

Neutron Diffraction Study of Nuclear Distributions in NH_4Cl

BY K. KURKI-SUONIO, M. MERISALO AND AINO VAHVASELKÄ

Department of Physics, University of Helsinki, SF-00170 Helsinki 17, Finland

AND F. K. LARSEN

Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus-C, Denmark

(Received 5 May 1975; accepted 12 July 1975)

Integrated intensities for the Bragg reflexion of 1.070 \AA neutrons by a single crystal of NH_4Cl have been measured at 295 K. The experimental data were corrected for extinction. An analysis based on direct calculation of properties of nuclear smearing functions is applied to the data. The results show that the motions of chlorine and the ammonium ion as a whole can be described within experimental accuracy by the harmonic model with the values $B_- = 1.90 \pm 0.08 \text{ \AA}^2$ and $B_+ = 2.00 \pm 0.08 \text{ \AA}^2$ of Debye-Waller factors for chlorine and the ammonium ion respectively. Values of parameters describing libration of the ammonium ion and the value $r_0 = 1.050 \pm 0.005 \text{ \AA}$ for the N-H bond length were determined from the radial scattering amplitudes of the ammonium ion. The radial nuclear density shows evidence for radial vibrations of the hydrogen atoms with mean-square amplitude $\Delta^2 = 0.006 \pm 0.001 \text{ \AA}^2$.

1. Introduction

Considerable attention has been drawn to joint X-ray and neutron diffraction studies in recent years. The potential of these studies, referred to below as XN-studies, is based essentially on the superiority of neutron diffraction over X-ray diffraction in inferring positional and thermal parameters of atoms in crystals (*cf. e.g.* Coppens, 1970; Coulson, 1970).

The aim of the present work is to examine the possibilities of an XN-study in analysing the electronic charge distribution and the thermal motions of a crystal. The physical approach to this problem requires the separation of the question of experimental reliability from the problem of adequacy of the theoretical model, as opposed to the conventional application of the criterion of fit in which the two questions are judged simultaneously. Experimentally this involves estimation of the accuracy of the data on the basis of physical knowledge of the experiment. In the analysis of data this means that a more direct approach should be used, where the adequacy of each parameter and the accuracy of the value obtained for it is concluded from the data independently of other parameters.

To be able to concentrate on the physical problems, it is necessary to take simple objects without particular experimental difficulties and with few structural parameters. It was decided to start with ammonium chloride, NH_4Cl , where, in spite of its simplicity, the necessity of complementary information from neutron diffraction is clearly demonstrated, since neither the positional nor the thermal parameters of the hydrogen atoms can be studied by X-rays with any satisfactory accuracy. The room-temperature study of NH_4Cl presented in this paper is part of a more extensive XN project which contains X-ray and neutron diffraction studies at various temperatures for normal and deuterated compounds.

A room-temperature X-ray diffraction measurement on NH_4Cl powder has been carried out previously (Pesonen, 1971). Analysis of those data and discussion of the possible conclusions on the basis of such a single set of X-ray data is given by Vahvaselkä & Kurki-Suonio (1975). Since the accuracy of the two neutron diffraction measurements made so far (Goldschmidt & Hurst, 1951; Levy & Peterson, 1952) cannot be considered high enough for the present purpose, a careful neutron measurement was made with the application of modern data-collection and processing techniques. This paper presents this measurement, the analysis of the data based on direct methods and a discussion of the combination of these results with the previous X-ray study.

2. Measurements and preliminary analysis

The structural modifications of ammonium chloride at various temperatures have been well established (*cf. e.g.* Levy & Peterson, 1952; Yelon, Cox & Kortman, 1974).

At room temperature ammonium chloride has the cubic CsCl structure and conforms to the space group $Pm\bar{3}m$ with cell edge $a = 3.8742 \text{ \AA}$ (Boiko, 1970). The four hydrogen atoms of the ammonium ion occupy two sets of crystallographically equivalent positions of tetrahedral symmetry, corresponding to a disorder between energetically equivalent orientations.

