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Electron Distribution and Charge Transfer in the Ammonium Ion

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A re-analysis of the single-crystal X-ray data of Adrian & Feil [*Acta Cryst.* (1969), A**25**, 438–444] for ammonium fluoride has shown that there is a transfer of negative charge from the 'surface' of the ammonium ion to the central nitrogen. In addition to charge transfer, models used in the analysis allow for non-rigid-body motion of the ammonium ion and asphericity in the hydrogen electron densities. This asphericitiy has been represented in two different ways, one involving a floated monopole and the other a polarized distribution centred on the neutron-determined position. Both models give comparable fits to the data and similar charge-transfer parameters are obtained, so that the floated-monopole model is considered adequate for obtaining properties of the total molecular electron distribution. However, the dipole model is to be preferred if information about the hydrogen pseudo-atom is desired. The present analysis is compared with previous ones employing structure factors derived from molecular wavefunctions for the ammonium ion. These previous analyses are less successful than might be expected and this is attributed to their over-simplified treatment of the ammonium ion as a rigid body and their neglect of crystal-field effects.

Introduction

The X-ray and neutron diffraction data of Adrian & Feil (1969) on ammonium fluoride were analysed by those authors to obtain structural and vibrational information only. Since the measurements were at liquid-nitrogen temperature and are believed to be quite accurate, the data were considered suitable for extracting electron-density information. The present study extends the original analysis to examine charge transfer within the ammonium ion and to explore various aspects of the bonded-hydrogen electron distribution.

It has been normal in electron-density studies to treat bonded hydrogen pseudo-atoms as spherically symmetric (*e.g.* Cromer, Larson & Stewart, 1976; Coppens, Csonka & Willoughby, 1970), so that their mean positions are artificially shifted with respect to the true nuclear positions as a result of electron-density concentration towards the bond centres. (This model is here referred to as the floated-monopole model.)

An early use of an aspherical model of the hydrogen electron distribution, centred on the proton position, is in the fit by Stewart, Davidson & Simpson (1965) of hydrogen pseudo-atoms to the electron distribution of the hydrogen molecule. This model includes a monopole, a dipole and a quadrupole component of the electron distribution for each hydrogen. It has been carefully analysed by Dawson (1975), who concluded that a straightforward atomic interpretation could indeed be applied to the static molecular electron distribution of H_2. The theoretical electron density considered by Stewart *et al.* (1965) for H_2 was, however, that appropriate to the non-vibrating molecule, whereas in all real situations not only are the hydrogen atoms vibrating, but their thermal motion is greater than that of their heavier neighbours. The total effect of this vibration on the observed electron distribution cannot be allowed for in a simple way.

Analyses of real data from vibrating molecules have been carried out by Coppens (1972) using aspherical hydrogen electron distributions. He introduced a dipole into the hydrogen scattering factor, based on $1s$–$2p$ orbital mixing, and initially centred the hydrogen multipoles on the neutron-determined sites. A comparison of the fits obtained using this model with those using the floated-monopole model showed that the polarized-hydrogen model did not provide better fits to the data, and that the optimum positions for the hydrogens with the dipole term included were still shifted into the bond with respect to the neutron positions. Coppens attributed at least part of the difficulty in representing the hydrogens to a breakdown of the rigid-ion approximation, which may lead to 'thermal shortening' of the bonds, as shown, for example by Coulson & Thomas (1971).

Another approach to the analysis of X-ray data for electron-density information is to employ structure factors based on molecular wave functions. This method was used to analyse the data of Adrian & Feil for NH_4F by Groenewegen & Feil (1969) and, very recently, by Bianchi, Cremaschi, Morosi & Simonetta (1977). Groenewegen & Feil employed the accurate multicentre wave functions of Krauss (1963) for the isolated ammonium ion, while Bianchi *et al.* used NH_4^+ wavefunctions obtained by *ab initio* SCF and SCF + CI methods, with both minimal and extended basis sets having standard or optimized exponents. Both groups of workers approximated the motion of the NH_4^+ ion to that of a rigid body and refined thermal vibration parameters and a scale factor. The later work was the more sophisticated, since librational modes were included and the hydrogens were placed at the neutron-determined positions. However, both groups made the considerable approximation that the internal vibrational modes of the ammonium ion were negligible. In addition they ignored the possibility of any effects on the NH_4^+ ion due to the crystalline state. Their thermal-vibration refinements presumably produced parameters which include some of these bonding effects.

