α_{mn} ($m, n=1, 2, 3$) of the corresponding row of the piezoelectric moduli by the $E_i^{(p)}$ given at the top of the table and then adding these products together. As an example

$$e'_{34} = \sum_{i=1}^{3} E_i^{(4)\mathrm{I}} \alpha_{3i} \,.$$

The piezoelectric stress constants $e'_{14}, e'_{25}, e'_{36}$ appear twice in this table.

A similar form of transformation can be applied to the elastic compliances s'_{pq} and the piezoelectric strain constants d'_{lq}. In Tables 2 and 3, the following substitutions should be made in order to define the elastic compliances:

In place of		Substitute
$\Gamma_t^{(p)}$	$t=1, 2, \ldots, 6$	$\Sigma_t^{(p)}$
c'_{pq} or c_{pq}	$p, q=1, 2, 3$	s'_{pq} or s_{pq}
c'_{pq} or c_{pq}	$p=1, 2, 3$ $q=4, 5, 6$ } or vice versa	$\frac{1}{2}s'_{pq}$ or $\frac{1}{2}s_{pq}$
c'_{pq} or c_{pq}	$p, q=4, 5, 6$	$\frac{1}{4}s'_{pq}$ or $\frac{1}{4}s_{pq}$

Correspondingly, Tables 4 and 5 hold for the piezoelectric strain constants when the following substitutions are made:

In place of		Substitute
$E_i^{(p)}$	$p=1, 2, \ldots, 6$	$\Delta_i^{(p)}$
e'_{lq} or e_{lq}	$q=1, 2, 3$	d'_{lq} or d_{lq}
e'_{lq} or e_{lq}	$q=4, 5, 6$	$\frac{1}{2}d'_{lq}$ or $\frac{1}{2}d_{lq}$

The piezoelectric strain constants g'_{lq} transform accordingly.

For application to elastic and piezoelectric problems, particularly to thickness vibrations of plates, this transformation is of practical value.

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The Electron Density Distribution in Ammonium Bifluoride

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An account is given of a three-dimensional X-ray analysis of NH_4HF_2 based upon Geiger-counter measurements of intensity. The electron density has been measured with a s.d. varying from 0·06 e.Å^{-3} in general positions to 0·11 e.Å^{-3} in special positions. It is found that the electron-density distribution in the H atoms of the NH_4^+ ion corresponds closely to that in an isolated atom with a temperature factor of $\exp(-2{\cdot}4 \sin^2\theta/\lambda^2)$. The electron density in the H atoms of the $(FHF)^-$ ions is subject to a rather larger random error, and the results are less clear cut. These atoms have a low peak density (0·47 and 0·52 e.Å^{-3}) but the electron count (average) over a sphere of radius 1·1 Å is normal. There is thus no evidence for a transfer of charge from H to F. The averaged electron density in these two atoms has spherical symmetry, within rather wide limits of error. The F atoms have strongly anisotropic vibrations, and their electron distributions appear to be more diffuse than that in an isolated atom. Attempts to determine the state of ionisation of the N and F atoms were not conclusive. The two independent F–H–F bond distances are 2·275 and 2·269 Å (s.d. 0·005 Å), and the N–H distances are both 0·88 Å (s.d. 0·03 Å) which is significantly less than the inter-nuclear distance of 1·025 Å.

Introduction

The fine structure of the bifluoride ion has aroused considerable interest in recent years and has been the subject of several experimental investigations. Peterson & Levy (1952) give a convenient summary of work done before 1952. It now appears to be established beyond reasonable doubt that the proton is located centrally between the fluorine atoms, and that the original postulate of a double potential well (Ketelaar,

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1941) is incorrect. Confirmation is provided by nuclear magnetic resonance studies (Waugh, Humphrey & Yost, 1953). Though the bifluoride ion is the only well established case of a symmetrical hydrogen bond, there are indications that it may not be unique (Godycki, Rundle, Voter & Banks, 1951; Rundle & Parasol, 1952; Cardwell, Dunitz & Orgel, 1953).

While establishing the location of the proton with reasonable certainty, these investigations yield no information about the distribution of electron density in the ion. The present X-ray analysis was undertaken in order to elucidate this aspect of the problem, and in that sense is to be regarded as complementary to the previous work.

The crystal structure of NH_4HF_2 is completely determined by hydrogen bonds, and there are two crystallographically independent examples of each type, N–H · · · F and F–H–F. The space group is *Pman* which has the equivalent positions

$$\pm(x, y, z;\ x, -y, -z;\ \tfrac{1}{2}-x, \tfrac{1}{2}-y, z;\ \tfrac{1}{2}-x, \tfrac{1}{2}+y, -z),$$

and the atoms are located at

$$F_1(x, 0, 0);\ F_2(0, y, z);\ N(\tfrac{1}{4}, \tfrac{1}{4}, z);\ H_1(0, 0, 0);$$
$$H_2(\tfrac{1}{2}, 0, 0);\ H_3(x, y, z);\ H_4(x, y, z)\,.$$

The four parameters (excluding H) which define the structure were first determined by Pauling (1933), and later refined by Rogers & Helmholtz (1940), who did not, however, make use of Fourier refinement techniques. With the redetermined values of the unit-cell dimensions, the new parameters led to F–F distances of 2·31 and 2·32 Å which the authors claimed were significantly longer than the corresponding distance of 2·26 Å in KHF_2 (Bozorth, 1923; Helmholtz & Rogers, 1939). It was suggested that the increase was to be attributed to a weakening of the F–H–F bond by the formation of the additional hydrogen bonds to the fluorine atoms.

Experimental

Crystal data

The crystals of NH_4HF_2 used in this work were grown from a solution of the commercial salt in aqueous HF in platinum dishes. The crystal habit was found to vary with the conditions of crystallization: (*a*) if grown rapidly from hot aqueous HF, the crystals appeared as thin needles parallel to [001], with poorly developed prism faces, and (*b*) when grown slowly from cold solutions the crystals developed a tabular habit showing the forms {001} and {110}. Cylindrical specimens of about 0·3 mm. diameter were ground from these.

As NH_4HF_2 decomposes rapidly when exposed to air, special precautions had to be taken to preserve the crystals. It was found that adequate protection was afforded by a thin layer of grease, 0·005 to 0·010 mm. in thickness. Specimens treated in this manner were preserved intact for several weeks. The scattering and absorption of X-rays by such a thin film are of course negligible.

The unit-cell dimensions were remeasured with the counter diffractometer (Cu $K\alpha$) with the following results:

$$a^* = 0{\cdot}1834 \pm 0{\cdot}0002,\ b^* = 0{\cdot}1889 \pm 0{\cdot}0002,$$
$$c^* = 0{\cdot}4202 \pm 0{\cdot}0005\,.$$

Within the range of measurement, the $\alpha_1\alpha_2$ doublet was not resolved. Taking a mean value of $\lambda = 1{\cdot}542$ Å, we obtain

$$a = 8{\cdot}40_8,\ b = 8{\cdot}16_3,\ c = 3{\cdot}67_0\ \text{Å}$$

which agree with the results of Rogers & Helmholtz (1940) to within the stated limits of error. The axial ratios corresponding to these unit-cell dimensions are

$$b:a:2c = 0{\cdot}971:1:0{\cdot}873\,.$$

The values given by Groth are (vol. 1, p. 312):

$$a:b:c = 0{\cdot}9710:1:0{\cdot}8626\,.$$

Twinning

For cylinders parallel to [001], it was found that each reflexion, with the exception of type *hhl*, was accompanied by two fainter ones with intensities proportional to that of the main reflexion. The relative positions of the main and subsidiary reflexions could be explained by assuming the existence of three reciprocal lattices related as shown in Fig. 1(*a*). The two secondary lattices are produced by rotation of the main lattice through 90° ± 1° 40′ around the common c^* axis, or alternatively, they can be regarded as arising from a rotation of the reciprocal lattice through 180° around the diagonals of the a^*b^* face of the reciprocal unit cell.

