This allows $\Delta\omega$ to be expressed in terms of the same quantities using equations (7), (8), (3), (10) and (12):

$$\Delta\omega = \frac{\Delta l . \sin(Y-\omega)}{\sin Y} . \qquad (13)$$

One then obtains the following expression using equations (1), (2), (12) and (13):

$$M = \frac{\Delta s}{\Delta l} = \frac{90}{\pi} \cdot \left[\frac{\cos^2\left(\omega - \dfrac{Y}{2}\right)}{\cos^2 \dfrac{Y}{2}} + \frac{\sin^2(Y-\omega)}{\sin^2 Y} \right]^{1/2} . \qquad (14)$$

The quantity M ('magnification') represents the ratio of the film separation Δs in millimetres of any two close reflexions, measured along a festoon, to their reciprocal-lattice separation Δl in reciprocal-lattice units. M is graphed in Fig.4. Fig.4 differs from Fig.2 in that it can be applied to *any* two close points on a festoon belonging to *any* crystal, twinned or untwinned, whereas Fig.2 applies only to *twin-pairs* belonging to a pseudo-merohedral twin. It is expected that Fig.4 will be useful in interpreting unusual patterns other than those covered by Fig.2.

In the case of pseudo-merohedral twinning we are especially concerned with the separation of the twin-pairs, and so must introduce the additional restriction

$$\Delta l_t = 2p \tan \chi , \qquad (15)$$

where the subscript t serves to remind us we are dealing with twin-pairs. Substituting this relation in equation (14), and using equation (11) for p, we get

$$\frac{\Delta s_t}{\tan \chi} = \frac{180}{\pi} \left[\frac{\cos^2\left(\omega - \dfrac{Y}{2}\right)}{\cos^2 \dfrac{Y}{2}} + \frac{\sin^2(Y-\omega)}{\sin^2 Y} \right]^{1/2}$$

$$\times [\cos(Y-\omega) - \cos\omega] . \qquad (16)$$

The calculations for Figs.2 and 4 were performed with the use of a FORTRAN program to compute the expressions given by (16) and (14) respectively, at all points on the Weissenberg film, with a grid interval of 0·5 mm along x and y. With the help of another program for linear interpolation, contours were constructed as shown in the Figures.

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The Structure of NH₄F as Determined by Neutron and X-ray Diffraction

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Neutron and X-ray intensities of NH₄F were measured at $-196\,^\circ$C and $-155\,^\circ$C respectively. The wurtzite type structure and space group $P6_3mc$ were confirmed. The displacement of the two h.c.p. sublattices, formed by each of the F^- - and NH_4^+ - ions, is such that all bond-distances are equivalent. The N–H bond distances as found from the X-ray data are about 0·1 Å shorter than those obtained from the neutron data. The final weighted R values were 1·9% and 2·6% for the X-ray and neutron data respectively.

Introduction

The structure of NH₄F was solved by Zachariasen (1927). The accuracy of the methods at that time was not high enough to show hydrogen atoms and provide information on bonding effects. Looking for compounds with small asymmetric units consisting of light atoms only, we decided to repeat the structure determination, this time by X-ray and neutron diffraction methods.

Previous work

In the following some previous work on NH₄F is summarized. Zachariasen (1927) established the space group to be $P6_3mc$ and found the following cell constants:

$a = 4.39 \pm 0.04$ Å ,

$c = 7.02 \pm 0.06$ Å ,

$c/a = 1.60 \pm 0.03$.

He reported the density to be 1.015 g.cm^{-3} giving two molecules per unit cell and the following positional parameters:

F$^-$: $(\frac{1}{3}, \frac{2}{3}, 0)$, $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$;

NH$_4^+$: $(\frac{1}{3}, \frac{2}{3}, u)$, $(\frac{2}{3}, \frac{1}{3}, u + \frac{1}{2})$.

He determined the parameter u to be about $\frac{3}{8}$ because he found no reflexions $hk4$. NH$_4$F, therefore, has the wurtzite structure.

The ideal wurtzite type structure consists of two h.c.p. sublattices displaced from each other by a distance $(\frac{3}{8})^{1/2}a_0$ where a_0 is the nearest neighbour distance within the h.c.p. sublattice. Hence the c/a ratio is expected to take on a value $= (\frac{8}{3})^{1/2} = 1.633$. Each atom is then at the centre of a tetrahedron formed by the atoms of the other h.c.p. sublattice and the fractional coordinate u then has a value $= \frac{3}{8}$.

