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Analysis of ionic charge distributions in NH_4Cl

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Abstract

Principles of direct analysis of charge density are discussed. The x-ray structure factors of NH_4Cl measured by PESONEN [Ann. Acad. Sci. Fennicae A VI, No. 378 (1971)] at room temperature are analysed. The values $B_- = 2.04 \pm 0.08$ Å^2 and $B_+ = 1.9 \pm 0.2$ Å^2 for the Debye-Waller factors of chlorine and ammonium can be concluded from the data. Small but significant changes in the radial charge distributions of both ions as compared to the free ion superposition model are observed yielding well defined Cl^- and NH_4^+ ions. In the ammonium ion the fourth order cubic harmonic component is significantly stronger than that predicte, by one center SCF wave functions; this indicates sharper angular concentration but wider radial distribution of charge in the hydrogen directions. These effects hide all information about librations or internal vibrations of the molecule.

1. Introduction

This work presents the initial part of a series of x-ray and neutron diffraction studies. The purpose is to clarify the nature of the information we can obtain about the resolution of observed thermally smeared charge distributions into a static charge density and its associated motions.

The simple model formed by superposition of theoretical free atoms (or molecules) in rigid harmonic motion is sufficient for routine structure determination. But since the physical meaning of the parameters of the model, the positions and mean square amplitudes, extend beyond the validity of the model itself, they form the natural basis of any more accurate analysis used together with terms such as anharmonicity, nonrigidity, deformations of atoms or bonding densities, which describe different kinds of deviations from this model. We concentrate on observation of these phenomena by direct analysis of experimental structure factors. Questions of reliability will couple these studies closely with experimental problems and the project will probably require the development of some experimental techniques.

In principle, direct study of positions and motions independently of any assumptions on charge density requires the use of neutron diffraction. Variation of the crystal dynamics by varying the temperature or particularly, in the case of light atoms, by making isotopic replacements, will also give separate information on dynamic parameters. Measurements at

different temperatures will be necessary for direct observation of deviations from rigid motion of the atoms. However, only limited conclusions can be made from a single set of accurate x-ray diffraction data and they are heavily based on assumptions concerning the validity of theoretical atomic factors.

The room temperature phase of ammonium chloride was chosen as the first object of this research project. With its easy structure and simple chemical nature it is expected to make possible sufficiently reliable measurements and a detailed direct analysis of all interesting features. The structural parameters, while few in number, are of different kinds and will offer the opportunity to clarify the above mentioned aspects of the basic problem and to demonstrate the relative virtues of the different methods. This paper treats the x-ray structure factors of NH_4Cl measured by PESONEN [1].

2. Strategy of direct charge density analysis

There are in principle two different ways to approach the problem of charge density analysis: 1. *parameter fitting* and 2. *direct calculation* of quantities describing characteristic properties of the charge distribution. The immediate result of a successful fitting analysis is a parametric representation of the experimental charge distribution in terms of the model developed. The direct method tends to derive experimental statements concerning the important features of the charge distribution or its deviations from a reference model. The idea is to conclude from the data each feature or parameter and its significance independently on the basis of its physical nature.

Most complicated structures can be treated by fitting procedures. Direct analysis is best applicable to simple structures without phase problem, but it may also be of fundamental importance in clarifying the basic nature of experimental information. Still, there need not be any real difference between the two approaches. If we are able to parametrize the important features in a proper way, fitting will lead to equivalent results.

Any analysis is based on some model. The ways of using the model vary with the ideas and procedures applied in the analysis. In principle the model has a triple role: First, it forms *a representation of the experimental information* or part of it. Second, it is used as *a tool for calculating* experimental results. Finally, it has the role of *a reference model,* which means that the experimental results yield corrections and improvements of the model or give rise to a more basic criticism of the nature of the model.

The fitting procedure in its ultimate sense concentrates on the first role. Therefore the best possible or most sophisticated models are needed. The validity of theoretical calculations on which the model is based is of primary importance in studies where a perfect fit with experimental data is the primary aim.

In a direct analysis we try to choose quantities X which would adequately describe the important features of the charge distribution and which can be calculated directly from experimental structure amplitudes e.g. in form of a series $X = \sum_{\nu} c_\nu F_\nu$ summed over the reciprocal lattice $\{\boldsymbol{b}_\nu\}$. In this context the model serves primarily for evaluation of the residual

term i.e. the contribution of structure factors beyond the experimental termination point. Thus, the second role, the use as a tool is emphasized. This does not put such strict requirements on the validity of the model as the fitting procedures. Sufficient accuracy of the model in the residual term region of the reciprocal space can be reached in most cases by superposition of theoretical free atoms in rigid harmonic motion, i.e. by taking theoretical free atom scattering factors and choosing suitable values for their positional parameters and Debye-Waller factors. The simplicity of the model is an advantage. The experimental information expressed by the model is reduced to the values of these parameters, which have a direct physical significance. Results of a direct analysis can then be expressed mainly as corrections due to »solid state effects». Direct experimental statements on occurrence and significance of phenomena like anharmonicity, nonrigidity, charge transfer, deformation, bonding etc. can thus be obtained without the necessity to resort to any predefined sophisticated parametrizations.

