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A STUDY OF ORIENTATIONAL DISORDER
IN NaCl-TYPE PHASE I OF ND$_4$I
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AND MAXIMUM ENTROPY METHODS

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1. Introduction

Ammonium halides NH_4X (ND_4X), X=I, Br, Cl are well known for a number of phase transitions which they undergo with respect to the disorder and relative orientation of the ammonium ions in the lattice [1].

Two cubic phases showing orientational disorder of ammonium ions are known to exist in ammonium halides [1], NaCl-type phase I and CsCl-type phase II. Thermal fluctuations of the lattice excite vibrations of ammonium ions around the equilibrium positions - i.e. librational motion, and also rotations between the allowed crystallographic positions - i.e. reorientational motion.

The CsCl-type phase II contains ammonium ions which are disordered between two equivalent crystallographic positions. The crystal structure, orientational disorder and ammonium reorientational motion in this phase were extensively studied by methods like neutron diffraction [2, 3], nuclear magnetic resonance (NMR) [4-6], quasielastic neutron scattering (QNS) [7-9] and by the reverse Monte Carlo method (RMC) [10].

The high temperature NaCl-type phase I of the ammonium halides is less well studied. In this structure (space group $Fm\bar{3}m$), tetrahedral NH_4^+ (ND_4^+) ions are located in the octahedral environment of the surrounding halide ions X^-. In this phase it is not possible to arrange all H (D) atoms at equal distances to halide atoms to form four N-H...X bonds of equal strength as it takes place in the phase II [1]. The ammonium ions were found to be highly disordered in the phase I and several models were proposed in order to describe the resulting H (D) distribution [2], see table 1.

Table 1. Structural models for the phase I of ND_4I, space group $Fm\bar{3}m$

Model	Number of atoms	Crystallographic position	Coordinates
a	1, D1	24 e	$x_{1a}, 0, 0$
	1, D2	96 j	$0, y_{2a}, z_{2a}$
	2, D3	192 l	x_{3a}, y_{3a}, z_{3a}
b	2, D1	96 j	$0, y_{1b}, z_{1b}$
	2, D2	96 k	x_{2b}, x_{2b}, z_{2b}
c	1, D1	32 f	x_{1c}, x_{1c}, x_{1c}
	3, D2	96 k	x_{2c}, x_{2c}, z_{2c}

In model (a) the three-fold axes of the ammonium ions match the four-fold axes of the crystal, i.e. one of the four N-H (N-D) bonds of the ammonium ion is oriented towards the nearest X^- ion. In model (b) two of the four H (D) atoms of the NH_4^+ (ND_4^+) ions make the closest approach to two neighboring X^- ions. The two-fold axes of the ammonium ions are aligned along the two-fold axes of the crystal. In model (c) the NH_4^+ (ND_4^+) ions are disordered between the equivalent positions with the closest approach of three H (D) atoms to three neighboring X^- ions. In this model the three-fold axes of the ammonium ions are oriented along the three-fold axes of the crystal. Resulting distributions of the H(D) atoms for the above described three model structures are shown in figure 1.
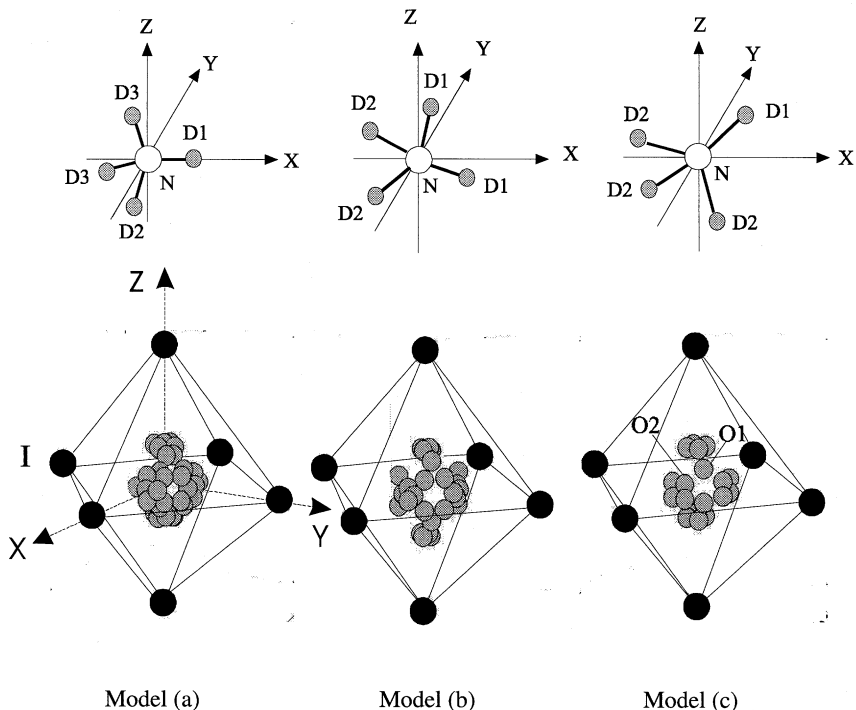
Figure 1. *Top: particular position of the ammonium ion in different model structures of the phase I of NH4I (ND4I). Bottom: distribution of H (D) atoms in different model structures of the phase I of NH4I (ND4I). Iodine atoms form an octahedron with the NH_4^+ (ND_4^+) ion in the center. Only atoms in ¼ part of the octahedron (X0Y quadrant) are shown. N atom in the center of the octahedron is not shown*

