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A STUDY OF ORIENTATIONAL DISORDER IN ND_4Cl BY THE REVERSE MONTE CARLO METHOD

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1. Introduction

The ammonium halides are well known for the number of phase transitions they undergo with respect to the disorder and relative orientation of ammonium ions in the lattice [1]. The order - disorder transition in ammonium chloride NH_4Cl (ND_4Cl) has been the subject of numerous studies because it has many interesting features and it is one of the ideal examples of the λ-transition in crystals [2].

Ammonium chloride is a typical system with orientational disorder. At room temperature it has a CsCl type cubic structure in which ammonium ions are randomly distributed between two equivalent positions which correspond to two possible orientations of ammonium tetrahedra, space group *Pm3m* [3] (figure 1). Hydrogen (deuterium) atoms are directed essentially towards four of the eight surrounding halogen ions. Thermal fluctuations of the lattice excite vibrations of ammonium ions around the equilibrium orientations – i.e. librational motion [4-6], and also rotations between the two allowed orientations – i.e. reorientational motion.

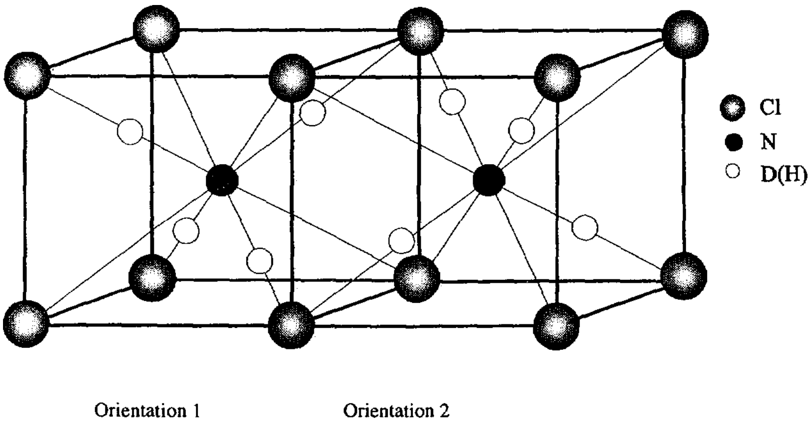


Figure 1. *Schematic structure of ND_4Cl. The two possible orientations of ammonium ions are shown*

To understand the nature of the order - disorder phase transitions in NH_4Cl (ND_4Cl) a knowledge of the disordering mechanisms is necessary. Nuclear magnetic resonance (NMR) [7-9] and quasielastic neutron scattering (QNS) [10-12] have been used to study disorder in ammonium halides. NMR results have clearly shown that the orientational disorder is dynamic. However this method is insensitive to the precise features of the reorientational mechanism. This can involve either 90° jumps around the two-fold axis of NH_4^+ (ND_4^+) ions, or a combination of reorientations around two-fold and three-fold axes (120° jumps), although calculations [7] based upon interionic potentials derived from a point charge model [13] predict a barrier for rotations around three-fold axes 80 % higher than for two-fold axes.

Information obtained by QNS gives two possible models for the reorientational motion. In a QNS study of NH_4Cl near the order - disorder transition [10] a model with statistically independent rotations of ammonium ions around two-fold and three-fold axes was used. It was found that the probabilities for these rotations per unit time, ν_4 and ν_3 respectively, have the same order of magnitude: $\nu_4 = 1.3 \cdot 10^9$ s^{-1} and $\nu_3 = 0.8 \cdot 10^9$ s^{-1} at $T_c = 242$ K. On the other hand, in a QNS study of NH_4Br at $T = 373$ K [11] it was shown that ammonium ion reorientations by 90° jumps dominate, with an average time between jumps of $\tau_4 = 3.2 \cdot 10^{-12}$ s (or a corresponding probability per unit time $\nu_4 = 1/2\pi\tau_4 = 4.9 \cdot 10^{10}$ s^{-1}), and the contribution from 120° jumps is negligible but can not be excluded. In a QNS investigation of NH_4Br [12] in the temperature region between 297 K and 409 K the experimental data were treated with a 90° jump model and good agreement was obtained.

