A low temperature neutron diffraction study of NH_4Cl

M. Merisalo, F.K. Larsen* and K. Kurki-Suonio
Department of Physics
University of Helsinki
Helsinki, Finland

*Department of Inorganic Chemistry
University of Århus
Århus, Denmark

Abstract

Neutron structure factors of NH_4Cl have been measured on a single crystal at 138 K by neutrons of 1.070 Å wavelength. Corrections for extinction and thermal diffuse scattering were estimated. Analysis of the nuclear motions was made by least-squares techniques using harmonic approximation for the vibrations and cubic harmonic expansion in treatment of librations of the NH_4 ion including radial vibrations of the NH bond. Parameter values necessary for combination with an X-ray diffraction analysis are given.

1. Introduction

This work constitutes part of a series of joint X-ray and neutron diffraction studies. The physical aim of this research project (referred to as XN-project) has been discussed in two earlier papers [1, 2], where the results of X-ray and neutron diffraction studies of ammonium chloride crystal at room temperature were reported. In these studies the importance of measurements on a different dynamical state was realized, in order to distinguish effects of dynamical origin in the average charge distribution observed, and thus to understand the relationship between neutron and X-ray measurements. This can be accomplished either by making isotopic replacement of nuclei or by varying the temperature.

In the present study the demand of variation of crystal dynamics was met by carrying out the neutron diffraction study of NH_4Cl at a low temperature. The low temperature phase of NH_4Cl presents, however, another type of problem in the analysis of charge and nuclear distributions. Since a center of symmetry is lacking, the direct approach used in the case of the room temperature data [1, 2] cannot be applied, and one must resort to determination of parameters by least-squares fitting. The problem then arises as to the equivalence of the parameter values obtained by the two different methods.

2. Measurements

The structural modifications of NH_4Cl crystal at various temperatures have been well established (cf. e.g. [3, 4]). At 249.5 K the crystal undergoes an order-disorder λ-transition. Below the transition temperature it has the cubic CsCl structure with essentially rigid hydrogen tetrahedra oriented in a parallel »ferromagnetic» arrangement. In the low temperature phase the crystal conforms to the space group $P\bar{4}3m$ with cell edge $a = 3.830$ Å [5].

The low temperature neutron diffraction data were collected on the same single crystal as was used in the room temperature study [2]. Measurements were made at 138 K on a Hilger-Ferranti automatic four-circle diffractometer at the wavelength 1.070 Å. Details of the measurements having been described previously [2], only special features of the low temperature system are presented here.

The crystal was cooled by a stream of cold nitrogen gas generated by an automatic low temperature system built for the neutron four-circle diffractometer [6]. The temperature distribution on the surface of the crystal, studied with a calibrated copper-constantan thermocouple, was found to be uniform within 1 K and the temperature at any particular point was found to be constant to better than ±1 K for several hundreds of hours. The diffractometer was sealed in a plexiglas enclosure, which was connected to an automatic drying system consisting of a molecular sieve dryer with dual chambers of desiccant and a compressor circulating gas in the system. This arrangement was found necessary to prevent the condensation of atmospheric water vapour onto the crystal. The cold gas flow of about 250 cm^3/s was found to be adequate to counteract heat leaks (conduction through the support pin of the crystal and radiation) to the crystal and to maintain a small overpressure in the enclosure. In spite of these precautions, some frost was observed to condense on the crystal during the long term operation. However, this had no significant effect on Bragg intensities as found by measuring the standard reflexions at regular time intervals.

A total of 550 reflexions with $\sin\theta/\lambda < 0.78$ Å^{-1} were measured, of which 32 were unrelated by symmetry. Integrated intensities were corrected for absorption by using the Gaussian integration method [7] and a neutron attenuation coefficient $\mu = 3.1$ cm^{-1} [2].

3. Analysis of data

The analysis of data was made by standard least-squares fitting procedures using two different models.

In the first model the constituent nuclei were allowed to execute independent harmonic vibrations (model iv) around their mean positions. Simultaneous correction of the experimental structure factors for isotropic extinction in the Zachariasen approximation [8] and determination of the absolute scale was included in the fitting procedure. Thus, the calculation involved 7 variable parameters: the scale factor, the isotropic extinction parameter g', the protonnitrogen bond length r_0, the isotropic Debye-Waller parameters B_N and B_{Cl} of nitrogen and chlorine, respectively, and the anisotropic Debye-Waller factors $B_{\parallel}$ and $B_{\perp}$ corresponding to the proton vibrations parallel and perpendicular to the bond direction, respectively. The values of the

Table I. Values of parameters for NH_4Cl in the independent atom model (model iv).

g'	0.069	(0.019)		$B_\parallel$	1.58 (0.30)	$Å^2$
r_0	1.042	(0.003)	Å	$B_\perp$	2.46 (0.16)	$Å^2$
B_N	0.86	(0.07)	$Å^2$	R-factor	3.49 %	
B_{Cl}	0.73	(0.06)	$Å^2$			

scattering lengths of chlorine, nitrogen and hydrogen were 0.958×10^{-12}, 0.944×10^{-12} and -0.374×10^{-12} cm, respectively [9].

