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The Structure of Ammonium Chloride by Neutron Diffraction

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From the intensities of powder diffraction lines the positions of the deuterons in ND_4Cl have been determined at liquid nitrogen and room temperatures. The experimental results confirm at low temperature the space group T_d^1 and the tetrahedral structure of the ammonium ion with an $N-D$ separation 1.03A. At room temperature the T_d^1 space group persists. Neither free rotation nor disordered orientations of the ammonium ions have been observed. Details concerning deuteron vibrations are discussed.

INTRODUCTION

ANOMALIES in the behavior of ammonium chloride were first observed by Simon[1] who detected a sharp transition at $-30°C$ in the specific heat at constant pressure. X-ray investigations[2] showed that the nitrogen and chlorine atoms were arranged in a lattice of the CsCl type and that a change of 1 percent in the lattice constant accompanied the transition, but these investigations gave no information about the hydrogen atoms. Pauling[3] suggested that onset of free rotation of the ammonium ion might account for the change in specific heat. Quanitative details of the onset of rotation for dipole interactions were discussed by Fowler[4] and in a somewhat different form by Kirkwood.[5] Eucken[6] pointed out that the rotational heat required for the ammonium ion above the critical temperature was not in agreement with experiment. In the meantime, Frenkel[7] had suggested an order-disorder transition for the ammonium ion, detailed mathematical treatment being given by Nagamiya.[8]

Concurrently experimental evidence in support of both the rotation and order-disorder theories accumulated. Hettich[9] observed the disappearance of the piezoelectric effect at the transition temperature and attributed it to rotation. Menzies and Mills[10] reported that below $-30°C$ the Raman line of 183 cm^{-1} was clearly visible, but that it was absent in the room temperature phase, while Krishnan[11] found that the line persisted in that phase but with much less intensity. Menzies and Mills, although favoring rotation, stated that a possible explanation for their results was onset of a simple torsional oscillation of the ammonium ion, while Couture and Mathieu[12] deduced rotation about a threefold axis from Raman polarization measurements. Similar differences occurred among the infrared results, where Beck[13] observed rotational structure on at least one vibrational band, while Wagner and Hornig[14] found evidence for the order-disorder theory. Solid state experiments by Bridgman,[15] and Lawson,[16] and electron diffraction measurements by Laschkarew[17] did not lead to conclusive results.

Since the difficulties arose from ignorance of the positions and behavior of the hydrogen atoms, it was decided to study ammonium chloride by neutron diffraction methods so that by comparison of experimental and calculated structure factors the correct distribution of the hydrogen atoms could be determined. Measurements by the powder method at liquid nitrogen and room temperature are reported in the present paper and it is shown that they establish the structures. For experimental reasons[18] deuterated ammonium chloride was used, and because the physical properties of deuterated and ordinary ammonium chloride are similar[14,19] the results of the structure determination may be expected to apply qualitatively to the ordinary chloride.

APPARATUS AND PROCEDURE

The general design of the spectrometer, the counting equipment, and the monitor of the neutron intensity have been previously discussed[20] and the collimation of the primary neutron beam has been described.[21] The monochromatic beam was selected from the primary beam by a sodium chloride crystal placed in the transmission position; diffraction by diamond powder gave the wavelength as 1.07A.

The spectrometer arm, carrying the main neutron counter and a defining collimator ($0.5\times1.5\times19$ inches long), was driven by a reversible synchronous motor and moved between two limit switches at the rate of

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[17] W. E. Laschkarew and I. D. Usyskin, Z. Physik **85**, 618 (1933).

[18] Shull, Wollan, Morton, and Davidson, Phys. Rev. **73**, 842 (1948).

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approximately 1.1 degree per hour. To check automatically the progress of the spectrometer arm, a phonograph crystal cartridge which was attached to the arm had its stylus adjusted to cross every 0.1-inch graduation (1.1°) of a graduated circle. The movement of the stylus into the graduations created a pulse in the crystal, which was recorded after amplification.

The specimen table was coupled to the arm by a belt system and followed at half the angular rate. The table carried a stainless steel Dewar flask with 0.007-inch windows and a separate support for the airtight cassette containing the powder specimen. The cassette could be centered accurately on the axis of rotation of the table. The windows of the cassette were made of 0.005-inch Dural, spaced approximately 0.1 inch apart, and large enough to accommodate the neutron beam (0.5×1 inch) at all required angles. The area occupied by the powder was determined from a radiograph of the filled cassette.