To resolve the question about the geometry of NH_4^+ (ND_4^+) ions reorientations and obtain more detailed information about disorder in ammonium chloride above T_c=242 K, it is necessary to use a method sensitive to the instantaneous crystal structure (i.e. deviations from the average structure). This possibility is given by the recently developed reverse Monte Carlo (RMC) method [14]. RMC analyzes the diffraction data (that is the total structure factor, which includes both Bragg and diffuse scattering) and allows one to obtain detailed information on structural disorder.

In this paper we present the first results of a RMC study of orientational disorder in deuterated ammonium chloride ND_4Cl at room temperature.

2. Experimental

Neutron powder diffraction data were obtained using the SLAD diffractometer [15] at the Studsvik Neutron Research Laboratory. The sample was contained in a thin walled vanadium cylinder of 6 mm diameter. The incident neutron wavelength was 1.11 Å and data were collected in the angular range $3° < 2\theta < 135°$. The resolution of the diffractometer at $2\theta = 56°$ is $\Delta d/d = 0.02$. Standard corrections for absorption, container and background scattering, multiple and inelastic scattering were applied. A vanadium measurement was used to normalize the cross-section to absolute units. All measurements were made at room temperature.

Initially the experimental data were refined by the Rietveld method in order to determine the hydrogen content in the sample. The value of 3.25 % H was obtained. Before RMC modeling it is necessary to subtract the background due to inelastic neutron scattering, in this case primarily incoherent scattering from the H component. This was done using the MCGR program [16]. The total radial distribution function, $G(r)$, is related to the total structure factor, $F(Q)$, by

$$F(Q) = \rho \int 4\pi r^2 G(r) \frac{\sin(Qr)}{Qr} dr \tag{1}$$

where ρ is the atomic number density of the sample and $Q = 4\pi \sin\theta / \lambda$ is the momentum transfer. $G(r)$ is generated by a Monte Carlo method and "fitted" to the experimental data. We apply two constraints. Firstly

$$G(r < r_0) = -\sum c_i c_j b_i b_j \tag{2}$$

where r_0 is the expected closest approach distance (0.95 Å) of any two atoms and c_i and b_i are the concentration and coherent scattering length of species i. Secondly the peak shapes must be appropriate given the experimental Q-space resolution and range. These constraints then allow the refinement of a background term $a + bQ + cQ^2$ in the fitting procedure. The MCGR fit of the experimental total structure factor and the background term are shown in figure 2.

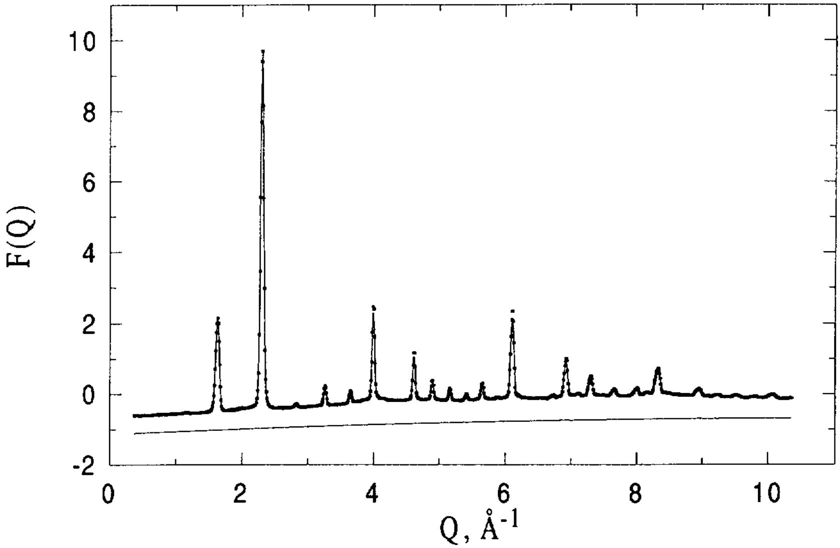


Figure 2. Corrected and normalized to absolute units experimental total structure factor for ND_4Cl (black squares), MCGR fit (solid and the refined background term (solid curve below)