A different attempt to model the proton disorder in the phase I of NH4Br and NH4I was made in the neutron diffraction study [11] by using orientation distribution functions based on spherical harmonics. The hydrogen density distribution calculated in this way for the NH_4^+ ions showed broad peaks along the <100> directions implying that N-H bonds point along these directions. However, from non of these descriptions a commonly accepted model of the phase I structure of ammonium halides could be derived [11].

In NMR study [12] the ammonium reorientational motion in phase I of NH4I was classified as a free rotation. However, in infrared study [13] an uni-axial rotation of ammonium ions was suggested. This is consistent with results from neutron diffraction experiments [2, 11] but not with neutron form-factor measurements [14] and other infrared spectroscopic data [15]. No libration modes were observed in the measurements of the phonon dispersion curves of ND4I(I) by inelastic neutron scattering [16] and hence no information could be obtained concerning the librational motion of ammonium ions. In QNS study of NH4I(I) [17] several models of the ammonium reorientational

motion have been tested involving free rotation, uni-axial diffusion, three-fold uni-axial rotation and several octahedral jump models but no definite model was finally chosen.

In order to obtain more information about structure, disorder and geometrically possible mechanisms of ammonium reorientational motion in the phase I of ammonium halides, it is necessary to apply methods sensitive to the instantaneous crystal structure, i.e. methods allowing to study deviations from the average crystal structure. Such a possibility is given by the recently developed reverse Monte Carlo (RMC) method [18]. RMC analyzes the diffraction data (the total structure factor , which includes both Bragg and diffuse scattering) and allows one to obtain detailed information on structural disorder.

Since the results of RMC modeling may depend on features of the initial configuration it is useful to combine the RMC modeling with a model-free (independent on the initial structural model) method for the reconstruction of the three dimensional scattering density distribution, in order to increase the confidence level of the obtained information. Such a possibility is given by the maximum entropy (ME) method [19] which has been found to be very useful for the reconstruction of scattering densities of dynamically disordered molecules from neutron [20] as well as X-ray powder diffraction data [21]. Consequently, RMC and ME are used in a joint approach here in order to study the structure and disorder mechanisms in the phase I of ammonium halides.

As a model compound, deuterated ammonium iodide ND_4I was selected. The phase I was reported to occur at temperatures above $T_c = 254$ K for ND_4I [2]. This is the lowest transition temperature into the phase I compared to the other ammonium halides [1, 2] and hence allowed to perform our study at ambient temperature.

2. Experimental and Data Analysis

Neutron time-of-flight powder diffraction data were measured with the DN-12 TOF spectrometer [22] at the IBR-2 high flux pulsed reactor in FLNP JINR, Dubna . The scattering angle was $2\theta = 90°$. For this angle, the resolution of the spectrometer at $d = 2$ Å is $\Delta d/d = 0.02$. Standard corrections for absorption, container and background scattering, multiple and inelastic scattering were applied. The sample was wrapped in a thin aluminum foil. The sample volume was $V \sim 100$ mm^3. A vanadium measurement was used to normalize the cross-section to absolute units. All measurements were made at room temperature.

The diffraction data were obtained in a Q-range 1.2 - 11 Å^{-1}. It is commonly considered nowadays that experimental data measured over a Q-range up to 30 Å^{-1} are necessary for the accurate structural studies of amorphous solids and liquids. However, it was shown recently [23, 24], that in case of molecular liquids and disordered crystals the detailed information may be obtained from the experimental data measured over more limited Q-range up to 10 Å^{-1}.

The experimental data were processed by the Rietveld method using the MRIA program [25] in order to determine the hydrogen content of the sample and to choose the most appropriate initial structural model from the above described models (a), (b) and (c) for RMC modeling. Structural parameters for all these models as well as the obtained R-factors and χ^2 values from Rietveld refinement are listed in table 2. A hydrogen content of 20 % was found from the refinement of the site occupation

parameters for H and D. According to this, an effective scattering length $b_D = 0.44 \times 10^{-14}$ cm for D atoms was used in the following RMC and ME calculations. The structure refinements revealed a better agreement of models (b) and (c) rather than (a). These two models resulted in almost the same quality of the fit. In a neutron diffraction study of the mixed crystal system $(NH_4I)_{0.73}(KI)_{0.27}$ [26] it was found that model (c) is in the best agreement with the experimental data, compared with the other models. According to this, model (c) was finally chosen to construct the initial configuration for RMC modeling.