Jeffrey, Parry & Mozzi (1956) listed actual c/a ratios for wurtzite type structures and found values ranging from 1.59 to 1.635. The exact tetrahedral arrangement is, therefore, destroyed and the parameter u may differ from the value $= \frac{3}{8}$. Keffer & Portis (1957) placed theoretical limits on the parameter u. If an atom of one h.c.p. sublattice is equidistant from the atoms of the other sublattice the parameter u becomes

$$u_1 = (\tfrac{1}{4}) + (\tfrac{1}{3})(a/c)^{1/2} , \qquad (1)$$

and for a tetrahedral arrangement of the bonds

$$u_2 = (\tfrac{1}{2}) - (\tfrac{1}{24})^{1/2}(a/c) . \qquad (2)$$

Morosin & Shirber (1965) reported the following cell constants for NH$_4$F at 23 °C:

$a = 4.4389 \pm 0.0004$ Å ,

$b = 7.1635 \pm 0.0004$ Å ,

$c/a = 1.6138 \pm 0.0001$

(from powder data using Cr $K\alpha_1$ of $\lambda = 2.28962$ Å).

With these values the theoretical limits for u as given by (1) and (2) would be

$u_1 = 0.3780$,

$u_2 = 0.3735$.

No phase change is undergone by NH$_4$F if the temperature is lowered. Earlier reports (Simon, Simpson & Ruhemann, 1927; Shulvas-Sorokina & Evdomikov, 1939; Kamiyoshi, 1956) that there exists a phase change at approximately -30 °C, as found from dielectric constant and heat capacity measurements, were disproved by Stevenson (1960) and Benjamin & Westrum (1957) who remeasured the dielectric constant and the heat capacity respectively and found no evidence of such a phase change. Benjamin & Westrum believe that the anomaly found previously was due to impurity water which they rigorously excluded in their work. NH$_4$F being very hygroscopic and possessing

nearly the same symmetry and cell constants as water (*cf*. Peterson & Levy, 1957) (H$_2$O: $a = 4.513$ Å, $c = 7.355$ Å at -50 °C *i.e.* a 3% difference in cell constants), it is not impossible that impurity H$_2$O molecules could lock themselves into the structure of NH$_4$F. The effect of such a possibility was not investigated.

Plumb & Hornig (1955) in their infrared studies on NH$_4$F found a strict $3m$ (C_{3v}) and an 'essentially' $\bar{4}3m$ (T_d) point group for the NH$_4^+$ ion as well as moderately strong H bonds. From the slow-neutron cross-section measurements made by Rush, Taylor & Havens (1960) on the ammonium halides, NH$_4$F proved to have the strongest H-bonding effect of that group. Batsanov & Gorogotskaya (1959) reported the energy of the H bond in NH$_4$F to be 3.5 kcal.mole^{-1}.

The crystals

For the X-ray experiments crystals were selected from normal BDH laboratory reagent NH$_4$F. They were rolled between filter paper resulting in cylindrical shapes whose ends were cut. The crystallographic c axis was found to be parallel to the axis of the cylinder in practically all cases. The crystals were dried over silica gel and sealed in thin-walled (1/100 mm wall-thickness) capillaries.

Larger crystals are required for neutron diffraction and these were prepared as follows: a saturated solution of ammonia in methanol was placed in the bottom of a desiccator. A saturated solution of NH$_4$F in water was placed in the top part of the desiccator which was closed, *cf*. Gmelin (1936). Within a couple of days large cylindrical crystals, tapered along their lengths, with hexagonal bases up to 0·8 cm diameter were obtained. The crystals were a few cm long, this dimension being limited by the size of the beaker containing the NH$_4$F solution in water. Many of the crystals thus obtained were hollow.

Samples of both batches from which the crystals were selected for the diffraction experiments were analysed for the water content. The amount of impurity water was found to be $0.6\% \pm 0.1\%$, as found by the Karl Fischer method of analysis. This water was not distributed homogeneously and most probably surface water adsorbed during the necessary handling of the samples in the open laboratory atmosphere.