3. RMC modeling

As an initial structure, the model obtained in a previous neutron diffraction studies [3, 17] was used. The positions of atoms in this structure are given in table 1. The lattice parameter, a = 3.845 Å, and the deuterium position parameter, u = 0.154, which are in agreement with [3, 17] within the experimental accuracy, were taken from the Rietveld refinement of the SLAD data.

The initial configuration consisted of 12x12x12 = 1728 unit cells (10368 atoms). 50 % of ammonium ions with orientation 1 and 50 % with orientation 2 were randomly distributed within the configuration. In order to maintain the covalent N-D bonding within the ammonium ions we have constrained the coordination of deuterium around each nitrogen to be four-fold in the range $0.85 < r < 1.15$ Å. All partial $g_{\alpha\beta}(r)$'s were set to zero for r less than some value $r_{\alpha\beta}$ which defines the closest approach distance between atoms of type α and β. Partial radial distribution functions $g_{\alpha\beta}(r)$'s are related to the total radial distribution function, $G(r)$, by

$$G(r) = \sum_{\alpha,\beta=N,D,Cl} c_\alpha c_\beta b_\alpha b_\beta (g_{\alpha\beta}(r) - 1) \tag{3}$$

where c_α are the concentrations and b_α the coherent scattering lengths of atom type α.

Table 1. Positions of atoms in ND_4Cl

Atom	X	Y	Z	
N	0.5	0.5	0.5	
Cl	0	0	0	
D	$\frac{1}{2}-u$	$\frac{1}{2}-u$	$\frac{1}{2}-u$	orientation 1
D	$\frac{1}{2}+u$	$\frac{1}{2}+u$	$\frac{1}{2}-u$	
D	$\frac{1}{2}+u$	$\frac{1}{2}-u$	$\frac{1}{2}+u$	
D	$\frac{1}{2}-u$	$\frac{1}{2}+u$	$\frac{1}{2}+u$	
D	$\frac{1}{2}+u$	$\frac{1}{2}-u$	$\frac{1}{2}-u$	orientation 2
D	$\frac{1}{2}-u$	$\frac{1}{2}+u$	$\frac{1}{2}-u$	
D	$\frac{1}{2}-u$	$\frac{1}{2}-u$	$\frac{1}{2}+u$	
D	$\frac{1}{2}+u$	$\frac{1}{2}+u$	$\frac{1}{2}+u$	

The starting values of $r_{\alpha\beta}$ have been estimated from the known crystal structure [17] and were then modified slightly according to the results of the initial fit. The final values of $r_{\alpha\beta}$ are given in table 2.

Table 2. Closest approach distances

$r_{\alpha\beta}$, Å	N	D	Cl
N	3.7	0.85	3.2
D	-	1.4	2.15
Cl	-	-	3.7

Because of the finite size of the RMC model (which is equal to L), the total radial distribution function is set to be $G(r > L/2) = 1$. Due to the long range order in crystals the radial distribution function is still oscillatory at the maximum distance, $r = L/2$, and so the Fourier transform to obtain $F(Q)$ is truncated, leading to unphysical oscillations. To avoid this the experimental structure factor must be convoluted with the Fourier transform of a step function corresponding to $L/2$ [18]. The convoluted structure factor $F'(Q)$ and the RMC model fit are shown in figure 3. The final configuration was obtained after more than 280000 accepted moves.

