Structure determination of sodium nitrate near the order-disorder phase transition

J. Lefebvre, R. Fouret, C.M.E. Zeyen

To cite this version:

J. Lefebvre, R. Fouret, C.M.E. Zeyen. Structure determination of sodium nitrate near the order-disorder phase transition. Journal de Physique, 1984, 45 (8), pp.1317-1327. <10.1051/jphys:019840045080131700>. <jpa-00209870>

HAL Id: jpa-00209870
https://hal.archives-ouvertes.fr/jpa-00209870

Submitted on 1 Jan 1984

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Structure determination of sodium nitrate near the order-disorder phase transition

J. Lefebvre (*), R. Fouret (*) and C. M. E. Zeyen (**)  

(*) Laboratoire de Dynamique des Cristaux Moléculaires, (E.R.A. 465), Université des Sciences et Techniques de Lille I, 59655 Villeneuve d'Ascq Cedex, France  
(**) Institut Laue-Langevin, 156 X, 38042 Grenoble Cedex, France  

(Reçu le 18 janvier 1984, accepté le 28 mars 1984)

Résumé. — Deux modèles sont proposés pour résoudre la structure du nitrate de sodium près de la transition de phase ordre-désordre \( T_c = 276 \, ^\circ C \). Le premier modèle est construit dans l'hypothèse d'un désordre statique entre les deux positions d'équilibre des ions \( \text{NO}_3^- \). Le désordre est alors caractérisé par un paramètre d'ordre \( \eta \). Dans le second modèle, le désordre est pris en compte par une fonction de probabilité orientationnelle unidimensionnelle. Dans le formalisme de ce modèle, il a été introduit un couplage entre la rotation des ions \( \text{NO}_3^- \) autour de l'axe ternaire et leur translation suivant la même direction. La comparaison des deux modèles montre que le modèle statique peut être considéré comme valable tant que la racine carrée de l'amplitude quadratique moyenne de rotation des ions \( \text{NO}_3^- \) autour de leur axe d'ordre trois est inférieure à 12°. La résolution de la structure par les deux modèles conduit à des affinements équivalents pour des températures inférieures à 250 °C ; pour des températures supérieures à 250 °C \( (T_c - 26 \, ^\circ C) \) le second modèle est mieux adapté. Les courbes d'équiprobabilité mettent en évidence le mécanisme de saut des ions \( \text{NO}_3^- \) entre deux positions d'équilibre : la rotation autour de l'axe ternaire s'accompagne d'une translation de telle manière à garder la distance entre les atomes d'oxygène et les ions \( \text{Na}^+ \) sensiblement constante pendant le saut.

Abstract. — Two models are proposed to solve the sodium nitrate structure near the order-disorder phase transition \( T_c = 276 \, ^\circ C \). The first model is built with the static disorder assumption between the two equilibrium positions of \( \text{NO}_3^- \) ions. In this case, disorder is characterized by an order parameter : \( \eta \). For the second model, a one-dimensional orientational probability function is introduced to take disorder into account. In the latter formalism, a coupling between \( \text{NO}_3^- \) rotations around the three fold axis and translations along the same axis has been introduced. Comparison between the two models shows that the static model can be held to be valid while the square root of the rotational mean square amplitude is lower than 12°. Structure determination by the two models yields equivalent fits for temperatures below ~ 250 °C, fits with the second model become better for temperatures above 250 °C \( (T_c - 26 \, ^\circ C) \). Equiprobability curves display the \( \text{NO}_3^- \) ion jump mechanism between their two equilibrium positions : the rotation around the three-fold axis is made via a translation so that the distance between oxygen atoms and the nearest neighbour \( \text{Na}^+ \) ion stays approximately constant during the jump.

1. Introduction.

Sodium nitrate undergoes an order-disorder phase transition at \( T_c = 276 \, ^\circ C \). In the ordered low temperature phase, the structure is trigonal (space group : R 3 c) with two molecules per unit cell. The \( \text{Na}^+ \) and \( \text{NO}_3^- \) ions are aligned along the three-fold axis and the oxygen atoms of two neighbouring \( \text{NO}_3^- \) groups are rotated by an angle of 180°. In the disordered high temperature phase, the structure is also trigonal, but with only one molecule per unit cell (space group : R 3 m), the \( \text{NO}_3^- \) ions occupying one of the two previous equilibrium positions [1] (Fig. 1). In fact, coherent neutron scattering measurements indicate the presence of a certain amount of disorder in the low temperature phase near the transition point [2, 3].