From the fundamental role of atoms as the basic building units of matter it follows that behaviour of the charge distribution around the atomic positions is of special interest. Therefore, the radial charge densities

$$\rho_n(r) = \frac{4\pi(-\mathrm{i})^n}{VA_n} \sum_\nu F_\nu j_n(2\pi b_\nu r) K_n(\theta_\nu, \varphi_\nu), \tag{1}$$

where A_n is the normalization constant $A_n = \int K_n^2 \, \mathrm{d}\Omega$, giving the charge density around the origin in the form of a lattice harmonic expansion

$$\rho(\boldsymbol{r}) = \sum \rho_n(r) K_n(\theta, \varphi) \tag{2}$$

in spherical coordinates r, θ, φ, are useful quantities in a direct analysis, cf. KURKI-SUONIO [2], PESONEN [3], VIDAL-VALAT *et al.* [4]. The original suggestion for their use was made by ATOJI [5]. Similarly the radial scattering factors $f_n(b)$ of the lattice harmonic expansion of the atomic scattering factor

$$f(\boldsymbol{b}) = \sum f_n(b) K_n(\theta_b, \varphi_b) \tag{3}$$

in spherical coordinates $b = 2\sin\theta/\lambda$, θ_b, φ_b of the reciprocal space, have proved useful. They have been introduced both in a fitting type analysis by DAWSON [6] and in a direct calculation analysis by KURKI-SUONIO and MEISALO [7] and by KURKI-SUONIO and RUUSKANEN [8], where they have been calculated by a method called by DAWSON [9] the SVP (Spherical Volume Partitioning) method involving the series

$$f_n(b;R) = \frac{(4\pi)^2 R^3}{VA_n} \sum_\nu F_\nu K_n(\theta_\nu, \varphi_\nu) \frac{x\, j_{n+1}(x)\, j_n(x_\nu) - x_\nu\, j_{n+1}(x_\nu)\, j_n(x)}{x^2 - x_\nu^2}, \tag{4}$$

representing the radial scattering factors for a distribution within a radius R around the origin. Here $x = 2\pi Rb$.

3. The model crystal

At room temperature NH_4Cl has CsCl structure with a lattice constant 3.8747 Å. Determinations of the bond length d_{NH} in the NH_4 molecule vary from 1.02 to 1.05 Å and there is complete disorder between the two possible orientations of the tetrahedral NH_4^+ ion leading to cubic site symmetry of both ions in a diffraction study. The structure factors given in Table I correspond to the choice of the origin at the chlorine ion.

The experimental values cover the CuKα region $b < 1.22$ Å^{-1} of the reciprocal space. For calculation of the necessary residual terms and for comparison with the experimental results obtained we build in the customary way a free ion superposition model. For chlorine we take the relativistic Hartree-Fock scattering factors $f_-(b)$ of the Cl^- ion given by DOYLE and TURNER [10]. As the molecular scattering factor $f_+(\boldsymbol{b})$ of NH_4^+ at rest we use two models: one (M) based on one-center SCF wave functions calculated by MOCCIA [11] for the bond

Table I.

h	k	l	$\sin\theta/\lambda$	1.	2.	3.	4.	5.	6.
1	0	0	0.1290	6.85	6.90	6.92	6.73	6.74	8.20
1	1	0	0.1825	17.36	17.16	17.18	17.32	17.33	16.38
1	1	1	0.2235	5.90	5.90	5.84	5.81	5.76	6.36
2	0	0	0.2581	12.33	12.59	12.48	12.62	12.52	12.32
2	1	0	0.2885	5.40	5.26	5.28	5.27	5.30	5.41
2	1	1	0.3161	10.15	10.10	10.12	10.06	10.09	10.02
2	2	0	0.3650	8.54	8.52	8.55	8.47	8.51	8.51
2	2	1	0.3871	4.33	4.30	4.26	4.34	4.28	4.29
3	0	0	0.3871	4.33	4.30	4.40	4.34	4.47	4.29
3	1	0	0.4081	7.30	7.40	7.35	7.37	7.30	7.42
3	1	1	0.4280	3.98	3.91	3.93	3.94	3.97	3.89
2	2	2	0.4470	6.46	6.55	6.60	6.53	6.60	6.57
3	2	0	0.4653	3.48	3.56	3.55	3.57	3.56	3.54
3	2	1	0.4828	5.91	5.86	5.87	5.85	5.87	5.88
4	0	0	0.5162	5.12	5.27	5.22	5.28	5.21	5.29
4	1	0	0.5321	2.96	2.94	2.97	2.93	2.98	2.93
3	2	2	0.5321	2.96	2.94	2.92	2.93	2.90	2.93
4	1	1	0.5475	4.82	4.77	4.75	4.78	4.75	4.78
3	3	0	0.5475	4.82	4.77	4.78	4.78	4.79	4.78
3	3	1	0.5625	2.57	2.67	2.65	2.66	2.69	2.66
4	2	0	0.5771	4.30	4.32	4.32	4.33	4.33	4.33
4	2	1	0.5913	2.43	2.42	2.42	2.41	2.41	2.41
3	3	2	0.6053	3.87	3.93	3.94	3.94	3.95	3.93