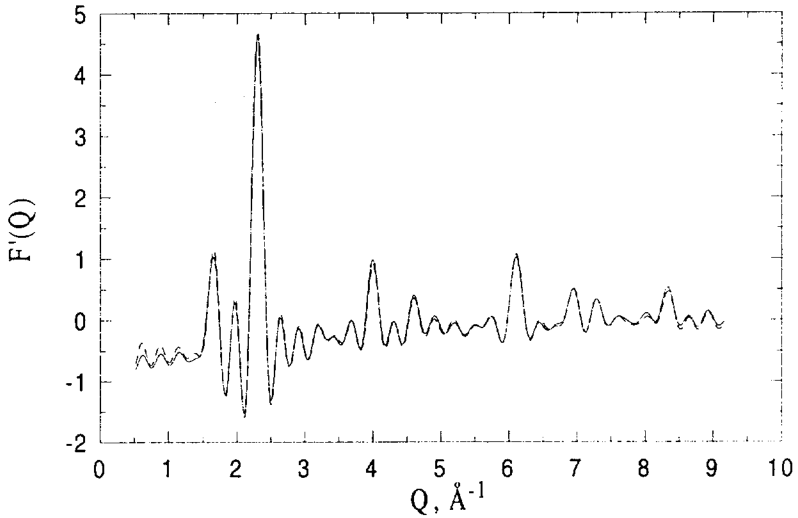


Figure 3. Experimental total structure factor convoluted with the Fourier transform of a step function corresponding to L/2 (half the box size) - solid curve and RMC fit - dashed curve

4. Results and Discussion

Partial radial distribution functions $g_{ND}(r)$, $g_{DD}(r)$ and $g_{DCl}(r)$ are shown in figure 4. The first peaks correspond to the average crystallographic distances between N, D and Cl atoms in the structure. Damped oscillations in $g_{DD}(r)$ for $r > 6$ Å show that long range correlations between deuteriums are weak, probably due to the orientational disorder.

As two equivalent positions of ammonium tetrahedra are possible, four peaks should be expected in the low r part of $g_{DCl}(r)$ at 2.30, 3.15, 3.8 and 4.35 Å. Instead of this just two overlapping peaks are found (figure 4), a narrower one at 2.30 Å and then a wider second peak which seems to consist of the other three expected peaks. All four peaks are broadened because of vibrations and rotations, the first one probably appears separate because it is slightly further from the other three.

In fig. 5 we show the space average D density distribution in the unit cell, obtained by averaging over all of the individual unit cells within the configuration, in the form of two constant density surfaces. In a general sense the distribution has the form of a cube. The corners of the cube correspond to the average crystallographic D positions and are broadened by librational motions of the ammonium ions. At approximately ¼ of the maximum D density these corners then ‘connect’, approximately along the edges of the cube. This is the path expected for jumps around two-fold axes. The path expected for three-fold jumps passes quite close to the face centre of the cube, but although the connection pathways broaden at lower densities they do not extend fully into the face centres until the very lowest densities. Although it is not possible to draw any strict dividing line between the two-fold and three-fold jump paths (fig. 6), since both are broadened by thermal vibrations and hence overlap, a rough estimate shows that the probability for the three fold reorientations is less than 5%.