The final values of the parameters are listed in Table I together with values of the crystallographic R-factor ($\Sigma|G^2_{obs} - G^2_{iv}|/\Sigma G^2_{obs}$). Observed and calculated squared structure factors G^2_{obs} and G^2_{iv}, along with the standard deviations σ and the extinction coefficients y, are listed in Table II, columns 2–5.

Since the frequencies of the internal modes of vibration of the NH_4 group in NH_4Cl are high compared to those of the lattice modes (cf. e.g. [10]), the group can be treated as an essentially rigid unit. Therefore a better description of the nuclear motion in NH_4 is expected with the rigid-body model. As discussed by PRESS and HÜLLER [11] and KURKI-SUONIO et al. [2], this can be done favourably by expanding the coherent scattering-length density of the NH_4 group into a series of site symmetrized harmonics. The librational motion of the rigid NH_4 group is taken into account by multiplication of each nonspherical term of the series by a constant libration coefficient (< 1). The vibrational motions of Cl and NH_4 are described by conventional (harmonic) Debye-Waller factors, and correlations between librational and translational motions of the NH_4 group are assumed to be negligible.

Following the notation of KURKI-SUONIO et al. [2] the neutron structure amplitudes of the rigid body model (model 1v) are expressed by the formula

$$G_{1v} = g_{Cl}e^{-B_{Cl}(b^2/4)} \pm e^{-B_N(b^2/4)}[g_N + 4g_H \sum_n a_n c_n i^n j_n(2\pi r_0 b) K_n(\theta_b, \varphi_b)], \qquad (1)$$

where $b = 2\sin\theta/\lambda$, θ_b, φ_b are the spherical coordinates of the reciprocal space, g_{Cl}, g_N, and g_H are the scattering lengths of chlorine, nitrogen and hydrogen, respectively, the a_n are the libration coefficients, and $j_n(x)$ are Bessel functions. The functions $K_n(\theta, \varphi)$ are the cubic harmonics of VON DER LAGE and BETHE [12]. The values of coefficients c_n for n up to 10 have been given by KURKI-SUONIO et al. [2].

This parametrization has the advantage of being applicable in charge density considerations. If the X-ray molecular scattering amplitude of the NH_4 group is expressed in terms of the site symmetrized harmonic series, a rigid body motion of the molecule corresponds to the same parametrization with the same numerical values for the parameters. With a view to combination of neutron and X-ray information it is essential to get estimates for the low order libration coefficients a_3 and a_4 (cf. VAHVASELKÄ and KURKI-SUONIO [1]).

The model (iv) was considered to give accurately enough the experimental scale and the extinction correction. Thus, the least-squares refinement of the model (1v) involved the NH

Table II. Squared neutron structure factors for NH_4Cl.

