[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Neutron Diffraction Determination of the Crystal Structure of Ammonium Bromide in Four Phases[1]

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The crystal structures of ND_4Br in four phases have been studied by neutron diffraction. Low temperature cubic ND_4Br contains ordered, parallel ammonium ions. In tetragonal ND_4Br, adjacent strings of ammonium ions are anti-parallel, and bromide ions are displaced toward a square array of near hydrogen atoms. Room temperature ND_4Br contains ammonium ions at random in two orientations. High temperature cubic ND_4Br appears to contain ammonium ions in which one, two or three hydrogen atoms make minimal approaches to bromide neighbors; further specification cannot be given from present data. In all structures there appears to be a significant attraction between D and Br. Information about thermal motions in the crystal is derived, including evidence for rotatory oscillation of the ammonium ions. The length of the N–D link is 1.03 ± 0.02 A.

Introduction

Polymorphism in the ammonium halides has attracted much experimental and theoretical interest since the discovery by Simon[2a] of a sharp anomaly in the specific heat of NH_4Cl at about $-30°$, and by Simon, von Simson and Ruhemann[2b] of similar anomalies in NH_4Br and NH_4I. Through the efforts of a number of workers[2-6] it has been established that the following transformations occur

$$\mathrm{NH_4Cl}\text{: phase I (NaCl)} \xleftrightarrow{184.3^\circ}$$

$$\text{phase II (CsCl)} \xleftrightarrow[\text{(2nd order)}]{-30.5^\circ} \text{phase III (CsCl)}$$

$$\mathrm{ND_4Cl}\text{: phase I (NaCl)} \xleftrightarrow{175^\circ}$$

$$\text{phase II (CsCl)} \xleftrightarrow[\text{(2nd order)}]{-23.8^\circ} \text{phase III (CsCl)}$$

$$\mathrm{NH_4Br}\text{:}^{7}\ \text{phase I (NaCl)} \xleftrightarrow{137.8^\circ}$$

$$\text{phase II (CsCl)} \xleftrightarrow{-38.1^\circ} \text{phase III (tetragonal)}$$

$$\mathrm{ND_4Br}\text{: phase I (NaCl)} \xleftrightarrow{\sim 125^\circ}$$

$$\text{phase II (CsCl)} \xleftrightarrow{-58.4^\circ} \text{phase III (tetragonal)}$$

$$\xleftrightarrow{-104^\circ} \text{phase IV (CsCl)}$$

$$\mathrm{NH_4I}\text{: phase I (NaCl)} \xleftrightarrow{-17.6^\circ}$$

$$\text{phase II (CsCl)} \xleftrightarrow{-41.6^\circ} \text{phase III (tetragonal)}$$

X-Ray diffraction methods have confirmed the existence of the above crystallographic phases and established the arrangements of nitrogen and halide ions to be as indicated in parentheses. In the tetragonal phases this arrangement is a slight distortion from that of CsCl. Complete structure determinations require also the placement of hydrogen atoms, and this information has not been given by the X-ray studies. It is required, of course, for an understanding of the λ-transition in the chloride and the corresponding transitions in the other salts. Pauling[8] once suggested that these transitions mark the onset of essentially free rotation of the ammonium ions in the crystal. Frenkel[9] suggested an alternative picture in which the transitions mark the onset of disorder; this view was given detailed description and a theoretical treatment of the Bragg–Williams type by Nagamiya.[10] A great deal of evidence has now accumulated favoring the second of these hypotheses, particularly the fact, pointed out by Lawson,[11] that in NH_4Cl phase II the specific heat at constant volume exceeds by 3 cal./mole-deg. the value expected for free rotation. The results of analysis of infrared and Raman data on the ordinary and deutero chlorides and bromides at various temperatures by Wagner and Hornig[12] also support the disorder hypothesis.

Neutron diffraction, because of the possibility of locating hydrogen atoms, is a most suitable tool for establishing the complete structures of these materials. Such studies of NH_4Cl and ND_4Cl in phase II[13] and ND_4Cl in phase III[14a] have already been reported and have confirmed the order–disorder hypothesis (a report that ND_4Cl in phase II is ordered[14a] has proved incorrect.[14a,b] We have extended these studies with determinations of the hydrogen positions in all four phases of ND_4Br and report the results below. A preliminary report covering phases IV and II was made earlier.[15]

Experimental

Deuteroammonium bromide was selected for investigation because of the existence of four phases, and because deuterium is better suited to powder neutron diffraction studies than is hydrogen.[16] Reagent grade NH_4Br was deuterated essentially to completion by means of repeated solution in 99.8% D_2O followed by evaporation of the solvent, with precautions to prevent exchange with atmospheric moisture. The chemical purity of the vacuum-dried sample was established by chemical analysis and by X-ray diffrac-

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(1) This work was performed under the auspices of the Atomic Energy Commission and was presented in part before the International Congress of Pure and Applied Chemistry, New York, 1951.

(2) (a) F. Simon, *Ann. Physik*, [4] **68**, 241 (1922); (b) F. Simon, Cl. von Simson and M. Ruhemann, *Z. physik. Chem.*, **129**, 339 (1927).

(3) F. Simon and R. Bergmann, *ibid.*, **B8**, 255 (1930).

(4) J. A. A. Ketalaar, *Nature*, **134**, 250 (1934).

(5) J. Weigle and H. Saini, *Helv. Phys. Acta*, **9**, 515 (1936).

(6) A. Smits, J. A. A. Ketelaar and G. J. Muller, *Z. physik. Chem.*, **A175**, 359 (1936).

(7) Recently C. C. Stephenson and H. E. Adams, *J. Chem. Phys.*, **20**, 1658 (1952), reported a new transition in NH_4Br at 78°K. on cooling, 108.5°K. on warming. This may correspond to conversion between phase III and phase IV.

(8) L. Pauling, *Phys. Rev.*, **36**, 480 (1930).

(9) J. Frenkel, *Acta Physicochem.*, **3**, 23 (1935).

(10) T. Nagamiya, *Proc. Phys. Math. Soc. Japan*, **24**, 137 (1942); **25**, 540 (1943).