Framework and assumptions of present study

The present study on ammonium fluoride assumes that the electron density as measured by the X-ray data of Adrian & Feil (1969) can be described by a superposition of pseudo-atoms, each of which may vibrate independently (*cf.* rigid-body assumption). The ammonium ion is constrained to be monovalent positive, but charge transfer can occur amongst the pseudo-atoms comprising that ion. The hydrogen pseudo-atoms are permitted either to have aspherical electron densities or to be represented by floated monopoles. Their thermal vibrations are derived from the neutron data of Adrian & Feil, rather than by refining the X-ray data to get both thermal and electron-density information for the hydrogens.

The aims of the present study of ammonium fluoride may be summarized as follows. (1) To compare polarized-hydrogen (P) models of the electron density with floated-monopole (FM) hydrogen models. (2) To carry out an analysis of the charge transfer within the ammonium ion and to assess the model dependence and significance of this analysis. (3) To compare the pseudo-atom model with the molecular wavefunction model of the ammonium ion used by Groenewegen & Feil (1969) and by Bianchi *et al.* (1977). (4) To examine the physical significance of the electron distribution obtained for the hydrogens.

The data refinement

The refinement for the electron-density parameters in NH_4F has been carried out on the X-ray data of Adrian & Feil (1969) using their neutron positional data and hydrogen thermal parameters. Table 1 gives details of the X-ray and neutron data. Most of the X-ray intensities were average values from two equivalent reflexions. Adrian & Feil did not quote any figures for internal agreement between equivalent reflexions, but they stated that their reference reflexions remained constant in intensity to within 1·5%. The data were collected on a relative rather than an absolute basis.

Table 1. *Single-crystal X-ray and neutron data on* NH_4F (*Adrian & Feii*, 1969)

	X-ray	Neutron
Temperature (°C)	−155	−196
Number of reflexions	95	48
Wavelength	0·7078 Å (Mo $K\overline{\alpha}$)	1·285 ± 0·03 Å
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0·80	0·57

A schematic representation of the modified wurtzite structure adopted by NH_4F is shown in Fig. 1. The hydrogen atoms occupy two types of special position, one of them axial (H1), the other non-axial (H2). Using the neutron data, Adrian & Feil (1969) found the thermal vibration of the hydrogen atoms to be anisotropic. Since the X-ray data show poor resolution of the hydrogen thermal motion, these neutron values of the hydrogen thermal parameters, corrected for the temperature difference of 41 K, were used in our analysis of the X-ray data. The differential temperature correction was calculated using the Debye theory (*International Tables for X-ray Crystallography,* 1959), an approximation which was assumed to be adequate since the hydrogen atoms are in the relatively flat quantum region of the mean square displacement ($\overline{u^2}$) *versus* temperature curve. Using this theory, we found the $\overline{u^2}$ to increase by 5%. In the notation of Adrian & Feil, the final values in Å^2 were $\overline{u_\perp^2} = 0{\cdot}029$, $\overline{u_\parallel^2} = 0{\cdot}015$ for H1: $\overline{u_\perp^2} = 0{\cdot}029$, $\overline{u_\parallel^2} = 0{\cdot}019$ for H2. The neutron values of $\overline{u^2}$ for nitrogen and fluorine were found to be isotropic. This constraint was applied in the X-ray analysis, but $\overline{u_N^2}$ and $\overline{u_F^2}$ were adjustable parameters.