Preliminaries

Cell constants were measured by means of a powder diffractometer while the powder was kept in a continuously refreshed atmosphere of dry nitrogen. Peaks were step-scanned and the cell constants were adjusted to the measured diffraction angles by means of a least-squares procedure. They refined to $a = 4.439 \pm 0.001$ Å, $c = 7.165 \pm 0.002$ Å (hence $c/a = 1.614 \pm 0.002$) at 20 °C using Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å).

The volume of the unit cell is, therefore, 122.14 ± 0.01 Å^3.

The density was measured by floating NH_4F crystals in a mixture of benzene and carbon tetrachloride and was found to be $1 \cdot 002 \pm 0 \cdot 005$ g.cm^{-3}. This agrees with two molecules per unit cell, the calculated density being $1 \cdot 006$ g.cm^{-3}.

The linear absorption coefficient, μ, for Mo $K\alpha$ radiation was calculated to be $1 \cdot 32$ cm^{-1}.

The space group

From rotation and Weissenberg photographs absences were determined and found to agree with space group $P6_3mc$ with two positions per unit cell. The fourth order reflexions were found to be observable after all by exposing this layer line for about ten times as long as the remaining layer lines. This indicates that the parameter u could differ from the value $\frac{3}{8}$, or that the scattering powers of the F$^-$- and NH$_4^+$-ions are not the same.

Test measurements of intensities on a diffractometer at room temperature produced a violation of the special extinction condition for the twofold positions in space group $P6_3mc$, i.e. if $h-k=3n$ then $l=2n$. Several low order reflexions, though weak, were found to be distinctly observable. This indicates that the fluorine, nitrogen and one of the H atoms lie in the special twofold position $(\frac{1}{3},\frac{2}{3},z)$, $(\frac{2}{3},\frac{1}{3},z+\frac{1}{2})$ whereas the six remaining H atoms lie in the sixfold positions $(x,\bar{x},z)$, $(x,2x,z)$, $(2\bar{x},\bar{x},z)$, $(\bar{x},x,\frac{1}{2}+z)$, $(\bar{x},2\bar{x},\frac{1}{2}+z)$, $(2x,x,\frac{1}{2}+z)$. It is evident that the NH$_4^+$ group cannot be a rotating group as this would lead to a spherically symmetric scattering centre at the twofold positions.

Measurement of X-ray intensities at -155°C

Intensity measurements were done by means of a Nonius three-circle, automatic diffractometer, with Mo $K\alpha$ radiation, on a crystal of $0 \cdot 03$ cm diameter and length $0 \cdot 05$ cm. The crystal was cooled by blowing a stream of cold nitrogen over it while the temperature, measured by means of a thermocouple to be -155°C ± 5°C, was continuously observed. In total 175 reflexions were measured of which 95 reflexions were unique, the remainder being equivalent and 15 reflexions were only measured once, using the θ–2θ method of scanning up to a value of $\sin \theta/\lambda = 0 \cdot 80$. Standard reflexions were measured periodically and found to be constant in intensity to within $1 \cdot 5\%$ throughout the experiment.

Neutron diffraction experiment at -196°C

The crystal selected for this experiment was a cylinder $0 \cdot 25$ cm in diameter and $3 \cdot 5$ cm long with the crystallographic c axis parallel to the axis of the cylinder. It was dipped several times into liquid nitrogen to increase its mosaic structure and sealed into a capillary of boron-free glass. This was fixed into a cryostat made of aluminum which was in turn placed on the large

goniometer head of the diffractometer. The arcs of this goniometer head (i.e. the φ- and χ-setting angles) had a limited travel of 30° and 60°. Because of this limitation the reflexions had to be measured in two orientations of the crystal, i.e. one with the crystal c axis, the other with the crystal a axis parallel to the ω-axis of the diffractometer. During the remounting process, achieved by bending the glass tube containing the crystal, a slight leak developed in the glass tube resulting in an evaporation of the crystal while the cryostat was again evacuated for the second half of the experiment. The crystal stopped evaporating at -196°C so that a correction factor could be obtained from the standard reflexion which was periodically measured. This correction factor was $5 \cdot 62 \pm 0 \cdot 23$.