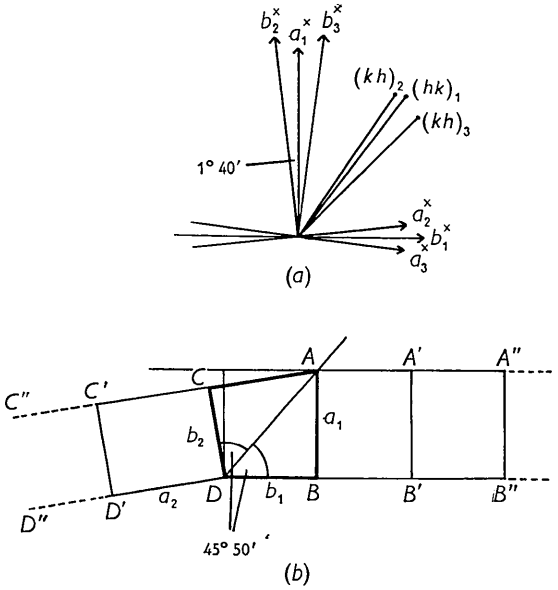

Fig. 1. Twinning in NH_4HF_2. (*a*) Twin reciprocal lattices, (*b*) postulated mechanism of twinning.

A possible mechanism for the twinning is illustrated in Fig. 1(*b*). It would appear that a block of unit cells ($AA'A''\ldots BB'B''$) is capable of changing direction either to the right hand or to the left hand to produce the set ($CC'C''\ldots DD'D''$) through the intermediate formation of a distorted cell such as *ABCD*. The twinning is intimately connected with the near-tetragonal symmetry of the lattice, and is apparently induced by mechanical stress.

Measurement of integrated intensity

The Geiger-counter equipment and the experimental techniques used in this work were essentially the same as those described by Cochran (1950), except that the diffractometer was modified to permit the recording of upper layer-line intensities.

All the counter measurements were made with filtered Cu $K\alpha$ radiation. During the count, the Geiger counter was kept stationary, and the crystal specimen was oscillated through an angle of about $1\frac{1}{2}°$, 45′ on either side of the peak reflecting position. In general, each reflexion was measured four times; the total number of pulses recorded, after correction for various factors, was taken as a measure of the integrated intensity. A total count of about 10,000 was usually recorded. For the very weakest reflexions, the count was made on the peak, and the ratio of peak to integrated intensity required to convert these readings was obtained empirically from measurements on the stronger reflexions.

Corrections were applied for 'lost counts', natural and X-ray background, and the presence of harmonics in the diffracted radiation. As these have been thoroughly discussed by Cochran (1950), it will not be necessary to go into any details here.

Extinction and absorption

Typical values of some of the stronger *hk*0 intensities measured with different crystal specimens are shown in Table 1. The values in column (1) were obtained with a cylinder of diameter 0·34 mm., while those in columns (2) and (3) were measured with un-cut needle-shaped crystals of roughly square cross-section (0·35 mm. and 0·15 mm.). The three sets of measurements are on the same (arbitrary) scale. Extinction effects are seen to be very serious with the un-cut crystals. In general, the intensities recorded with crystal (3) were greater than those from crystal (2), but even with this very small crystal, some of the intensities were reduced to less than 50% of their true values. Because of this, most of these measurements were discarded as completely unreliable. The intensities measured with the cylindrical specimens, on the other hand, were not noticeably affected by extinction, except for a few of the very strongest. The effect of dipping the crystals in liquid air was not investigated.

Table 1. *Illustrating extinction effects*

Comparison of $I(hk0)$ measured with different crystals

(*hk*0)	(1)	(2)	(3)
040	59100	40700	46000
080	30500	24900	23700
130	308000	120000	142000
220	133000	69500	83300
240	172000	84400	94500
310	340000	99000	159000
400	62000	35300	47400
420	163000	75000	99000
800	35000	22300	25600

Values of the absorption factor A appropriate to the equatorial reflexions of the cylindrical crystals were obtained from Bradley's tables (1935), while for the measurements made with the irregularly shaped specimens, and the upper layer line intensities from the cylindrical crystals, Albrecht's method (1939) was used with slight modifications. For any crystal, the maximum and minimum values of A differed by only a few percent.

Scaling of intensity measurements

(i) *Relative scaling.* For each crystal setting, the upper layer-line intensities were scaled experimentally against the zero layer by measuring selected standards at the same time under as nearly as possible identical conditions. The three axial sets of *hkl* data were then scaled together by direct comparison of common reflexions, after correction for geometrical factors and absorption.

A value of 3·0% was obtained for the discrepancy factor $R=\Sigma(|F_1|-|F_2|)/\Sigma|F_1|$, summed over all the reflexions common to the three sets of measurements. The degree of reproducibility which could be achieved with the apparatus was rather better than this. The discrepancy between two sets of *hk*0 measurements, for example, made with the same crystal, was only 2·0%. The difference is probably to be accounted for mainly by extinction, though other small errors associated with alignment, scaling, etc., undoubtedly play a part. Cochran (1950), using essentially the same apparatus, obtained a discrepancy factor of $R=2{\cdot}6\%$ for two sets of *h*0*l* measurements on adenine–HCl with different crystals and counting tubes.

In all, 169 independent *hkl* reflexions were measured with the Geiger counter, out to a limit of $\sin\theta/\lambda = 0{\cdot}55$ Å^{-1}. The range was extended to $\sin\theta/\lambda = 0{\cdot}85$ by photographic measurements made with Mo radiation. A total of 350 independent intensities was measured in this way.

(ii) *Absolute scaling.* The advantages of placing the measured intensities on an absolute scale have often been stressed. It is particularly important to do so if, as in the present case, the object of the investigation is to measure electron density and not simply atomic positions.

The method adopted consisted in comparing the reflecting power of cylinders of NH_4HF_2 and of a standard crystal (NaCl) under identical experimental conditions. If the experimental arrangement is such that a constant length h of the crystals is irradiated (volume $\pi r^2 h$), then it can readily be shown that the absolute value of F^2 is given by

$$F_1^2 = \frac{F_2^2 E_1 r_2^2 (V_c)_1^2 \omega_1}{E_2 r_1^2 (V_c)_2^2 \omega_2}\,, \quad \text{i.e. } F_1^2 = K.E_1\,,$$

where the subscripts (1) and (2) refer to NH_4HF_2 and NaCl respectively. E is the total intensity as measured with the counter (after correction for absorption and geometrical factors) when the crystal is oscillated through the reflecting position with a constant angular velocity ω. V_c is the unit-cell volume, and r is the radius of the cylindrical crystal specimen.

The values of F^2(abs.) for NaCl given in the literature are not in good agreement. The original measurements of Bragg, James & Bosanquet (1921), and James & Firth (1927), are generally smaller and presumably less accurate than the later measurements made by Brill *et al.* (1939), Renninger (1952), and Krug *et al.* (1953). Standards for the present work were obtained by averaging the results of the three later sets of measurements.

Of the few equatorial reflexions of NaCl occurring within the experimental range, the 400 and 440 were chosen as suitable experimental standards. As for the NH_4HF_2 crystals, extinction was found to be virtually negligible in the crystals of NaCl after they had been shaped into cylinders. Several independent measurements of these two reflexion intensities gave an average value of $K = 0{\cdot}00520$ for the experimental constant. Absolute values of F_o obtained in this way are listed in Table 10. The accuracy of this method is not high, ±5% in F probably being a reasonable estimate of the maximum error.