The crystals were grown from an aqueous solution of ammonium chloride to which about 10% urea had been added in order to promote a cubic growth habit. A crystal with linear dimensions $3.00 \times 3.14 \times 1.96 \text{ mm}$ and bounded by $\{100\}$ planes was used for data collection. The neutron diffraction data were collected at 296 K on a Hilger-Ferranti four-circle diffractometer at the DR3 reactor of the Danish Atomic Energy Commission Research Establishment, Risø. The 002 re-

flexion from a Be monochromator crystal provided the incident neutron beam of wavelength 1.070 Å. The Bragg intensities were measured with a BF₃ detector using ω - 2θ step-scan technique with a step length of 0.08° in 2θ . The integrated intensities were evaluated by a method which divides the step-scanned profile into peak and background in such a way that $\sigma_{\text{COUNT}}(I)/I$ is minimized (Lehmann & Larsen, 1974), where I is the integrated intensity and $\sigma_{\text{COUNT}}(I)$ its estimated standard deviation based on counting statistics. Two standard reflexions 400 and 004 were measured every 20 reflexions, and revealed a systematic increase (< 2%) in the standard intensities for the data collection period. The intensities were scaled accordingly and corrected for absorption by the Gaussian integration method (Coppens, Leiserowitz & Rabinovich, 1965) using a neutron absorption coefficient, $\mu = 3.1 \text{ cm}^{-1}$, calculated from tabulated mass absorption coefficients and incoherent scattering cross sections (*International Tables for X-ray Crystallography*, 1968), except for the proton, for which the incoherent scattering cross section was given the value of 40 barns. 766 reflexions with $\sin \theta / \lambda < 0.83 \text{ \AA}^{-1}$ were measured, of which 44 were unrelated by symmetry. The internal consistency R value,

$$R = \frac{\sum |G_{hkl, \text{obs}}^2 - \langle G_{hkl, \text{obs}}^2 \rangle|}{\sum G_{hkl, \text{obs}}^2}$$

was 2.55%, where G is the neutron structure factor.

Full-matrix least-squares refinement was performed by applying a correction for isotropic extinction in the Zachariasen approximation (Coppens & Hamilton, 1970) using a reference model with independent harmonic vibrations of the nuclei (model iv). The variable quantities were the scale factor, the isotropic extinction parameter g' , the proton-nitrogen bond length r_0 , the isotropic Debye-Waller parameters B_+ and B_- of nitrogen and chlorine, respectively, and the proton anisotropic thermal parameters β_{11} and β_{12} . Scattering lengths g for the nuclei were those recommended by the Neutron Diffraction Commission (Bacon, 1972). The value of the discrepancy index $R = \sum |G_{hkl}^{\text{obs}} - G_{hkl}^{\text{iv}}| / \sum |G_{hkl}^{\text{obs}}|$ arrived at in the least-squares refinement was 2.54%.

Observed and calculated structure factors G^{obs} and G^{iv} , respectively, along with the corresponding standard deviations σ and the extinction coefficients γ are listed in Table 1. The final values of the parameters are given in Table 2. Here the values of $B_{\parallel} [= 4a^2(\beta_{11} + 2\beta_{12})]$ and $B_{\perp} [= 4a^2(\beta_{11} - \beta_{12})]$ related to r.m.s. amplitudes parallel and perpendicular to the N-H bond, respectively, are given instead of β_{11} and β_{12} .

If the extinction is mosaic-spread-dominated - Type I (Zachariasen, 1967) - the extinction parameter g' can be interpreted as a mosaic spread of 0.045°.

3. Basic formalism

The observed nuclear distribution $s(\mathbf{r})$ is the weighted sum

$$s(\mathbf{r}) = \sum_n g_n \tau_n(\mathbf{r} - \mathbf{r}_n) \quad (1)$$

of the nuclear smearing functions $\tau_n(\mathbf{r})$. Its analysis on the basis of observed neutron structure amplitudes G_j does not differ in principle from the analysis of charge density. Both can be based either on a fitting procedure or on direct calculation, as discussed by Vahvaselkä & Kurki-Suonio (1975). The model in this case consists of the values g_n of the neutron scattering amplitudes of the nuclei and parameters for nuclear posi-