Table 2. Structural parameters and obtained from Rietveld refinement R-factors and χ^2 values for the different models of the phase I structure of ND_4I

Lattice parameter a, Å	7.245(5)		
Atomic positions			
Atom	x	y	z
N	0	0	0
I	0.5	0.5	0.5
D positions, model (a)			
D1	0.1408	0	0
D2	0	-0.0469	-0.1327
D3	-0.0469	0.1149	0.0664
D positions, model (b)			
D1	0	0.1387	0.0238
D2	0.0575	0.0575	0.1149
D positions, model (c)			
D1	0.0813	0.0813	0.0813
D2	0.0271	0.0271	-0.1355
Deuterium isotropic thermal factor B_D, Å^2	3.0		
χ^2. and R - factors			
Model	χ^2.	R_p, %	R_{wp}, %
(a)	2.61	2.87	2.18
(b)	2.51	2.85	2.14
(c)	2.50	2.84	2.14

Prior to RMC modeling it is necessary to subtract the background originating from inelastic neutron scattering, in this case primarily incoherent scattering from the H component. This was done using the MCGR program [27]. 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 applied two constraints. Firstly

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

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, respectively. Secondly the peak shapes must be appropriately given for the experimental Q-space resolution and the measuring 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.
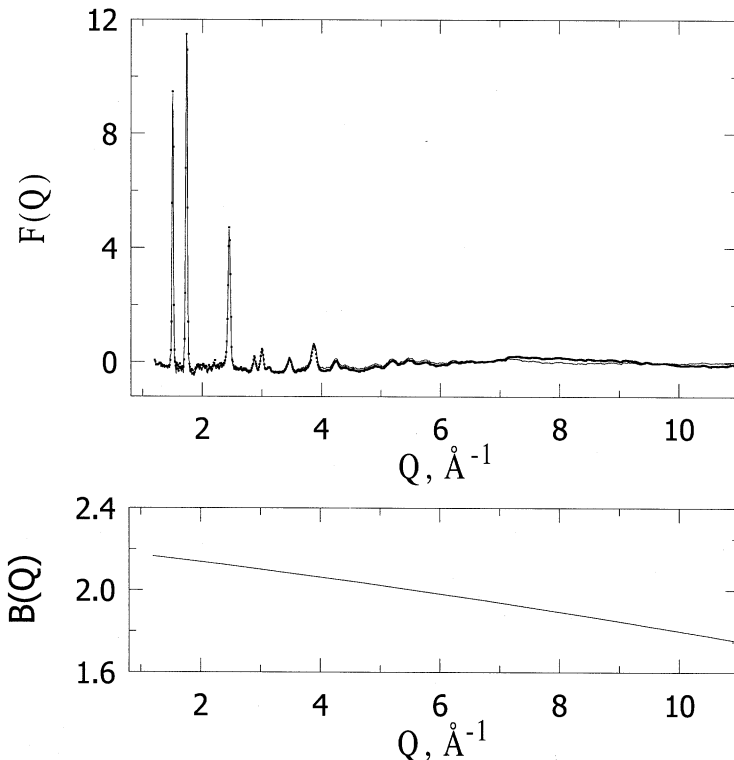
Figure 2. Top: corrected and normalized to absolute units experimental total structure factor for $ND_4I(I)$ (black squares) and MCGR fit (solid). Bottom: the refined background term

     The initial configuration for the RMC modeling consisted of $8 \times 8 \times 8 = 512$ unit cells (12288 atoms). Ammonium ions were randomly distributed among eight possible equivalent positions within the initial configuration based on the structural model (c). 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 $0.9 < r < 1.1$ Å. All partial radial distribution functions $g_{\alpha\beta}(r)$ were set to zero for r being smaller than some value $r_{\alpha\beta}$ which defines the closest approach distance between atoms of type α and β. Partial radial distribution functions $g_{\alpha\beta}(r)$ are related to the total radial distribution function, $G(r)$, by

$$G(r) = \sum_{\alpha,\beta=N,D,I} c_\alpha c_\beta b_\alpha b_\beta \left(g_{\alpha\beta}(r) - 1\right) \qquad (3)$$

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

The starting values of $r_{\alpha\beta}$ have been estimated for model (c) of the average crystal structure (for discussion see below) and slightly modified according to the results of the initial RMC fit. The final values of $r_{\alpha\beta}$ are given in table 3.