The weighting scheme employed by Adrian & Feil for the X-ray data was of the form $w = 1/I$ for $I > 10\,000$ and $w = 3/(4I)$ for $I < 10\,000$, where w is the weight and I is the peak integrated intensity. The resulting overemphasis of the low intensities (Mackenzie, 1974) may be appropriate for obtaining temperature factor information but is quite unsuitable for

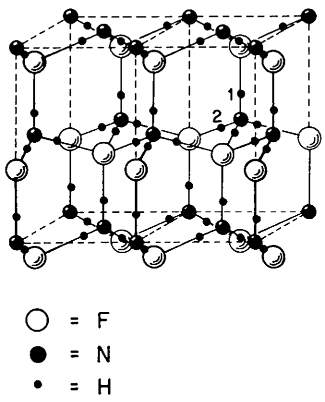

Fig. 1. The structure of ammonium fluoride. The labels 1 and 2 refer to the two types of hydrogen position.

detecting electron density effects. Consequently, a unit-weighting scheme was used here. This had the effect of giving the higher intensities greater weight.

With this weighting scheme a small correction for extinction was found necessary. Using Zachariasen's (1967) formula, the maximum extinction correction was 2%, so that a more sophisticated treatment of extinction was considered unwarranted. The effect of including extinction in the refinement led to changes in the electron-density parameters which were smaller than their standard deviations.

Four models for the total electron distribution in NH_4F were investigated in the present work. These are briefly described as follows.

Model 1*P*

The fluoride ion is assumed to be monovalent negative, with Hartree–Fock isolated-ion scattering factors as listed in *International Tables for X-ray Crystallography* (1974). The hydrogens are assumed neutral, and the spherical component of their scattering factor is taken as that of Stewart *et al.* (1965), which is also listed in *International Tables* (1974). A dipole component, directed along the nearest-neighbour bond, is introduced into the hydrogen scattering factor. In terms of the electron density, this is of the form:

$$\rho_D = \frac{\alpha_i^4}{16\pi} D_i \exp(-\alpha_i r) r \cos \varphi \begin{cases} i = 1 \text{ for H1} \\ i = 2 \text{ for H2} \end{cases}, \quad (1)$$

where we have employed polar coordinates; φ is the angle between r and the bond axis, α_i is the decay factor, D_i the weight and $\alpha_i^4/16\pi$ is introduced to normalize the number of electrons per lobe to D_i.

Although the symmetry of the hydrogens of type H2 permits the dipole to point in a direction inclined to the bond axis, in the present work it was constrained to lie parallel to the axis. This use of apparent symmetry is commonly employed in electron-density studies (*e.g.* Harel & Hirshfeld, 1975) where over-parametrization of the problem might otherwise occur and where the electron difference-density maps show that it is reasonable, as in our case.

A quadrupole term on each of the hydrogen centres and octupole components (of types O_2 and O_7, as defined by Stewart, 1973) on the nitrogen centres were initially included, but these were so poorly resolved that they were omitted from later analyses.

To maintain charge neutrality in the molecule, the nitrogen was assigned a single positive charge. An assumed form for the N^+ scattering factor was calculated from the spherically-averaged ^3P wavefunction of Clementi (1965). This resulted in a scattering-factor curve not significantly different from that of neutral nitrogen above $\sin \theta/\lambda \sim 0{\cdot}3$ Å^{-1}.

Model 2*P*

Model 2P is a modification of model 1P in which the possibility of charge transfer between the hydrogen and nitrogen atoms is introduced. A uniform expansion or contraction of the spherical part of the hydrogen electron density was permitted by scaling $\sin \theta/\lambda$ in the scattering factor by the factor κ, and the electron population, P_H, of the hydrogens was allowed to vary from 1·0. These two hydrogen parameters were constrained to be the same for both hydrogen types (H1 and H2) in order to reduce the number of adjustable parameters. The transferred charge was added to the N^+ ion charge density in the form of a single Slater term

$$(1 - P_H) \frac{\gamma^5}{24\pi} r^2 \exp(-\gamma r), \quad (2)$$

where γ is a variable parameter.