Table 1. Neutron structure factors for NH₄Cl

$h k l$	G^{obs}	σ	γ	G^{iv}	G^{ivr}
1 0 0	0.8326	0.0031	0.9638	0.8190	0.8263
1 1 0	1.3461	0.0042	0.9304	1.3715	1.3620
1 1 1	0.2846	0.0040	0.9984	0.2140	0.2247
2 0 0	2.0522	0.0074	0.9067	2.0638	2.0656
2 1 0	-0.2223	0.0016	0.9985	-0.2335	-0.2378
2 1 1	1.6797	0.0045	0.9406	1.7186	1.7172
2 2 0	1.4349	0.0005	0.9602	1.4411	1.4544
3 0 0	-0.7822	0.0033	0.9889	-0.7812	-0.8011
2 2 1	0.0959	0.0068	0.9999	0.0557	0.0631
3 1 0	1.8272	0.0040	0.9462	1.8208	1.8403
3 1 1	-0.2592	0.0031	0.9992	-0.2126	-0.2222
2 2 2	1.2521	0.0060	0.9736	1.2541	1.2197
3 2 0	0.2027	0.0027	0.9993	0.2090	0.1936
3 2 1	1.0674	0.0023	0.9819	1.0797	1.0740
4 0 0	1.5067	0.0018	0.9695	1.5373	1.5331
4 1 0	-0.1637	0.0046	0.9995	-0.1720	-0.1715
3 2 2	0.0728	0.0130	1.0000	0.0265	0.0597
4 1 1	1.1439	0.0033	0.9829	1.1469	1.1423
3 3 0	0.6171	0.0037	0.9942	0.6339	0.6431
3 3 1	0.2825	0.0037	0.9989	0.2691	0.2786
4 2 0	0.8442	0.0024	0.9906	0.8445	0.8471
4 2 1	0.1082	0.0060	0.9998	0.1118	0.1194
3 3 2	1.1014	0.0029	0.9853	1.0214	0.9940
4 2 2	0.8922	0.0034	0.9894	0.9052	0.8886
5 0 0	—	—	—	0.0447	0.0825
4 3 0	0.2581	0.0037	0.9991	0.2577	0.2516
5 1 0	0.7626	0.0025	0.9925	0.7831	0.7558
4 3 1	0.7006	0.0022	0.9936	0.7057	0.7028
5 1 1	0.0794	0.0082	0.9999	0.0557	0.0766
3 3 3	-0.2433	0.0087	0.9994	-0.2138	-0.2010
5 2 0	0.0693	0.0397	0.9999	0.0632	0.0701
4 3 2	-0.0985	0.0137	0.9999	-0.0686	-0.0604
5 2 1	0.7149	0.0023	0.9938	0.7078	0.7008
4 4 0	0.5884	0.0045	0.9955	0.5918	0.6025
5 2 2	—	—	—	-0.0100	-0.0069
4 4 1	0.0557	0.0135	0.9999	0.0458	0.0422
5 3 0	0.6591	0.0030	0.9951	0.6344	0.6415
4 3 3	0.7987	0.0041	0.9914	0.7821	0.7859
5 3 1	—	—	—	-0.0000	-0.0020
4 4 2	0.6545	0.0038	0.9940	0.6567	0.6566
6 0 0	0.4202	0.0080	0.9959	0.4746	0.4469
6 1 0	0.0866	0.0075	0.9998	0.0917	0.1102
6 1 1	0.5080	0.0055	0.9954	0.5176	0.5060
5 3 2	0.5914	0.0032	0.9942	0.5954	0.5951

Table 2. Values of parameters for NH₄Cl in the model with independent vibrations

g_{N}	$0.944 \times 10^{-12} \text{ cm}$
g_{Cl}	$0.958 \times 10^{-12} \text{ cm}$
g_{H}	$-0.374 \times 10^{-12} \text{ cm}$
g'	0.0359 (0.0094)
r_0	1.0246 (0.0034) Å
B_+	1.974 (0.044) Å ²
B_-	1.897 (0.038) Å ²
B_{\parallel}	2.508 (1.08) Å ²
B_{\perp}	4.661 (0.54) Å ²

tions and motions. Because of this simplicity parameters which make the fitting procedure equivalent to the direct approach are more easily found than in the case of X-ray analysis, and they will be distinguished only when deviations from harmonic motion or from the Gaussian form of the smearing function are studied.