Table 3. Closest approach distances

$r_{\alpha\beta}$, Å	I	N	D
I	4.95	3.45	2.4
N	-	4.95	0.9
D	-	-	1.5

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 $L/2$ [28]. The convoluted structure factor $F'(Q)$ and the RMC model fit are shown in figure 3. The final configuration was obtained after more than 253000 accepted moves.
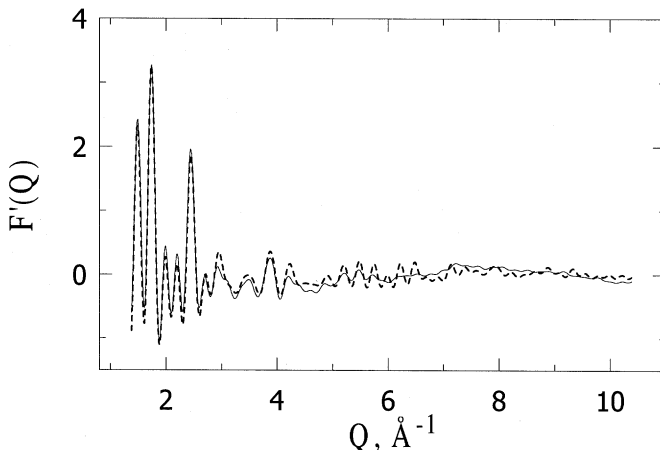

Figure 3. Experimental total structure factor convoluted with the Fourier transform of a step function corresponding to L/2 (half the box size) - solid curve and RMC fit - dashed curve

The Maximum Entropy method [19] results from a Bayesian analysis aimed at maximizing the quantity

$$\text{Prob} (\rho \mid \boldsymbol{F}, \boldsymbol{m}) \propto \text{Prob} (\boldsymbol{F} \mid \rho) \cdot \text{Prob} (\rho \mid \boldsymbol{m}) \qquad (4)$$

in order to find the most suitable scattering density ρ where Prob $(X|Y)$ is the conditional probability of obtaining X when Y is unknown. $\boldsymbol{F} = (F_H, \sigma_H)$ is a limited and noisy data set of structure factors F_H and the related error bars $\sigma_H = \sigma (F_H)$ with $H = (h, k, l)$, $\boldsymbol{m}$ is the *a priori* model density for ρ. The algorithm for ρ is iterative and starts from $\boldsymbol{m}$. The resulting density ρ is the closest to $\boldsymbol{m}$ which fits the data $\boldsymbol{F}$ with the smallest amount of spurious spatial correlations. One of the advantages of ME over standard Fourier synthesis is its reduction of truncation effects and noise-suppressing capability.

For the ME reconstruction of the scattering density in the phase I of ND_4I the program MEED [29] was used. Observed $|F(H)|$ values for 11 resolved reflections, their phases and error bars (table 4) were obtained from the initially performed Rietveld refinement with MRIA program [25]. In case of N strongly overlapped reflections, when only their intensity sum $\sum j_k \mid F(H_k)\mid^2$ can be measured (j_k - multiplicity), the combined structure factor values were calculated,

$$G(H) = \sqrt{\sum_{k=1}^{N} j_k \mid F(H_k)\mid^2 / \sum_{k=1}^{N} j_k} \; . \qquad (5)$$

Three groups of completely overlapping reflections were derived in this way and used for the ME reconstruction (see table 4).

Table 4. *Observed and calculated from the obtained ME density distribution structure factor values for the phase I of ND_4I*

h k l	F_{obs}	$\sigma(F_{obs})$	F_{cal}
1 1 1	-59.26	0.20	-59.25
2 0 0	95.73	0.76	94.21
2 2 0	69.52	0.57	69.47
3 1 1	-20.99	0.90	-20.46
2 2 2	50.33	1.00	51.19
4 0 0	53.37	1.50	53.90
3 3 1	-3.79	1.85	-3.11
4 2 0	43.88	0.95	44.81
4 2 2	33.90	2.00	36.32
4 4 0	40.93	0.76	40.18
6 2 0	51.85	3.61	45.86
5 1 1 3 3 3	9.67	0.38	9.70
5 3 1 6 0 0 4 4 2	22.89	0.31	22.95
5 3 3 6 2 2	33.43	2.37	29.62

Applying the disorder models from table 1 it was tested that phase angles of the structure factors determined from the Rietveld refinement are independent on the underlying structural model. For the calculation of the scattering density distribution, the unit cell was divided into an equidistant grid of 60×60×60 pixels, giving a spatial resolution of 0.12 Å. An uniform *a priori* density distribution **m** was chosen. Calculations were performed for an asymmetric unit cell, and the density distribution in the whole unit cell was obtained using symmetry operations of the space group $Fm\overline{3}m$. Sections through the resulting density distribution were calculated using MECO program [30]. Observed and calculated from the obtained ME density distribution structure factor values for $ND_4I(I)$ are presented in table 4. The resulting *R*-factor is $R = 3.1\%$.