Again the θ–2θ method of scanning was used, the wavelength was $\lambda = 1 \cdot 285 \pm 0 \cdot 03$ Å (hence $\mu = 4 \cdot 12$ cm^{-1}) and 48 independent reflexions were measured up to $\sin \theta/\lambda = 0 \cdot 57$.

Refinement on the X-ray data

The program used for refinement was a modification of ORFLS written by Busing, Martin & Levy (1962).

The scattering factor curves used were for

F$^-$ *International Tables for X-ray Crystallography* (1962),

N Hansen, Herman, Lea & Skillman (1964),

H Stewart, Davidson & Simpson (1965).

The scattering factor curve for the H atom was calculated by Stewart, Davidson & Simpson (1965) on the model of an H–H bonded molecule.

The weight for each reflexion was taken to be $w = 1/\sigma^2$ where σ is the standard deviation of the measured intensity. In calculating the standard deviations the following procedure was used: for intensities greater than 10,000 counts (132 of the 175 reflexions) the background was neglected, for smaller intensities the background was taken to be $\frac{1}{3}$ of the peak count so that

$$w = \frac{1}{I} \text{ for } I > 10,000,$$

$$w = \frac{1}{\frac{4}{3}I} \text{ for } I < 10,000.$$

Weighting schemes different to the above were tried, but the discrepancies in the results were found to be insignificant.

The function minimized was $w(|F_o| - 1/s|F_c|)^2$ where

$s = $ scaling factor,
$F_o = $ observed structure factor,
$F_c = $ calculated structure factor.

Only the N and F atoms were included in the first refinement on the scaling factor, the isotropic temperature factors of these two atoms and the z parameter of the N atom. This yielded $R = 5 \cdot 0\%$ and $R_w = 8 \cdot 1\%$.

Fig. 1 shows a difference-Fourier of a section bounded by the c axis and the longer diagonal through the $x-y$ plane of the unit cell. The positions of the four H atoms expected in this plane are clearly indicated.

Including the H atoms and refining the necessary positional parameters and the isotropic thermal parameters of all atoms gave $R=1.4\%$ and $R_w=2.0\%$. Refining the F^- ion anisotropically gave $R=1.4\%$ and $R_w=1.9\%$. Any further refinements with the N atom or the H atoms anisotropic gave no further drop in the R values. Hamilton's (1965) test was applied to check for the significance of the anisotropic thermal

Fig. 1. X-ray difference-Fourier synthesis showing positions of the H atoms.

Fig. 2. X-ray final difference-Fourier synthesis.

motion of the F^- ion using an R_w ratio of $1.99/1.90 = 1.05$ (adding one valid digit to the R_w values). The test showed that the anisotropic motion of the F^--ion is valid at the 99% level of significance, the relevant value from Hamilton's Tables being

$$R_{1,85,0.01} = 1.04 .$$

Fig. 2 shows the final difference-Fourier of the same section as above and Table 1 lists the parameters obtained in this refinement.

Table 1. *Parameters obtained from X-ray data*

Standard deviations are given in parentheses.

$\overline{u^2}$ = isotropic thermal mean square displacement,
$\overline{u_\parallel^2}$ = thermal mean square displacement parallel to c axis,
$\overline{u_\perp^2}$ = thermal mean square displacement perpendicular to c axis

	Parameter	Value
F^-	$\overline{u_\parallel^2}$	0·0133 (6) Å²
	$\overline{u_\perp^2}$	0·0122 (5) Å²
N	z/c	0·3782 (3)
	$\overline{u^2}$	0·0129 (4) Å²
H(1)	z/c	0·244 (6)
	$\overline{u^2}$	0·018 (5) Å²
H(2)	x/a	0·441 (3)
	z/c	0·416 (2)
	$\overline{u^2}$	0·019 (3) Å²

Refinement on neutron data

Again the function minimized was $\Sigma\ w(|F_o| - 1/s|F_c|)^2$ with $w = 1/\sigma^2$ where σ is the standard deviation of the intensity. The scattering lengths used were (Bacon, 1955): $b_H = -0.38 \times 10^{-12}$ cm, $b_N = 0.94 \times 10^{-12}$ cm, $b_F = 0.55 \times 10^{-12}$ cm.