(11) A. W. Lawson, *Phys. Rev.*, **57**, 417 (1940).

(12) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296, 305 (1950).

(13) Henri A. Levy and S. W. Peterson, *Phys. Rev.*, **86**, 766 (1952).

(14) (a) G. H. Goldschmidt and D. G. Hurst, *ibid.*, **83**, 88 (1951). (b) G. H. Goldschmidt and D. G. Hurst, *ibid.*, **86**, 797 (1952).

(15) Henri A. Levy and S. W. Peterson, *ibid.*, **83**, 1270 (1951).

(16) C. G. Shull, E. O. Wollan, G. A. Morton and W. L. Davidson, *ibid.*, **73**, 842 (1948).

tion. The isotopic purity was measured by neutron transmission and also by determination of the density of a recovered final portion of solvent; the two methods were in excellent agreement, giving 97.5% D.

Diffraction patterns were obtained from the finely powdered sample packed into a cylindrical, thin-walled (about 0.006") aluminum container about 1 cm. in diameter. The neutron spectrometer is similar to one described by Wollan and Shull,[17] but differing from it in that the scattered neutron intensity is measured with a linear count-rate meter and recorded continuously as a function of scattering angle on a strip-chart recorder. A servo mechanism holds the primary neutron beam to constant intensity by adjusting the thickness of an interposed absorber. The primary beam is monochromatized by reflection from a (111) face of a single crystal of copper, yielding a narrow band of wave lengths centering at 1.16 Å. Soller slits can be inserted ahead of the monochromator and in the entrance of the detector to adjust the resolution of spectrometer to the optimum for the problem at hand. For data at temperatures other than ambient, the sample and cell were placed in an evacuated aluminum cryostat.

The total number of neutrons recorded in each Bragg reflection (E_{hkl} in the equation below) was determined directly from the chart recording of counting rate *versus* time, integrating by means of the trapezoid rule, and occasionally checking by a triangle approximation. For this purpose the diffuse background level must be estimated from values of the scattered intensity between resolved peaks. A considerable uncertainty sometimes is attached to this estimation because of incomplete resolution of peaks and the considerable structure which appears in the background of some of the patterns. This uncertainty is reflected in the precision of the resulting structure factor values. Suitable corrections, where necessary, were made for scattering from the aluminum container. Observed values from several patterns, suitably normalized, were averaged, and from them absolute values of jF^2 were obtained by means of the following formula appropriate to the case of a cylindrical sample bathed in radiation

$$E_{.kl} = \left(\frac{I_0 \epsilon V l w \lambda^3}{8\pi r^2 \omega}\right) \frac{\rho'}{\rho} \frac{N^2}{\sin\theta \sin 2\theta} AjF^2_{hkl}$$

This expression is a minor adaptation of that commonly used for the X-ray case. The symbol I_0 represents the incident intensity, ϵ the counting yield of the detector, V the sample volume, l, w, ω and r the height, width, angular velocity and radius of travel of the sensitive aperture of the detector, ρ' and ρ, respectively, the packed powder and crystal densities, θ the Bragg angle, N the number of unit cells per unit volume, j the multiplicity of the reflection and F its structure factor. The factor A corrects for absorption in the sample; it has been tabulated[18] as a function of μR and θ, where μ is the total linear attenuation coefficient of the sample, measured for 1.16 Å. neutrons, and R is the radius of the sample. The quantity in parentheses was numerically evaluated from similar neutron diffraction data, prepared under identical conditions, from the (111), (200) and (220) reflections of pure powdered nickel. The coherent cross section[19] σ_{Ni} was taken as 13.4 barns, and the temperature factor for nickel was calculated from the Debye characteristic temperature, 400°K. Observed data are listed in Tables I-V. Uncertainties appended correspond to estimated standard deviations arising from counting statistics, background estimation and systematic error in standardization.

Calculated values of jF^2 were obtained from specializations of the usual formula[20]

$$F_{hkl} = \Sigma f_i \exp\left[-B_i (\sin\theta/\lambda)^2\right] \exp\left[2\pi i(hx_i + ky_i\, lz_i)\right]$$

where the summation is over a unit cell, x_i, y_i and z_i are the position parameters of atom i in terms of fractions of the unit cell dimensions, B_i is a temperature factor coefficient, and, in the neutron case, the coherent scattering amplitude f_i is given by $(\sigma_{coh}/4\pi)^{1/2}$. Values of the coherent scattering cross sections σ_{coh} for many elements and nuclides have been measured by Shull and Wollan.[19] In this work the values used were $f_N = 0.94$,[21] $f_{Br} = 0.67$ and $f_D = 0.62$ (for 97.5% D, 2.5% H).[19] In the early stages of the study, an earlier value of f_N, 0.85, was used; this resulted in the shorter N-D distance reported previously.[15]

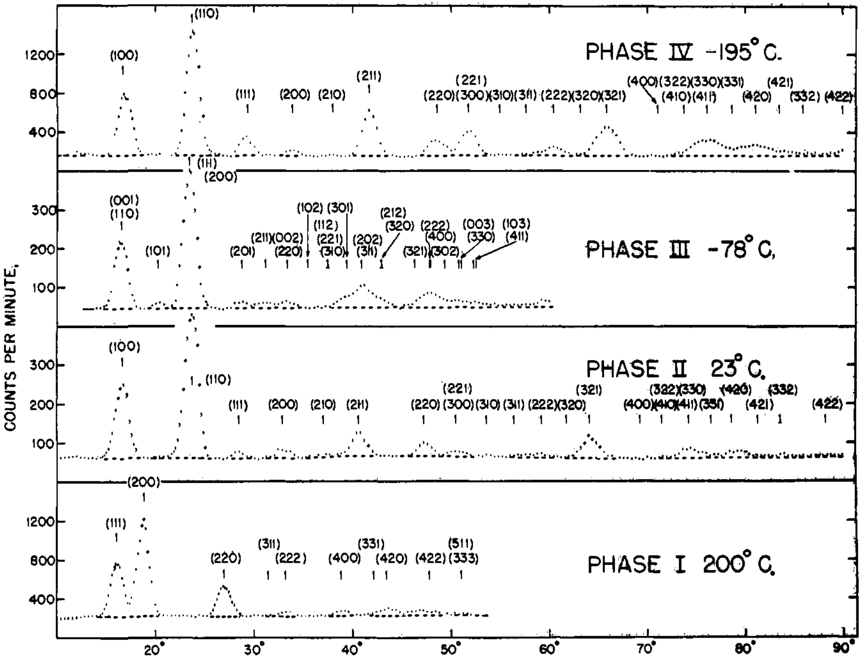

Fig. 1.—Typical neutron diffraction patterns from four phases of ND_4Br. The patterns shown for phases II and III were made with greater collimination, produced by insertion of soller slits. The points were read from chart recordings of the counting rate. The dashed lines represent estimated diffuse background counting rates.