3. Results and Discussion

Partial radial distribution functions $g_{ND}(r)$, $g_{DD}(r)$ and $g_{DI}(r)$ obtained from RMC modeling are shown in figure 4. The first peaks of the partial radial distribution functions correspond to the average crystallographic distances between the N, D and I atoms in the structure. Since eight equivalent positions of ammonium tetrahedra are possible in the average crystal structure (model (c)), six peaks should also be expected in the low *r* part of $g_{DI}(r)$ at 2.65, 3.15, 3.55, 3.95, 4.3 and 4.6 Å, respectively. However, only two broad overlapping peaks are found (see figure 4), a narrower one at 2.65 Å and a wider second peak which seems to consist of the remaining five expected peaks. The broadening of the peaks is due to ammonium librations and rotations.

The spatial average D density distribution in the unit cell obtained from RMC modeling is shown in figure 5 as an iso-density surface, for two density levels. The density data were averaged over all 512 individual unit cells of the configuration using cubic symmetry operations. Generally, the distribution has the shape of an octahedron. This corresponds to the site symmetry of N atom position in the space group.

The distribution of scattering density obtained from the ME reconstruction is very similar to that obtained from RMC modeling. A sequence of three contour plots through the center of the unit cell is given for both methods in figure 6 showing the close agreement of the RMC model with the ME density data.

It is also important to realize that there is a distinction between the ME and RMC results - even though they look very similar. The ME result is a time average of the crystal structure based on elastic scattering data only. RMC result is a space average of the instantaneous local structure based on total scattering data (both elastic and diffuse scattering).

Considering the average crystal structure based on the model (c), two possible types of N-D bond orientations exist. One N-D bond of each ND_4^+ ion with D atom located at one of (*xxx*) sites of the space group is oriented along one of <111> directions. We will refer to this type of orientation as O1 below (figures 1 and 7). The other three N-D bonds of each ND_4^+ ion with D atoms at (*xxz*) sites are oriented at the angle $\alpha=15.77°$ with respect to <100> directions. This type of orientation will be labeled as O2 afterwards (figures 1 and 7). Averaging over eight equivalent positions of ND_4^+ ions gives configuration with eight D atoms centered along <111> directions and square-shaped arrangements of D atoms centered along <100> directions (figure 1).
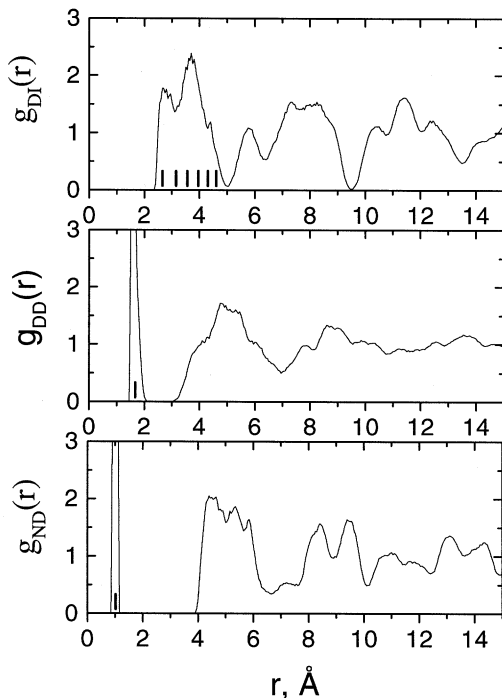
Figure 4. *Partial radial distribution functions $g_{ND}(r)$ (bottom), $g_{DD}(r)$ (center) and $g_{DI}(r)$ (top). The bars represent the shortest distances between N, D and I atoms (as appropriate) within the average crystal structure*