The Debye–Waller factors can be defined by the best fit to the smearing functions at the mean positions, and their values can be refined, together with the scale, by the same procedures as in case of X-ray analysis (Vahvaselkä & Kurki-Suonio, 1975). The anharmonicity will then appear as a low-scattering-angle effect. It can be analyzed by studying the behaviour of the smearing function $\tau(\mathbf{r})$ or its Fourier transform, the temperature factor $T(\mathbf{b})$. Here the expansions

$$s(\mathbf{r}) = \sum_n s_n(r) K_n(\theta, \varphi) \quad (2)$$

$$gT(\mathbf{b}) = \sum_n g_n(b) K_n(\theta_b, \varphi_b), \quad (3)$$

in terms of site-symmetrized harmonics K_n in spherical coordinates (r, θ, φ) and (b, θ_b, φ_b) , lend themselves for proper use. The radial densities $s_n(r)$ and radial scattering amplitudes $g_n(b)$ can be calculated from the series

$$s_n(r) = \frac{4\pi(-i)^n}{VA_n} \sum_j G_j j_n(2\pi b_j r) K_n(\theta_j, \varphi_j) \quad (4)$$

$$g_n(b) = \frac{16\pi^2 R^3}{VA_n} \sum_j G_j \times \frac{x j_{n+1}(x) j_n(x_j) - x_j j_{n+1}(x_j) j_n(x)}{x^2 - x_j^2} K_n(\theta_j, \varphi_j) \quad (5)$$

(cf. Kurki-Suonio, 1967). The notations involve the spherical Bessel functions $j_n(x)$ with $x = 2\pi Rb$, normalization integrals $A_n = \int K_n^2 d\Omega$, and a computational atomic radius R . For the atom considered, a sphere of radius R is assumed to contain the whole region of non-zero smearing function but no significant contributions from the neighbouring atoms. This requirement is easier to fulfil than the corresponding requirement in charge-density analysis.

In the case of NH₄Cl the expansions (2) and (3) can also be appropriately used for representation of the nuclear density of the NH₄⁺ group. The functions $K_n(\theta, \varphi)$ are then the cubic harmonics of von der Lage & Bethe (1947), which are used here with the normalization $\text{Max}\{K_n\} = 1$ of Kurki-Suonio & Ruuskanen (1971). At rest the contribution of the four protons is given by four δ functions at the distance r_0 in tetrahedral coordination around the central nitrogen atom:

$$s_H(\mathbf{r}) = 4g_H \sum_{i=1}^4 \delta(\mathbf{r} - \mathbf{r}_i) = 4g_H \frac{\delta(r - r_0)}{4\pi r^2} \sum_{i=1}^4 \frac{\delta(\theta - \theta_i)}{\sin \theta} \delta(\varphi - \varphi_i). \quad (6)$$

This corresponds to cubic harmonic expansions (2) and (3) with

$$s_n^0(r) = 4g_H c_n \frac{\delta(r - r_0)}{4\pi r^2} \quad (7)$$

$$g_n^0(b) = 4g_H i^n c_n j_n(2\pi r_0 b), \quad (8)$$

where $n = 0, 3, 4, 6, 7, 8, 9, 10, \dots$, and $c_n = K_n(111)/A_n$ or $c_0 = 1, c_3 = 35/9, c_4 = -7/2, c_6 = 416/81, c_7 = 455/81, c_8 = 561/64, c_9 = -5.25049, c_{10} = 58240/6561$. These values are equivalent to those given by Press (1973, 1976).

As stated by Press & Hüller (1973), any librations or orientational disorder of the rigid group will introduce certain librational factors a_n which depend only on the time-averaged orientational distribution of the group. We get thus

$$s_n^1(r) = 4g_H a_n c_n \frac{\delta(r - r_0)}{4\pi r^2} \quad (9)$$

$$g_n^1(b) = 4g_H i^n a_n c_n j_n(2\pi r_0 b). \quad (10)$$

The spherical term always remains unchanged, $a_0 = 1$. The orientational disorder of NH₄ in NH₄Cl at room temperature makes all odd terms vanish, *i.e.* $a_3 = a_7 = a_9 = \dots = 0$. A free rotation of the group would make all $a_n = 0$ ($n > 1$).