Low Temperature Cubic ND_4Br (Phase IV)

X-Ray studies of ND_4Br at −140° have shown[22] that nitrogen and bromine atoms have the CsCl arrangement and that the unit cell dimension a_0 is 3.981 Å. A determination at this laboratory by Mr. B. S. Borie yielded $a_0 = 4.010 \pm 0.001$ Å. (based on CuKα = 1.5418 Å.) at about −140°. A neutron pattern obtained at liquid nitrogen temperature and illustrated in Fig. 1 was consistent with $a_0 = 4.00$ Å., showing that the arrangement of deuterium atoms in the crystal does not call for a unit cell different from that given by X-ray data.

Reasonable deuterium positions giving tetrahedral coordination around nitrogen are provided by positions[23] (e) of space group T_d^1: xxx, $x\bar{x}\bar{x}$, $\bar{x}x\bar{x}$, $\bar{x}\bar{x}x$, with nitrogen in (a): 000 and Br in (b): $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Refinement of the model required the introduction of separate Debye–Waller temperature factors for N, D and Br, and yielded excellent agreement.

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(17) E. O. Wollan and C. G. Shull, *Phys. Rev.*, **73**, 830 (1948).

(18) "International Tables for the Determination of Crystal Structures," Vol. II, Gebrüder Borntraeger, Berlin, 1935, and Edwards Bros., Ann Arbor, Mich., 1944, p. 584.

(19) C. G. Shull and E. O. Wollan, *Phys. Rev.*, **18**, 527 (1951).

(20) References 18, p. 557.

(21) S. W. Peterson and Henri A. Levy, *Phys. Rev.*, **87**, 462 (1952).

(22) A. Smits and D. Tollenaer, *Z. physik. Chem.*, **B52**, 222 (1942).

(23) The notation is that of reference 18.

The effect of a rotatory oscillation of the ammonium ion, as found in phase II and described in the following section, was tested; an oscillation with half-angle α of 5° is consistent with but not necessarily required by the data. A comparison of jF^2 is presented in Table I. The preferred parameter values are: $x = 0.148$, $\alpha = 5°$, $B_N = 0.8$ Å.², $B_{Br} = 0.2$ Å.², $B_D = 1.0$ Å.². The N–D bond distance is 1.026 ± 0.02 Å.

TABLE I

NEUTRON DIFFRACTION DATA FROM ND_4Br, PHASE IV, AT −195°

hkl	jF^2 Obsd.	jF^2 Calcd.[a]		hkl	jF^2 Obsd.	jF^2 Calcd.[a]	
100	17.9 ± 0.4	18.0		320	5.8 ± 4	9.6	
110	72.3 ± 1.4	71.8		321	163.2 ± 8	156.7	
111	16.1 ± 0.8	15.6		400	<1	0.1	
200	5.0 ± 0.6	5.1		410	27.4 ± 5	15.1	23.3
210	1.7 ± 1.0	0.6		322		8.2	
211	87.1 ± 2.4	84.6		411	118 ± 15	25.3	127.0
220	30.8 ± 2.0	31.9		330		101.7	
221	76.0 ± 3.5	59.1	77.7	331	33 ± 15	25.5	
300		18.6		420	93 ± 15	76.4	
310	4.1 ± 2.1	2.5		421	41 ± 15	27.6	
311	13.3 ± 3.5	11.9		332	25 ± 10	23.7	
222	41.5 ± 8	41.0					

[a] For the final model: $x = 0.148$, $\alpha = 5°$, $B_D = 1.0$, $B_N = 0.8$, $B_{Br} = 0.2$ Å.².

Room Temperature Cubic ND_4Br (Phase II)

The neutron diffraction pattern of ND_4Br at room temperature, shown in Fig. 1, was consistent with a cubic unit with a spacing of 4.060 Å., a value determined in this Laboratory by X-ray diffraction with a precision of ±0.001. That there are marked differences between this pattern and that at low temperature is immediately apparent; in particular, the intensity ratio of (111) and (200) is reversed, and there is a more rapid decrease in general intensity with scattering angle. There is also a marked hump in the diffuse background similar to that observed in room-temperature ND_4Cl[13] and probably ascribable also to the disordered structure.

No agreement between calculated and observed intensities was found possible with a model in which deuterium atoms were placed in positions (e) of space group T_d^1. Models containing freely rotating and orientationally disordered ammonium ions were among those next tested. For the free rotation model, deuterium contributions to the structure factors were computed as

$$(4f_D/2rh_0)\sin 2\pi rh_0;\quad h_0 = (h^2 + k^2 + l^2)^{1/2} \qquad (1)$$

Expression (1) is appropriate for four deuterium atoms distributed uniformly over a spherical shell whose radius is the fraction r of the unit cell length a_0. Models involving orientational disorder are described by placing four deuterium atoms at random in the eightfold positions (g) of space group O_h^1.

Table II compares the experimental jF^2 values for several reflections with those calculated without temperature factors from an ordered T_d^1 model, and O_h^1 model with orientational disorder, and an O_h^1 model with free rotation. The disordered model shows the best approach to agreement with experiment. Application of temperature factors, especially to deuterium, brought improvement but was not sufficient to give satisfactory agreement.