After a refinement with all atoms isotropic ($R = 3.8\%$, $R_w = 4.9\%$) it was noticed that the intensities must have suffered slightly from secondary extinction. Hamilton's (1957) correction was applied and then four sets of refinement were carried out:

(1) All atoms isotropic, 9 parameters, $R = 2.4\%$, $R_w = 3.2\%$.

(2) N and F isotropic, H's anisotropic, 13 parameters, $R = 2.2\%$, $R_w = 2.6\%$.

(3) N isotropic, F and H's anisotropic, 14 parameters, $R = 2.2\%$, $R_w = 2.5\%$.

(4) All atoms anisotropic, 15 parameters, $R = 2.2\%$, $R_w = 2.5\%$.

Significance tests were then carried out by use of Hamilton's (1965) procedure in order to decide on the proper model. Model (2) was found to be preferable over model (1) at a 99% level of significance, the relevant R value ratio being $3.2/2.6 = 1.2$ while from Ha-milton's Tables $R_{4,35,0.01} = 1.203$. Model (3) shows a level of significance of 75% over model (2) while model (4) is not significant. Model (2) was, therefore, chosen to be the most justifiable. The parameters of this model are shown in Table 2.
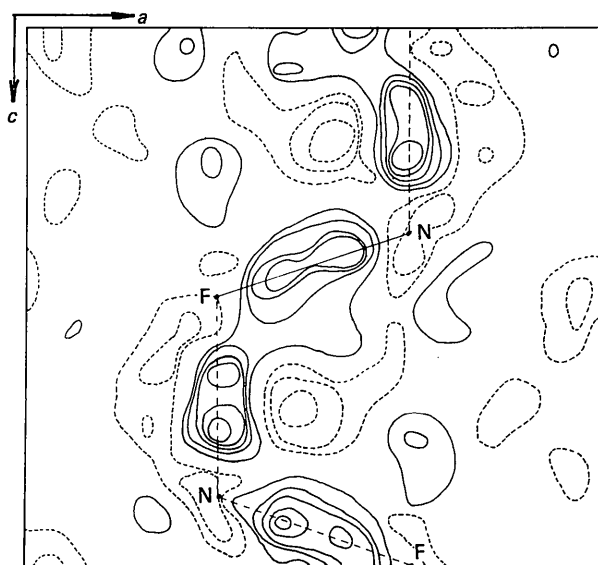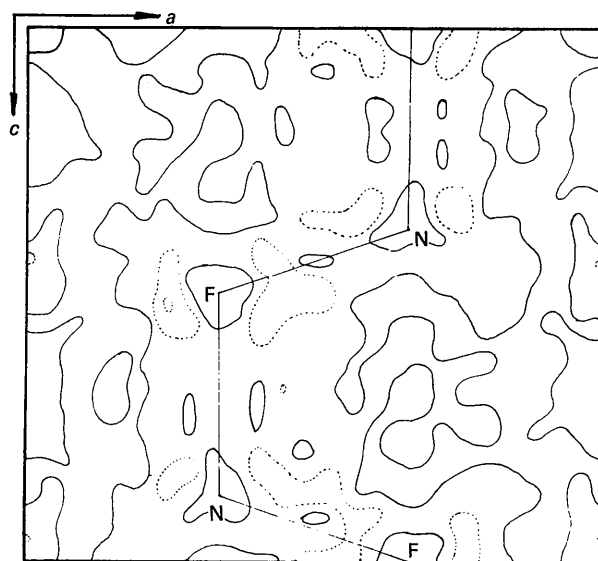
Table 2. *Parameters obtained from neutron data*

Standard deviations are given in parentheses.

$\overline{u^2}$ = isotropic thermal mean square displacement,

$\overline{u_\parallel^2}$ = thermal mean square displacement parallel to H-bond,

$\overline{u_{1\perp}^2}$ = first thermal mean square displacement perpendicular to H-bond,

$\overline{u_{2\perp}^2}$ = second thermal mean square displacement perpendicular to H-bond and $\overline{u_{1\perp}^2}$.