Refinement

In the refinement of the structure, atomic coordinates, temperature factors and scattering factors were treated as variable parameters. It was found that the use of empirical scattering factors was essential if the difference maps were to be interpreted correctly, because other significant features were obscured by the presence of false detail due to inaccuracies in the standard curves. There can be no objection to the use of empirical f-curves if, as in the present case, the F_o are on an absolute scale.

The refinement was carried out by means of $(F_o - F_c)$ syntheses, the atomic coordinates and temperature-factor parameters being chosen to make the difference density

$$\begin{aligned} D(x, y, z) &= \varrho_o - \varrho_c \\ &= (1/V)\Sigma\Sigma\Sigma(F_o - F_c)\cos 2\pi(hx + ky + lz) \end{aligned}$$

as flat as possible near the centres of the fluorine and nitrogen atoms. The atomic coordinates obtained in this way (Table 2) are free from series termination errors (Cochran, 1951).

Table 2. *Fractional atomic coordinates and standard deviations*

	x	y	z
N	0·2500	0·2500	0·4498
F_1	0·1353	0	0
F_2	0	0·3706	0·8872
H_1	0	0	0
H_2	0·500	0	0
H_3	0·212	0·173	0·307
H_4	0·327	0·212	0·586
	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
N	0	0	0·00095
F_1	0·00027	0	0
F_2	0	0·00036	0·00071
H_1	0	0	0
H_2	0	0	0
H_3	0·0036	0·0037	0·0082
H_4	0·0039	0·0040	0·0090

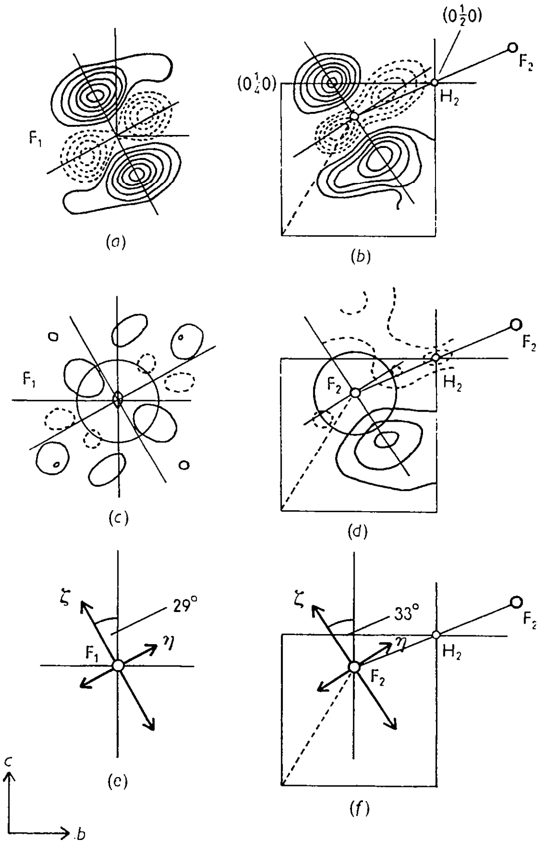

Fig. 2. Illustrating anisotropic vibration of F atoms. (*a*) and (*b*): y, z sections of the $(\varrho_o - \varrho_c)$ density through the centres of F_1 and F_2 before correction for anisotropic vibration; (*c*) and (*d*): after correction for anisotropic vibration; (*e*) and (*f*): principal vibration directions of F_1 and F_2 (third vibration direction normal to plane of paper). Contour interval 0·13 e.Å^{-3} for (*a*) and (*b*), 0·10 e.Å^{-3} for (*c*) and (*d*).

Difference syntheses are particularly useful for studying anisotropic vibrations, as is illustrated in Figs. 2(*a*) and 2(*b*) which show sections of the difference density through the fluorine atoms. In calculating these sections, the fluorine atoms were given an isotropic temperature factor of $B=2{\cdot}4$ Å^2, but in fact, as is shown by the shape of the $(\varrho_o-\varrho_c)$ distributions, their vibrations are markedly anisotropic, the value of B being twice as great in one direction as in the other. Two of the principal vibration directions are defined by these sections. The third is normal to the plane of the paper, in both cases. Their direction cosines with respect to the crystallographic axes are given in Table 3. It is interesting to note that, for both fluorine atoms, the direction of maximum vibration is approximately perpendicular to the mean plane of the three hydrogen bonds ending on the atom (an attempt has been made to show this in Fig. 7). The vibration of the nitrogen atoms was found to be isotropic, as expected from the symmetry of the environment.

Table 3. *Direction cosines of principal vibration directions of fluorine atoms*

		n_x	n_y	n_z
F_1	ξ	1	0	0
	η	0	0·875	0·485
	ζ	0	−0·485	0·875
F_2	ξ	1	0	0
	η	0	0·839	0·545
	ζ	0	−0·545	0·839

Correction for anisotropic vibration

To allow for anisotropic vibration, we write

$$f_j=f_{oj}\exp\left[-\sin^2\theta/\lambda^2(u_jn_{j1}^2+v_jn_{j2}^2+w_jn_{j3}^2)\right]$$

as the scattering factor of the jth atom (Cochran, 1951), where the u_j are constants proportional to the mean-square amplitude of vibration in the three vibration directions, and the n_{ji} are the direction cosines of the reciprocal vector s with respect to these directions. It is convenient to work in terms of small corrections to an average temperature factor. Then the contribution of the jth atom to (F_o-F_c) will be given by

$$(F_o-F_c)_j=f_{oj}\cos 2\pi(hx+ky+lz)_j\exp\left[-B(\sin^2\theta/\lambda^2)\right] \times\{\exp\left[-(\delta u\xi^2+\delta v\eta^2+\delta w\zeta^2)\right]_j-1\}$$

with $\xi=n_1\sin\theta/\lambda$ etc. This equation was applied by transforming the axes of the vibrational ellipsoid to coincide with the crystallographic axes. The (δu) can in principle be obtained from the $(\varrho_o-\varrho_c)$ distribution (Cochran, 1951), but in practice, estimation by trial and error is generally satisfactory, at least in the case of simple structures with few parameters.

Owing to the high symmetry, the problem was essentially a two-dimensional one, and it was possible to apply the graphical method of distorting the reciprocal lattice suggested by Cochran (1954). This method was found to be rapid and convenient in practice, and capable of three-figure accuracy if proper care was taken.

The final temperature-factor parameters for the nitrogen and fluorine atoms are listed in Table 4. They are probably accurate to ±0·05. A value of $B=2{\cdot}4$ Å^2 was assumed for the hydrogen atoms.

Table 4. *Temperature-factor parameters* (Å^2)

	u	v	w	
N	1·88	1·88	1·88	
F_1	2·08	1·91	3·91	
F_2	2·15	1·98	3·98	
H	2·4	2·4	2·4	(assumed)

After the corrections for anisotropic vibrations had been applied, the difference density at the centres of F_1 and F_2 was reduced to less than 0·1 e.Å^{-3}, and was satisfactorily flat in the immediate neighborhood of the atomic centres (Figs. 2(*c*) and 2(*d*)). It will be observed, however, that there is a rather large residual peak of height 0·35 e.Å^{-3} near F_2 (Fig. 2(*d*)), which can have no physical significance and must be ascribed to random errors in the F measurements. The magnitude of this peak suggests that the values given for the s.d. of electron density in Table 7 have been slightly under-estimated, but the general conclusions are unaffected.