Table II suggests that a more satisfactory model might be achieved by superposing on the orientational disorder a severe temperature motion corresponding to a rotatory oscillation of the ammonium ion. This sort of model was approximated by considering that each deuterium atom is distributed not only in a spherical cloud corresponding to the usual temperature factor, but that the center of this cloud is distributed around a circle centered on one of the body diagonals of the unit cell. If α is the central half-angle of the cone defined by the nitrogen position and this circle, the corresponding contribution of deuterium to the structure factor is

$$^1/_2 f_D \exp\left[-B_D(\sin\theta/\lambda)^2\right] \Sigma \exp[2\pi i \cos\alpha\,(hx_0 + ky_0 + lz_0)]\,J_0(2\pi\sqrt{S}\sin\alpha) \qquad (2)$$

where ($x_0\ y_0\ z_0$) describe in turn the eightfold positions (g) of space group O_h^1 at the correct interatomic distance from nitrogen, the summation is over these positions, J_0 is the Bessel function of zero order and

$$S = (hy_0 - kx_0)^2 + (lx_0 - hz_0)^2 + (kz_0 - ly_0)^2$$

This expression is adapted from a more general one given by King and Lipscomb.[24] While this model is artificial in that an appropriate distribution over α would more realistically describe a rotatory oscillation of the ion, the sensitivity of the neutron intensities to this parameter did not justify the more elaborate procedure.

TABLE II

COMPARISON OF OBSERVED DATA FROM ND_4Br, PHASE II, WITH THOSE FROM VARIOUS MODELS

hkl	jF^2 obsd.	jF^2 calcd.[a] Ordered (T_d^1)	jF^2 calcd.[a] Disordered (O_h^1)	jF^2 calcd.[a] Freely rotating
100	17.2	19.7	19.7	20.1
110	65.3	78.7	78.7	73.2
111	3.5	17.7	5.6	2.9
200	6.6	6.5	6.5	14.5
211	31.2	96.0	42.2	26.4
220	18.9	31.0	31.0	11.3
221–300	7.6	113.8	26.9	4.1
311	2.9	25.7	12.9	1.8
222	11.0	65.2	18.1	10.5
321	75.5	195.3	153.6	83.6
400	0	4.5	4.5	13.3

[a] No temperature factors were included in these calculated values. The parameter value corresponded to an N–D distance of 1.00 Å. in each model.

After adjustment of the parameters x_0 and α and the various temperature factor coefficients, a satisfactory fit to the experimental data was obtained. The final values are $x_0 = 0.1475 \pm 0.003$, $\alpha = 12.5 \pm 3°$, $B_D = 2.5$ Å.², $B_N = 1.7$ Å.², $B_{Br} = 1.7$ Å.². Table III presents a comparison of experimental jF^2 values with those calculated for the final model for all reflections in the available angular range. The N–D distance is 1.037 ± 0.02 Å.

TABLE III

NEUTRON DIFFRACTION DATA FROM ND_4Br, PHASE II, AT 23°

hkl	jF^2 Obsd.	jF^2 Calcd.[a]		hkl	jF^2 Obsd.	jF^2 Calcd.[a]	
100	17.2 + 0.4	17.2		320	3.6 ± 1.8	3.5	
110	65.3 ± 1.3	65.5		321	75.5 ± 6	78.3	
111	3.5 ± 0.4	3.8		400	<1.0	0.3	
200	6.0 ± 0.7	5.9		410	5.9 ± 3	1.9	3.3
210	<1.0	0.2		322		1.4	
211	31.2 ± 1.6	32.4		411	46.6 ± 5	15.0	49.1
220	18.9 ± 1.4	19.2		330		34.1	
221	7.6 ± 0.8	1.1	8.4	331	9.3 ± 5	8.4	
300		7.3		420	35.8 ± 6	34.3	
310	3.6 ± 1.8	4.9		421	5.0 ± 3	4.7	
311	2.9 ± 1.5	1.6		332	17.6 ± 3	18.7	
222	11.0 ± 1.7	12.3		422	17.3 ± 3	18.6	

[a] For the final disordered model: $x_0 = 0.1475$, $\alpha = 12.5°$, $B_D = 2.5$, $B_N = 1.7$, $B_{Br} = 1.7$ Å.².

Tetragonal ND_4Br (Phase III)

Tetragonal ammonium bromide was studied by X-ray diffraction by Ketelaar[4] and by Weigle and Saini[5]; their data are consistent with the space-group assignment D^7_{4h}–P^4/nmm. Since these authors reported non-concordant unit cell dimensions, Mr. Bernard Borie of this Laboratory has made precision determinations of the unit cell dimensions at three temperatures, with the following results in substantial agreement with those of Weigle and Saini at −145° and −71.5°

T, °C.	a, Å.	c, Å.
−100	5.826	4.136
−124	5.818	4.130
−145	5.810	4.125

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[24] M. V. King and W. N. Lipscomb, *Acta Cryst.*, **3**, 318 (1950).

The axial ratio is 1.409 at the three temperatures. The values are based on CuKα = 1.5418 Å.

In this structure the unit cell is bimolecular with N in positions (a) 000, $\frac{1}{2}\,\frac{1}{2}\,0$ and Br in positions (c) $0\,\frac{1}{2}\,u$, $\frac{1}{2}\,0\,\bar{u}$. The vaue of u has been reported as 0.53 (or 0.47)[4] and 0.52 (or 0.48).[5] Thus the arrangement is a slight distortion of the CsCl structure, for which u would be $\frac{1}{2}$ and a/c would be $\sqrt{2}$.

The deuterium atoms would be expected to be in positions (i): $0xz$; $x0\bar{z}$; $\frac{1}{2}, \frac{1}{2} + x, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2}, z$; $0\bar{x}z$; $\bar{x}0\bar{z}$; $\frac{1}{2}, \frac{1}{2} - x, \bar{z}, \frac{1}{2} - x, \frac{1}{2}, z$. If the ammonium ion is tetrahedral, x and z will be nearly equal. With these hydrogen positions, the N–D arms of the ammonium ions are directed essentially toward four of the eight surrounding bromide ions; however, unlike the phase IV structure, the arrangement of close hydrogen atoms around Br is not tetrahedral, but square, the bromide ion lying some distance out of the plane of the square along the fourfold axis. If the values of x and z are taken positive, the displacement of Br from the ideal CsCl location is toward the approaching hydrogen atoms if u is less than $\frac{1}{2}$ and away if u is greater than $\frac{1}{2}$.