A chromel-alumel thermocouple was soldered to the surface of the cassette and the temperature of the cassette was recorded. For low temperature experiments liquid nitrogen was maintained in the Dewar flash by an automatic refill system connected to a 50 liter flask; the temperature fluctuated between −170°C and −190°C.

All counts were recorded on a multiple pen recorder and analyzed by the following method. The number of counts in each fifteen minute interval was corrected for fluctuations in the intensity of the primary neutron beam. The difference between measurements with full and empty cassettes gave the effect of the powder. The resulting diffraction pattern of the powder was plotted as an integral curve against angle. An example of such a plot, which includes two diffraction peaks, is shown in Fig. 1. The incoherent background appears as straight lines and the integrated intensity of the peaks is given by the height of the steps I and I'. Because the width of each step depended on the resolution of the spectrometer, overlapping of peaks sometimes occurred even with simple cubic compounds and it was then difficult to assign the correct position and slope to the background lines. In such a case the point of minimum slope between unresolved peaks was selected and a line parallel to the nearest resolved background line was drawn through this point.

GENERAL THEORY

For a flat slab of crystalline powder whose normal makes an angle θ with the incident beam[22] the integrated intensity in a peak is

$$I_{hkl}=BP_0\frac{W\exp(-ut\sec\theta)}{\rho A\sin^2 2\theta}j_{hkl}N^2|F_{hkl}|^2, \qquad (1)$$

where hkl is the reflection index, P_0 is the power in the primary beam, B is an instrumental constant determined by calibration, t is the thickness of the slab, W is the weight of powder in the cassette, A is the area of the powder, ρ is the crystalline density, u is the absorption coefficient, 2θ is the angle between incident and diffracted beams, j_{hkl} is the multiplicity factor, and N is the number of unit cells per cm^3. F_{hkl} is the structure factor for the unit cell and may be written

$$F_{hkl}=\sum_n f_n R_n \exp\{-2\pi i(hx_n+ky_n+lz_n)\} \qquad (2)$$

where the summation is carried out over all the atoms in the unit cell; $x_n y_n z_n$ are the fractional coordinates of nucleus n, f_n is the bound nuclear scattering length, and R_n is a correction factor for thermal and zero-point vibrations. Instead of the coherent scattering amplitude f_n, it is usual to state the coherent cross section, σ_n, which is defined by

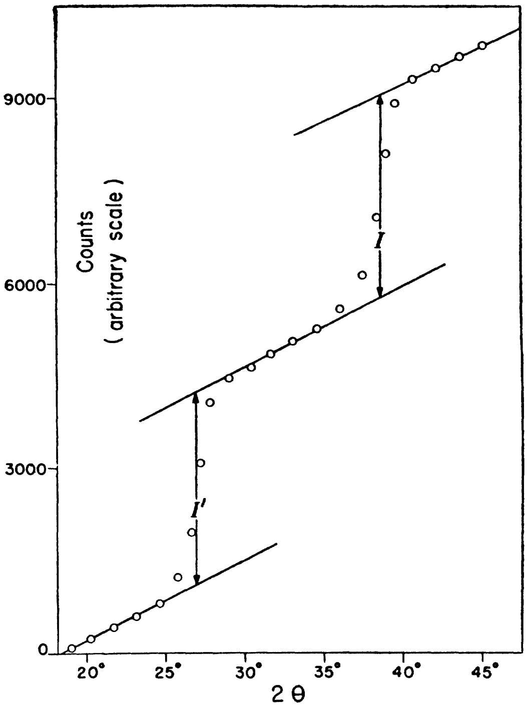

FIG. 1. An integral plot for a specimen of ZrN. The detector moved at a constant angular rate and the accumulated counts are plotted against angular position of the detector. The steps I and I' are the integrated intensities of two diffraction peaks.

$$\sigma_n=4\pi|f_n|^2. \qquad (3)$$

The factor R_n has been calculated by Debye and Waller for x-rays, and Weinstock[23] has discussed the application to neutrons. For isotropic binding

$$R_n=\exp(-K_n\sin^2\theta) \qquad (4)$$

with

$$K_n=\frac{6h^2}{\lambda^2 m_n k\Theta}\left(\frac{\varphi(x)}{x}+\tfrac{1}{4}\right) \qquad (5)$$

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

[23] R. Weinstock, Phys. Rev. **65**, 1 (1944).