Models 1*FM and* 2*FM*

Models 1FM and 2FM were, respectively, modifications of models 1P and 2P, in which the hydrogen dipole terms were set to zero, but the H positions were allowed to shift to account for the non-spherical charge distributions (*i.e.* floated-monopole models).

The distinguishing features of the above models are summarized in Table 2.

Table 2. *Summary of models*

Model			
1P	H positions from neutron results	H dipoles included (weights D_i, exponents α_i)	No charge transfer allowed
1FM	H positions refined	H dipoles not included	
2P	H positions from neutron results	H dipoles included (weights D_i, exponents α_i)	Charge transfer allowed (P_H is the population of electrons on the hydrogens; γ the exponent for charge transferred to nitrogen; and κ the contraction of H monopoles)
2FM	H positions refined	H dipoles not included	

All least-squares refinements were carried out with the *BOTM* (*POWELL*) algorithm described in Kuester & Mize (1973), which finds the minimum of an unconstrained, multivariate non-linear function. Conventional crystallographic least-squares programs, which use only first derivatives in calculating the parameter shifts, were found to converge too slowly when refining exponents such as α_i and γ of (1) and (2) above. Using the *BOTM* algorithm such parameters reached convergence, although the process was still rather slow. As the algorithm required no derivatives, it was especially flexible for testing different models.

Results

(*a*) *Models without charge transfer* (*models* 1*P*, 1*FM*)

A difference-density section for a refinement, in which the hydrogens are placed at their nuclear positions and represented by monopoles only, is shown in Fig. 2. The effect of the non-centrosymmetric hydrogen electron-density is evident in the residual dipole components centred about the nuclear positions and pointing towards the adjacent nitrogens.

The results for the model 1P refinement (including the dipole components) are listed in column 2 of Table 3. The standard deviations for D_i and α_i show that the H1 dipole term is poorly defined compared with the H2 term. The 1:3 ratio of the H1 and H2 hydrogens presumably contributes to this effect. The exponents, α_i, of 5·37 (2·75) and 4·27 (0·35) Å^{-1} are of similar magnitude to the corresponding exponent obtained by Stewart *et al.* (1965) for the hydrogen molecule, *viz* 5·08 Å^{-1}.

Comparing the results of model 1FM, shown in column 3 of Table 3, with those of model 1P, we find that the dipole model, with its lower weighted *R* factor, R_w, and lower agreement index (both of which are defined in Table 3) gives a slightly better representation of the charge density than the floated-monopole model at this level of sophistication of the models. The unweighted *R* factor, *R*, is less sensitive to the high-intensity reflexions (Mackenzie, 1974), where most of the hydrogen-bonding information is contained, and shows a corresponding insensitivity to the difference in the models.

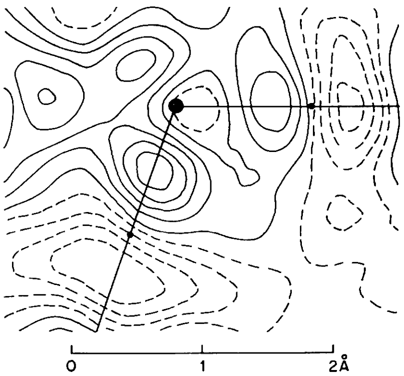

Fig. 2. The difference density in the region of an ammonium ion for a refinement in which the hydrogens are placed at their nuclear positions (small black circles) and represented by monopoles with a population of one electron. The large black circle represents a nitrogen position. Contour intervals are at 0·034 e Å^{-3} and negative contours are broken.

(*b*) *Models with charge transfer* (*models* 2*P* *and* 2*FM*)

The results for model 2P, which allows the possibility of charge transfer within the ammonium ion, are listed in the fourth column of Table 3. It can be seen that a significantly better fit to the data has been achieved with a transfer of 0·09 ± 0·03 e from each of the hydrogen atoms to the nitrogen.