Neutron diffraction data were obtained from ND_4Br powder at −78° as shown in Fig. 1. Limited resolution limits the useful portion of the pattern to about 52° in 2θ; in this range no peaks were observed which were inconsistent with the X-ray unit and space group. Because of the limitations of the data, a complete, systematic variation of all parameters was not feasible; hence the N–D distance was assumed to be 1.03 Å., as found in phases IV and II, and models with other than tetrahedral ammonium ions were given only brief consideration.

Separate temperature factors were assumed for N, D and Br, and a distribution corresponding to a rotatory oscillation of ND_4^+ was assumed for the deuterium atoms. This treatment appeared necessary to obtain satisfactory agreement with the data. The contribution of D to the structure factors is thus given by Eq. (2) with $(x_0\,y_0\,z_0)$ taking in turn the values for positions (i) of D^7_{4h} and the factor $\frac{1}{2}$ omitted (since there is no disorder in this model).

A model which gave satisfactory agreement with the neutron data is described by the parameters: $x = z = 0.147$, $u = 0.47$, $B_D = 3.7$ Å.^{2}, $B_{Br} = 0.4$ Å.^{2}, $B_N = 1.2$ Å.^{2}. Values of u greater than $\frac{1}{2}$ were completely unsatisfactory, indicating that the displacement of Br is toward the approaching hydrogen atoms. The values of α and B_D were most sensitive in achieving a fit and received most attention. In addition, a limited number of other trial structures were examined, with no indication that any was in accord with the data; these included small rotations of ammonium ions around the c axis (space group C^3_{4h}) and flattened NH_4^+ ions ($x > z$). A comparison of observed structure factors with those calculated from the final model is shown in Table IV.

TABLE IV

OBSERVED AND CALCULATED NEUTRON DIFFRACTION INTENSITIES[a] FOR ND_4Br, PHASE III, AT −78°

hkl	Obsd.	Calcd.[b]	*hkl*	Obsd.		Calcd.[b]	
001 110	1600 ± 70	1616	301	(276)	1069 ± 40	280	1162
101	129 ± 15	109	202 311	(533)		667	
111 200	3285 ± 100	3292	212	(260)		215	
201	129 ± 20	116	321	(57)	789 ± 50	58	705
211	157 ± 40	122	222 400	(365)		333	
002 220	143 ± 40	168	302	(84)		110	
102	<20	2	003 330	(151)		114	
112 221 310	<20	4	103 411	(132)		90	

[a] The quantities listed are $jF^2/\sin\theta \sin 2\theta$. Observed values in parentheses are from incompletely resolved peaks. [b] For the final model: $x = z = 0.147$, $\alpha = 10°$, $B_D = 3.7$s $B_N = 1.2$, $B_{Br} = 0.4$ Å.^{2}, $\mu = 0.47$.

High-temperature Cubic ND_4Br (Phase I)

X-Ray data[25] from the high-temperature phase of ammonium bromide indicate the structure to be of the NaCl type with the cubic cell dimension 6.90 Å. and space group O^5_H. This unit is tetramolecular with N at positions (a) 000, F.C. and Br at (b) $\frac{1}{2}$ 0 0, F.C. Neutron diffraction data obtained from ND_4Br powder at 150° and 200° were similar and consistent with the above unit cell and space group. The patterns, illustrated in Fig. 1, show severe attentuation of intensity with scattering angle, as expected at these temperatures; this feature limits the number and precision of the data.

The structures found for phases II, III and IV all achieve a close approach between D and Br. In phase I it is not possible to place four hydrogen atoms simultaneously close to four of the octahedrally distributed bromide ions. This fact suggests that either the attractive interaction evident in the other phases is overcome, or that fewer than four simultaneous approaches is achieved. Testing of models in which the ammonium ions are rotating and models with various numbers of close approaches of D to Br is accordingly suggested. Some other models with ammonium ion orientations suggested by the ion and crystal symmetry, but not conforming to the above criteria, were also tested.

The models examined include the following, in all of which N is placed in positions 4(a) and Br in 4(b) of space group O^5_h.

Model	Hydrogen positions[23]
(1) Free rotation	16 D uniformly on 4 spheres centered at 4(a)
(2) Single approach	4 D in 24(e), $x = b$ 12 D uniformly distributed around 24 circles centered at 24(e), $x = b/3$
(3) Double approach	8 D in 96(j), $y_1 = b \cos 9°44'$, $z_1 = b \sin 9°44'$ 8 D in 96(k), $x_2 = (b/\sqrt{2}) \cos 54°44'$, $z_2 = b \sin 54°44'$
(4) Triple approach	12 D in 96(k), $x_1 = b/3\sqrt{3}$, $z_1 = 5b/3\sqrt{3}$ 4 D in 32(f), $x_2 = b/\sqrt{3}$
(5)	16 D in 32(f), $x = b/\sqrt{3}$
(6)	16 D in 96(j), $y = b \sin 54°44'$, $z = b \cos 54°44'$
(7)	16 D around 24 circles centered at 24(e), $x = b \cos 54°44'$
(8)	4 D in 32(f), $x = b/\sqrt{3}$ 12 D around 32 circles centered at 32(f), $x = b/3\sqrt{3}$

In each case the parameter b represents the ratio of the N–D distance (taken close to 1.03 Å.) to the unit cell edge. No deviations from tetrahedral angles were considered. Model (2) represents an ammonium ion rotating freely about a single 3-axis set parallel to a 4-axis of the crystal and minimizes the approach of the axial hydrogen atom to a bromide ion. Model (8) represents similar rotation with the axis set parallel to a 3-axis of the crystal. Model (3) places two hydrogen atoms in (100) planes and two in (110) planes of the crystal and minimizes the approach of the former to near bromide ions. Model (4) places one hydrogen atom along a [111] axis, each of the other three in the $(01\bar{1})$, $(10\bar{1})$ and $(1\bar{1}0)$ planes containing this axis, and minimizes the approach of the latter to bromide ions. Model (5), the arrangement of highest symmetry, maximizes the D–Br distances. It was tested both with and without rotatory oscillation with $\alpha = 20°$. Model (6) places the ion $\bar{4}$-axis parallel with a crystal 4-axis and the ion mirror planes parallel to basal crystal planes. In Model (7) the ion rotates about a $\bar{4}$ axis set parallel to a crystal 4-axis. In all cases the over-all crystal symmetry is achieved statistically by randomness.