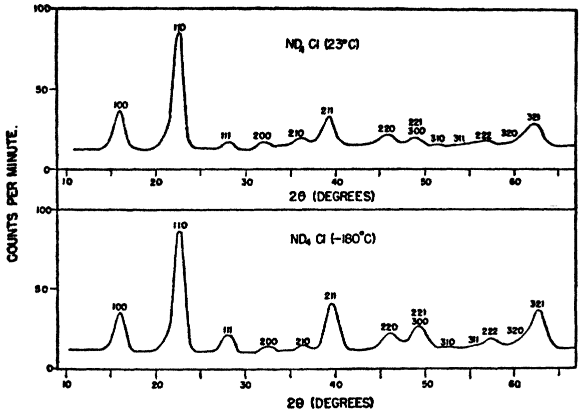

FIG. 2. Neutron diffraction patterns of powdered ND_4Cl at two temperatures, for a neutron wavelength of 1.07A.

where Θ is the Debye characteristic temperature of the material, h is Planck's constant, λ is the wavelength, m_n is the mass of the atom, k is Boltzmann's constant, $\varphi(x)$ is the Debye characteristic function, and $x=\Theta/T$ where T is the temperature.

For anisotropic binding K_n is a function of θ and is proportional to the mean square displacement of the scatterer perpendicular to the reflecting plane.[24]

CALIBRATION OF SPECTROMETER AND MEASUREMENT OF CROSS SECTIONS

The instrument constant B was determined at liquid nitrogen and room temperatures from diffraction measurements with diamond powder[22] of particle size 6 to 12 microns, the bound coherent cross section of carbon being taken as 5.52 barns.[25]

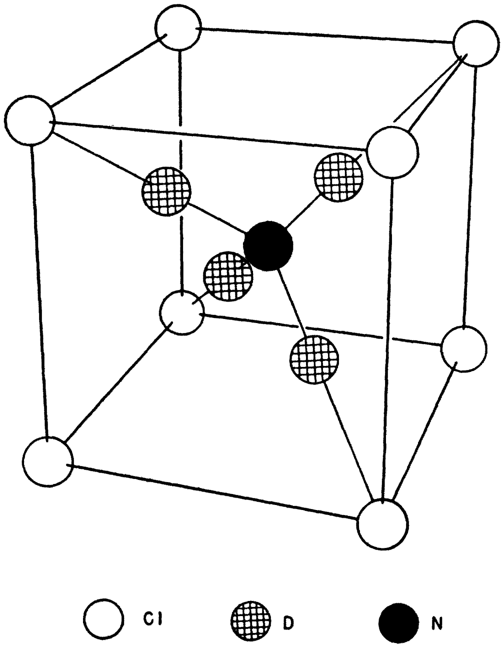

FIG. 3. The unit cell of ND_4Cl.

Preliminary comparison of observed and calculated intensities for the ammonium chloride diffraction pattern at low temperature cast doubt on the values available for the coherent cross sections of chlorine and nitrogen. They were therefore redetermined from powder diffraction patterns of NaCl and ZrN at liquid air temperatures. Special precautions were taken to prepare crystals of NaCl with maximum particle size 10 microns; the ZrN was obtained commercially at 600 mesh. ZrN was used in spite of its hafnium impurity of 3 percent because no pure simple cubic nitride was available. The following values were obtained for the bound coherent cross sections:—

$$\sigma_{\mathrm{Cl}}=11.9 \text{ barns}$$
$$\sigma_{\mathrm{Na}}=1.63 \text{ barns}$$
$$\sigma_{\mathrm{Zr}}=5.1 \text{ barns}$$
$$\sigma_{\mathrm{N}}=9.1 \text{ barns.}$$

The chlorine and sodium cross sections are in fair agreement with the values of 12.8 barns and 1.51 barns published by Wollan and Shull,[22] while the high value of the nitrogen cross section shows that there is little spin incoherence, in disagreement with other results.[26] Gas scattering experiments carried out in this laboratory have also given the higher value for the nitrogen cross section. The deuterium cross section was taken to be 5.8 barns.[20]

STRUCTURE DETERMINATION OF ND_4Cl

Diffraction measurements were made at liquid nitrogen and room temperatures using deuterated ammonium chloride with a deuterium purity of 99.4 percent.[27] The diffraction patterns are shown in Fig. 2. Integrated intensities I_{hkl} were found from integral plots as previously described, and experimental structure factor moduli $|F_{hkl}|_E$ were derived by Eq. (1). These are tabulated for the low and high temperatures in Table I, column 11, and Table IV, column 4, respectively, the units being 10^{-12} cm. The errors quoted are the maximum deviations from the mean of several measurements.