1. Dispersion corrected experimental structure factors of PESONEN [1].
2. Structure factors of the spherical model M [11].
3. Structure factors of the nonspherical model M [11].
4. Structure factors of the spherical model AC [12].
5. Structure factors of the nonspherical model AC [12].
6. Structure factors of the N^-Cl^- model.

length d_{NH} = 1.0530 Å and the other (AC) based on a one-center basis set SCF MO calculation of ALBASINY and COOPER [12] for bond length d_{NH} = 1.0054 Å. Both of these models allow immediate expression of the molecular scattering factor in the form of a cubic harmonic expansion (3) with angular functions $K_n(\theta, \varphi)$ given by KURKI-SUONIO and RUUSKANEN [8] identical with the cubic harmonics of VON DER LAGE and BETHE [13] except for normalization, which for practical reasons is chosen to give $\mathrm{Max}\{K_n\} = 1$. The orientational disorder of NH_4^+ destroys all odd components without affecting the even ones. Components with $n > 6$ are seen to be negligible. Thus both models of NH_4^+ consist of merely the spherical component f_0 modified by an additional term f_4K_4 of the cubic shape $K_4(\theta, \varphi)$ and a small correction $f_6K_6(\theta, \varphi)$.

In addition, to demonstrate the role of the model in a direct analysis and the independence of the results of the model, we take a third model, where the NH_4^+ ion is replaced by a free N^- ion, whose Roothaan-Hartree-Fock scattering factors are given by MIRANSKII, POGORELOV and KHAENKO [14].

We let both ions of the model perform rigid, harmonic, translational vibrations involving one spherical Debye-Waller parameter each, B_- for Cl^- and B_+ for NH_4^+. This is obviously the best we can do at this stage for the reliability of the model in the residual term region. Librational motion of NH_4^+ corresponds to multiplication of the nonspherical components f_n by libration factors $a_n < 1$ (cf. PRESS and HÜLLER [15]) to be determined. However, the effect of the nonspherical f_n in the residual term region is small in any event. Independent vibrations of the hydrogens cannot be taken into account by any simple parameter in the theoretical molecular form factors. The effect of vibrations perpendicular to the bond can obviously not be distinguished from librations of the whole molecule and will, thus, not cause any further discrepancy in the calculations. Vibrations along the bond form a real source of uncertainty due to their unpredictable effect in the residual term region together with other uncertainties in the calculation of wave functions for NH_4^+.

The structure amplitudes of the model are thus expressed by the formula

$$F_\nu = f_-(b_\nu)\, e^{-B_- b_\nu^2/4} + (-1)^{h_\nu + k_\nu + l_\nu}[f_0(b_\nu) + a_4 f_4(b_\nu)\, K_4(\theta_\nu, \varphi_\nu) + a_6 f_6 K_6]\, e^{-B_+ b_\nu^2/4}, \quad (5)$$

where the functions f_-, f_0, f_4 and f_6 are taken from the theoretical calculations. The libration factor a_4 is to be determined by further analysis. The magnitude of f_6 is below any experimental observability, and will not allow determination of a_6. For the calculations we take either a spherical model with $a_4 = a_6 = 0$, which corresponds to a freely rotating molecule, or a non-librating model with $a_4 = a_6 = 1$.

The Debye-Waller factors B_- and B_+ must be adapted to the motions of the atomic cores so as to yield the best possible estimates of the residual terms. This is realized by a computational procedure which adjusts their values iteratively such that the difference $\Delta\rho_0 = \rho_{0,\mathrm{obs}} - \rho_{0,\mathrm{model}}$ in the average spherical charge distributions at the ionic centra is flat, as calculated from the difference series corresponding to eq. (1) with $n = 0$. The procedure includes the possibility of adjusting simultaneously the scale of the experimental structure factors by the same criterion. It also corrects the structure factors for dispersion. This procedure has been

developed from the method of KURKI-SUONIO and FONTELL [16], which applied the same criteria using the conventional Fourier series. In the present case the adjusted scale was found to be consistent within 0.5 % with the experimental scale determination and in further treatment of the data the experimental scale was preserved. Dispersion correction for Cl^- was made according to CROMER [17].