Of these models, only numbers (2), (3) and (4) gave agreement with the observed data, and these are equally satisfactory. It is thus not possible with the present data to select among these three models.

Table V shows a comparison of observed structure factors at 200° and those calculated for models (1) to (5) inclusive. The temperature factor parameters used were $B_D = 4$ Å.^{2},

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(25) G. Bartlett and I. Langmuir, THIS JOURNAL, **43**, 84 (1921).

$B_N = 3$ Å.^{2}, $B_{Br} = 3$ Å.^{2}. The N–D distance for the satisfactory models was 1.03 Å.

TABLE V

NEUTRON DIFFRACTION STRUCTURE FACTORS FOR ND_4Br PHASE I, AT 200°

		|F| calcd.					
hkl	|F| obsd.	Free rotation[a]	1-Approach[b]	2-Approach[b]	3-Approach[b]	Model (5)[c]	
111	6.7 ± 0.1	6.86	6.69	6.70	6.68	6.77	
200	11.1 ± .1	10.75	10.82	10.84	10.85	10.14	10.33
220	6.8 ± .1	7.17	7.00	7.05	7.03	7.35	
311	0.7 ± .35	0.99	0.91	1.14	1.15	0.41	
222	4.0 ± .3	5.00	4.49	4.41	4.34	6.03	
400	5.0 ± .2	3.91	4.82	5.04	5.08	0.76	2.53
331	1.0 ± .5	0.52	0.93	0.97	0.99	0.85	
420	3.8 ± .2	3.35	3.67	3.75	3.77	2.92	
422	2.9 ± .3	3.09	2.69	2.58	2.54	3.67	
620	3.0 ± .45		3.82	3.95	3.92		

[a] N–D taken as 1.015 Å. This model with N–D = 1.05 Å. was also unsatisfactory. [b] Acceptable models, incorporating N–D = 1.03 Å., $B_D = 4$, $B_N = B_{Br} = 3$ Å.^{2}. [c] Left column, no rotatory oscillation; right column, $\alpha = 20°$.

Discussion of the Structures

The phase IV structure, illustrated in Fig. 2, consists of an ordered, parallel, simple cubic array of ammonium ions and bromide ions, as anticipated by several earlier workers. Each deuterium atom lies along a line connecting a nitrogen and bromine position, and each bromide ion is tetrahedrally surrounded by deuterium. An entirely similar structure has been previously given[13] for ND_4Cl phase III, and it may be presumed that NH_4Cl is also similar.

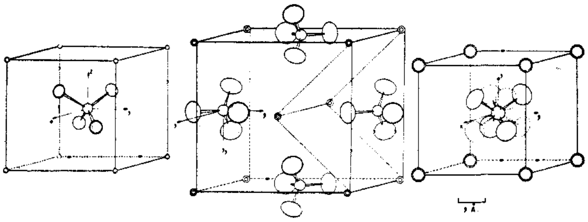

Fig. 2.—Drawings of the structures of ND_4Br in phases IV, III and II. The circles and ellipses represent approximately the extent of thermal motion of the nuclei. The dotted lines in the phase III drawing outline a monomolecular pseudocell comparable to the cubic units of phases IV and II. In phase II, one orientation of the ion is shown with solid lines and the other with dotted lines.

Tetragonal ND_4Br, phase III, has the structure illustrated in Fig. 2. It contains columns of parallel ammonium ions extending along the *c*-axis, and neighboring columns are oppositely oriented. Again the deuterium atoms lie substantially along N . . . Br lines; however, the environment of Br is unsymmetrical as previously described, and the bromide ions are displaced about 0.012 Å. toward the plane of the near deuterium atoms. Alternate bromide ions are oppositely displaced, preserving the centro-symmetric character of the structure, in agreement with the absence of piezoelectricity.[26] It seems reasonable that this structure is shared by NH_4Br and NH_4I in phase III.

The structure of phase II, illustrated in Fig. 2, contains ammonium ions at random in two orientations, in each of which the deuterium ions lie along N . . . Br lines. The environment about the bromine position is random, and may vary statistically from zero to eight near deuterium atoms in a variety of arrangements. Wagner and Hornig[12] have suggested that the anion is probably displaced in a random manner away from the body-center position, depending on the particular environment in which it occurs. This suggestion finds some measure of confirmation in the neutron diffraction data, inasmuch as in phase II a temperature factor coefficient B_{Br} equal to B_N was necessary, whereas in phases IV and III B_{Br} is considerably smaller than B_N, in qualitative accord with their mass ratio. The phase II structure has been shown to be common to ND_4Cl,[13,14b] NH_4Cl[13] and ND_4Br; in all likelihood it is also assumed by the remaining compounds.

The acceptable models for phase I are shown in part in Fig. 3. Each illustration shows one orientation of the ammonium ion of the several equivalent ones occupied at random in its relation to the coördination octahedron of bromide ions. (In the case of the single approach model, one orientation of the rotating ion is shown.)

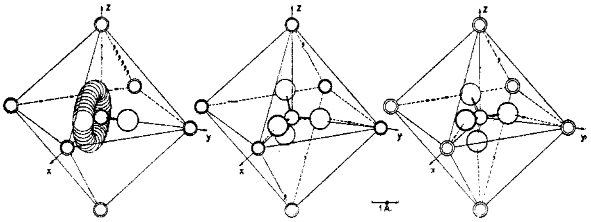

Fig. 3.—Drawings showing the coördination of ammonium ion in acceptable models of ND_4Br, phase I. In each case there is shown one orientation of the ammonium ion of the six, twelve and eight, respectively, occupied at random.

In these structures, the environment of Br is again random; the relatively large value of B_{Br} found may well represent random displacements of the ion from ideal positions as well as thermal motion, as suggested for phase II. A neutron diffraction study[27] of ND_4I has shown that in this crystal also the ammonium ion is not rotating freely and that three models similar to those here described for a bromide give satisfactory agreement with the observed reflections.