The experimental moduli were compared with the moduli of structure factors calculated by Eq. (2) for models suggested by the previous experimental work. In these models several minor parameters were available for adjustment: the nitrogen deuterium distance was known to be about 1A but some variation from this was permissible; the R factors in Eq. (2), even if taken as following Eq. (4), still gave latitude because the Debye temperature was not found in the literature and because Eq. (5) may not apply accurately; and the cross sections could be varied within the experimental error of their determination.

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[24] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1948), Chapter V.

[25] E. Melkonian, Phys. Rev. 76, 1750 (1949).

[26] C. G. Shull and E. O. Wollan, Phys. Rev. 75, 1302 (1949).

[27] The ND_4Cl was prepared and analyzed by the Analytical Development Section, Chemical Control Branch, Chalk River.

TABLE I. Variation of parameters in the low temperature case.

	Trial calculations									Experimental results	
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Final[a] choice		
K_{Cl}	0.36	0.36	0.36	0.20	0.20	0.20	0.20	0.20	0.15		
K_{N}	0.78	0.78	0.78	0.52	0.52	0.52	0.52	0.52	0.39		
K_{D}	5.5	5.5	3.6	3.6	3.6	2.7	2.7	2.7	2.7		
r(A)	1.00	1.10	1.00	1.00	1.05	1.05	1.04	1.03	1.03		
hkl	$\lvert F_{hkl}\rvert$	$\lvert F_{hkl}\rvert$	$\lvert F_{hkl}\rvert$	$\lvert F_{hkl}\rvert$	$\lvert F_{hkl}\rvert$	$\lvert F_{hkl}\rvert$	$\lvert F_{hkl}\rvert$	$\lvert F_{hkl}\rvert$	$\lvert F_{hkl}\rvert$	$\lvert F_{hkl}\rvert_E$	Error
100	1.32	1.13	1.37	1.37	1.28	1.31	1.34	1.35	1.38	1.39	2%
110	2.58	2.41	2.62	2.63	2.53	2.56	2.59	2.60	2.59	2.54	2%
111	1.08	1.25	1.18	1.19	1.29	1.39	1.33	1.32	1.33	1.35	4%
200	1.21	0.90	1.13	1.12	1.00				1.01	0.98	4%
210	0.44	0.64	0.49	0.48	0.55				0.53	0.55	4%
211	1.74	1.82	1.89	1.92	1.97				1.97	1.95	4%
220	1.78	1.93	1.81	1.87	1.95				1.94	1.92	4%
222	1.73	1.60	1.85	1.94	1.87				2.02	1.94	20%
321	1.68	1.72	1.78	1.85	1.88				1.93	1.94	5%

[a] For the structure factors in this column the chlorine cross section was taken as 11.5 barns. The change from 11.9 barns gave better agreement, and is within the experimental error of the measurement. (The intensities from the planes (310), (311), and (320) were too small for accurate measurement. The peaks due to (300), and (221) are coincident and are omitted from this table.)

LOW TEMPERATURE PHASE

The low temperature structure suggested by the previous experimental work is illustrated by the model shown in Fig. 3. In this model the nitrogen and chlorine atoms are in positions $(xyz)_{\mathrm{N}}=000$, $(xyz)_{\mathrm{Cl}}=\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The ammonium ion is tetrahedral with the deuterium atoms on the diagonals of the unit cell at a distance r from the nitrogen atoms so that the coordinates of the four deuterium atoms are $(xyz)_{\mathrm{D}}=xxx$, $x\bar{x}\bar{x}$, $\bar{x}\bar{x}x$, $\bar{x}x\bar{x}$ where $x=r/(\sqrt{3}a)$ and a is the length of the cube edge. The space group of this lattice is $T_d{}^1$, and the structure factor with R of the form given by Eq. (4) becomes

$$\begin{aligned}F_{hkl}=&f_{\mathrm{N}}\exp(-K_{\mathrm{N}}\sin^2\theta)+(-1)^{h+k+l}f_{\mathrm{Cl}}\\&\times\exp(-K_{\mathrm{Cl}}\sin^2\theta)+4f_{\mathrm{D}}\exp(-K_{\mathrm{D}}\sin^2\theta)\\&\times\{\cos(2\pi hx)\cos(2\pi kx)\cos(2\pi lx)\\&\qquad-i\sin(2\pi hx)\sin(2\pi kx)\sin(2\pi lx)\}.\qquad(6)\end{aligned}$$