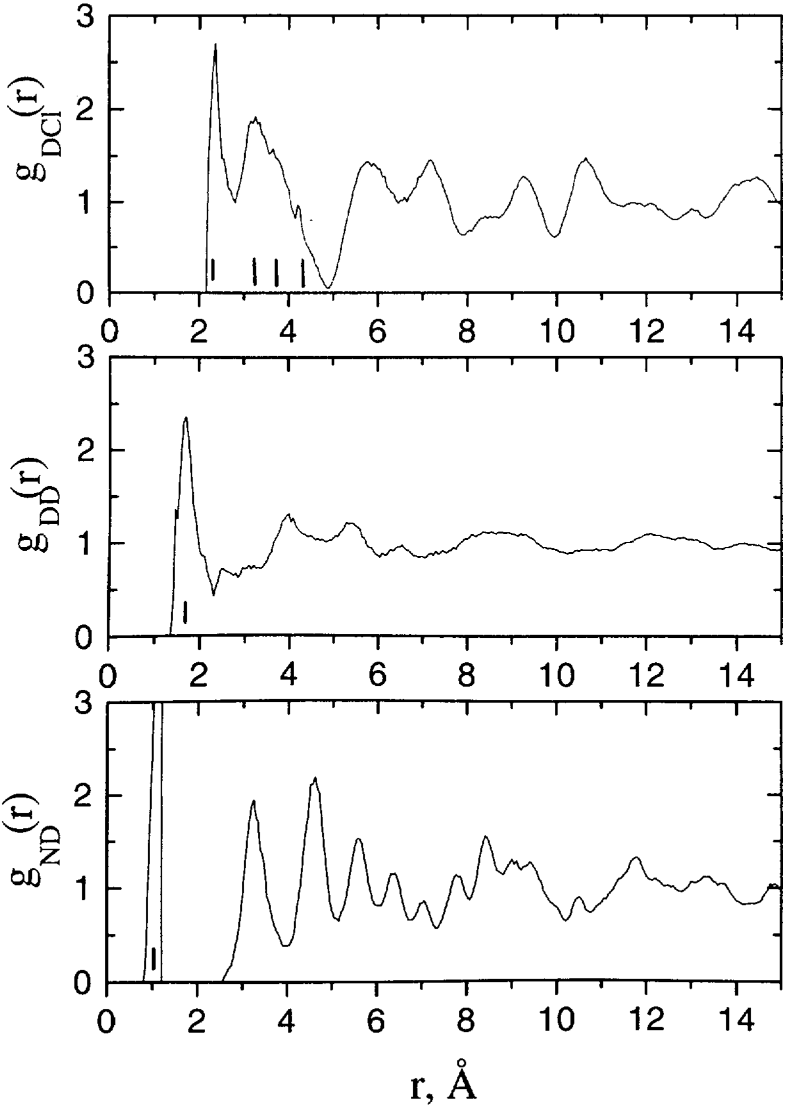
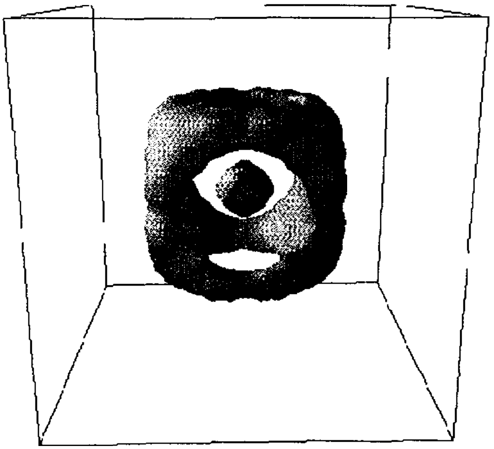


Figure 4. *Partial radial distribution functions $g_{ND}(r)$ (bottom), $g_{DD}(r)$ (centre) and $g_{DCl}(r)$ (top). The bars represent the shortest distances between N, D and Cl atoms (as appropriate) within the average crystal structure*