	Parameter	Value
F	$\overline{u^2}$	0·0103 (7) Å²
N	z/c	0·3780 (4)
	$\overline{u^2}$	0·0109 (8) Å²
H(1)	z/c	0·2337 (10)
	$\overline{u_\parallel^2}$	0·015 (4) Å²
	$\overline{u_{1\perp}^2} = \overline{u_{2\perp}^2}$	0·028 (3) Å²
H(2)	x/a	0·4614 (8)
	z	0·4270 (5)
	$\overline{u_\parallel^2}$	0·018 (3) Å²
	$\overline{u_{1\perp}^2}$	0·030 (4) Å²
	$\overline{u_{2\perp}^2}$	0·026 (3) Å²
Average of $\overline{u_{1\perp}^2}$, $\overline{u_{2\perp}^2}$		0·028 (4) Å²

Fig.3 is a Fourier, and Fig.4 a difference-Fourier of the section described above based on model (2). Fig.5 shows the thermal motion parameters of this model.

Application of neutron parameters to X-ray data

The application of the anisotropic thermal parameters of the H atoms obtained from the neutron data did not result in a drop in the R values: $R = 1\cdot4\%$. The complete model as determined by neutron diffraction resulted in a worse agreement: $R = 2\cdot4\%$. Most of the disagreement was the result of the lack of parameters to compensate for the effect of the bonding electrons in the NH₄ group. Application of neutron parameters and scattering factors based on molecular wave functions gave a result which was nearly as good as the fully refined X-ray model: $R = 1\cdot8\%$. (Groenewegen & Feil, 1969.)

Table 3. *Bond lengths and angles*

Parameter	From −155°C X-ray data	From −196°C neutron data
Distance		
N–H(1)	0·96 (5) Å	1·035 (8) Å
N–H(2)	0·88 (3)	1·045 (6)
N–F(1)	2·709 (2)	2·707 (3)
N–F(2)	2·707 (2)	2·708 (3)
Angles		
F(1)–N–F(2)	108·80 (5)°	108·85 (11)°
H(1)–N–H(2)	108·9 (1·2)	109·60 (25)

Results

Table 3 lists the bond lengths and angles calculated from the two experiments and based on the room tem-

perature cell-constants reported by Morosin & Shirber (1965). In the calculations the thermal motion of the atoms and the standard deviations in the cell-constants were not taken into account.

Observed and calculated structure factors for the cases of X-ray and neutron diffraction are given in Tables 4 and 5 respectively.

Discussion of the structure

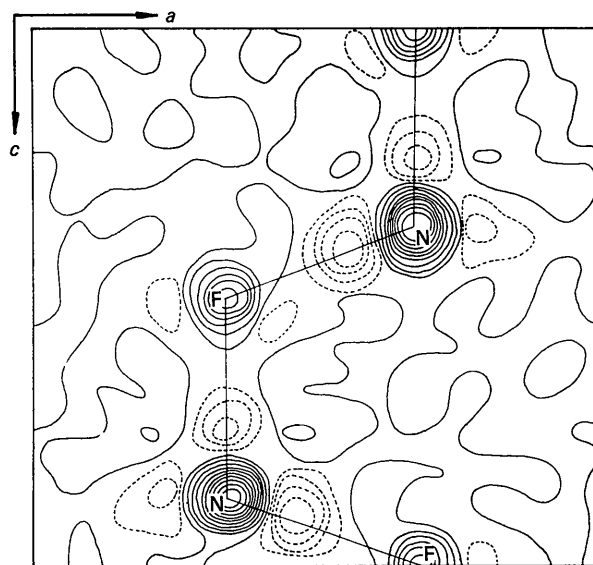The displacement between the two h.c.p. sublattices is such that each ion is equidistant from its four nearest
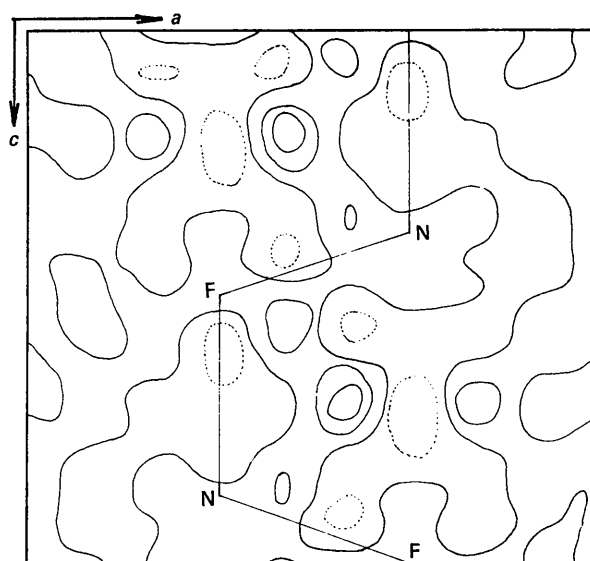

Fig.3. Neutron Fourier synthesis.