Since no Debye temperature for ND_4Cl could be found in the literature, the K values in preliminary calculations were based on the Debye temperature of NaCl. This temperature is 281°K and its use was suggested by the similarity in the low temperature specific heats of ND_4Cl and NaCl[28] and by the similarity of the ionic masses. r was taken as 1A. The initial agreement was good and calculations were continued by the methods of successive approximation. The course of the calculations is summarized in Table I, where the adjustable parameters are shown at the top of the table and the corresponding $|F_{hkl}|$ below. The choice of parameters implies that the nitrogen chlorine and deuterium atoms are considered as separate units. It might be more correct to assume that the lattice is made up of chlorine and ammonium ions with the deuterons as internal constituents of the ammonium ions. However, this would introduce complexity which is not justified at present, especially as the calculated structure factors were relatively insensitive to changes in K_{N} and K_{Cl}.

The parameters r and K_{D} were first changed, and then K_{N} and K_{Cl} were adjusted so that $K_{\mathrm{N}}m_{\mathrm{N}}=K_{\mathrm{Cl}}m_{\mathrm{Cl}}=K_{\mathrm{D}}m_{\mathrm{D}}$ in conformity with Eq. (5). In the final calculation it was found that changing σ_{Cl} from 11.9 barns to 11.5 barns gave best agreement. The agreement of the final set of calculated structure factors with the experimental results was very good, and the number of planes was sufficient to make unlikely any other structure. The value of $r=1.03\mathrm{A}\pm0.02\mathrm{A}$, is consistent with the recent result[29] $r=1.025\pm0.01\mathrm{A}$ obtained from magnetic resonance experiments on NH_4Cl.

The extent of the deuteron vibration can be estimated from K_{D}, if it is assumed that the reduction factor $\exp(-K_{\mathrm{D}}\sin^2\theta)$ is due to the spreading of each deuteron over the finite volume of the ground state of an isotropic harmonic vibration. On this assumption $K_{\mathrm{D}}=(2\pi s/\lambda)^2$ where s determines the width of the ground state with density proportional to $\exp[-\{\mathrm{radius}/s\}^2]$. For $K_{\mathrm{D}}=2.7$ (Table I, column 10) the value of s is 0.28A, and this value is an upper limit because inelastic scattering was neglected.

ROOM TEMPERATURE PHASE

It was suggested by Pauling and Frenkel that the transition at −30°C in NH_4Cl marks the onset of vibrations which are large enough to lead to a disordered arrangement of the ammonium ion in the lattice. Pauling suggested that the tetrahedra rotate freely above the transition temperature, while Frenkel proposed that some ammonium ions have sufficient energy to cross the potential barrier and rotate about the {100} axis, taking up a position at 90° to the original orientation. These disordered arrangements introduced a center of symmetry into the lattice and offered an

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[28] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 57.

[29] Gutowsky, Kistiakowsky, Pake, and Purcell, J. Chem. Phys. **17**, 972 (1949).

TABLE II. Comparison of $|F|$'s observed at room temperature with $|F|$'s calculated for three models.

	Calculated			Experimental
hkl	Model (a) $\lvert F_{hkl}\rvert$	Model (b) $\lvert F_{hkl}\rvert$	Model (d) $\lvert F_{hkl}\rvert$	$\lvert F_{hkl}\rvert_E$
100	1.54	0.97	0.97	1.41
110	2.57	2.19	2.19	2.47
111	0.13	0.01	0.48	0.89
200	1.50	1.40	1.40	1.09
210	0.59	0.30	0.30	0.68
211	0.97	1.45	1.49	1.43
220	0.81	1.40	1.40	1.39
222	0.94	1.22	1.22	1.08
321	1.06	1.14	1.14	1.32

easy explanation for the disappearance of the piezoelectric effect. There was, however, not sufficient evidence to prove whether either of the two suggestions was correct, and to cover all important possibilities, four models (a), (b), (c), and (d) have been considered in the present work. These models differ in the behavior of the ammonium ion, but not in the positions of the nitrogen and chlorine atoms because these are known from x-ray studies.

In model (a), called the spherical shell model, the ammonium ion is assumed to be rotating freely. The four deuterium atoms present a thin spherical shell of radius r to the incoming neutrons, insofar as the coherent scattering is concerned. The deuterium contribution to the structure factor for this thin shell is

$$F_D = 4f_D \sin y / y, \tag{7}$$

where

$$y = (4\pi r \sin\theta)/\lambda.$$

Model (b) corresponds to Frenkel's suggestion of total disorder in the arrangement of the tetrahedra on the two sets of diagonals in each cube. For coherent scattering this is equivalent to placing one-half deuteron on each diagonal in the unit cubes and is called the half-hydrogen model. Such an arrangement would arise from a "resonance" between the two sets of diagonals.