Vibration of the rigid molecule means convolution of $s(\mathbf{r})$ with the vibrational smearing function and multiplication of $g(\mathbf{b})$ by the corresponding temperature factor. The use of the nitrogen Debye–Waller factor B_+ leads to

$$s_n^{1v}(r) = 4g_H a_n c_n C \exp[-a(r^2 + r_0^2)] j_n(2\pi r_0 r) \quad (11)$$

$$g_n^{1v}(b) = 4g_H i^n a_n c_n \exp(-B_+ b^2/4) j_n(2\pi r_0 b), \quad (12)$$

where $C = (4\pi/B_+)^{3/2}$, $a = 4\pi^2/B_+$ and $i_n(x)$ are the modified spherical Bessel functions.

If the protons are allowed to execute radial vibrations independently of the two other modes of motion, the radial δ function in equations (6), (7) and (9) will be replaced by a radial smearing function $R(r)$. This finally leads to the expressions

$$s_n^{1vr}(r) = 4g_H a_n c_n \int_0^\infty R(r') \times \exp[-a(r^2 + r'^2)] j_n(2\pi r' r) dr' \quad (13)$$

$$g_n^{1vr}(b) = 4g_H i^n a_n c_n \times \exp(-B_+ b^2/4) \int_0^\infty R(r) j_n(2\pi r b) dr. \quad (14)$$

If the r.m.s. amplitude Δ of the radial vibrations is small ($\Delta \ll r_0$) we can, to a good approximation, use the Gaussian smearing function:

$$R(r) = \frac{\Delta}{\sqrt{2\pi}} \exp\left[-\frac{1}{2} \left(\frac{r - r_0}{\Delta}\right)^2\right]. \quad (15)$$

Anharmonicity of the vibrations would only require non-Gaussian smearing functions, but as long as the nitrogen smearing function is spherical the basic

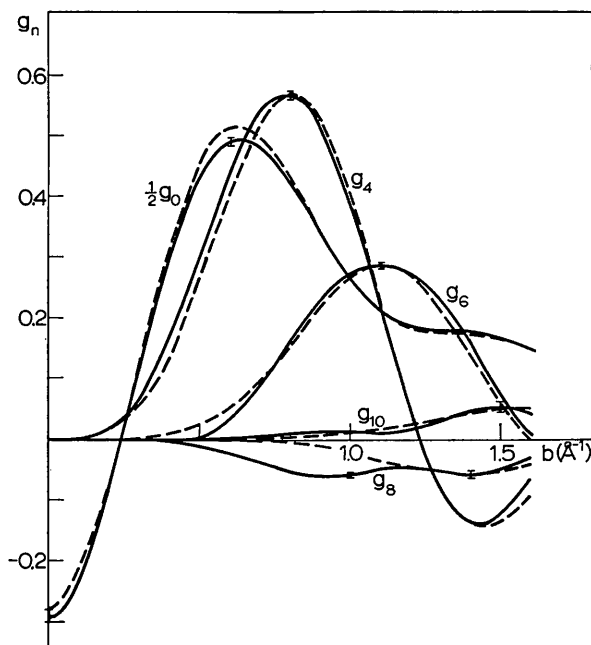


Fig. 1. Experimental radial scattering amplitudes $g_n(b)$ of the NH_4 group (solid line) calculated from equation (11) with the preliminary model as the reference model, together with those of the rigid model (broken line) calculated from equation (18) with the parameters of Table 3. The error bars indicate statistical accuracy.

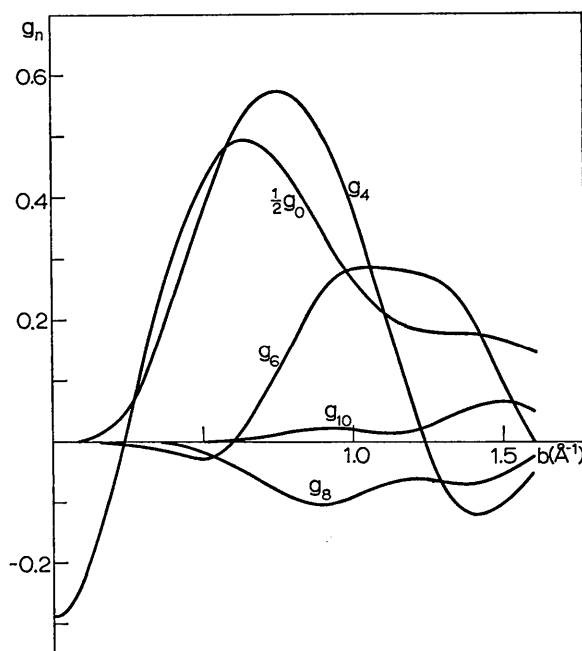


Fig. 2. Experimental radial scattering amplitudes $g_n(b)$ of the NH_4 group calculated with the rigid model of Table 3 as the reference model.