Fig.4. Neutron final difference-Fourier synthesis. Contours at arbitrary intervals. Negative contours are dotted.

neighbours, in agreement with equation (1). All four hydrogen-bridged distances are 2·708 (3) Å.

The N–H distances exhibit the usual feature that X-ray determined bonds are shorter than those found by neutron diffraction (Cromer, Kay & Larson, 1967). The difference between the N–H distances in either experiment is not significant. The average N–H distance from the X-ray data is 0·92 (4) Å. From the neutron data this distance is 1·040 (7) Å in agreement with the value given by Ibers & Stevenson (1958) who found a value of 1·041 (17) Å from neutron magnetic resonance data. This indicates that the spherical atomic form factor approximation is unsatisfactory and that a form factor based on molecular wave functions is to be preferred (Groenewegen & Feil, 1969).
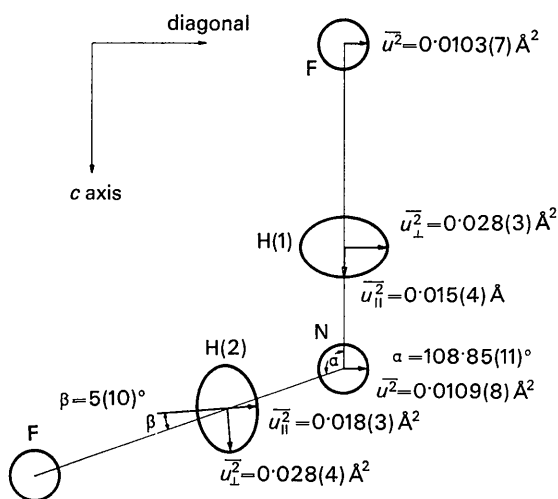
The X-ray data showed there to be a slight anisotropic motion of the F⁻-ion. This is not as evident from the neutron data possibly because the relative scattering power is smaller in the latter case.

Neutron data showed anisotropic thermal motion of the H atoms. Any difference between the atoms is not significant. Averaging the results, the mean square displacement in the direction of the H bond is 0·017 (3) Å² and in directions perpendicular to the H bond, 0·028 (3) Å². This model is identical with the thermal motion found by Peterson & Levy (1957) for heavy ice.

Fig. 5. Thermal mean-square displacements obtained from neutron data.

Table 5. *Neutron observed and calculated structure factors*

h	k	l	F_o	$|F_c|$	h	k	l	F_o	$|F_c|$
0	0	4	712	733	0	3	2	1050	1015
0	0	6	1158	1109	0	3	3	417	414
0	0	8	1036	989	0	3	4	451	451
0	1	2	207	205	0	3	5	347	353
0	1	3	862	840	0	3	6	361	366
0	1	4	272	286	1	2	0	201	204
0	1	5	745	760	1	2	1	476	480
0	1	6	478	465	1	2	2	268	258
0	1	7	230	231	1	2	3	914	982
0	1	8	440	436	1	2	4	213	206
0	2	0	848	882	1	2	5	743	724
0	2	1	189	177	1	2	6	360	364
0	2	2	940	923	0	4	0	424	427
0	2	3	884	858	0	4	1	259	254
0	2	4	531	524	0	4	2	434	434
0	2	5	702	704	0	4	3	713	724
0	2	6	165	165	1	3	0	434	443
0	2	7	237	239	1	3	1	133	134
1	1	0	809	849	1	3	2	463	461
1	1	2	1000	982	1	3	3	720	697
1	1	4	459	459	2	2	0	465	473
1	1	6	499	498	2	2	4	317	328
0	3	0	949	950	2	3	0	158	158
0	3	1	450	448	2	3	1	223	222