Atomic scattering factors

Inaccuracies in the theoretical f curves and errors in the temperature factors were allowed for simultaneously by setting up the equations

$$A_F\delta f_F+A_N\delta f_N=(F_o-F_c)_{hkl}$$

and solving by least-squares for the best values of the δf at different values of $\sin\theta/\lambda$ (A_F and A_N are the trigonometric parts of the structure factor). It is not of course possible, without carrying out experiments at different temperatures, to separate the vibrational and non-vibrational parts of the empirical scattering curves so obtained. However, for large values of $\sin\theta/\lambda$, where the theoretical f-values are expected to be most accurate, we may put

$$f_{\text{theor.}}\exp(-B\sin^2\theta/\lambda^2)=f_{\text{exp.}}$$

and so obtain a value of the temperature factor B which can then be used to calculate the shape of the modified scattering curve for the non-vibrating atom at all angles. This was done and the resulting values of the atomic scattering factors are listed in Table 5, and compared with the most recent theoretical curves (Berghuis *et al.*, 1955) in Fig. 3. The agreement is close

Table 5. *Empirical scattering factors for fluorine and nitrogen*

$\sin\theta/\lambda$	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8
F	7·76	6·49	4·94	3·62	2·70	2·15	1·87	1·77
N	5·60	4·32	3·11	2·20	1·74	1·56	1·46	1·41

in the case of fluorine, except at small angles, but the experimental curve for nitrogen is everywhere depressed compared with the theoretical curve. The significance of the discrepancies at small angles will be discussed later.

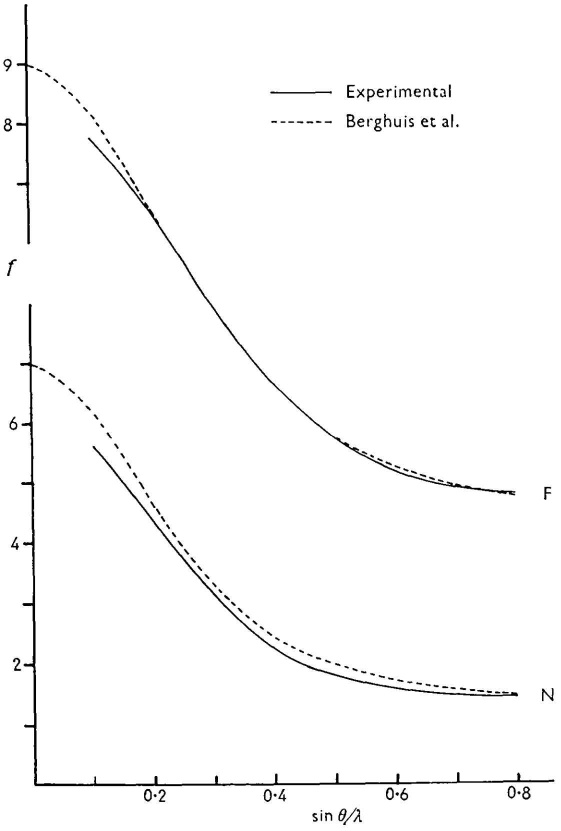

Fig. 3. Comparison of experimental (full line) and theoretical (dotted) *f*-curves.

Final F values calculated with these scattering factors and the coordinates and temperature factor parameters in Tables 2 and 4 are listed in Table 10 for comparison with the F_o. The final value of $R(hkl)$ was 0·050 for the F values measured with the counter, and 0·077 if the photographic measurements were included.

Electron-density sections

The electron density in the hydrogen atoms was investigated by calculating

$$D_H = (1/V)\Sigma\Sigma\Sigma(F_o - F_c') \cos 2\pi(hx+ky+lz)$$

F_c' being the structure factor for the nitrogen and fluorine atoms only. This function was evaluated at every point of the grid $a/60 \times b/60 \times c/15$ and the sections through the centres of the hydrogen atoms, shown in Figs. 4 and 5, were obtained by interpolation. The empirical *f*-values for F and N, listed in Table 5, were used in the calculation of F_c'. In order to keep the random errors to a minimum, the photographic data were excluded from these calculations. (It can be shown that terminating the Fourier series at $\sin\theta/\lambda = 0·55$ Å^{-1} has the effect of reducing the electron density at the atomic centres by a factor of about 0·85. This should be taken into account when

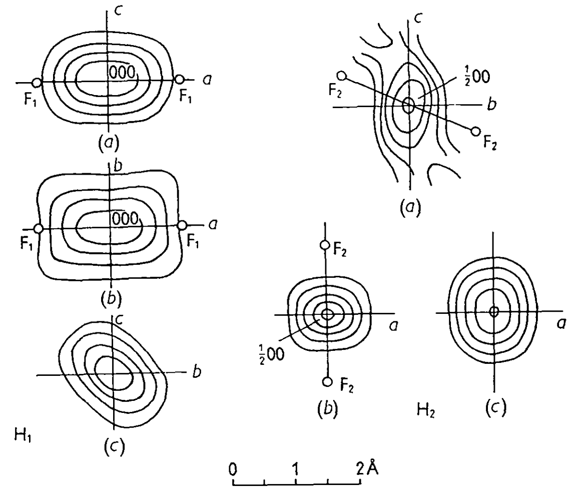

Fig. 4. Sections of the electron density in H_1 and H_2. (*a*) and (*b*) parallel, and (*c*) perpendicular to the axis of the $(FHF)^-$ ion. Contour interval 0·1 e.Å^{-3} starting at 0·1.

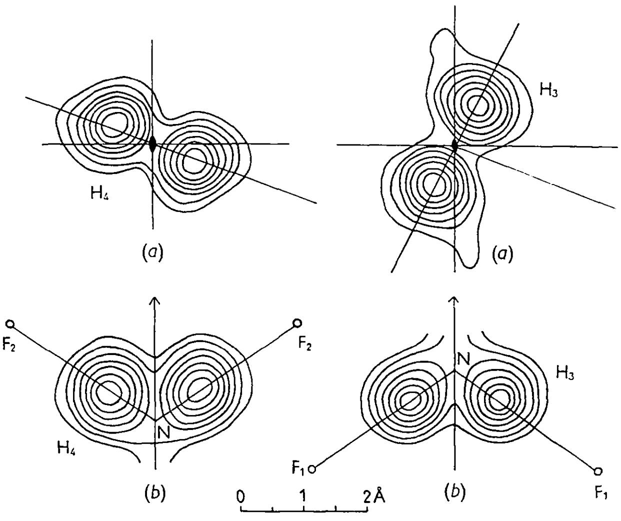

Fig. 5. Sections of the electron density in H_3 and H_4. (*a*) perpendicular, and (*b*) parallel to the 2-fold axis. Contours as for Fig. 4.

Table 6. *Peak densities and electron counts* ($r = 1·1$ Å) *for hydrogen atoms*

	$\varrho(0)$ (e.Å^{-3})	n (e.)
H_1	0·47	0·91
H_2	0·52	0·67
H_3	0·76	0·79
H_4	0·79	0·79
Averaged atom	0·50	0·79
Calculated	0·70	0·76

comparing experimental and calculated peak densities). The peak densities and numbers of electrons associated with each of the hydrogen atoms are listed in Table 6. The electron distributions will be discussed in more detail later.

Finally, the electron density in the bifluoride ion is shown in Fig. 6, which is a section of the 3-dimensional ϱ_o distribution computed with all the data out to a limit of $\sin\theta/\lambda=0{\cdot}85$ Å^{-1}. At room temperature, the electron densities at the atomic centres are 19·8 e.Å^{-3} for F and 2·1 e.Å^{-3} for H, and the minimum of electron density (0·4 e.Å^{-3}) is found at a point on the axis of the ion at 0·35 Å from the centre. Series-termination effects were not allowed for, so that the errors associated with this section are not accurately known, but they are probably not much greater than the values given in column 2 of Table 7.