The hydrogen electron population is a fairly model-independent parameter, since the model 2FM value (Table 3, column 5) is within the error limits of that for model 2P. The electron transfer for model 2FM is 0·12 ± 0·03 e, a slight increase over the model 2P value. A similar comparison of models by Coppens (1972) for some small organic molecules also showed a small difference in hydrogen population, but in the opposite direction.

In terms of agreement indices, there is little to choose between models 2P and 2FM, in contrast to the corresponding case when no charge transfer is allowed. The exponent, γ, for the distribution of the electron transfer to the nitrogen [expression (2)] is, for model 2FM, closer to twice the *L*-shell standard molecular-orbital value* (Hehre, Ditchfield, Stewart & Pople, 1970) of 7·38 Å^{-1} than for model 2P. Whilst there is no direct correspondence between the definitions of the latter exponent and of γ, one might expect that the two would be of similar size if the electron transfer took place in the region of the *L* shell.

Both models predict through the κ parameter that the spherical component of the hydrogen electron density is contracted with respect to the Stewart *et al.* (1965) case. This may in part be due to an overestimate of the hydrogen temperature factors, although the effect is not significant in models 1P or 1FM.

(*c*) *Comparison with molecular wavefunction models*

The molecular wavefunction models used by previous workers to fit the NH_4F X-ray data of Adrian & Feil (1969) have been described in the *Introduction.* The lowest agreement factor obtained by Groenewegen & Feil (1969), using a multicentre wavefunction for NH_4^+, was $R = 1{\cdot}8$ ($R_w = 2{\cdot}6$, four parameters refined). Bianchi *et al.* (1977) were able to obtain a value $R = 1{\cdot}6$ ($R_w = 2{\cdot}2$, nine parameters refined) for

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* The standard molecular-orbital exponent refers to a wavefunction. It must be doubled for comparison with an electron density.

Table 3. *Results of least-squares fits using models described in the text*

Standard deviations are given in parentheses below the refined values.

	Model 1P	Model 1FM	Model 2P	Model 2FM
Scale factor	33·06 (0·15)	33·31 (0·15)	32·64 (0·18)	32·80 (0·17)
Extinction parameter, r^* (μm)	0·62 (0·20)	0·69 (0·17)	0·51 (0·16)	0·74 (0·15)
$\overline{u_{\rm N}^2}$ (Å^2)	0·0130 (0·0004)	0·0131 (0·0004)	0·0136 (0·0005)	0·0132 (0·0004)
$\overline{u_{\rm F}^2}$ (Å^2)	0·0142 (0·0004)	0·0145 (0·0004)	0·0133 (0·0004)	0·0137 (0·0004)
Hydrogen population, $P_{\rm H}$ (e)	1·0	1·0	0·91 (0·03)	0·88 (0·03)
Hydrogen expansion parameter, κ	1·0	1·0	0·93 (0·03)	0·89 (0·02)
D_1 (e)	0·36 (0·28)	0·0	0·17 (0·06)	0·0
α_1 (Å^{-1})	5·37 (2·75)	–	10·54 (4·81)	–
D_2 (e)	1·01 (0·14)	0·0	0·74 (0·12)	0·0
α_2 (Å^{-1})	4·27 (0·35)	–	4·84 (0·43)	–
γ (Å^{-1})	–	–	8·9 (1·6)	7·3 (0·8)
$R_w = 100\left(\frac{\sum_i w_i\lvert F_{o,i}-F_{c,i}\rvert^2}{\sum_i w_i\lvert F_{o,i}\rvert^2}\right)^{\frac{1}{2}}$	1·5	1·7	1·4	1·4
$R = 100\,\frac{\sum_i\lvert F_{o,i}-F_{c,i}\rvert}{\sum_i\lvert F_{o,i}\rvert}$	1·4	1·4	1·3	1·2
Agreement index $= \left(\frac{\sum_i w_i\lvert F_{o,i}-F_{c,i}\rvert^2}{(n-m)}\right)^{\frac{1}{2}}$	3·0	3·3	2·7	2·7

(n = number of observations; m = number of parameters)

their best fit. All of the models used in the present work give substantially lower R factors than this, using between 4 and 11 refinable parameters. This relative lack of success with the molecular wavefunction models is probably due to their over-simplified treatment of the thermal motion as that of a rigid body. The weighting schemes used by both groups of workers would undoubtedly have aggravated this shortcoming, as small structure factors were given relatively higher weighting than large ones. Nevertheless, it is clear that internal modes should be included in such models, especially before introducing such subtle refinements as electron correlation.