Due to librations and reorientations of ammonium ions, the resulting density distribution consists of wide spherical D distributions centered along <111> directions which are connected with the nearest square - shaped D distributions centered along <100> directions (figures 5, 6). Such a picture suggests that ammonium ions reorient by 39° jumps of N-D bonds between the nearest O1 and O2 orientations and vice versa (figures 5, 7). Ammonium reorientations by 90° jumps between the equivalent crystallographic positions of ND_4^+ ions (O1-O1 and O2-O2 reorientations) are not consistent with the obtained distribution of D density (figures 5, 8). It means that the probability for O1-O1 and O2-O2 reorientations is very low in comparison with O1-O2 reorientations. Although this type of reorientational motion can not be excluded, since jump paths corresponding to O1-O2 and O1-O1 (O2-O2) reorientations may be broadened by thermal vibrations and could overlap.
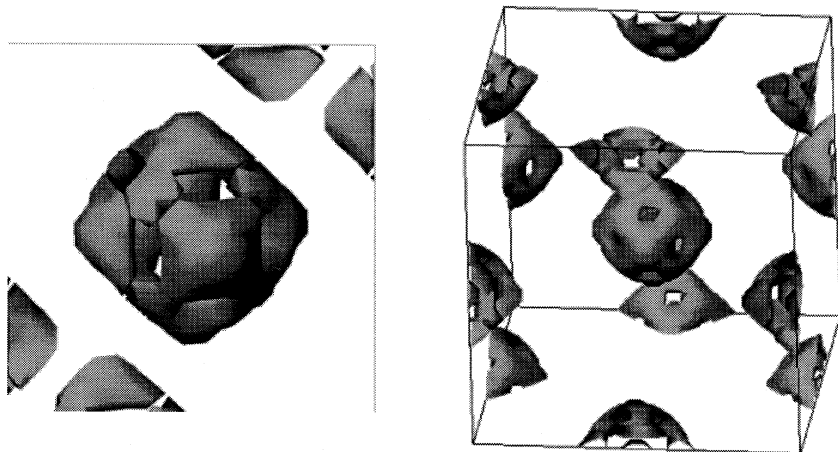
Figure 5. *Space average D density distribution in the unit cell of ND$_4$I in the form of constant density surfaces for density levels 1/3 (left, only the central part of the unit cell is shown) and 1/4 (right) of the maximum density. Calculation was done using cubic symmetry operations*

In QNS study of the phase I of NH$_4$I [17] it was found that the correlation time τ for ammonium reorientations is almost independent on temperature between 100 K and 300 K. However, a rotational potential barrier for reorientations by octahedral 90° jumps of $V \sim 2$ kcal/mole [17] would predict that τ should increase by a factor of 8.2×10^2 when the temperature increases from 100 K to 300 K. Only models involving reorientations over angles smaller than 90°, such as O1-O2 reorientations, can explain the QNS results.

One may expect that with the temperature increase effective radii of the D density distributions centered along <111> and <100> directions would increase due to an increase of the angular libration amplitude and the reorientation frequency of ammonium ions. It means, that the probability of O1-O1 (O2-O2) reorientations by 90° jumps would also increase with the temperature increase. At rather high temperatures, a free rotation of ammonium ions is expected. The corresponding D density distribution is a spherical one and in this case it would not be possible to distinguish between different types of ammonium reorientations.
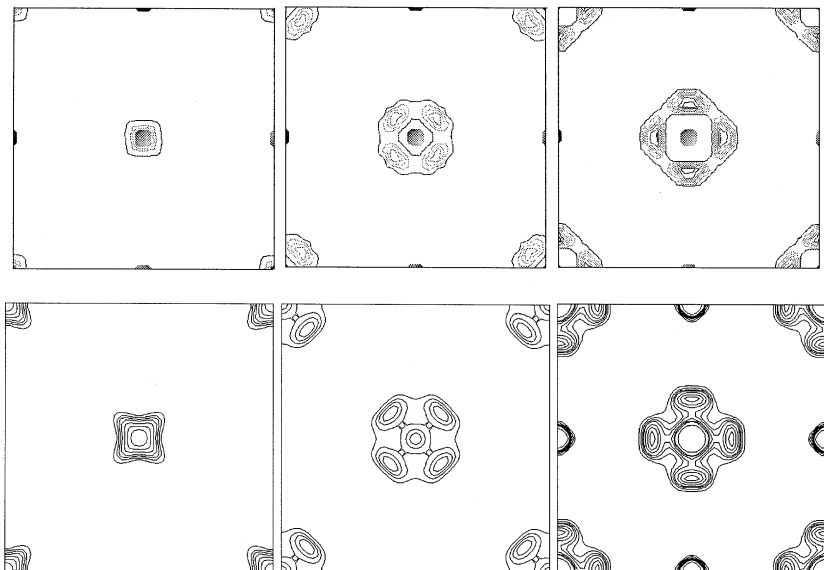
Figure 6. *Contour plots of scattering density of ND₄I in a sequence of planes perpendicular to (001) direction. The distance to the center of the cube is 0.966 Å for the left plane and 0.483 Å for the central plane. Right plane is cutting through the center of the cube. Top: result derived from RMC modeling. Eight levels between the minimum and maximum density values are shown. Bottom: result obtained from ME reconstruction. Eight levels between ME density values 0 and 10 are shown*