There is thus shown to exist a significant potential barrier to free rotation of ammonium ions in phase I of both bromide and iodide. The minima of the potential clearly correspond to orientations in which one, two or three hydrogen atoms make close approaches to bromide ions, but which of these possibilities is most stable is not disclosed by the present neutron data. An investigation of the form of the potential expected from electrostatic considerations is being undertaken by V. Schomaker.

Stephenson, Landers and Cole[22] have interpreted heat capacity measurements on NH_4I and mixed crystals of KI–NH_4I (which crystallizes with the same structure) to indicate ammonium ion rotation, in the latter even at low temperatures. Their observations are twofold: (1) the heat capacity of

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(26) A. Hettich, *Z. physik. Chem.*, [A] 168, 353 (1934).

(27) H. A. Levy and S. W. Peterson, submitted to *J. Chem. Phys.*

NH_4I in phase I is 3.8 cal./mole degree lower than that in phase II, and (2) that of the mixed crystal is higher than that of either KI or NH_4I at temperatures between 14 and 100°K. The first observation was recognized as suggestive of but not requiring rotation, as lattice contributions to the heat capacity might be quite different in the two structures. The second observation indicates that there exists a spectrum of energy levels with spacings comparable to 14°K. and this was taken by Stephenson and co-workers to indicate one or more degrees of freedom which are rotational in nature. In fact, however, a closely-spaced spectrum of energy levels could well result from any of the models found to be in agreement with the neutron data: in the double and triple approach models by virtue of the multiple potential minima resulting from the superposition of tetrahedral and cubic symmetries, and in the single approach model also from the single-axis rotation. We must conclude that qualitative interpretation of heat capacities does not favor any one of these models over the others.

A study of the infrared absorption spectrum of NH_4I and ND_4I in phase I has been made by Plumb and Hornig. Their interpretation led them to a single-axis rotation model identical to our single-approach model.

We plan to extend our neutron diffraction study to single crystals of NH_4I and mixed single crystals of KI–NH_4I in order to determine more clearly the details of the phase I structure.

The length of the nitrogen-to-hydrogen bond in the ammonium ion appears to be established as 1.03 ± 0.02 Å. Individual determinations are summarized in Table IV. The value in the ammonia molecule appears to be slightly smaller.

TABLE VI

NITROGEN-TO-HYDROGEN BOND LENGTHS

Substance	Bond length, Å.	Method[a]	Reference
NH_4Cl	1.025	NMR	(28a)
NH_4Cl	1.03	ND	(12)
ND_4Cl	1.03	ND	(12, 13)
NH_4Br	1.039	NMR	(28a)
ND_4Br	1.03	ND	This research
NH_3, ND_3	1.014	S	(28b)

[a] NMR, nuclear magnetic resonance; ND, neutron diffraction; S, spectroscopy.

The nature of the phase III to-phase II transitions is now firmly established to be order-to-disorder in both ammonium chloride and ammonium bromide, confirming the suggestions of Frenkel[9] and Nagamiya[10] and the conclusions of Wagner and Hornig.[12]

Consideration of this group of structures indicates that an important factor in their stability is the attraction of the anion for the hydrogen atom. This attraction is particularly evident in displacement of the bromide ion toward the hydrogen atoms in the tetragonal structure. Nagamiya[10] has discussed the energies of both the chloride and bromide systems on the basis of simple electrostatics, assigning a positive electrostatic charge to each hydrogen atom. It appears that this discussion considerably underestimates the hydrogen–anion attraction for the following reasons: (a) the treatment requires too large an N–H distance (>1.13 Å.) or a rather large electrostatic charge on hydrogen, (>0.28 e) or both, and (b) it badly underestimates the frequency of rotatory oscillation of the ammonium ions in NH_4Cl. The stronger attraction that appears to be required might be described as formation of N—H · · · X hydrogen bonds, and might arise from a (multipolar) polarization of the anion by the charge on the approaching hydrogen atoms. Nagamiya's calculations suggest that (dipolar) polarization of Br^- is important in stabilizing the phase II structure.

The existence of the Phase IV structure in ND_4Br and its absence[29] in NH_4Br provides an interesting problem for theoretical discussion. We offer the suggestion that the zero-point energy associated with the rotatory oscillation is an important factor in this situation. That this is plausible is shown by the following argument. We assign zero-point energy 3/2 $h\nu$ per ammonium ion, taking Wagner and Hornig's[12] inferred frequencies for ND_4Br in phases IV and III and NH_4Br in phase III. For hypothetical NH_4Br in phase IV we take $\sqrt{2}$ times the frequency for ND_4Br in this phase. We further assign an energy ϵ to both phase III structures, corresponding to a small difference in lattice energy between the two structures. We then have the following energy assignments, in $cm.^{-1}$

	Phase IV	Phase III
NH_4Br	(525)	$478 + \epsilon$
ND_4Br	372	$345 + \epsilon$

With a suitable value of ϵ, between 27 and 47 $cm.^{-1}$, the order of stability is as observed.

Nagamiya[10] discussed the difference in phase II–phase III transition temperatures between NH_4Cl ND_4Cl, ascribing the difference to quantum effects associated with the rotatory oscillation, and predicted that the deuterium compound should transform at a temperature 4° higher, to be compared with 7° observed. However, recalculation using the observed frequencies in place of Nagamiya's calculated values yields the much less satisfactory temperature difference of 48°, although still in the right direction. It is interesting that if Nagamiya's expression is applied to the bromide case, again with the observed frequencies, a lowering of the transition temperature of 22° for ND_4Br as compared with NH_4Br is predicted. The observed lowering is 19°. While the close agreement is fortuitous, the correct prediction of the direction of the effect in two cases is gratifying.

We are greatly indebted to Dr. E. O. Wollan and Dr. C. G. Shull of the Physics Division of this Laboratory for much aid and discussion in the theory and application of the neutron diffraction method, and for the use of a spectrometer whose basic design and construction is due to them. Thanks are

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(28) (a) H. S. Gutowsky, G. B. Kistiakowsky, G. E. Pake and E. M. Purcell, *J. Chem. Phys.*, **17**, 972 (1949); (b) D. M. Dennison, *Rev. Mod. Phys.*, **12**, 175 (1940).