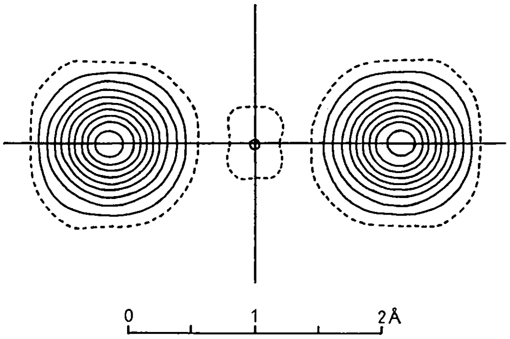

Fig. 6. Electron density in the (FHF)$^-$ ion at room temperature. Contour interval 2 e.Å^{-3} (1-electron contour broken).

Accuracy

The methods of Cruickshank & Rollett (1953) were found particularly useful for calculating the s.d. of electron density and of the atomic coordinates at special positions in the unit cell. Column 1 of Table 7 gives values of $\sigma(\varrho)$ appropriate to the sections in Figs. 4 and 5, and column 2 those appropriate to Fig. 6 (the values of $\sigma(\varrho)$ are of course dependent upon the number of terms in the series). The values of $\sigma(x)$ are given in Table 2.

Table 7. *Standard deviation of electron density at special positions* (e.Å^{-3})

The values in column (1) refer to electron-density maps computed with the counter-measured F's only ($\sin\theta/\lambda\le 0{\cdot}55$ Å^{-1}), and those in column (2) to maps computed with all the data ($\sin\theta/\lambda\le 0{\cdot}85$ Å^{-1})

	(1) $\sigma(\varrho)$	(2) $\sigma(\varrho)$
x, y, z	0·059	0·105
0, 0, 0	0·110	0·194
$\frac{1}{2}$, 0, 0	0·110	0·194
x, 0, 0	0·078	0·137
$\frac{1}{2}, y, z$	0·081	0·138
$\frac{1}{4}, \frac{1}{4}, z$	0·083	0·150

Discussion of results

The spatial relations of the various atoms in the structure are clearly shown in Fig. 7, a drawing of one quarter of the unit cell. Bond-lengths and angles calculated from the final coordinates in Table 2 are given in Tables 8 and 9, together with the standard deviations calculated by the methods of Cruickshank & Rollett (1953).

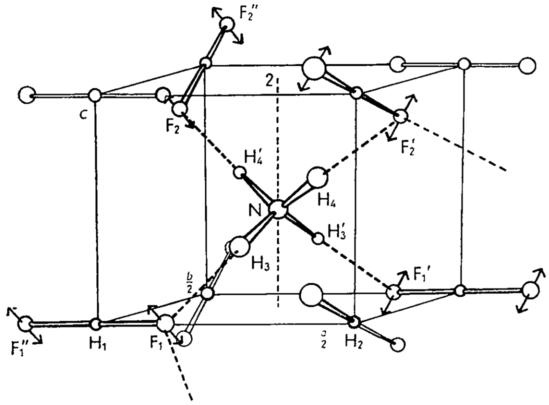

Fig. 7. Environment of the NH_4^+ ion in NH_4HF_2. The directions of maximum vibration of the fluorine atoms are indicated by arrows.

Table 8. *Bond lengths and standard deviations* (Å)

		s.d.
F_1–H_1–F_1	2·275	0·0046
F_2–H_2–F_2	2·269	0·0055
N–H_3–F_1	2·797	0·0022
N–H_4–F_2	2·822	0·0025
Longer N–F contacts		
F_1–N	3·028	0·0022
F_2–N	3·106	0·0030
Ammonium ion		
N–H_3	0·878	0·033
N–H_4	0·875	0·033

Table 9. *Bond angles and standard deviations in degrees*

(See Fig. 7 for numbering of atoms)

	Angle	s.d.
N–F_1–F_1''	110·2	0·05
N–F_1–N	139·7	0·10
N–F_2–F_2''	122·2	0·05
N–F_2–N	96·3	0·12
F_1–N–F_1'	107·6	0·12
F_2–N–F_2'	110·7	0·12
F_1–N–F_2	109·5	0·06
F_1–N–F_2'	109·8	0·06
H_3–N–H_3'	106·8	4·0
H_4–N–H_4'	110·2	4·0
H_3–N–H_4'	109·0	2·8
H_3–N–H_4	110·9	2·8

The hydrogen atoms in the N–H · · · F bonds are within 0·02 Å of the lines joining the N and F atoms. This distance is smaller than the s.d. of the error in the hydrogen-atom coordinates. Thus, to within the limits of error, the N, H, and F atoms are collinear. Of the four F–N–F angles around the nitrogen atoms, two differ significantly from the tetrahedral value (F_1–N–F_1' = 107·6° and F_2–N–F_2' = 110·7°).

The ammonium ion

(i) *Dimensions.*—The dimensions of the ammonium ion are shown in Fig. 8. The angles, calculated from the coordinates of the hydrogen atoms, are seen to vary between 106·8° and 110·9°, with a mean value of 109·2°. These values are not significantly different from the tetrahedral value. If it is assumed, however, that the hydrogen atoms lie exactly on the lines joining the N and F atoms, then the differences do become significant, for two of the angles at any rate, as pointed out above.

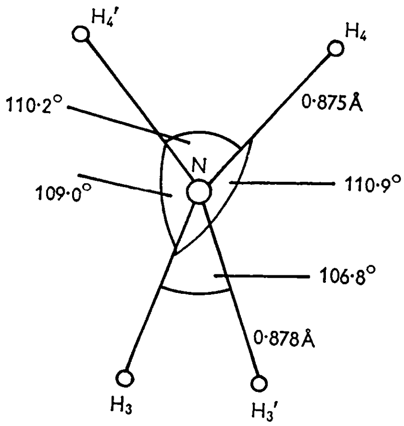

Fig. 8. Dimensions of the NH_4^+ ion.

The two independent N–H bonds are of equal length, 0·88 Å, a value which is significantly shorter than the inter-nuclear distance of 1·025 ± 0·005 Å (Gutowsky, Kistiakowsky, Pake & Purcell, 1949). A similar shortening is by now well substantiated in the case of C–H bonds measured by X-rays. An explanation of this effect is probably to be found in the partial ionic character of these bonds, as Tomiie (1958) has recently demonstrated.

(ii) *Electron distribution.*—Line sections of the final $(\varrho_o - \varrho_c)$ synthesis through the centres of the hydrogen atoms of the ammonium ion are shown in Fig. 9. The broken curves represent the profile of an isolated atom in the (1*s*) state with a temperature factor of $\exp(-2{\cdot}4 \sin^2\theta/\lambda^2)$ (McDonald, 1956). The effect of terminating the Fourier series at $\sin\theta/\lambda = 0{\cdot}55$ Å^{-1} is to reduce the peak height to about 85% of its true value; thus, the experimental profiles, if corrected for series termination, would lie slightly above the theoretical curves at the peak. The agreement between the experimental and theoretical curves is good, the difference being everywhere less than the s.d. of the measurement. Electron counts (r = 1·1 Å) over these two atoms gave 0·79 e. for both, in good agreement with the calculated value of 0·76 e.. It is interesting to note that the experimental distributions can, as for heavier atoms, be accurately approximated near the atomic centres by one-term Gaussian functions.