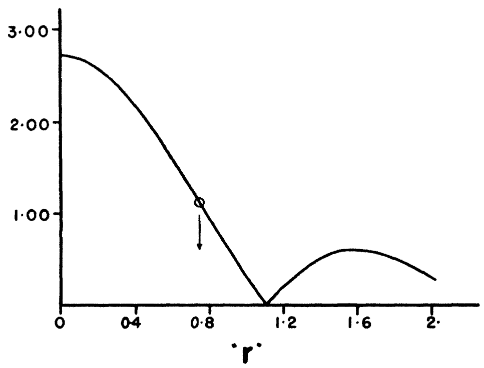

FIG. 4. The contribution to the (111) structure factor of ND_4Cl by the four deuterons, on the assumption of free rotation of a rigid ammonium ion. The variable r is the nitrogen deuterium distance and the arrow indicates the value which would be required to make this model fit the experimental result for the (111) reflection.

The structure factor is that of Eq. (6) without the imaginary term. In model (c) the ammonium ions lie in mirror image positions in neighboring cells, and the original unit cell has to be enlarged eight times to conform with the altered symmetry conditions. The resulting space group is O_h^5 with $a = 7.73$A. A diffraction line whose intensity is comparable with the line marked (111) in Fig. 2 should be observed at $2\theta = 14°$ and this line can be regarded as a characteristic feature of this model. Finally, in model (d), the low temperature form is assumed to persist at room temperature and the space group remains unaltered. The structure factor is given by Eq. (6) on the assumption that Eq. (4) applies.

Since no new lines were observed in the spectrum, calculations on model (c) were unnecessary, and this model was not considered further. Preliminary calculations of $|F_{hkl}|$ for each of the models (a), (b), and (d) were undertaken with $r = 1.00$A and $\Theta = 281°$K, and the results were tabulated with the experimental values (Table II). Although the agreement was poor, further calculations led to the choice of a satisfactory model.

The value of $|F_{111}|$ was found to be particularly sensitive to the deuterium contributions because the contributions of the chlorine and nitrogen nearly cancel, and this quantity was of primary importance in the attempts to get a fit by variation of the parameters. For agreement with the experimental value of $|F_{111}|$ the deuterium contribution must equal 1.12. For model (a) the deuterium contribution to $|F_{111}|$ was plotted as a function of the radius r for $0 < r < 2$A (Fig. 4). Only one radius ($r = 0.74$A) gave agreement with the required value 1.12. This radius, besides being unlikely, brought $|F_{100}|$ up to 2.0 compared to the experimental value 1.41. Introducing a factor $\exp(-K_D \sin^2\theta)$ into Eq. (7), i.e., changing the thickness of the spherical shell, did not help, and further calculations clearly indicated that the spherical model had to be abandoned. It also proved impossible to adjust model (b) satisfactorily because the calculated $|F_{111}|$ was too small for all reasonable values of the nitrogen deuterium separation. In fact, the introduction of a center of symmetry, as in models (a) and (b), destroyed the strong imaginary component of the (111) structure factor. This left only unsymmetrical structures such as model (d) to be considered.

In the calculation of the structure factor of model (d) the K's and r's were varied as before. With $K_D = 9.5$ fair agreement was obtained for the $|F_{hkl}|$ values (Table III). However, when the agreement for the low index plane (100) was good $|F_{200}|$ was unsatisfactory (columns 2 and 3), or when the agreement for the higher index 200 improved $|F_{100}|$ deteriorated (columns 4 and 5). This suggested that the correction factor $\exp(-K_D \sin^2\theta)$ no longer applied, and that the deuterium distribution should not be treated as isotropic in the high temperature modification.

