_c - T)/T_c < 0.1$  to a power law  $I \sim \epsilon^{2\beta}$  yielded an exponent  $\beta = 0.26 \pm 0.01$ , which indicates the vicinity of a TCP. A more detailed investigation of the TCP with neutrons on a  $\text{ND}_4\text{Br}$  single crystal is clearly desirable.

#### IV. CUBIC TO TETRAGONAL TRANSITION (II-III)

For quite some time there has been a question as to whether the II-III transition in  $\text{NH}_4\text{Br}$  at atmospheric pressure is continuous or not. This is related to the possible presence of a TCP on the II-III phase line. A recent measurement of the optical birefringence in  $\text{NH}_4\text{Br}$  by Brunskill *et al.*<sup>15</sup> shows a jump in the birefringence as well as hysteresis, both indicating a discontinuous transition. We have made measurements of the order parameter of the antiparallel-ordered phase III by scanning a superlattice reflection (301) as a function of temperature during heating and cooling cycles at different pressures. The integrated intensities derived from these scans are shown in Fig. 5. The hysteresis at a given pressure will be taken as a measure of the discontinuity of the transition. A more complete analysis of the data, including the effects of nucleation, to determine true stability limits of the respective phases, as made by Jahn and co-workers,<sup>12,15</sup> was not attempted. Figure 6 shows the values obtained for the hysteresis as a function of pressure. At pressures close to the triple point but still in a regime where  $dP_{\text{II-III}}/dT$  is fairly linear, a rather pronounced temperature hysteresis  $H$  is observed.  $H$  decreases with decreasing pressure—that is, with increasing distance from the triple point—so one might expect  $H$  to become zero at a finite pressure. Yet at lower pressures  $H$  seems to level out at some constant value, or maybe even increase slightly, as indicated by the broken line in Fig. 6. This rules out the presence of a second TCP in  $\text{NH}_4\text{Br}$ . For a detailed understanding of this behavior the inclusion of both the lattice compressibility and the effect of pressure on the competing interactions would be necessary. The  $P$ - $T$  values of the II-III phase lines obtained in these measurements agree well with Garland and Young's data.

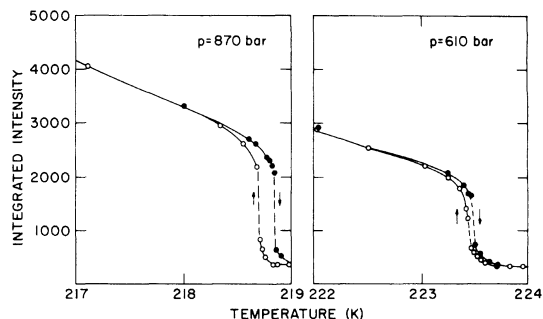


FIG. 5. Integrated intensity of the (301) reflection from single-crystal  $\text{NH}_4\text{Br}$  as a function of temperature close to the transition temperature  $T_{\text{II} \rightarrow \text{III}}$ , at (a) 870 bar and (b) 610 bar. Open and solid circles correspond to points taken on heating and cooling cycles, respectively.

### V. EFFECT OF DEUTERATION

As it is not possible to apply external fields conjugate to the order parameters of the parallel-ordered and antiparallel-ordered phases, respectively, the mixed system  $\text{NH}_4\text{Cl}_x\text{Br}_{1-x}$  has been studied in much detail.<sup>11,12</sup> By replacing Cl with Br the direct interaction, which favors parallel order, is only slightly affected (decreasing slightly due to the larger lattice spacing), while the indirect interaction increases in a more pronounced way due to the larger polarizability of the bromine ion. There is another isotope effect, however; namely, the effect of deuteration on the phase diagram of the ammonium halides. We would like to emphasize this feature in the following discussion.