Let us discuss the average crystal structures corresponding to the other two possible models of the ND₄I(I) structure - models (a) and (b). In the case of model (a) one of D (H) atoms of ND_4^+ ion is at (*x00*) sites and the other three D atoms are distributed among circles perpendicular to the <100> directions having the distance $l_c = 0.34$ Å to the center of the octahedron forming by the nearest I⁻ ions (figure 1). Taking into account thermal large-amplitude librations and reorientations of ammonium ions, the resulting density distribution should be close to a spherical one. This is clearly in contrast to our results (see figure 5). For model (b) the distribution of D (H) atoms in the average crystal structure consists of "triangular" arrangements of atoms at (*xxz*) sites which are centered along the <111> directions with the angle $\psi = 35.56°$ between the nearest N-D bonds and "rhombe shape" arrangements of D (H) atoms at (*0yz*) sites which are centered along the <100> directions with the angle $\psi = 13.9°$ between the nearest N-D bonds (figure 1). It is reasonable to suppose that the ratio of the effective radii of these distributions remains constant or increases with ammonium librations and reorientations. Therefore, the resulting density distribution should contain overlapping distributions centered along the <111> directions (with a large effective radius) and along <100> (with an effective radius which is considerably smaller). Such a

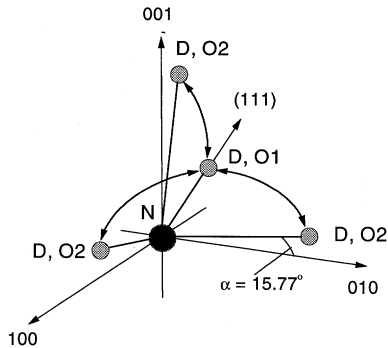distribution is in poor agreement with the obtained density distribution (figure 5).

Figure 7. *Two types of N-D bonds orientations - O1 and O2 in the model (c) of ND$_4$I(I) structure. The O1 orientation with D atom in (xxx) position and the nearest O2 orientations with D atoms in (xxz) positions are shown. Solid curves indicate possible pathways for O1-O2 ammonium reorientations via 39° jumps*
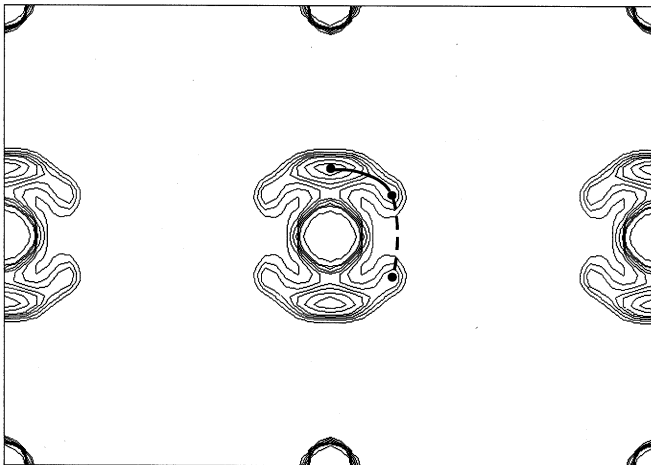

Figure 8. *ME density distribution for ND$_4$I in [110] plane. Eight levels between density values 0 and 10 are shown. Thick solid and broken curves indicate possible pathways for O1-O2 reorientations by 39° jumps and O1-O1 reorientations by 90° jumps between equivalent positions, respectively. The absence of the scattering density along the latter pathways may indicate that the ammonium reorientations by 90° have a very low probability*

The distribution of the N-D-I bond angle θ obtained from RMC modeling is shown in figure 9. It has maximum at $\theta = 180°$ which is close to the value for the average crystal structure, $\theta_0 = 157°$. The average N-D-I bond angle calculated from this distribution is $\theta = 132.5°$. This corresponds to an average libration amplitude for ND_4^+ ions $\gamma = 20°$.
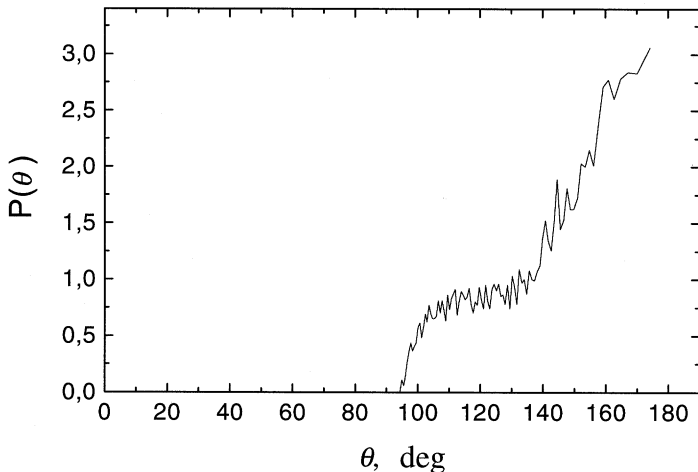

Figure 9. *Bond angle distribution $P_{N-D-I}(cos\theta)$*

In figure 10 we show the angular correlations between the ammonium ions (as defined by the set of four normalized vectors related to the four N-D bonds) and the (100) direction (averaged over all <100> type directions) obtained from RMC modeling. In the average crystal structure one would expect peaks at $cos\varphi = \pm 0.962, \pm 0.577, \pm 0.193$. However, due to the disorder of ammonium ions, just two peaks at $cos\varphi = \pm 1$ and one wide peak at $cos\varphi = 0$ are found. This corresponds to the observation of two overlapped peaks in the low r values part of $g_{DI}(r)$ (figure 4).