h	k	l	G^2_{obs}	σ	y	G^2_{iv}	G^2_{1v}	G^2_{1vr}
0	0	1	0.6379	0.0061	0.8653	0.6575	0.6771	0.6746
0	0	2	5.4309	0.1105	0.6624	5.3247	5.2281	5.2433
0	0	3	1.0206	0.0114	0.9259	1.0527	1.0247	1.0328
0	0	4	4.3941	0.0139	0.8007	4.4313	4.4016	4.4442
0	1	1	1.9198	0.0150	0.7562	2.0690	2.0707	2.0516
0	1	2	0.1491	0.0029	0.9924	0.0702	0.0788	0.0703
0	1	3	5.1554	0.0256	0.7547	4.9576	5.0312	5.0117
0	1	5	1.5088	0.0086	0.9074	1.5494	1.4543	1.5173
0	2	2	2.7159	0.0213	0.8368	2.4740	2.6729	2.5678
0	2	3	0.1964	0.0030	0.9903	0.1467	0.1326	0.1376
0	2	4	1.4887	0.0080	0.9268	1.4839	1.4033	1.4746
0	3	3	0.6369	0.0095	0.9684	0.5554	0.5266	0.5451
0	3	4	0.2089	0.0048	0.9888	0.2157	0.2668	0.2485
0	3	5	1.6422	0.0128	0.9238	1.6436	1.6311	1.6295
0	4	4	1.0701	0.0083	0.9459	1.0989	1.1477	1.1068
1	1	1	0.6002	0.0077	0.9176	0.6411	0.5570	0.5819
1	1	2	4.1740	0.0246	0.7374	4.2585	4.3412	4.2643
1	1	3	0.1453	0.0036	0.9935	0.0926	0.1156	0.1058
1	1	4	2.7193	0.0148	0.8722	2.7832	2.7254	2.7972
1	1	5	0.1714	0.0029	0.9923	0.1558	0.1685	0.1716
1	2	2	0.5537	0.0050	0.9535	0.5931	0.5677	0.5686
1	2	3	1.9588	0.0089	0.8927	1.8968	1.9098	1.9226
1	2	4	0.1554	0.0021	0.9901	0.1790	0.1600	0.1542
1	2	5	1.7848	0.0081	0.9201	1.7684	1.8187	1.8135
1	3	3	0.2230	0.0034	0.9882	0.1991	0.2329	0.2211
1	3	4	1.2584	0.0052	0.9371	1.2845	1.2859	1.2599
2	2	2	3.2543	0.0337	0.8225	3.2098	3.0501	3.1262
2	2	4	2.3553	0.0225	0.8946	2.2637	2.3964	2.3182
2	2	5	0.1309	0.0035	0.9933	0.1295	0.1170	0.1140
2	3	3	2.8289	0.0166	0.8672	2.7257	2.6701	2.6804
3	3	3	0.2167	0.0058	0.9865	0.2284	0.2564	0.2362
3	3	4	2.3368	0.0196	0.8932	2.2638	2.4153	2.3667

bond length r_0, the Debye-Waller factors B_{Cl} and B_N plus the libration coefficients a_n, up to $n = 10$.

The radial vibrations of the protons (assumed to be uncorrelated with the two other modes of motion) can be taken into account using the parametrization presented by KURKI-SUONIO et al. [2]. The structure amplitudes of this model (model 1vr) are obtained from eq. (1) by replacing the Bessel functions $j_n(2\pi r_0 b)$ by the expression

$$\int_0^\infty R(r) j_n(2\pi r_0 b)\, dr, \qquad (2)$$

where $R(r)$ is the radial smearing function.

In the least-squares refinement of this model the Debye-Waller factors B_{Cl}, B_N and the libration coefficients up to $n = 10$ were allowed to vary. The smearing function $R(r)$ in eq.

Table III. Values of parameters for NH_4Cl in the rigid-body model (model 1v) and in the model with bond vibrations (model 1vr).

	model 1v			model 1vr	
B_N	0.83	(0.05)	$Å^2$	0.85	$Å^2$
B_{Cl}	0.71	(0.05)	$Å^2$	0.71	$Å^2$
r_0	1.055	(0.003)	$Å$	—	
a_3	0.840	(0.006)		0.859	
a_4	0.781	(0.015)		0.815	
a_6	0.627	(0.010)		0.661	
a_7	0.445	(0.020)		0.510	
a_8	0.644	(0.020)		0.639	
a_9	0.491	(0.026)		0.523	
a_{10}	0.228	(0.015)		0.330	
R-factor	3.82 %			3.28 %	

(2) was represented by five δ-functions at the positions r_0, $r_0 \pm \alpha\Delta$, $r_0 \pm \beta\Delta$ with weights m_0, m_1 and m_2, respectively, and with the values $\alpha = 0.7731$, $\beta = 2.1470$, $m_0 = 0.1988$, $m_1 = 0.3357$, $m_2 = 0.0649$ fitted to yield moments $\langle |r - r_0|^n \rangle$ up to $n = 4$ equal to the moments of a Gaussian smearing function with the r.m.s. amplitude Δ. The values $r_0 = 1.055$ Å, obtained in refinement of the model (1v), and $\Delta = 0.0775$ Å [2, 16] were adopted and kept constant during the calculation.

The final values of the model parameters are assembled in Table III, and the corresponding values of the structure factors are listed in Table II, columns 6–7.

4. Discussion

The statistical accuracy of the data is good, with the main source of uncertainty arising from systematic errors. The error limits given in Table III are based on the considerations presented in the room temperature study [2], and include the uncertainty due to the extinction correction. This was found to affect primarily the values of the Debye-Waller factors, and to be comparable with the statistical inaccuracy in the case of low order libration coefficients, but of no concern for higher orders.