Upon deuteration the II-III transition temperature at atmospheric pressure decreases by about 10% from 235 to 215 K. This is quite unusual, since in most systems in which ordering of hydrogen or hydrogenous groups plays a dominant role transition temperatures increase with deuteration. In the case of multipolar interactions this is due to the fact that the effective multipole moment—in the present instance the effective octupole moment  $\langle I_3 \rangle$  of the  $\text{NH}_4^+$  group—increases upon replacement of hydrogen by deuterium, as the orientational distribution is more confined to the equilibrium orientation. Within the framework of Hüller's model for the competing interactions,<sup>5-7</sup> the direct and the indirect interactions increase by a constant factor, which does not account for the differences between the phase diagrams of  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$ .

Apart from the anomalous change of the transition temperature  $T_{\text{II} \rightarrow \text{III}}$  at atmospheric pressure, the triple-point (coexistence of phases II, III, and IV) pressure decreases from about 1.6 kbar ( $\text{NH}_4\text{Br}$ )

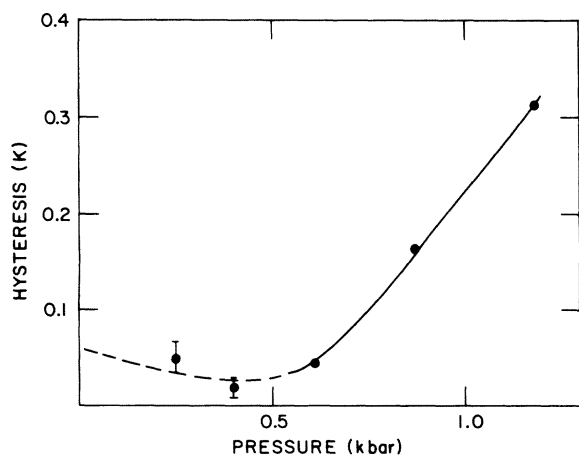


FIG. 6. Hysteresis at the II  $\rightarrow$  III transition in  $\text{NH}_4\text{Br}$  as a function of pressure.

to about 0.6 kbar ( $\text{ND}_4\text{Br}$ ). This indicates that deuteration strongly reduces the indirect interaction and thus the regime in which the antiparallel-ordered phase is stable. There is one further piece of evidence for this, namely the pressures at which the TCP's on the II-IV phase line occur.

In<sup>8,9</sup>  $\text{NH}_4\text{Cl}$  and<sup>10</sup>  $\text{ND}_4\text{Cl}$  the TCP has been located at 1.5 kbar and 128 bar, respectively, while the present measurements show the II-IV transition to change from first to second order in the range 2.5–3.65 kbar in  $\text{NH}_4\text{Br}$  and 2–3 kbar in  $\text{ND}_4\text{Br}$ . We therefore suggest that the TCP is at an approximately constant pressure distance from the triple point in all systems, as is indicated in the generalized phase diagram, Fig. 1(b). It therefore appears to us that deuteration has almost the same effect as replacement of Cl with Br. While it is understood how the interaction is influenced in the latter case, the effect of deuteration has not been discussed in the literature.

As an explanation of the effect of deuteration within the framework of the Landau theory of Yamada *et al.*, the quantity  $A_{ij}$ , which describes the strain dependence of the effective interaction  $J_{\text{eff}}$ , is likely to be important. It gives rise to terms of the form  $(1/C_0)(A_{ij}\sigma^2/v - P)$  in the free energy ( $\sigma$  is the order parameter,  $v$  the volume of unit cell,  $P$  the pressure,  $C_0$  a linear combination of elastic constants), with  $A_{ij}$  positive for phase III and negative for phase IV. The fact that the stability of the antiparallel-ordered phase III is limited to low pressures is due to this term. As the  $A_{ij}$  were calculated from the spontaneous strain in phases III and IV extrapolated to  $T = 0$ , it seemed useful to compare the temperature dependence of the lattice parameters of<sup>16</sup>  $\text{NH}_4\text{Br}$  and<sup>1</sup>  $\text{ND}_4\text{Br}$ . In particular, a drastic difference in the anomalous expansion in phase III shows up in the literature. While Bonilla and Garland find  $\Delta\bar{a}/\bar{a} = +0.7\%$  (with  $\bar{a} = \frac{2}{3}a + \frac{1}{3}c$  for  $\text{NH}_4\text{Br}$ ,<sup>16</sup> the values given for  $\text{ND}_4\text{Br}$  by Levy and Peterson,<sup>1</sup> obtained by x-ray diffraction, yield  $\Delta\bar{a}/\bar{a} \approx 2\%$ .