simplicity is preserved. Coupling between the librations and the radial vibrations of the protons would formally appear as different smearing functions $R_n(r)$ in different terms of the cubic harmonic expansion. Calculation of the radial densities $s_n(r)$ or scattering amplitude g_n of the ammonium group by equations (4) and (5) will give direct information on all these aspects.

4. Analysis

The experimental structure amplitudes scaled and corrected for extinction by the preliminary least-squares treatment were taken as the data for the analysis. The two Debye-Waller parameters B_- and B_+ were obtained by adjustment of the spherical average nuclear density of the rigid harmonic model at the mean positions of Cl and N. On the basis of the B values the computational radii R were determined to be $R_- = 1.25 \text{ \AA}$ for chlorine, $R_N = 0.65 \text{ \AA}$ for nitrogen and $R_+ = 2.25 \text{ \AA}$ for the whole ammonium group. The corresponding radial scattering amplitudes g_n were calculated from (5) with the difference series added to the relevant components of the model.

In these calculations the rigid model, (11) and (12), was used. In the first reference model only the libration-independent spherical term was included. In the chlorine smearing function a fourth-order component $g_4(b)$ was observed to exceed by a factor of five the statistical limit of error. Its significance is discussed later. The nitrogen shows no deviations from the model. Its smearing function is, thus, Gaussian within the experimental accuracy. The higher-order components were very small, indicating consistency of the non-spherical information included in the data (Kurki-Suonio & Ruuskanen, 1971).

Fig. 1 shows the results for the ammonium group together with radial scattering factors of the rigid model, equation (12). The libration factors and the bond length were fitted to yield the same maximum values and positions of maxima for the model curves as for the experimental ones. The resulting values are given in Table 3. The higher orders, $n > 10$, are expected to be insignificant and were not included in the calculation. The convergence of g_n towards larger n is, however, not strong enough to justify this omission at lower temperatures.

Table 3. Values of parameters for NH_4Cl from direct analysis in the rigid model and the model with bond vibrations

	B_+	2.00 (0.08) \AA^2
	B_-	1.90 (0.08) \AA^2
	r_0	1.050 (0.005) \AA
	Rigid model	Model with bond vibrations
a_4	0.755	a_4 0.771 (0.007)
a_6	0.466	a_6 0.479 (0.008)
a_8	0.341	a_8 0.350 (0.029)
a_{10}	0.184	a_{10} 0.186 (0.033)
		Δ^2 0.006 (0.001) \AA^2

Our model already has quite a good fit to the data. The nature of the residual differences can be seen more exactly if another calculation is made using the model obtained as a new and better reference model. The results are shown in Fig. 2. There is no need to re-evaluate the bond length or the libration factors.

To see the significance of the radial vibrations of the hydrogen atoms the difference in radial nuclear density $4\pi r^2 \Delta s_0(r)$ was calculated from (4) with the rigid model of Table 3 as the reference model. The result is compared in Fig. 3 with the change $4\pi r^2(s_0^{iv} - s_0^{iv})$ of the model due to inclusion of radial vibrations with $\Delta^2 = 0.0036 \text{ \AA}^2$, according to (11) and (13). This comparison does, however, not give a quantitative determination of Δ^2 because of the natural truncation of the series (4). Comparison with the effect of Δ^2 on the truncated series corresponding to the model leads to the estimate $\Delta^2 = 0.006 \pm 0.001 \text{ \AA}^2$.

Inclusion of this radial oscillation has a minor effect on the radial scattering amplitudes g_i . After the necessary readjustment of the libration factors, Table 3, it is sufficient to yield a practically complete fit with the experimental g_0 , g_4 and g_6 . It does, however, not explain the behaviour of g_8 and g_{10} . If these differences are real, they must be interpreted as a coupling between librations and vibrations. The behaviour of g_8 would indicate that the protons spend more time in the free octahedral directions [100] and at a larger distance from the centre than allowed by the model.