The values of temperature factors (and the scale factor) as given by the procedure and, hence, the dispersion corrections depend on the theoretical form factors used. For Cl^- we get $B_- = 2.04$ Å^2 independently of the model of the other ion. B_+ varies as expected. We get $B_+(\mathrm{M}) = 1.87$ Å^2 and $B_+(\mathrm{AC}) = 1.95$ Å^2. Omission of nonspherical components has no effect. Use of N^- leads to $B_+ = 1.98$ Å^2. The model structure amplitudes corresponding to these B values are given in Table I. In principle the corrected experimental structure amplitudes forming the basis of further analysis also depend on the model, through the scale factor and through the dispersion correction which depends on the Debye-Waller factors. The differences in B_+ are, however, too small to cause any effect in the corrected data shown in column 1 of Table I.

The B values with their uncertainties express the experimental information included in the model. They give estimates for the nuclear mean square amplitudes of chlorine and nitrogen. B_- can be considered more reliable than B_+, because of the rather well defined and stable core of chlorine and because of the smaller uncertainty in its theoretical scattering amplitude. Its uncertainty is mainly of experimental nature and is roughly estimated to correspond to an uncertainty of ±2 % in the scale determination. This correspondence follows from the mutual coupling of scale and temperature factors in their determination and gives $\delta B_- = \pm 0.08$ Å^2.

The indeterminacy in B_+ is, to the contrary, strongly increased by the uncertainty in the theoretical model. More accurate multicenter molecular wave functions would certainly reduce it. In this context the only estimate of the accuracy of B_+ can be obtained from the interval of variation when different models are used with an additional experimental component of the order of ±0.09 Å^2 estimated similarly to δB_-. According to this argument the value of the Debye-Waller factor corresponding to translational librations of the NH_4^+ group cannot be determined more accurately than by the estimate $B_+ = 1.9 \pm 0.2$ Å^2.

4. Spherical average ionic charge distributions

The spherical average behaviour of the atomic charge distributions has proved to give a good basis for discussing the nature of the atoms in the crystal, cf. KURKI-SUONIO and SALMO [18], RUUSKANEN and KURKI-SUONIO [19], VIDAL-VALAT *et al.* [4]. For this purpose we calculated *the radial charge density* $4\pi r^2 \rho_0(r)$ from the series (1) with $n = 0$, or

$$\rho_0(r) = \frac{1}{V} \sum_{\nu} F_\nu \frac{\sin 2\pi b_\nu r}{2\pi b_\nu r} \tag{6}$$

and *the spherical electron count* $Z(r) = \int_0^r 4\pi r^2 \rho_0(r)\, \mathrm{d}r$ given by the series