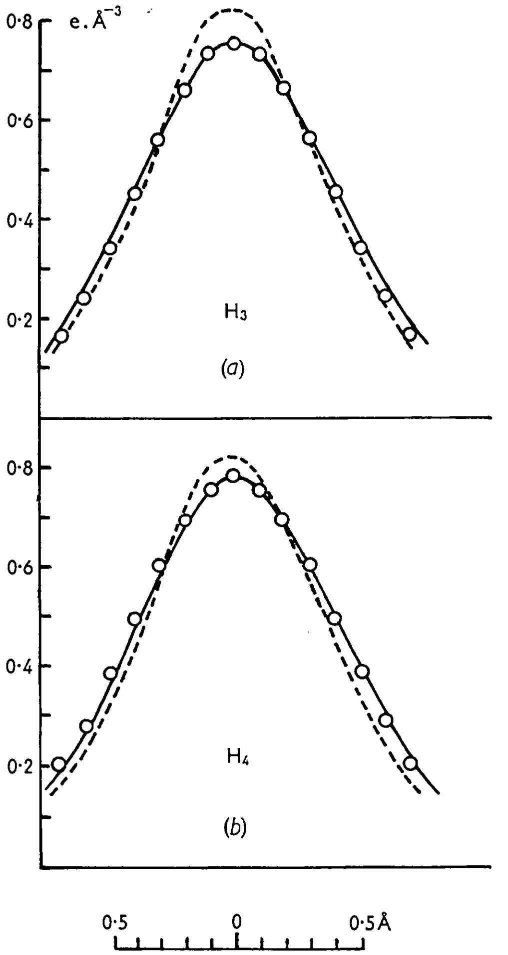

Fig. 9. Line sections of the electron density in H_3 and H_4: (*a*) the section (x, 0·17, 0·31) through the centre of H_3, and (*b*) the section (0·33, y, 0·51) through the centre of H_4. The full line represents the experimental density, and the broken line the density in a (1*s*) hydrogen atom with a temperature factor of $\exp(-2{\cdot}4 \sin^2\theta/\lambda^2)$. The circles outline the best Gaussian approximations, $0{\cdot}76 \exp(-3.2r^2)$ for H_3, and $0{\cdot}79 \exp(-2{\cdot}8r^2)$ for H_4.

We have the result, then, that the electron distribution in the hydrogen atoms of the ammonium ion does not differ significantly from that in an isolated atom with the same temperature factor. It may be objected that such a comparison is not valid, because the temperature factors of the hydrogen atoms have not been determined experimentally, one experimental measurement being used to determine two unknown quantities, namely, the extent of thermal vibration of the atoms and their degree of departure from the isolated state. The validity of this objection cannot be denied. It is generally possible, however, to make a good guess at the value of B for the hydrogen atoms from a consideration of the temperature factors of the heavier atoms in the structure. Reference to Table 9 of the above article (McDonald, 1956) shows that theoretical electron distributions obtained in this way are generally in good agreement with the experimental distributions in 'normal' covalently-bonded hydrogen atoms. The quality of this agreement shows that the (1*s*) orbital of the hydrogen atom is not greatly perturbed by bonding, and also gives us confidence to conclude in those cases where large discrepancies are found between the theoretical and experimental distributions that the hydrogen atoms in question are in some respect 'abnormal'.

The fundamental nature of the difficulty is recognized, however. Possibly, the tables in the paper referred to above will be found most useful when the temperature factors of the hydrogen atoms have been measured accurately by some other physical method, and not simply obtained by inference from the electron distributions. It may in this way be possible to draw significant conclusions about the redistribution of electrons resulting from bonding.

The electron density in the ammonium ion corresponds closely to a superposition of spherically symmetrical nitrogen and hydrogen atoms with no (detectable) perturbations of the electron clouds produced by bonding, apart from an inward movement of the hydrogen distributions. It will be well at this point to correct a false impression which may have been conveyed in a previous communication (Cochran, 1958), where it was stated that these experimental results contradicted the conclusions of Banyard & March (1956). These authors calculated X-ray scattering factors for a series of molecules, H_2O, NH_3, CH_4 by a variational method, using central-field wave-functions corresponding to neon-like configurations, and they found that their results were in close agreement with the observed X-ray scattering by these gases. The authors stated 'we believe that the spherical density we have calculated here should be regarded as providing a reasonable approximation to the leading terms in an expansion of the actual density in the NH_3 molecule in spherical harmonics, or, put another way, to the actual density in the molecule, when this is averaged over angles, a view which was fully substantiated by later work (Banyard & March, 1957; Carter, March & Vincent, 1958). The fact that the angular terms in the density make only a negligible contribution to the scattered intensity does not imply of course that the distributions are spherical, nor does it mean that, in principle, central-field functions can be made to give a better approximation to the spherically-averaged molecular density than any superposition of suitably modified atomic densities centred on the nuclei, as we were inclined to believe at first. The experimental atomic distributions which we have found for NH_4^+ approximate to normal non-bonded distributions, though the N atom is electron-deficient (see later) and the H atoms are drawn in towards the centre of the ion. It is possible that these modifications may lead to a radial density distribution in agreement with that obtained by Banyard & March's approach, and it would be interesting to compare the spherically averaged NH_4^+ scattering from our single-crystal results with that calculated by their method.

The bifluoride ion

(i) *Bond length.*—To within the limits of error (s.d. $= 0{\cdot}005$), the two independent F–H–F bonds are of equal length (Table 8), and they are not significantly different from the distance of 2·26 Å found for this bond in KHF_2. Thus there is no increase in the length of this bond on passing from KHF_2 to NH_4HF_2 as a result of the additional hydrogen-bond formation, as was previously suggested by Rogers & Helmholtz (1940).

It is to be noted that there are two additional sources of inaccuracy which are not taken into account in the s.d.:

(1) The unit-cell dimensions are subject to an error of $\sim 0{\cdot}1\%$.

(2) The effect of the large rotational oscillations of the F–H–F ions has not been considered. The apparent bond contraction resulting from such oscillations can be quite appreciable as Cruickshank (1956) has pointed out. A detailed analysis has not been attempted, but a rough calculation has shown that the error might well be of the order of 1%.

(ii) *Electron distribution.*—The peak densities of atoms H_1 and H_2 (Table 6) are considerably less than those of H_3 and H_4, though the differences are only possibly significant. The calculated peak height for an isolated atom with a temperature factor of $B = 2{\cdot}4$ Å^2 is 0·70 e.Å^{-3} after correction for series termination at $\sin\theta/\lambda = 0{\cdot}55$ Å^{-1}. With a s.d. of 0·11 e.Å^{-3} this difference is again only possibly significant, but the fact that both H_1 and H_2 are deficient to about the same extent tends to increase the significance of this result.

The detailed electron-density distributions in these atoms are shown in Fig. 4. Atom H_1 is seen to be drawn out along the direction of the axis of the ion. This elongation corresponds to a small maximum of electron density of height 0·2 e.Å^{-3} in the $(\varrho_o - \varrho_c)$ synthesis from which all the hydrogen atoms were subtracted. The s.d. of the electron density at this point is rather high (0·137 e.Å^{-3}), and, as H_2 is not similarly elongated, no significance is to be attached to this result.

There is no reason to suppose that these hydrogen atoms should differ in any respect, since they are in almost identical environments in the crystal. The individual sections through H_1 and H_2 shown in Fig. 4 are subject to fairly large random errors (Table 7). There is therefore some justification for averaging the two distributions. This has been done, and the resulting sections have been further modified in accordance with reasonable assumptions about the symmetry of the force field in the bifluoride ion. The two final sections, shown in Fig. 10, are probably the best representation of the electron density in the hydrogen atom of the bifluoride ion that can be obtained from the experimental results.

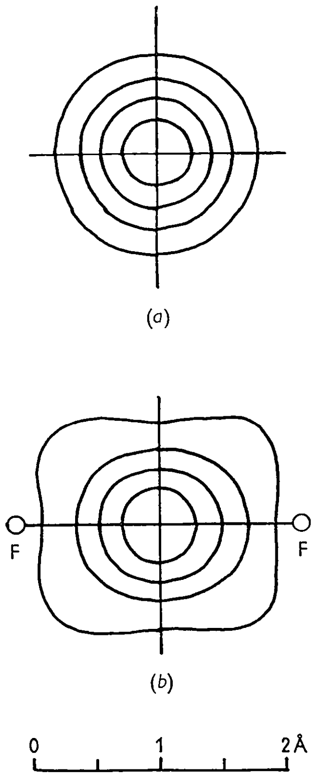

Fig. 10. Sections of the electron density in the 'symmetrized' hydrogen atom: (*a*) normal, and (*b*) parallel to the axis of the $(FHF)^-$ ion. Contour interval 0·1 e.Å^{-3}, starting at 0·1.