The aim of this study is to determine the structure of \( \text{NaN}_3 \) below the transition temperature. To take into account the disorder of the \( \text{NO}_3^- \) groups, two models are proposed corresponding to two different disorder mechanisms :

(i) Static disorder (Ising model) with an order parameter characterizing the occupation of the two possible positions ;
(ii) Orientational probability function ; this method is more convenient when the disorder becomes dynamic, that is to say when the residence time of the \( \text{NO}_3^- \)
Fig. 1. — Unit cell and order-disorder phase transition of sodium nitrate.

group on one of its equilibrium positions is of the order of magnitude of the lattice vibration period.

In the first case, for a lattice such as NaN0₃, the order parameter can be defined as [2]:

\[ \eta = \frac{P_+ - P_-}{P_+ + P_-} \]

where \( P_+ (P_-) \) is the probability for a NO₃ group to be in the one (or other) position on its site for the space group R 3 c. The NO₃ ions are regarded as rigid and for the thermal vibration, « classical » T-L-S tensors are introduced. In a previous structure determination of sodium nitrate [4], an attempt has been made to introduce the order parameter \( \eta \) below \( T_c \); but unfortunately, certain temperature factors decrease suddenly when the temperature rises close to \( T_c \). In the same way, the reliability index increases (from 4 % at 230 °C to 9.2 % at 268 °C).

In the second case, the oxygen atom positions are determined using an orientational probability function, the NO₃ ions being also regarded as rigid. This method, introduced by Press and Hiiller [5] has been extensively applied to crystals with cubic symmetry : CD₄, p-D₂, ND₄Br [6], C₂D₂ [7] CB₄ [8], KOD [9] and substituted compounds of adamantane [10]. The structure of \( \beta \)-Nitrogen with a hexagonal symmetry has also been resolved with this formalism [10]. More recently, Press et al. [11] included the effects of correlations between orientation and position of the molecule. In the case of NaNO₃ this effect could be important because the symmetry of the NO₃ groups allows the existence of translation-rotation coupling terms. It is in this framework that the orientational probability function \( f(r, \Omega) \) has been expressed [\( r \) represents the displacement of the centre of mass with respect to its equilibrium position; \( \Omega = (\theta, \varphi) \) are the two angles of the spherical coordinates].

In fact, two possibilities are offered according to the nature of the disorder [5]. If the disorder is three-dimensional, the probability function must be expanded using cubic harmonics. The second possibility is the case of a one-dimensional disorder and whence the angular part of \( f(r, \Omega) \) is expressed using multiple trigonometric functions of \( \varphi \), where \( \varphi \) is the rotation angle around the three fold axis. The application of the three-dimensional disorder requires a large number of parameters to provide a good convergence of the structure; thus, the results of this method are not reported in this paper, and only the one-dimensional probability function will be investigated on the present work.

The plan of the paper is as follows. We start with a short description of the experiment (section 2). The theoretical background to calculate structure factors is developed in the case of static disorder (section 3) and for an orientational probability function (section 4). Relations between these two models are given in section 5. Results of the different structure refinements are given and discussed in section 6.

For the structure factor, the hexagonal system will be used. NaNO₃ having trigonal symmetry, the following relation between the Miller indices holds:

\[ h + k + l = 3n \]

The comparison between the reciprocal lattices of the low and high temperature phases shows that the reflections of the low temperature phase with \( l \) odd vanish in the high temperature phase.

2. Experimental.

As the aim of the experiment was to obtain a good determination of the temperature factors, it was necessary to measure reflections up to large \( Q \) momentum transfer vectors. For this reason, the experiment was performed in two steps:

(i) At room temperature where the Debye-Waller factors are small, an X-ray automatic four circle diffractometer (Université de Lille) was used. The wavelength was 0.7107 Å (MoKα); \( \theta - 2 \theta \) scans were made up to \( \theta = 63^\circ \). The background was counted for half the total scan time on each side of the Ka position. 674 non-equivalent reflections were collected (most of them were measured in two equivalent positions) of which 499 such as \( I > 3 \sigma (I) \) have been used on the fitting procedure. The absorption coefficient being small for this wavelength (\( \mu \approx 4 \text{ cm}^{-1}, \mu R \approx 0.036 \)), no absorption correction was applied.