Calculation of the distribution of the relative N-D bond orientations for the neighboring ammonium ions has shown that there is no preferred orientational correlations between them.
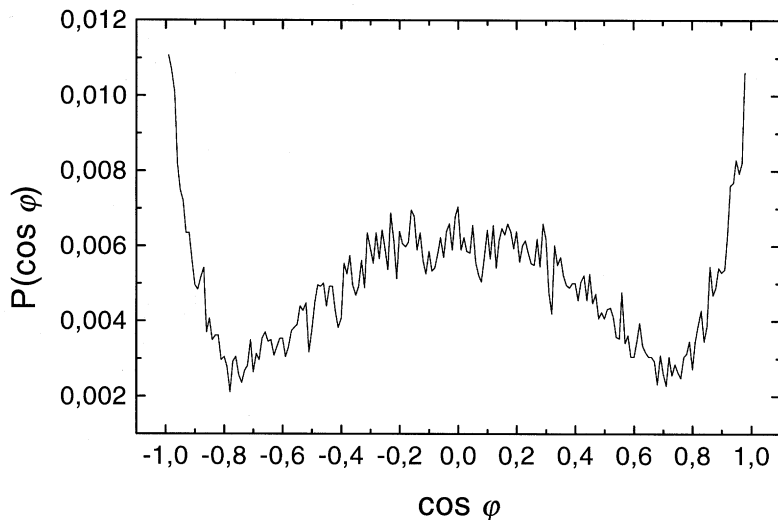
Figure 10. Orientational correlations between N-D bond vectors and (100) axes

6. Conclusions

The analysis of powder neutron diffraction data of the phase I of ND_4I by RMC and ME methods has provided detailed information on the orientational disorder and possible mechanisms of the reorientational motion of ammonium ions.

It was found that the structural model in which three D (H) atoms of ND_4^+ (NH_4^+) ion make the closest approach to the nearest Γ ions, such as the three-fold axes of ammonium ions are oriented along the three-fold axes of the crystal, is in the best agreement with experimental data. Our results show that ammonium ions may reorient by 39° jumps of their N-D bonds between the (*xxx*) positions and the neighboring (*xxz*) positions in the structure. Ammonium reorientations by 90° jumps between the equivalent crystallographic positions have a very low probability. This agrees well with the assumption of QNS study [17] that ammonium ions are expected to reorient over angles smaller than 90° in the phase I of NH_4I.

A clear indication was obtained that ammonium ion reorientations are stochastic and no correlation exists between the motion of neighboring ions in the high temperature phase I.

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Козленко Д.П. и др.   E14-2000-221

Исследование ориентационного беспорядка в фазе I ND_4I
методами обратного Монте-Карло и максимальной энтропии

Методом время-пролетной нейтронной дифракции измерен структурный фактор высокотемпературной фазы I ND_4I. Для исследования структуры и геометрических особенностей ориентационного беспорядка ионов аммония в этой фазе проведено моделирование экспериментально измеренного структурного фактора методами обратного Монте-Карло и максимальной энтропии. Результаты анализа показали, что ионы аммония совершают либрационные колебания вокруг положений равновесия со средней угловой либрационной амплитудой $\gamma = 20°$. Установлено, что основным механизмом реориентационного движения являются реориентации ионов ND_4^+ на угол 39° между ближайшими положениями типа (xxx) и (xxz) пространственной группы. Вероятность реориентаций ионов аммония на 90° между ближайшими позициями типа $(xxx) - (xxx)$ или $(xxz) - (xxz)$ очень мала.

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

Kozlenko D.P. et al.   E14-2000-221

A Study of Orientational Disorder in NaCl-Type Phase I of ND_4I
by Reverse Monte Carlo and Maximum Entropy Methods

Structure and orientational disorder of ammonium ions in the high temperature phase I of ND_4I were studied by reverse Monte Carlo and maximum entropy methods using powder neutron diffraction data. The ammonium ions were found to perform a librational motion with an average angular libration amplitude of $\gamma = 20°$ and reorientational motion by 39° jumps of the N–D bonds between (xxx) and (xxz) positions in the structure. Reorientations by 90° jumps were found to have a low probability.

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

Макет Т.Е.Попеко