We have made a careful determination of the lattice constant of  $\text{ND}_4\text{Br}$  with reasonably high-angle x-ray-diffraction data from a powder sample. A complete powder pattern was recorded at  $T = 195.6$  K (the dry-ice point) to ensure correct indexing. The results are shown in Fig. 7 together with a smoothed plot of the data of Bonilla and Garland.<sup>16</sup> As can be seen from Fig. 7 there is only a small difference between  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$ . In particular, the anomalous expansion is about the same in both systems, the tetragonal distortion in the deuterated system being slightly smaller than in  $\text{NH}_4\text{Br}$ . Unfortunately, the range in which the tetragonal phase exists is too narrow to allow an extrapolation of  $a(T)$  and  $c(T)$  to  $T = 0$  with

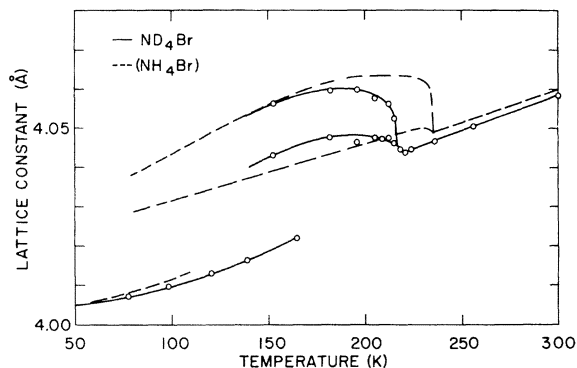


FIG. 7. Lattice constant of polycrystalline ND<sub>4</sub>Br, obtained by x-ray diffraction. The dashed line represents the lattice constant of NH<sub>4</sub>Br (Ref. 16).

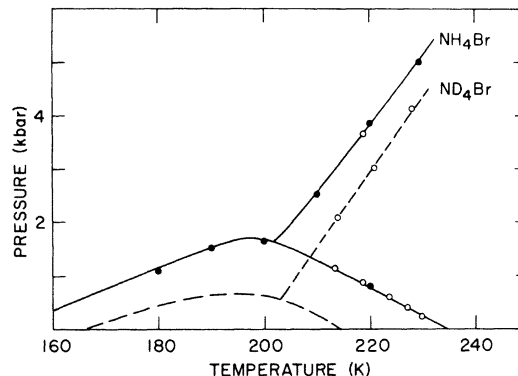


FIG. 8. Phase diagrams of NH<sub>4</sub>Br and ND<sub>4</sub>Br. Open circles: this work; solid circles: Ref. 3. The phase line separating phases III and IV is not very well defined because of strong hysteresis.

the desired accuracy. Therefore the effect of deuteration on the phase diagram, which corresponds to a shift of the pressure axis by about 1 kbar (Fig. 8), can be understood only qualitatively. Both deuteration and replacement of bromine by chlorine (Fig. 1) seem to change  $A_{ij}$  or—in terms of a microscopic picture—the “hydrogen bond” energy<sup>4</sup> in a similar way. A discussion of the ammonium halides in terms of hydrogen bonds has been given by Megaw.<sup>17</sup>

Within the framework of Hüller’s approach deuteration affects only the effective octupole moment  $\langle I_3 \rangle$ , which increases slightly.<sup>6</sup> Since all terms

in the Hamiltonian depend on  $\langle I_3 \rangle^2$ , the observed change in the phase diagram cannot be accounted for. It seems necessary to include indirect interaction terms which are not of electrostatic origin for further investigation of the topic.

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