It is noticeable that the electron-density difference map shown by Bianchi *et al.* (1977) for their best model shows a peak at the nitrogen atom. This is consistent with the charge-transfer effect obtained in the present study.

(*d*) *The bonded-hydrogen charge distribution*

A profile of the total bonded-hydrogen charge distribution along the N–H2 bond is shown in Fig. 3 for a stationary non-axial hydrogen with the parameters of model 2P. The dipole contribution is shown by the broken line. It can be seen that the latter is so large that in the fluorine direction the hydrogen charge-distribution component (though not the total charge distribution) has become slightly negative. A similar plot (not shown) for model 1P shows the same effect. These results are especially remarkable, since the basis set of (1) has been used by Stewart *et al.* (1965) to fit the static hydrogen molecule electron distribution without producing a negative region. Similar work by Bentley & Stewart (1976) on a series of diatomic hydrides, also treated in the static condition, yielded atomic electron densities which were all effectively positive definite. The appearance of the negative region in our hydrogen pseudo-atom densities raises questions about the interpretation of these 'atomic' distributions, even though there is no absolute necessity for the separated component corresponding to the hydrogen electron distribution to be everywhere positive.

Noting that the above examples involving diatomic molecules dealt with static systems, the effect of thermal motion must be considered as a possible cause of our negative electron density. The negative region cannot be explained in terms of the probable presence of small anharmonic vibrational components for the hydrogens, which have been included to a first-order approximation in the neutron positional parameters. It can, however, be eliminated for practical purposes by allowing the non-axial polarized hydrogens to move away from the neutron-determined positions to optimum positions in a model 2P refinement. The resultant shift of 0·08 ± 0·03 Å towards the nitrogens may be due, at least partly, to thermal shortening as a result of breakdown of the rigid-ion approximation (see Coulson & Thomas, 1971). However, the evidence for such a breakdown is by no means conclusive, as the rather weak negative region may have other causes.

Shortening of hydrogen bonds, even when the hydrogen electron-density is given a dipole component, was observed by Coppens (1972) in deutero-oxalic acid and in pyrene tetracyanoethylene. Coppens also attributed at least part of this shortening to non-rigidity of the hydrogen electron distribution. Price, Varghese & Maslen (1978) have observed analogous effects in melamine.

Conclusions

The analysis of the electron distribution in ammonium fluoride has shown that the floated-monopole model fits the electron density surprisingly well. If there is no allowance for charge transfer, the polarized hydrogen model gives a slightly better fit. Both models give quite similar results for the charge transfer. It may be concluded that the simple floated-monopole model is adequate for representing properties of the total electron distribution.

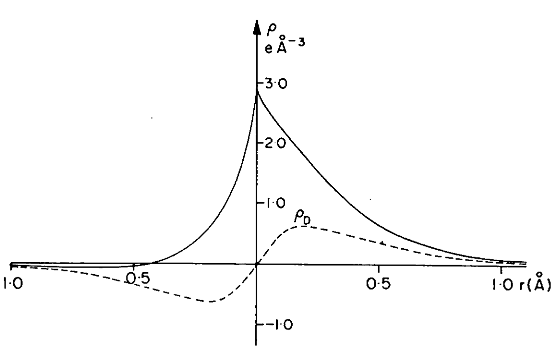

Fig. 3. The total static charge density for the non-axial hydrogens (H2), from the model 2P refinement showing the slightly negative region at the left of the plot. The broken curve represents the dipole contributions.