An anisotropic distribution of the deuterium nuclei could arise from small torsional oscillations of the ammonium ion about its center. This motion would cause each vertex of the tetrahedron to move on a spherical cap of radius 1.03A. The structure factor of this model was obtained by methods based on unpublished work of Dr. N. K. Pope. Each deuteron was considered to be spread out into a spherical cloud corresponding to the simple interpretation given above of the low temperature value of K_D. The center of this cloud was assumed to move over the spherical cap with a probability density proportional to $\exp(-u^2/l_D^2)$ where u is the distance of the center of the cloud from the appropriate diagonal of the unit cell, and l_D is a parameter. For simplicity of calculation, the curvature of the spherical cap was neglected, and the cap was treated as a flat plate perpendicular to the diagonal and at a distance r_1 from the nitrogen. The structure factor of this plate is

$$f_D \exp\{-K_D \sin^2\theta \sin^2\psi - 2\pi i(hx_1+ky_1+lz_1)\}$$

where (x_1, y_1, z_1) are the fractional coordinates of the point of intersection with the diagonal, and ψ is the angle between the normal to the plate and the direction $\{hkl\}$.

The contribution of the deuterium to the structure factor of the unit cell is the sum of four such terms corresponding to the four deuterons. The result is

$$\begin{aligned}F_D = {} & f_D \exp(-K_D \sin^2\theta)\exp(-4\pi l_D^2 \sin^2\theta/\lambda^2)\\ & \times[\{\cos 2\pi x_1(h+k+l) - i \sin 2\pi x_1(h+k+l)\}\\ & \times \exp\beta(h+k+l)^2 + \{\cos 2\pi x_1(h-k-l)\\ & - i \sin 2\pi x_1(h-k-l)\}\exp\beta(h-k-l)^2\\ & + \{\cos 2\pi x_1(-h-k+l) - i \sin 2\pi x_1(-h-k+l)\}\\ & \times \exp\beta(-h-k+l)^2 + \{\cos 2\pi x_1(-h+k-l)\\ & - i \sin 2\pi x_1(-h+k-l)\}\exp\beta(-h+k-l)^2]\end{aligned}$$

where

$$x_1 = r_1/(a\sqrt{3})$$

and

$$\beta = \pi^2 l_D^2/(3a^2).$$

In the calculations of the structure factors K_N and K_{Cl} were 2.7 and 1.1 corresponding to $\Theta = 281°K$ and $T = 296°K$, K_D was 2.7, the final low temperature value, and l_D was chosen equal to 0.3A. Different values of r_1 were tried and maximum agreement was obtained for $r_1 = 0.97A$ (Table IV). Since the agreement was within experimental error, further refinement of the K values and l_D was considered meaningless. The agreement proves that the model contains the essential features of the deuterium distribution.

It seems reasonable to assume that the nitrogen deuterium distance does not change from 1.03A, and that r_1 is the apparent mean distance of the deuteron density distribution in the $\{111\}$ direction. For the case of the spherical cap, this leads to an approximate amplitude of oscillation of 18±2° which is consistent with the l_D value.

The anisotropic distribution may also be interpreted as a motion of the deuterons around the diagonals. However, the present results cannot be used to distinguish between these fine details of deuterium behavior.

TABLE III. Variation of parameters of model (d).

K_{Cl}	1.1	0.53	0.53	1.1	
K_N	2.7	1.36	1.36	2.7	
K_D	9.5	9.5	9.5	9.5	
r	0.90	0.90	1.03	1.03	
hkl	$\|F_{hkl}\|$	$\|F_{hkl}\|$	$\|F_{hkl}\|$	$\|F_{hkl}\|$	$\|F_{hkl}\|_E$
100	1.37	1.37	1.16	1.16	1.41
110	2.57	2.62	2.58	2.33	2.47
111	0.71	0.92	0.87	0.88	0.89
200	1.44	1.54	1.22	1.13	1.09
210	0.30	0.29	0.43	0.44	0.68
211	1.52	1.63	1.60	1.48	1.43
220	1.39	1.55	1.56	1.41	1.39
222	1.25	1.46	1.45	1.25	1.08
321	1.29	1.50	1.40	1.18	1.32

CONCLUSION

The structure of deuterated ammonium chloride has been shown to possess T_d^1 symmetry at both −180°C and 23°C. No evidence for free rotation or disorder has been found.

In the low temperature modification the nitrogen deuterium distance is 1.03±0.02A and the distribution of each deuteron is spherical to within the experimental resolution. This distribution is largely due to zero-point vibrations and its characteristic radius is 0.28A.

In the room temperature modification the distribution of the deuteron is spread transversely to the cube diagonal. This anisotropic distribution can be interpreted in several ways, for example, as an angular oscillation of the tetrahedron about the nitrogen as center, or as a motion of the deuterons around the diagonals. In the former the deuterium distribution has the shape of a spherical cap with radius (nitrogen deuterium distance) equal to 1.03A, and the apparent nitrogen deuterium distance along the cube diagonal is 0.97A. In the latter the center of the deuteron moves approximately in a circle in a plane which cuts the cube diagonal at 0.97A from the nitrogen. (It is of

TABLE IV. Comparison of final model with experimental results (room temperature). A value of $\sigma_{Cl} = 11.5$ barns was used for this table.