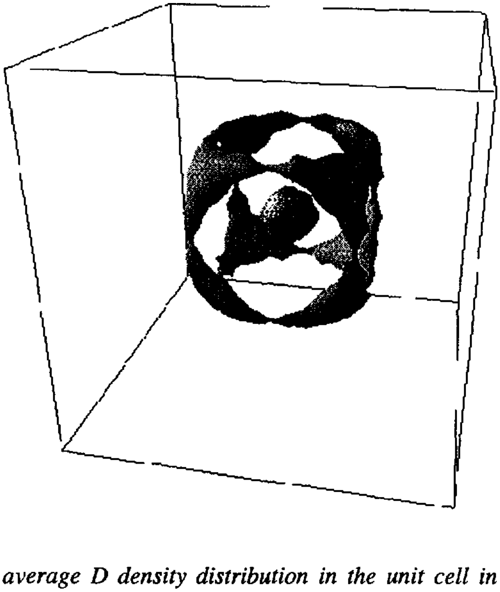


Figure 5. *Space average D density distribution in the unit cell in the form of constant density surfaces for density levels 1/8 (top) and 2/8 (bottom) of the maximum density*

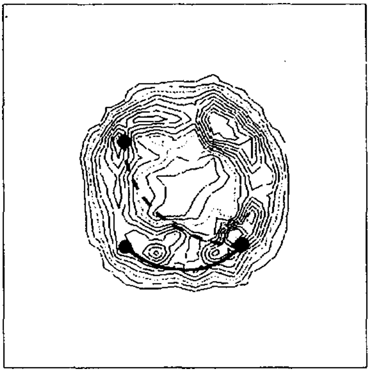


Figure 6. Contour plot of the D density in a plane cutting through four corners of the D density 'cube' (as shown in figure 5). The plane thickness is 10% of the lattice parameter; 10 contour levels between 0.4 and 8 % of the maximum density are shown. Thick solid and broken curves indicate two of the possible pathways for two-fold and three-fold reorientations respectively. One can see that the three-fold reorientations have a very low probability

The cosine distribution of the N-D-Cl bond angle is shown in figure 7. This has maximum at $\theta = 180°$ in agreement with the average crystal structure. The average N-D-Cl bond angle calculated from this distribution is $\theta = 155°$. This corresponds to an average libration amplitude for ND_4^+ ions $\alpha = 17°$. The value obtained by neutron diffraction [17] is $\alpha = 10°$. Note that the RMC value should be higher since a normal crystallographic refinement effectively corresponds to approximately the Gaussian angular distribution is (something like) Gaussian (e.g. librations only), whereas in fact there is also a long 'tail' down to angles of about 105°, corresponding to reorientational motions.

In figure 8 we show the angular correlation between ammonium ions (as defined by the set of four normalized vectors related to the four N-D bonds) and the (111) direction (averaged over all (111) type directions). The peaks at $\cos\varphi = \pm 1$ come from N-D bonds oriented along (111) directions and reflect the two possible orientations of ammonium ions. In the average crystal structure one would also expect peaks at $\cos\varphi = \pm 0.33$. However, due to the disorder of ammonium ions, just one wide peak is found at $\cos\varphi = 0$. This result corresponds to the observation of one narrow and one broad peak in $g_{DCl}(r)$ (figure 4).

We have divided ammonium ions into two groups, depending on which of the two 'ideal' orientations they are closest to. On average, ions with orientation 1 have almost exactly 3 neighboring ions with the same orientation and 3 with the opposite orientation, and vice-versa. This shows that there are no preferred orientational correlations between neighbouring ions.