However, for a physically reasonable representation of the hydrogen electron distribution, the floated monopole model is unacceptable (since it implies that the static pseudo-atom has a cusp away from the nucleus), and the introduction of an antisymmetric term in the hydrogen charge distribution becomes mandatory. Using such a polarized-hydrogen model, the results obtained here, as well as those of other workers, suggest that it may be necessary to relax the restriction of rigidity of the hydrogen electron distribution in order to obtain a sensible result. A more complete picture of the hydrogen electron distribution would require studies at several temperatures, so that the effects of thermal motion might more readily be assessed. Comparative measurements with deuterated samples might also be useful.

The comparison made here between various molecular wavefunction models and our empirical atomic models of the electron distribution has illustrated the importance of a realistic treatment of thermal vibrations. Where internal modes of vibration are significant, then a rigid-body treatment of the molecule can only give a rather approximate representation of the thermally-smeared electron distribution. If one tries to remedy this situation by including internal modes of vibration in the molecular wavefunction description, serious difficulties arise in treating the two-centre products. Stevens, Rys & Coppens (1977) have proposed an approximate but apparently reasonable formalism for treating internal modes. Atomic models, by contrast, present no such problem, since they are one-centred.

The chemical significance of the work has been to show that the electron distribution for the NH_4^+ ion in NH_4F corresponds to a transfer of electron density from the hydrogens to the central nitrogen. The overall effect on the NH_4^+ group corresponds to a transfer of positive charge to its exterior, and a consequent partial neutralization of the central nitrogen atom. This charge transfer may be viewed as a molecular analogue to a Faraday's ice-pail effect. Each hydrogen has a charge of +0·09 (±0·03) e, leaving the central nitrogen with +0·6 (±0·1) e. Partial neutralization of the charge on the central atom in a complex ion has also been observed by Iwata (1977), in both $[Co(NH_3)_6]^{3+}$ and $[Cr(CN)_6]^{3-}$ in $Co(NH_3)_6Cr(CN)_6$.

The process of refinement of charge transfer is open to the criticism that the values obtained are basis-specific. Nevertheless, it would seem that the hydrogen electron populations obtained here are meaningful quantities since the models consistently predict that the hydrogens have a positive charge and that this is small. Comparable small positive charges (of order 0·19 e) on the hydrogens of the ammonium ion have moreover been found to be compatible with the lattice energies of NH_4Cl, NH_4Br and NH_4I, which have the alternative CsCl structure (Goodliffe, Jenkins, Martin & Waddington, 1971).

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The Magnetic Structure of $Bi_2Fe_4O_9$ – Analysis of Neutron Diffraction Measurements

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The compound $Bi_2Fe_4O_9$ belongs to the space group *Pbam* (D_{2h}^9), with two formula units per unit cell. Neutron diffraction measurements showed that it is paramagnetic at room temperature and undergoes a transition to an antiferromagnetic state at $T_N = (264 \pm 3)$ K in agreement with previous susceptibility and Mössbauer measurements. Analysis of the 80 K neutron diffraction pattern yielded a magnetic structure with the following features: (*a*) The basic translations $\mathbf{a}_o$, $\mathbf{b}_o$, $\mathbf{c}_o$ of the chemical lattice change into antitranslations in the magnetic lattice. (*b*) The spins are perpendicular to $\mathbf{c}_o$. (*c*) The magnetic structure belongs to the P_C2/m space group and is a basis vector to an irreducible space under the *Pbam* irreducible representations, in accord with Landau's theory of second-order phase transition. The position parameters of the Fe^{3+} ions in the unit cell were refined. The magnetic moment of the compound was found to be $(4{\cdot}95 \pm 0{\cdot}08)\mu_B$, compared with the value of $5\mu_B$ for the Fe^{3+} free ion. The temperature dependence of the {131} magnetic reflection peak intensity was measured and found to be in agreement with the sublattice magnetization predicted by the molecular field approximation.