	Calculated		Experimental	
hkl	$\|F_{hkl}\|$ $r_1 = 1.00A$	$\|F_{hkl}\|$ $r_1 = 0.97A$	$\|F_{hkl}\|_E$	Error
100	1.35	1.41	1.41	2%
110	2.42	2.48	2.47	2%
111	1.03	0.95	0.89	5%
200	1.00	1.11	1.09	20%
210	0.61	0.56	0.68	20%
211	1.52	1.54	1.43	20%
220	1.28	1.25	1.39	20%
222	1.53	1.54	1.08	40%
321	1.28	1.28	1.32	5%

interest to note that electron diffraction[17] has given a value of 0.95±0.07A for the nitrogen hydrogen separation in NH_4Cl at room temperature.) Interpretations in terms of stationary tetrahedra involving angular displacement disorder are much less likely.

The disappearance of the piezoelectric effect and the absence or weakening of the Raman line, 183 cm^{-1}, above −30°C can now no longer be explained in terms of disorder or a centro-symmetric structure. However, angular oscillations of the ammonium tetrahedra may disturb the charge distribution in the lattice sufficiently to weaken the Raman line and to make the piezoelectric effect unobservable. A sudden onset of such oscillations may also be the cause of the lattice expansion at the transition temperature and the discontinuity in specific heat.

Theoretical studies are being undertaken to explain the observed behavior, and further experiments are planned to study as a function of temperature the change from the −180°C form to the room temperature form. This is of particular interest because of the existence of a magnetic resonance line width transition at −140°C.[30]

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The Theory of Pressure Broadening and Its Application to Microwave Spectra

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In this paper the calculation of the widths of several absorption lines in the microwave region is attempted. First, the fourier integral formula for transition probability is deduced with the adiabatic assumption. Then the width and the shift of the absorption line are calculated, assuming the well type and the inverse power intermolecular potential. Applying the latter model, the width is calculated for several kinds of self-broadened microwave absorption line. A theoretical formula which gives the width of the ammonia inversion line is obtained as a function of $K/[J(J+1)]^{\frac{1}{2}}$, where K and J are the rotational quantum number. It agrees with experiment for large $K/[J(J+1)]^{\frac{1}{2}}$, and its temperature dependence is also good. In the microwave absorption of oxygen, the quadrupole interaction is shown to be responsible for the width, and our theoretical result agrees with experiment if the quadrupole moment of this molecule is 2.5 to 2.0×10^{-26}. It is also shown that the widths of the rotational lines of linear and symmetric top molecules can be explained by the dipole interaction.

I. INTRODUCTION

It was about half a century ago that the first theory of pressure broadening was proposed by Lorentz.[1] Since then much theoretical and experimental work has been performed on this subject. In microwave spectra, the technique of which has been developed in the past few years, the width can be measured fairly accurately; and recently many interesting data have been obtained in this region. Thus, it may still be interesting and valuable to give further consideration to this subject.

In his theory Lorentz[1] assumed that the molecule is represented by a classical oscillator and that the intermolecular collisions are so strong that the oscillation process is absolutely interrupted by them. His formula which gives the intensity at circular frequency ω is

$$I(\omega)=(c/\pi)[\pi a^2\bar{V}N/\{(\omega-\omega_0)^2+(\pi a^2\bar{V}N)^2\}], \quad (1)$$

where $\bar{V}$ is the mean relative velocity of the molecules, a is the radius of the molecule, N is the number of molecules in unit volume, and c is the total intensity. At $|\omega-\omega_0|=\pi a^2\bar{V}N$ the intensity is just half of the maximum intensity, and thus this quantity gives the half-width of the spectral line. Van Vleck and Weisskopf[2] revised this formula, and Van Vleck and Margenau[3] proved that absorption and emission lines have the same shape in this model. In applying the above formula, the collision radius a was found to be very different from the kinetic collision radius; thus, a was taken as a mere parameter with whose physical meaning we are not concerned.

Kuhn,[4] Margenau,[5] and some others developed a theory in which molecules are assumed to be randomly distributed in space and simultaneously interacting with the radiating molecule. This theory is valid at high pressure and can explain the asymmetry of line shape which is observed in this region. But since we are treating the low pressure region, we cannot use this theory.

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