The 'symmetrized' atom is seen to have nearly spherical symmetry. It must be remembered, however, that the limits of error are rather wide, and it is equally true to say that the experimental density does not differ significantly from a slightly ellipsoidal distribution as could result from random location or anisotropic vibration of the hydrogen atom. The peak density is slightly reduced compared with that in an isolated atom, but the electron content is the same.

Now that a theoretical electron distribution for the $(FHF)^-$ ion has become available (Hamano, 1957), a detailed comparison of the theoretical and experimental densities should be possible. Until this is done, it hardly seems profitable to discuss the experimental results, except to say that they obviously are not in accord with the generally accepted view that the ionic form $F^-H^+F^-$ is the predominant resonance structure. In this connection it is interesting to recall that in the case of the strong O–H · · · O bonds in salicylic acid (Cochran, 1953*a*) and sodium sesquicarbonate (Candlin, 1956), the number of electrons associated with the hydrogen atoms was smaller than for the other hydrogen atoms in these structures.

Electron distribution in the N and F atoms

Attempts have been made in the past to determine the number of electrons associated with particular atoms by extrapolating their f-curves to $\sin\theta/\lambda = 0$, the point of intersection with the axis being taken as the apparent atomic number Z' of the atom. Such methods are unreliable because of the uncertain nature of the extrapolation, and the results should be accepted with caution.

Cochran (1953*b*) has suggested a method of obtaining the number of electrons associated with an f-curve which is independent of any extrapolation into the non-observable domain. The minimum value of the one-dimensional periodic function

$$\varrho'(x) = 2\sum_{n=1}^{\infty} f(nq)\cos 2\pi nx/a$$

is a measure of Z', the number of electrons in the atom, *above a certain level*. If the sampling interval q is chosen in such a way that the atoms are well resolved, and the electron density falls to zero between them, then the minimum value of this function is simply $-Z$. If, on the other hand, the minimum density between the atoms is say ε (in line projection), then $\varrho'(x) = -Z' = -(Z - a\varepsilon)$. Evidently, if the atomic charge clouds are extensive, Z' will not be a true measure of the electron content of the atom, and will give no reliable indication of its state of ionisation.

The method was applied to the experimentally determined scattering curves for N and F, taking a sampling interval $q = \sin\theta/\lambda = 0{\cdot}084$ Å^{-1}, equal to the lowest observable reciprocal spacing for NH_4HF_2, and corresponding to a separation of $1/2q = a = 5{\cdot}9$ Å. The scattering curves were modified by an artificial temperature factor of $\exp(-4{\cdot}75 \sin^2\theta/\lambda^2)$ to ensure convergence of the series. The results were $Z' = 6{\cdot}1$ for N and 8·3 for F.

The low result for N may be taken as evidence that the electron density in the nitrogen atom is still appreciable at 2·95 Å from the centre. Alternatively, it can be taken to mean that the experimental f-curve in the region $0{\cdot}08 < \sin\theta/\lambda < 0{\cdot}8$ Å^{-1} corresponds to an atomic distribution which falls to zero within 2·95 Å but which contains only 6·1 electrons. As the hydrogen atoms appear to have their full complement of electrons, this corresponds to a deficiency of 0·9 electrons for the ammonium ion as a whole. It is tempting to attach significance to this result and claim it as evidence of ionisation. However, as is evident from the result for F, we must be rather more cautious in our interpretation. The low result for fluorine cannot, of course, be interpreted to mean that the fluorine atoms are deficient in electrons, but must rather be accepted as evidence of the large spread of the electron clouds of these atoms. As the 'missing' electrons are spread throughout a volume comparable with that of the unit cell, they can scarcely be regarded as belonging to any particular nucleus, and should perhaps be

Table 10. *Observed and calculated structure factors*

The columns in this table give respectively, for each value of l: h, k, $10F_o$ measured with the Geiger counter, $10F_o$ measured photographically, and $10F_c$. An asterisk denotes that the observed values are affected by extinction. These terms were included in the ϱ_0 syntheses as F_c, and in the D_H syntheses as F_c for hydrogen

$\ell = 0$

0	2	033	029	014	5	1	184	190	176-
0	4	157	135	152	5	3	020	029	034
0	6	071	069	070	5	5	009	•	013
0	8	165	153	164	5	7	•	063	066-
0	10		007	005-	5	9		033	032-
1	1	012	•	008-	6	0	099	114	107
1	3*	322	•	345	6	2	105	110	109
1	5	191	175	183	6	4	104	100	103-
1	7	007	•	008-	6	6	073	070	074
1	9		009	007	6	8		016	017
1	11		041	038	6	10		029	027
2	0	006	•	007-	7	1	023	•	022
2	2	190	163	193	7	3	134	137	137
2	4	298	•	304-	7	5		079	085
2	6	071	070	071	7	7		000	006
2	8	009	•	006	7	9		014	013
2	10		012	018	7	11		027	030
3	1*	321	•	378-	8	0	175	194	179
3	3	021	•	014-	8	2	015	•	011
3	5	021	020	024-	8	4		039	036
3	7	125	122	121-	8	6		010	007
3	9		051	050-	8	8		060	074
4	0	157	167	160	9	1	022	•	024-
4	2	284	281	296-	9	3		044	042
4	4	172	181	171-	9	5		025	030
4	6	121	124	117-	10	0		017	017-
4	8		036	038	10	2		000	007
4	10		059	062-	10	4		076	081-
4	12		016	012-	11	1		054	053-

$\ell = 1$

0	0*	239	222	260	5	1	136	135	131-
0	2*	392	•	450	5	3	011	•	016
0	4	070	070	063-	5	5	007	•	002-
0	6	183	187	188	5	7		060	054-
0	8	058	058	056	5	9		021	022-
0	10		048	052	6	0	178	•	190
0	14		025	030	6	2	028	027	023-
1	1	049	049	042	6	4	022	024	022
1	3	250	269	245	6	6	008	•	009-
1	5	149	135	144	6	8		062	067
1	7	006	•	001-	6	10		018	020-
1	9		016	016	7	1	037	039	037
1	11		032	032	7	3	102	100	104
2	0*	322	•	368	7	5	066	068	070
2	2	196	184	185-	7	7		018	011
2	4	028	025	023-	7	11		030	026
2	6	053	052	052-	8	0	063	•	062
2	8	069	074	070	8	2	084	091	088
2	10		012	039-	8	4		028	030-
3	1	277	230	282-	8	6		065	068
3	3	034	033	030-	8	8		020	014
3	5	055	053	052-	8	10		029	031
3	7	092	092	090-	9	3		032	034
3	9		042	043-	9	5		023	020
4	0	150	156	137-	10	0		042	036
4	2	063	064	055-	10	2		054	053-
4	4	253	220	266-	10	4		021	013-
4	6	009	•	006-	10	6		028	033-
4	8		047	049-	10	8		023	021
4	12		038	046-	11	1		042	043-