(29) But see reference (7). The argument here presented is in any case pertinent to the exceptionally large difference in transition temperatures resulting from deuterium substitution.

due also to Mr. B. S. Borie for X-ray diffraction measurements. We are especially grateful to Professor V. Schomaker for several illuminating discussions.

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

An Electron Diffraction Investigation of the Molecular Structures of 1,1,1-Trichloroethane, 2,2-Dichloropropane and 2-Chloro-2-methylpropane[1]

BY J. W. COUTTS AND R. L. LIVINGSTON

RECEIVED JULY 28, 1952

An electron diffraction investigation of the molecular structures of 1,1,1-trichloroethane, 2,2-dichloropropane and *t*-butyl chloride has yielded the following results: 1,1,1-trichloroethane, C–Cl = $1.77_5 \pm 0.02$ Å., C–C = 1.50 to 1.58 Å. (assumed), ∠C–C–Cl = 110 ± 1.5°; 2,2-dichloropropane, C–Cl = $1.77_6 \pm 0.02$ Å., C–C = 1.54 ± 0.04 Å., ∠Cl–C–Cl = 109.5 ± 2°, ∠C–C–Cl = 109 ± 3°; *t*-butyl chloride, C–Cl = 1.80 ± 0.04 Å., C–C = 1.54 ± 0.03 Å., ∠C–C–Cl = 107.5 ± 1.5°.

Introduction

One of the important applications of electron diffraction has been the study of the effects produced in the configuration of a molecule when certain groups or atoms therein are replaced by other groups or atoms. The purpose of the present investigation was to determine whether any structural differences result from the substitution of methyl groups for chlorine atoms in the series: 1,1,1-trichloroethane, 2,2-dichloropropane and 2-chloro-2-methylpropane (*t*-butyl chloride). It was also hoped that accurate values could be obtained for the bond distances and angles in these compounds so that comparisons with distances and angles in other compounds would be possible. Of these compounds, the first and third have been previously investigated by Beach and Stevenson.[2,3] The diffraction patterns obtained by Beach and Stevenson did not extend to as large a scattering angle as is generally obtained with the apparatus available in this Laboratory. Since the outer part of the diffraction pattern is often the most valuable in structure determinations, repetition of their work was considered worthwhile in the hope that a more precise determination would result. Furthermore, their determinations were made without allowance for the displacements of atoms caused by intramolecular vibration. In the case of a molecule such as *t*-butyl chloride with a large number of hydrogen atoms, vibration factors assume considerable importance and the study of this compound cannot be considered complete without an investigation of their effects.

When this investigation was undertaken there was no report in the literature of a structural investigation of 2,2-dichloropropane. When the work was near its completion, however, mention was made in a review article[4] of an unpublished diffraction investigation of this compound by J. O'Gorman and V. Schomaker. The authors have been informed by Dr. Schomaker that the values given in the review article were based upon an incomplete study.

Experimental

Commercial samples of 1,1,1-trichloroethane and *t*-butyl chloride were purified by washing with appropriate reagents followed by rectification in all-glass columns. The sample of 2,2-dichloropropane was prepared from acetone and phosphorus pentachloride following in most essentials the method outlined by Smyth and Turkevich.[5] The refractive indices of the samples used were as follows: 1,1,1-trichloroethane, $n^{20}\text{D}$ 1.4380; 2,2-dichloropropane, $n^{20}\text{D}$ 1.4148; *t*-butyl chloride, $n^{20}\text{D}$ 1.3852.

The electron diffraction photographs were prepared using an apparatus built by Professor H. J. Yearian of the Department of Physics of Purdue University. The wave length of the electrons as determined from the transmission patterns of zinc oxide was about 0.055 Å. and the camera distance was about 11 cm. The diffraction patterns extend to approximately q = 90 for each compound and are represented by curves VIS in Figs. 2, 4 and 6. The q_0 values are given in Tables I, II and III.

Interpretation.—In interpreting the photographs both the visual correlation method[6] and the radial distribution method[7] were employed. The intensity curves used in the visual correlation were calculated from the equation

$$I(q) = \sum_{\mathrm{i}}\sum_{\mathrm{j}} \frac{Z_{\mathrm{i}}Z_{\mathrm{j}}}{r_{\mathrm{ij}}} \exp\,(-b_{\mathrm{ij}}q^2) \sin \frac{(\pi q r_{\mathrm{ij}})}{(10)}$$

The summations were performed from punched cards[7,8] by an I.B.M. tabulating machine. In the calculation of all intensity curves the bonded C–H distance (1.09 Å.) and the short non-bonded C–H distance (2.16 Å.) were damped by the factors b = 0.00018 and b = 0.00035, respectively. These values have been found by Schomaker[9,10] to account adequately for the distribution of these distances due to vibration in several similar compounds. The values of b_{ij} assigned to other distances will be discussed separately for each compound. The radial distribution functions were calculated from the equation[7]

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[1] Contains material from the doctoral thesis of J. W. Coutts, Research Corporation Fellow in Chemistry, Purdue University, 1949–1950.

[2] J. Y. Beach and D. P. Stevenson, THIS JOURNAL, **60**, 475 (1938).

[3] J. Y. Beach and D. P. Stevenson, *ibid.*, **61**, 2643 (1939).

[4] P. W. Allen and L. E. Sutton, *Acta Crystallographica*, **3**, 46 (1950).

[5] C. P. Smyth and A. Turkevich, THIS JOURNAL, **62**, 2468 (1940).

[6] L. O. Brockway, *Revs. Mod. Phys.*, **8**, 231 (1936).

[7] P. A. Shaffer, V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

[8] P. A. Shaffer, V. Schomaker and L. Pauling, *ibid.*, **14**, 648 (1946).

[9] V. Schomaker and P. Shaffer, THIS JOURNAL, **69**, 1555 (1947).

[10] W. N. Lipscomb and V. Schomaker, *J. Chem. Phys.*, **14**, 475 (1946).