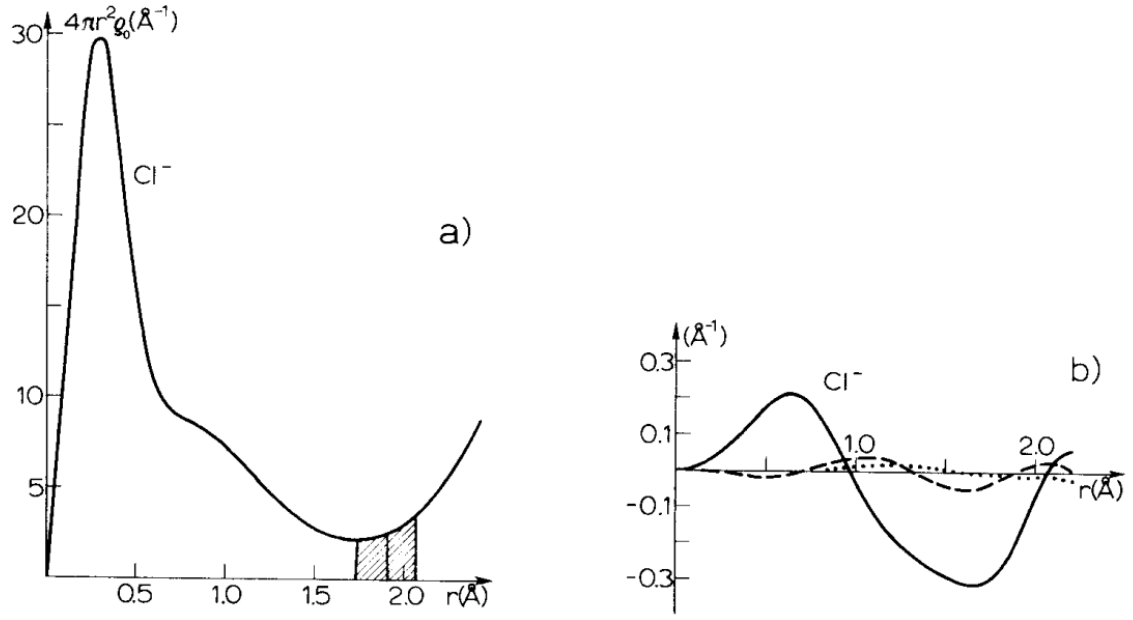

Fig. 1. (a) Experimental radial charge density $4\pi r^2\rho_0(r)$ of chlorine in NH_4Cl with a limit for integrated electron count equal to 18 ± 0.5 e. (b) deviation of the experimental radial density from the free ion superposition model (solid line) with NH_4 (MOCCIA); differences between experimental results derived using two different models (dotted line = (M) - (AC), dashed line = NH_4Cl(M) - N^-Cl^-).

$$Z(r) = \frac{4\pi r^3}{V} \sum_{\nu} F_{\nu} \frac{j_1(2\pi b_{\nu} r)}{2\pi b_{\nu} r} \,. \tag{7}$$

The calculation procedure is based on Gaussian representation of the model ionic form factors. The number of Gaussian terms per atom is here irrelevant, and no physical meaning is attached to this representation. It is only important that the compatibility is as precise as possible in the residual term region of the reciprocal space. The radial charge densities and the spherical electron counts for the Gaussian crystal can be calculated using the analytic expressions. Experimental values and model values are then obtained by adding to the Gaussian result the relevant difference series corresponding to the series (6) and (7). This procedure, which is an extention of the method of HOSEMANN and BAGCHI [20] for treating charge density maps, is equivalent to using residual terms corresponding to the model (see KURKI-SUONIO and SALMO [18]). The experimental radial charge densities $4\pi r^2\rho_0(r)$ of the two ions obtained by this procedure are shown in Figs. 1a and 2a. Results obtained using different models did not differ in the scale of these figures. Fig. 2a gives also the radial density of N^- in the Cl^-N^- model, showing clearly the difference of a total of two electrons. The solid curves in Figs. 1b and 2b in a x 20 magnified scale show the deviations from the models. Differences between calculations using different models are shown in the same magnification to demonstrate the stability of these results against changes of model and, thus, the reliability of the residual terms.

Radii within which the integrated electron counts amount to 18 ± 0.5 e and 10 ± 0.5 e corresponding to ionised states Cl^- and NH_4^+, respectively, are indicated by limits and shaded

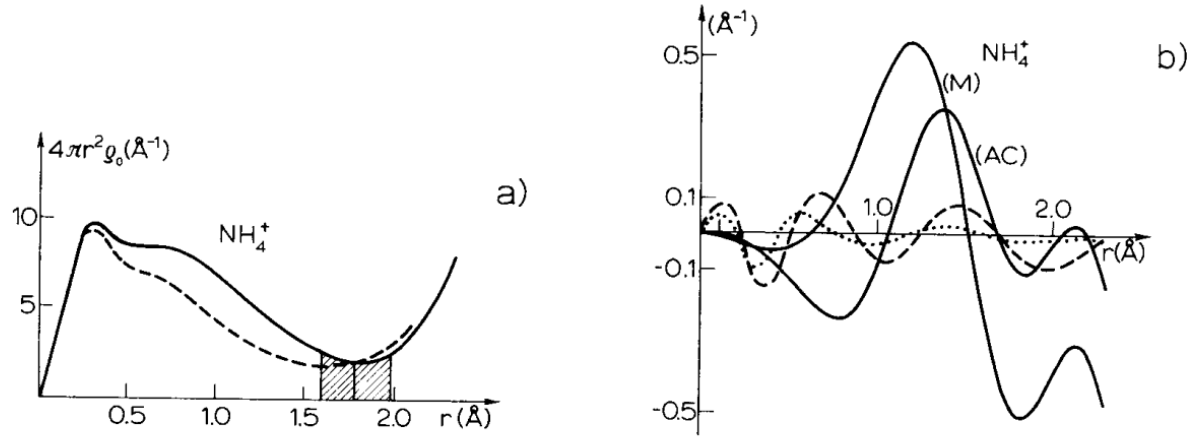

Fig. 2. (a) Radial charge density $4\pi r^2\rho_0(r)$ of ammonium in NH_4Cl (solid line) and N^- in the N^-Cl^- model (dashed line); limit for integrated electron count equal to 10 ± 0.5 e is shown. (b) deviations of the experimental radial density from the free ion superposition models (M) and (AC) (solid lines); differences between experimental results derived using two different models as for Fig. 1 (b).

regions in Figs. 1a and 2a. The radii corresponding to 18 and 10 electrons varied in the different calculations from 1.92 Å to 1.98 Å for Cl^- and from 1.67 Å to 1.78 Å for NH_4^+.