A further source of uncertainty arises from thermal diffuse scattering, for which a reliable correction could not be made. To get an idea of the order of magnitude of this effect, the data were corrected for TDS using the isotropic approximation of COOPER and ROUSE [13] for first order scattering, which is not valid if the neutron velocity (4000 m/s in the present case) is less than that of the phonons (2700–5500 m/s for NH_4Cl). The values $B_N = 0.976$ Å^2 and $B_{Cl} = 0.853$ Å^2 were obtained for the Debye-Waller factors by the least-squares refinement with the TDS-corrected data, and again the values of libration coefficients remained practically unchanged; e.g. for a_4 the change was 0.0014. It should be noted that the present calculation

will lead to overestimation of the contribution of TDS, and consequently to overestimation of the Debye-Waller factors, since to good approximation there is no TDS correction for slower-than-sound neutrons [14]. A considerable over-correction is also likely to result when the resolution function has been ignored [15].

Terms up to $n = 10$ were included in the expansion of the thermally smeared nuclear scattering length of the NH_4 group. It should be noted that the convergence of the expansion is not strong enough to justify the omission of higher orders $n > 10$ if a full representation (within experimental accuracy) is desired. This is a consequence of the strong orientational localization of the NH_4 group and of the fairly small libration amplitudes at lower temperatures.

However, because of mutual orthogonality of terms in the harmonic expansion in eq. (1), it is expected that the values of low order libration coefficients are insensitive to the addition of higher order terms. A control calculation confirming this showed that inclusion of orders $n = 8, 9, 10$ had only minor effects on the values of a_3 to a_6.

In comparison of these results with those of the room temperature study [2] the question of comparableness of the parameter values obtained by the two different methods arises. In the direct approach [1, 2] the determination of the value of a parameter is based on the physical nature of the parameter and is largely independent of features which cannot be described by the model, whereas the fitted values include some averages of such features. In the room temperature study [2] the fourth order radial scattering amplitude of NH_4 was found to follow very accurately this librating model, while there were some deviations in the higher orders. From the nature of these deviations we can conclude that least-squares fitting would give larger values for a_6, a_8 and a_{10}, while there is no significant difference in a_4.

It is concluded that the values of a_3 and a_4 which are of major interest in the charge distribution study [1] are given reliably within the error limits of Table III.

The present values of the Debye-Waller factors (model 1vr) correspond to the values 0.0090 (8) $Å^2$ and 0.0108 (8) $Å^2$ for mean-square amplitudes of chlorine and nitrogen respectively. These results are in good agreement with the values 0.0094 $Å^2$ and 0.0107 $Å^2$ calculated by KURITTU and MERISALO [16] from a rigid ion-rigid molecule lattice dynamical model based on inelastic neutron scattering data.

References

1. Aino Vahvaselkä and K. Kurki-Suonio, Phys. Fenn. 10, 87 (1975)
2. K. Kurki-Suonio, M. Merisalo, Aino Vahvaselkä and F.K. Larsen, Acta Crystallogr. A32, 110 (1976).
3. H.A. Levy and S.W. Peterson, Phys. Rev. 86, 766 (1952).
4. W.B. Yelon, D.E. Cox and P.J. Kortman, Phys. Rev. B9, 4843 (1974).

5. A.A. Boiko, Kristallografiya (USSR) **14**, 639 (1969) [transl. Sov. Phys. – Crystallogr. **14**, 539 (1970)].

6. M. Merisalo, M.H. Nielsen and K. Henriksen, Danish Atomic Energy Commission Research Establishment Risø Report No. 279 (1973).

7. P. Coppens, L. Leiserowitz and D. Rabinovich, Acta Crystallogr. **18**, 1035 (1965).

8. P. Coppens and W.C. Hamilton, Acta Crystallogr. **A26**, 71 (1970).

9. G.E. Bacon, Acta Crystallogr. **A28**, 357 (1972).

10. E.R. Cowley, Phys. Rev. **B3**, 2743 (1971).

11. W. Press and A. Hüller, Acta Crystallogr. **A29**, 252 (1973).

12. F.C. von der Lage and H.A. Bethe, Phys. Rev. **71**, 612 (1947).

13. M.J. Cooper and K.D. Rouse, Acta Crystallogr. **A24**, 405 (1968).

14. B.T.M. Willis, Acta Crystallogr. **A26**, 396 (1970).

15. W. Cochran, Acta Crystallogr. **A25**, 95 (1969).

16. J. Kurittu and M. Merisalo, University of Helsinki, Report Series in Physics, No. 104 (1975).

Department of Physics
Siltavuorenpenger 20 c
SF-00170 Helsinki 17
Finland

Department of Inorganic Chemistry
University of Århus
DK-8000 Århus C
Denmark