5. Discussion

The statistical accuracy of the data is very good. If the experimental structure amplitudes G_j are treated as independent statistical variables, we get the error bars shown in Fig. 1, according to which even small details of the behaviour should be considered significant. Random errors may accumulate in some high-order component; this affects the reliability of conclusions drawn from g_8 and g_{10} . In general the main problem arises from systematic sources of error.

We have no quantitative way of estimating the reliability of the model on which the extinction correction is based. The extinction corrections obtained by the preliminary fitting are rather small. Since the fit itself is no physical criterion, we can take this only as an indication of the order of magnitude of this effect. To have an idea of its significance we analysed also the uncorrected data. This yielded the values $B_- = 1.758 \text{ \AA}^2$, $B_+ = 1.864 \text{ \AA}^2$ and the scale factor $k = 1.077$. The fourth-order component $g_4(b)$ of chlorine became about twice as large. Changes of the libration factors were small. The value of bond length and the estimate of Δ^2 did not change.

As a whole there is little difference in the effect of the extinction correction from that of changing the scale by about 8%. It is not possible to conclude whether this is valid for the actual extinction. Thus, in the absence of any better criteria, we assume the

uncertainty due to extinction to be half of the effect caused by the extinction correction. In this way extinction becomes the main source of uncertainty in the Debye-Waller factors and in estimation of the anharmonicity of the chlorine motion. It is comparable to the statistical inaccuracy in the case of a_4 and a_6 and of no concern for a_8 , a_{10} , r_0 and Δ^2 , for which the inaccuracy is mainly due to the indeterminacy in the curve fitting used for their evaluation.

Another obvious source of error is the thermal diffuse scattering, which has not been corrected. It also principally affects the values of Debye-Waller factors.

Table 3 gives error limits concluded according to these considerations. The g_4 of chlorine is slightly larger than the uncertainty deduced in this way, but not large enough to be considered as a measure of anharmonicity of chlorine motion. If it is real, it indicates a slightly larger probability of vibrations in the directions of the neighbouring ammonium ions.

The results should be compared with the corresponding X-ray study by Vahvaselkä & Kurki-Suonio (1975). The superior power of neutron diffraction in the analysis of atomic motions is clearly seen. The X-ray values for B_- and B_+ are in accordance with the neutron results, but the X-ray determination of B_+ is much less reliable.

The information concerning librations, bond vibrations and refinement of the N-H bond length was not accessible by X-rays. Of the two models for the ammonium ion used in the X-ray analysis, that of Moccia (1964) had the more correct bond length. This was also suggested by the X-ray analysis, but it could not be definitely concluded because of other possible interfering effects.

At the present stage combination of the neutron information with the results of X-ray analysis does not essentially increase our knowledge about the charge distribution of NH₄Cl. If the rigid-body assumption were correct, we could use the observed Debye-Waller parameter B_+ and the libration factor a_4 to derive the

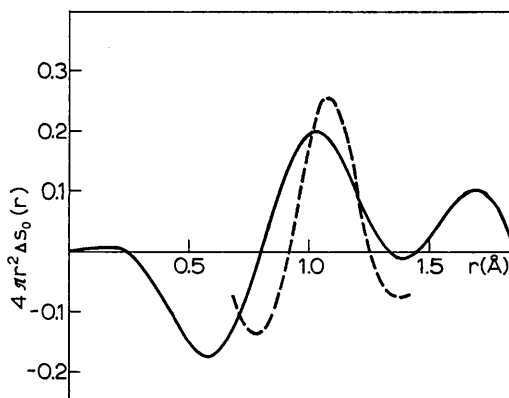


Fig. 3. Difference series calculation of $4\pi r^2(s_0^{iv} - s_0^{iv})$ for the radial nuclear density of the NH₄ group (solid line) compared with the effect, $4\pi r^2(s_0^{iv} - s_0^{iv})$, of bond vibrations with r.m.s. amplitude 0.06 Å on the radial density of the model (broken line).