We find that both ions are clearly separated from their surroundings by distinct minima in the radial charge density, 2.2 e/Å for Cl^- and 1.8 e/Å for NH_4^+. The »radii of best separation» have the values $R_{Cl} = 1.75$ Å and $R_{NH_4} = 1.76$ Å, corresponding to a small overlap ($R_{Cl} + R_{NH_4}$ exceeds the ionic distance by 4.6 %). The integrated electron counts of the distribution peaks correspond to single ionization, as shown by Figs. 1 and 2. The values of $Z(R)$ at the minima being 17.55 e and 9.95 e for Cl and NH_4 respectively show that the positive ion is compact, whereas a total of about 0.5 electrons of the negative ion is more widely distributed.

Comparison of the experimental distributions with the free ion superposition model indicates a compression of the chlorine, and in ammonium there is a concentration of charge at the bond length distance from the center when compared to the model M and a displacement of charge outwards from the bond region when compared to the AC model. Numerically these effects are small. They are not sensitive to changes of model (including variations of Debye-Waller parameters). Their significance in the light of experimental uncertainty must, however, be checked by calculation of the radial scattering factors. Similar features have been observed in other cases and they seem to be typical of ionic crystals. In fact, already the superposition models show the state of ionization of the atoms quite well. The experimental data just slightly improve the separation of the ions from each other. Thus, the information of the nature of the crystal is included to a first approximation in the structure of the crystal and in the charge distributions of the free atoms or molecules, cf. KURKI-SUONIO and SALMO [18]. Numerical comparison with other crystals indicates that the ions are here not quite as well defined as they are in the alkali halide crystals, but there is a clear distinction in this respect when compared to, say, metal oxides with doubly ionized atoms, cf. KURKI-SUONIO and SALMO [18], VIDAL-VALAT *et al.* [4].

5. Radial ionic scattering factors f_n

To consider deviations of the ionic charge distributions from their spherical average the difference series (4) or Δf_n with $n \leqslant 10$ was calculated for both ions. The computational radii $R_- = 1.7$ Å $= 0.5066\, d$ for Cl^- and $R_+ = 1.8$ Å $= 0.5364\, d$ for NH_4^+, where $d = 3.3556$ Å is the mutual distance of the ions, were chosen on the basis of Figs. 1 and 2. To check the dependence of the results on the model, Δf_n with respect to all the models introduced in sec. 3 were calculated.

Since the libration coefficients a_n of eq. (5) were not known, the first calculations were made with spherical models. The results corresponding to the spherical model M are shown by the dashed lines in Figs. 3 and 4. The error bars attached to some points of the curves indicate the experimental uncertainty. Spherical AC as well as the Cl^-N^- model gave equal results to within limits an order of magnitude narrower than the experimental error bars. This means that the nonspherical components were equal, and that the differences in Δf_0 were equal to the differences in the models themselves, as shown by Fig. 4a, which also gives the AC result and the difference $f_0^{(M)} - f_0^{(AC)}$ (including the temperature factors). According to the nonspherical standard of adequacy of KURKI-SUONIO and RUUSKANEN [8], occurrence of high order components would indicate experimental inaccuracy. The 8th order component of Cl^- is probably such a »ghost». It is not large enough to destroy the consistency of information about the strong fourth order component in NH_4, but its presence certainly reduces the significance of possible statements about the nonsphericity of chlorine.

The spherical components Δf_0 in Figs. 3a and 4a confirm the significance of the statements based on the radial densities (Figs. 1 and 2) concerning deviations of the ions from the

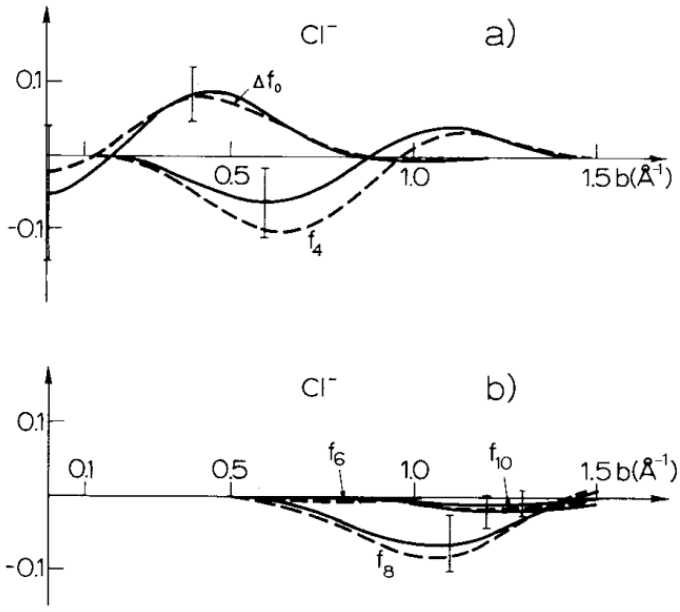

Fig. 3. Radial scattering factors of the cubic harmonic expansion of chlorine in NH_4Cl with statistical error bars as calculated for a sphere of radius $R = 1.7$ Å using the spherical (dashed line) and nonspherical model of MOCCIA for NH_4: (a) spherical component Δf_0 and the nonspherical f_4; (b) higher order components.