Table 4. *X-ray observed and calculated structure factors*

h	k	l	F_o	$|F_c|$	h	k	l	F_o	$|F_c|$	h	k	l	F_o	$|F_c|$	h	k	l	F_o	$|F_c|$
0	0	2	702	726	0	2	7	88	87	0	4	0	121	118	2	2	8	132	132
0	0	4	129	130	0	2	8	89	88	0	4	1	82	83	1	4	2	124	123
0	0	6	190	193	0	2	9	41	42	0	4	2	80	79	1	4	4	21	22
0	0	8	203	203	0	2	10	47	48	0	4	3	158	156	1	4	6	85	84
0	0	10	109	107	1	1	0	695	691	0	4	5	133	133	0	6	0	112	110
0	1	0	501	524	1	1	2	400	399	0	4	6	51	49	0	6	2	75	76
0	1	1	323	326	1	1	4	99	98	0	4	7	51	51	2	3	0	102	102
0	1	2	300	294	1	1	6	177	173	0	4	8	59	58	2	3	1	68	68
0	1	3	482	485	1	1	8	185	181	1	3	0	126	125	2	3	2	71	69
0	1	4	58	57	0	3	0	348	347	1	3	1	99	96	2	3	3	141	139
0	1	5	322	321	0	3	1	25	24	1	3	2	83	81	2	3	5	121	123
0	1	6	94	92	0	3	2	217	217	1	3	3	184	182	2	3	6	45	44
0	1	7	109	106	0	3	3	18	17	1	3	5	153	153	2	3	8	53	54
0	1	8	99	98	0	3	6	133	133	1	3	6	58	58	1	5	2	43	43
0	1	9	44	46	0	3	8	146	146	1	3	7	58	59	1	5	5	82	85
0	1	10	53	52	1	2	0	228	223	1	3	8	63	65	2	4	0	71	72
0	1	11	83	85	1	2	1	164	163	0	5	0	79	79	2	4	1	47	47
0	2	0	269	263	1	2	2	142	139	0	5	2	54	54	2	4	2	49	49
0	2	1	215	216	1	2	3	259	259	0	5	3	112	111	2	4	5	91	93
0	2	2	153	152	1	2	4	32	30	0	5	5	99	100	3	3	6	73	70
0	2	3	342	342	1	2	5	200	198	0	5	6	36	37	3	4	0	51	55
0	2	4	53	52	1	2	6	71	70	2	2	0	287	285	3	4	1	34	36
0	2	5	244	246	1	2	8	78	78	2	2	4	42	43	3	4	2	36	38
0	2	6	90	88	1	2	10	41	44	2	2	6	114	115					

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Molecular Form Factors in X-ray Crystallography

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The calculation of molecular form factors from *ab initio* molecular electronic wave functions is discussed, and a scheme for application to X-ray diffraction structure analysis is given. The method is used to calculate the form factor of the NH_4^+ molecular ion from three accurate molecular wave functions, as well as for the corresponding isolated-atoms arrangement. The merits of the different form factors obtained are tested on experimental single-crystal X-ray diffraction data for NH_4F. It appears that the quality of the form factor is determined by the number of centres in the wave function basis rather than by the wave function energy.

Introduction

In X-ray diffraction structure analysis the electron density distribution in crystalline solids is usually resolved in terms of distinct, *i.e.* isolated, atoms or ions. Interatomic effects of chemical and general solid state binding are obscured in this scheme and resist quantitative evaluation. Efforts to account *a priori* for the effect of binding have been directed mainly at evaluating scattering factors for 'bonded' and 'valence state' atoms (McWeeny, 1951, 1952, 1953, 1954; Freeman, 1959; Dawson, 1964; Stewart, Davidson & Simpson, 1965). The use of molecular form factors calculated from *ab initio* molecular wave functions is feasible for structures that may be resolved in terms of small molecules or molecular ions. Application of this method to X-ray crystallography seems to be non-existent or of questionable significance (Webb, 1965; amended by Davis & Whitaker, 1966). Some success has been had with the use of a molecular form factor in the interpretation of electron scattering data from CH_4 (Iijima, Bonham, Tavard & Roux, 1965).

In this work we discuss the calculation of molecular form factors from *ab initio* wave functions and their application to X-ray diffraction structure analysis. The method is demonstrated for the NH_4^+ molecular ion in the NH_4F structure. Results of subsequent few parameter structure refinements are given.