X-ray scattering factor for NH_4^+ at rest from the observed radial scattering factors f_0, f_4 . Such a result yields, however, only the qualitative conclusion, already reached in the X-ray analysis, that the one-centre SCF calculations do not give large enough non-spherical components, *i.e.*, they do not yield a sharp enough concentration of charge around the hydrogen atoms. Observations on another dynamical state (*e.g.* temperature variation, isotopic replacement ND_4) would give, at least in principle, complementary information on the physical basis of this deviation. Such studies would gain substantially from theoretical scattering factors of free NH_4^+ , with the observed bond length and with some internal dynamics included to account for the observed average bond vibrations. The anisotropy of chlorine vibrations is, in any case, far too small to cause observable effects in the X-ray scattering factor of chlorine.

We are indebted to Dr. R. Tellgren for providing the single crystal used for the neutron diffraction work, and to Miss S. Rosten for her invaluable help with the computational work. This study was financially supported by the National Council for Science, Finland (K.K-S. and M.M.) and by the University of Helsinki (M.M.).

References

- BACON, G. E. (1972). *Acta Cryst.* A28, 357–358.
 BOIKO, A. A. (1970). *Sov. Phys. Crystallogr.* 14, 539–543.
 COPPENS, P. (1970). *Thermal Neutron Diffraction*, Edited by B. T. M. WILLIS, pp. 82–100. Oxford Univ. Press.
 COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.
 COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* 18, 1035–1038.
 COULSON, C. A. (1970). *Thermal Neutron Diffraction*, Edited by B. T. M. WILLIS, pp. 68–81. Oxford Univ. Press.
 GOLDSCHMIDT, G. H. & HURST, D. G. (1951). *Phys. Rev.* 83, 88–94.
International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.
 KURKI-SUONIO, K. (1967). *Ann. Acad. Sci. Fenn.* A VI, 263.
 KURKI-SUONIO, K. & RUUSKANEN, A. (1971). *Ann. Acad. Sci. Fenn.* A VI, 358.
 LAGE, F. C. VON DER & BETHE, H. A. (1947). *Phys. Rev.* 71, 612–622.
 LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A30, 580–584.
 LEVY, H. A. & PETERSON, S. W. (1952). *Phys. Rev.* 86, 766–770.
 MOCCIA, R. J. (1964). *J. Chem. Phys.* 40, 2176–2185.
 PESONEN, A. (1971). *Ann. Acad. Sci. Fenn.* A VI, 378.
 PRESS, W. (1973). *Acta Cryst.* A29, 257–263.
 PRESS, W. (1976). *Acta Cryst.* A32, 170.
 PRESS, W. & HÜLLER, A. (1973). *Acta Cryst.* A29, 252–256.
 VAHVASELKÄ, A. & KURKI-SUONIO, K. (1975). *Phys. Fenn.* 10, 87–99.
 YELON, W. B., COX, D. E. & KORTMAN, P. J. (1974). *Phys. Rev.* B9, 4843–4856.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* 23, 558–564.

Acta Cryst. (1976). A32, 115

Restriction of the Number of Terms in the Sayre–Hughes Equation Connected with a Criterion to Establish the Absence of Atomic Overlap in Projection

BY J. J. L. HEINERMAN AND J. KROON

Laboratorium voor Structuurchemie, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands

(Received 28 July 1975; accepted 1 August 1975)

In the Sayre–Hughes equation the variable reciprocal-lattice vector ranges over the whole reciprocal net. It is shown that under the condition that a projection along a zone axis has no overlapping atoms the variable reciprocal-lattice vector can be restricted to range over a plane of the reciprocal net. *A fortiori* if a projection on an axis is free from overlap the variable vector can be restricted to range over a row of the reciprocal net. Criteria to determine the projections for which these conditions are best fulfilled are given. These criteria involve the absolute values of the structure factors only. The theory is illustrated by a test employing normalized structure factors calculated from atomic coordinates.

Introduction

It is always possible to determine the three-dimensional structure from any two resolved two-dimensional projections for which the projection on their intersecting line is resolved. In the case that only one two-

dimensional projection is resolved use can be made of generalized projections to find the three-dimensional structure.

For reciprocal space it follows that under the conditions mentioned above, a restricted number of structure factors determines the others (at the given