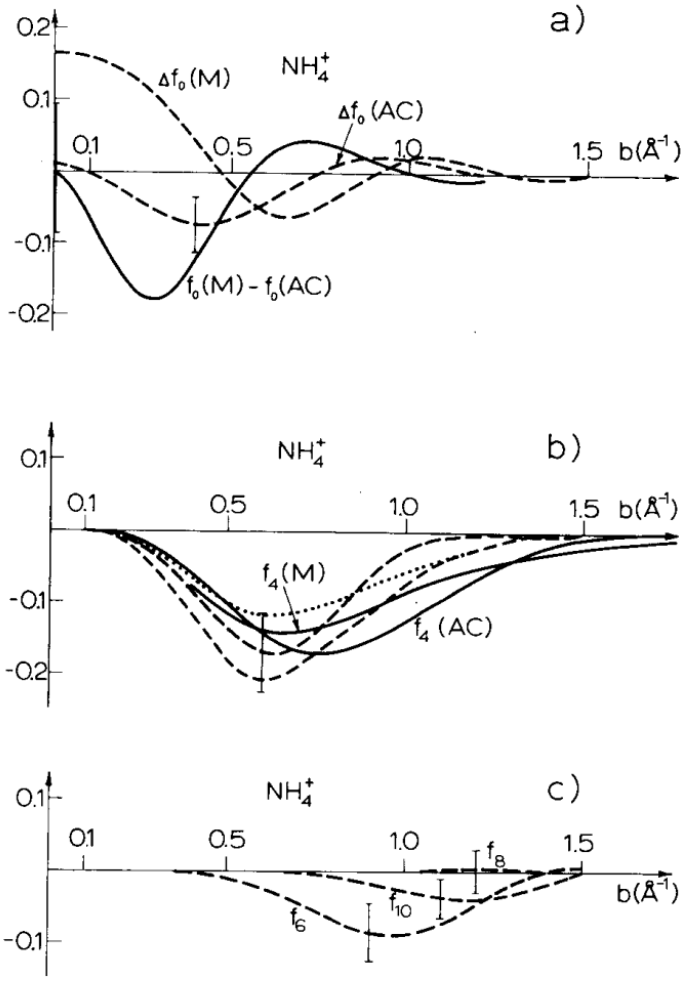

Fig. 4. Radial scattering factors of the cubic harmonic expansion of ammonium in NH_4Cl: (a) the spherical component, deviations Δf_0 from the model (M) and from the model (AC) and the difference f_0(M) - f_0(AC) between the two models including the temperature factors; (b) fourth order component f_4 obtained using the spherical model (M) (upper dashed line) and the nonspherical model (M) (lower dashed line), the components in the theoretical models (M) and (AC) at rest and in (M) including rigid vibrations of the molecule (dotted line); (c) higher order components f_n obtained using the spherical model (M).

models. The spherical component of the AC model seems to be closer to the experimental one, the deviation being characterized as a slight average broadening of the charge distribution, which can have its explanation in the short bond length of (AC). This, however, does not necessarily mean that the AC model is better in its average behaviour. The models have also the difference equivalent to the difference in the temperature factor. A final judgement cannot be made until we know which of the temperature factors is closer to the correct one.

This first calculation shows significant fourth order deformation components in both ions. They correspond to angular displacement of charge from the (100) directions to the nearest neighbour directions (111). In NH_4^+, Fig. 4b, we know its existence already from the shape of the molecule. The sixth order component of NH_4^+, Fig. 4c, may also be real, although this cannot be stated with confidence, because the eighth order »ghost» of chlorine is of the

Table II. Structure factor ratios of coincident reflexions according to different models and observed nonsphericities.

	Theor(M)	Exp(M)	Theor(AC)	Exp(AC)
F_{300}/F_{221}	0.968	0.946	0.957	0.942
F_{410}/F_{322}	1.017	1.017	1.028	1.028
F_{411}/F_{330}	0.994	0.994	0.992	0.992

same magnitude and puts a lower limit on the consistent nonspherical information of data. In any event, simultaneous occurrence of f_4 and f_6 of this kind would be consistent with charge concentrations in cubic coordination around the nitrogen. Qualitatively this can be seen, e.g., from the coefficients of cubic harmonic expansion of cubically (or tetrahedrally) coordinated δ-function charges, cf. Table 2 of PRESS [21][1]. The sixth order component would have the effect of making the angular distribution of this charge concentration sharper and would cancel part of the reduction in the (100) directions.