$\ell = 1$

0	1	066	061	047-	4	3	090	095	086-
0	3	148	144	138-	4	5	067	071	068
0	5	067	066	071	4	7	019	018	016
0	7	012	020	011	5	2	095	099	094
0	9		019	012-	5	4	020	•	007-
0	11		023	022-	5	6	034	033	035-
1	2	172	160	160	5	10		014	015
1	4	017	016	018-	6	1	078	081	076-
1	6	067	070	067-	6	3	020	023	021-
1	8	003	•	001-	6	5	015	016	014
1	10		014	016	6	7		028	027
2	1	185	169	182-	6	9		021	022-
2	3	057	057	045-	7	2	044	043	044
2	5	042	039	041	7	4	003	•	003-
2	7	043	042	042	7	6		032	029-
2	9		026	029-	7	10		019	010
3	2	116	117	109	8	1	015	•	015-
3	4	025	022	014	8	3	038	040	039-
3	6	053	053	050-	8	5		029	029
3	8	008	•	007	9	2		026	030
3	10		020	021	9	6		021	019-
4	1	029	032	029-					

$\ell = 2$

0	0*	270	250	291	4	0	029	035	029-
0	2	053	053	058	4	2	159	146	156-
0	4	165	160	168	4	4		040	038-
0	6	039	041	038	4	6		080	075-
0	8		077	078	4	10		039	046-
0	12		027	032	5	1	051	056	051-
1	1	092	091	086	5	3	012	018	016-
1	3	112	114	110	5	5		033	028-
1	5	054	051	052	5	7		025	024-
1	7	022	021	023	6	0	000	018	001
1	9		027	026	6	2	061	066	062
1	11		019	018	6	4		022	020-
2	0	075	079	067-	6	6		052	052
2	2	058	057	057	6	10		014	020
2	4	089	090	084-	7	1	051	053	050
2	6	053	051	049	7	3	050	057	053
2	8		028	030-	7	5		040	036
2	10		022	011	7	7		019	020
3	1	111	110	113-	7	9		022	021
3	3	079	079	078-	8	0		056	080
3	5	058	058	057-	8	4		052	054
3	7	053	055	050-	8	8		035	039
3	9		019	020-	9	3		018	012
3	11		010	011-	10	4		039	037-

$\ell = 2$

0	1	185	185	180-	4	3	008	•	011-
0	3	051	051	047-	4	5		032	029
0	5	025	026	022	4	7		053	053
0	7	041	043	044	4	9		029	030-
0	9		051	053-	5	2	082	078	088
1	2	125	125	132	5	6		040	041-
1	4	016	018	014-	5	8		018	008
1	6	077	079	074-	5	10		023	021
1	10		018	018	6	1	014	014	017-
2	1	041	046	042-	6	3	069	072	071-
2	3	122	116	122-	6	5		057	056
2	5	093	091	096	7	2	049	054	050
2	7	007	•	005	7	6		038	037-
2	11		032	022-	8	1		054	056-
3	2	133	124	130	8	7		023	024
3	4	011	•	006-	8	9		025	030-
3	6	045	046	045-	9	2		035	033
3	8		013	013	9	6		023	022-
3	10		026	026	10	3		030	031-
4	1	130	124	126-	10	5		035	032

$\ell = 3$

0	0	008	•	006	4	0	108	093	114-
0	2	101	104	105	4	2	024	026	025-
0	4	056	057	058	4	4		046	041-
0	6		071	070	4	8		048	050-
0	8		024	005-	5	1	004	•	002-
0	10		020	029	5	3	031	038	035-
1	1	078	081	080	5	5		029	029-
1	3	020	020	020	6	4		050	051
1	5	010	008	010	7	1		046	043
1	7		029	031	7	3		026	020
1	9		025	026	7	5		009	012
2	0	019	•	014-	7	7		028	023
2	2	043	044	040-	7	9		016	021
2	4	051	051	051	8	2		043	040
2	6		025	023-	8	4		016	018
2	10		011	018-	8	6		033	033
3	1	032	032	030-	10	2		029	026-
3	3	058	059	061-	10	4		010	011
3	5		056	053-					
3	7		018	016-					

$\ell = 3$

0	1	008	•	013-	4	1	006	•	006
0	3	079	079	080-	4	3	052	056	055-
0	5	060	058	061	4	5		067	067
0	7		027	028-	5	2	039	043	040
0	9		016	004-	5	6		023	020-
0	11		031	026-	5	8		010	009
1	2	056	051	057	6	1		060	056-
1	4	024	022	017-	6	7		023	026
1	6		042	037-	6	9		028	032-
1	8		013	004	7	2		024	027
2	1	089	085	085-	7	4		015	011-
2	3	013	014	011	7	6		024	023-
2	5	003	•	000	7	8		019	001
2	7		033	039	8	3		042	031-
2	9		035	037-	8	5		033	039
3	2	055	056	055	8	7		020	007-
3	4	004	•	001-	9	2		016	019
3	6		026	022-	9	4		027	003-
3	8		018	016	10	1		031	032-
3	10		012	018					

$\ell = 4$

0	2		047	022	8	4		028	033
0	4		064	065	0	1		046	045-
0	6		027	013	0	3		023	026
0	8		013	008	0	5		026	026-
1	1		043	045	0	9		028	034-
1	7		025	025	1	2		•	006
2	4		013	013	1	4		013	008-
2	6		010	004	2	1		054	027
2	8		023	024-	2	3		036	034-
3	3		040	040-	2	5		043	038
3	5		033	033-	2	7		024	025-
4	2		034	034-	3	2		009	011
4	6		031	025-	3	8		010	013
4	8		022	021-	4	1		034	034-
5	3		024	026-	4	3		034	032
5	5		015	020-	4	7		023	026
6	2		025	017	5	2		015	009
6	4		020	017	6	1		019	021
7	1		030	030	6	3		025	028-
7	7		023	021	6	5		028	028
8	0		023	006	6	7		019	024-
					8	1		028	027-

$\ell = 5$

0	0		017	001
0	4		025	026
1	1		015	019
1	7		016	016
2	4		018	010
3	3		015	021-
0	1		024	029
0	3		024	021-
0	5		025	017
0	7		031	030-
2	1		020	022-
2	3		025	030
3	2		021	005-
6	3		023	024

thought of as forming a continuous background of electron density.

It is evident from these results that we cannot come to any definite conclusions about the state of ionisation of the atoms. The difficulties involved in detecting ionisation in crystals by X-ray methods have been discussed by Bijvoet & Lonsdale (1953). According to these authors, it will generally speaking not be possible to do so, since the charge redistributions involved in ionisation will only take place in regions of the atom which correspond to experimentally inaccessible regions of reciprocal space. This is a fundamental difficulty which is not to be overcome by altering the experimental conditions. It will be understood from the above discussion that the value of the atomic number of an atom or ion obtained by Fourier transformation of the f-curve inside the experimental range will depend ultimately upon the spread of the charge clouds in relation to the size of the unit cell, and the electron contents of the various atoms measured in this way need bear no very direct relation to their states of ionisation, if indeed the phrase has any meaning in this context. The hydrogen atom, because of its relatively small volume, appears to be an exception to this general rule.

The results of an investigation such as this depend critically upon the accuracy of the experimental measurements, and will be particularly influenced by errors in the absolute scale. It is unfortunate that it is experimentally so difficult to establish the latter with any accuracy, and the method adopted here is certainly not the most accurate. Errors in the F-values of the smallest-angle reflexions will also have a profound effect upon the results. For these reasons the effects discussed in this section may be exaggerated but there can be little doubt of their reality. Generalising from these results, we conclude that the electron distributions in ionic crystals are more diffuse than is perhaps generally realised, and that the classical picture of isolated positive and negative ions must be regarded as a rather crude approximation to the truth. This point has been more fully discussed by Lundqvist (1954).

The direct measurement of the electron density at points remote from the atomic centres is difficult because of the relatively high experimental error at these points (Brill *et al.*, 1939; Krug *et al.*, 1953). But, as is demonstrated above, it is a fairly simple matter to get some idea of the number of electrons which have 'gone into the background' and hence of the general background level.

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