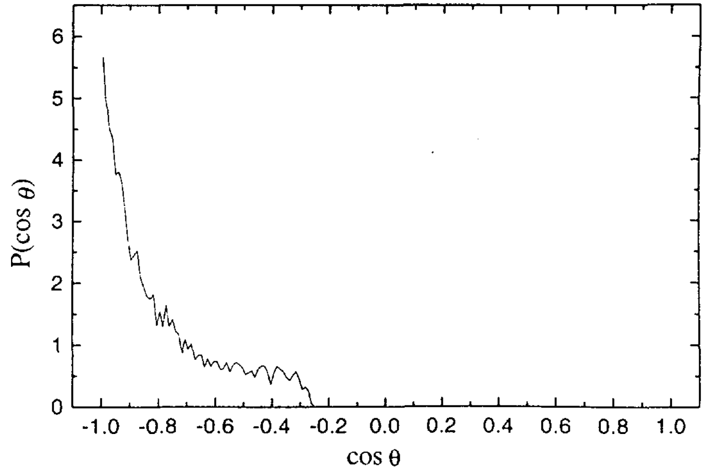


Figure 7. Bond angle distribution $P_{N\text{-}D\text{-}Cl}(\cos\theta)$

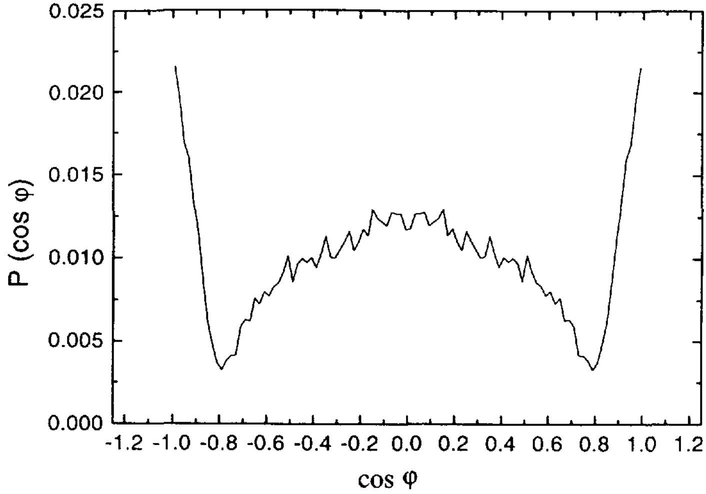


Figure 8. Orientational correlations between N-D bond vectors and (111) axes

5. Conclusions

RMC modeling of the total structure factor for ND_4Cl has provided detailed information on the orientational disorder and the mechanisms of reorientational motion of ammonium ions. A clear indication was obtained that ammonium ion reorientations are stochastic and no correlations exist between the motion of neighboring ions in the high temperature phase. The value of the average angular libration amplitude of the ammonium is consistent with that calculated from diffraction data if one takes into account the ammonium reorientations. Our results confirm that 90° ammonium ion jumps around two-fold axes dominate, the probability of three fold jumps being less than 5%. This is quite consistent with what would be expected from simple considerations of the ionic potential [7,13], and also with QNS studies of NH_4Br [11, 12] which has the same structure as NH_4Cl in a dynamically disordered phase. However it differs from QNS results for NH_4Cl at 242K where the proportion of three-fold jumps was about 40% [10]. This difference clearly cannot be explained simply by the temperature difference, so further RMC studies as a function of temperature are required to verify it.

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Белушкин А.В. и др. E14-98-332
Исследование ориентационного беспорядка
в ND_4Cl обратным методом Монте-Карло (RMC-методом)

Проведено моделирование структурного фактора дейтерированного хлорида аммония ND_4Cl, полученного методом нейтронной дифракции, с помощью обратного метода Монте-Карло (RMC-метода). Результаты моделирования показали, что основной механизм ориентационного беспорядка в ND_4Cl — либрационные колебания ионов аммония вокруг положений равновесия со средней угловой амплитудой $\alpha = 17°$ и реориентационное движение ионов аммония — скачкообразные реориентации вокруг осей 2-го порядка на 90 °. Вклад от реориентаций вокруг осей 3-го порядка на 120 ° пренебрежимо мал.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ.

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Belushkin A.V. et al. E14-98-332
A Study of Orientational Disorder in ND_4Cl
by the Reverse Monte Carlo Method

The total structure factor for deuterated ammonium chloride measured by neutron diffraction has been modeled using the reverse Monte Carlo method. The results show that the orientational disorder of the ammonium ions consists of a local librational motion with an average angular amplitude $\alpha = 17°$ and reorientations of ammonium ions by 90 ° jumps around two-fold axes. Reorientations around three-fold axes have a very low probability.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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