When the calculations are made using the nonspherical models with $a_4 = 1$ and the Debye-Waller factors obtained in sec. 3, the fourth order components change a little, as shown by the solid lines in Figs. 3a and 4b. The others remain essentially unchanged. For NH_4^+ the curve is obtained by adding the difference series to f_4 of the model. M and AC results do not differ in the scale of the figure. The growth of f_4 in NH_4 as compared to the spherical model calculation is typical of these calculations. Part of the effect can be explained as a residual term effect, since f_4 of the model extends beyond the cut-off value of experiments, cf. KURKI-SUONIO [22]. Part of it – in this case quite small – can be assigned to the lack of experimental information on the difference of coincident reflexions. By use of nonspherical models this is taken into account by dividing the total intensity of the coincident reflexions in the relation indicated by the model. For both reasons a spherical model is likely to yield smaller nonsphericities and the result obtained with the nonspherical one will be regarded here as the experimental result. The experimental outcome also indicates different values for the structure amplitudes of coincident reflexions, as shown in Table II.

For comparison, the fourth order components corresponding to the models M and AC are drawn in the same Fig. 4b, M also with the relevant temperature factor. The observed f_4 (and f_6) is considerably stronger than in the vibrating model. The maximum is even larger than in the models at rest. It is, thus, not possible to give any estimate of the libration parameter a_4 on the basis of the x-ray data.

The result indicates that the angular concentration of charge in the directions of the hydrogen atoms is sharper than in any of the two models. The occurrence of f_6 would further enhance this effect. The difference in the radial behaviour is of the opposite nature. The maximum of the experimental curve is closer to the origin and is sharper, which indicates

[1] In comparison, note the difference in normalization of the cubic harmonics, the phase factor due to Fourier transformation and the misprints: $c_{61}^{T} = \sqrt{26}\,4/9$, $c_{71}^{T} = -\sqrt{455}/9$.

that the charge of the hydrogen atoms is concentrated at somewhat larger radial distance and is radially more widely distributed than in the models. We think that these differences demonstrate a difficulty in the calculations based on one center wave functions, although a larger bond length in the calculation of ALBASINY and COOPER would probably have corrected for most of the differences. Qualitatively, also vibrations of the hydrogen atoms along the bond would make the radial distribution of the model wider in the observed manner. However, it should be noted that we expect the crystalline field to cause changes of just the observed nature both in the angular and in the radial behaviour of the NH_4^+ ion. The observed f_4 of chlorine indicates that they can account for a significant part of the observations. Such small adjustments of the model are therefore not well motivated on the basis of these data.

6. Conclusions

The analysis of the room temperature data on NH_4Cl demonstrates clearly some advantages and weaknesses of the x-ray analysis. The information observed is conditional, in that it depends on the basic assumption of reliability of theoretical atomic or molecular form factors *in the residual term region.* The values of Debye-Waller parameters are sensitive to this assumption, while, on the other hand, the statements describing the deviations of ionic charge distributions from the model are much less sensitive.

The information obtained cannot immediately be parametrized or analyzed in terms of charge density and structural dynamical parameters, except for Debye-Waller parameters which refer to the dynamics. Even the obvious parameters, bond length in NH_4^+, vibrations of hydrogens along the bond or librations (or vibrations of hydrogens perpendicular to the bond) cannot be determined or refined any further on the basis of the results, since the effects of the crystalline field and, in the case of NH_4^+, also the inaccuracy of the theoretical model are similar in nature and possibly of the same order of magnitude as the effects of the parameters.

Improvement offered by more accurate theoretical wave functions in this situation is probably unessential, although it would give some added confidence in the Debye-Waller factors. A sophisticated model might further give the possibility to make some vague estimates of the vibrations of hydrogens or librations of the molecule and a checking of the bond length, but still this information would be of a highly conditional nature. On the other hand, fit with data would not give any real test of the reliability of such improvements of the theoretical model, because crystalline field effects may cause similar changes of the charge distribution.

Direct information on thermally smeared nuclear distributions would in principle essentially reduce these difficulties. Data of comparable accuracy would give directly, not only Debye-Waller factors, but also the whole thermal smearing functions including possible anharmonicities and, hence, libration parameters as well as the vibration of hydrogens along the bond. This information would then serve both as a check of the theoretical x-ray form factors of the ions and as a means of more detailed parametrization of the x-ray diffraction results. Therefore as the next step in our XN-project we shall make an effort to study these possibilities in practice.

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