(ii) At higher temperature, neutron diffraction (four-circle diffractometer D10, Institut Laüe Langevin,
Grenoble) was used as this yields the temperature factors with better accuracy than X-rays. The crystal was heated by a gas-flow furnace which allows temperature settings with a stability and a homogeneity over the whole sample better than 2 °C. The wavelength was 1.2626 Å and intensity was measured using « w step scans ». For each temperature studied (T = 228, 245, 257 and 266 °C), about 110 reflections were collected. The absorption coefficient measured from a thick sample was found equal to 0.30 ± 0.03 cm⁻¹ (µR = 0.056) and absorption corrections were neglected. On the other hand, isotropic extinction [14] and T.D.S. corrections were made. In particular, T.D.S. corrections were of the order of 12% for reflections with large Q vectors.

3. Structure factor in the case of static disorder (Model I).

The disorder is characterized by the order parameter η. In the low temperature phase with a space group R 3 c, and in the triple hexagonal cell, the Na⁺ ions are in positions 6(a) of the International tables of Crystallography [12], the N atoms in position 6(b) and the « ordered » oxygen atoms in position 18(e). The probability of finding an oxygen atom on an « ordered » position is \( \frac{1}{2} (1 + \eta) \). The position of the « disordered » oxygen atoms [with a probability \( \frac{1}{2} (1 - \eta) \)] is obtained using inversion of the previous 18(e) positions with respect to the N atoms. In the high temperature phase, the NO₃⁻ ions are equally distributed among the two stable orientations and the order parameter becomes equal to zero.

If the NO₃⁻ ions can be regarded as rigid bodies, thermal vibrations are taken into account by the T-L-S tensors. The tensor T takes into account translational thermal vibrations of the group, L, rotational thermal vibrations around the centre of mass and S gives the possibility to couple translational and librational thermal vibrations. With the D₃ symmetry of the NO₃⁻ ions, these tensors have the following diagonal form:

\[
\begin{pmatrix}
T_{11} & 0 & S_{11} \\
0 & T_{11} & S_{11} \\
S_{11} & S_{33} & S_{33}
\end{pmatrix}
\]

These tensors are expressed along the orthogonal system a, b*, c. It is to be noted that the S₁₁ and S₃₃ coupling terms have opposite signs according to whether the NO₃⁻ ions are on an « ordered » or a « disordered » position in the cell.

With this assumption, the structure factor \( F(h, k, l) \) becomes η independent if \( l \) is even, and directly proportional to η if \( l \) is odd: the structure factor vanishes at the transition temperature for odd values of \( l \).

4. Structure factor using an orientational probability function (Model II).

With this formalism, the oxygen atoms of the NO₃⁻ groups are considered not to vibrate around their equilibrium positions. A probability function is introduced to characterize the orientation of the NO₃⁻ groups with respect to a fixed reference system. Two cases have been considered including correlations between orientation and position of the molecule. All data show that the oxygen atoms stay essentially in planes perpendicular to the three-fold axis. In such cases the three-dimensional model needs a large number of parameters to allow the localization of the NO₃⁻ group without giving further information about the disorder. Therefore, only the one-dimensional case will be developed. According to the T-L-S tensors, the only non-vanishing coupling term between the rotation perpendicular to the three fold axis and position of the group is \( S_{33} \). Consequently, it will be supposed that only the rotation of the group perpendicular to the three-fold axis is correlated with the translation along this axis.

As in [11], the coupled orientational probability function for the site \( K \) of the unit cell can be expressed by the following relation:

\[
\begin{equation}
\mathcal{f}^K(r) = \int f_{\text{T}}^K(R) f_{\text{rot}}^K(r - R | R) \, dR
\end{equation}
\]

where \( R \) is the instantaneous centre of mass position of group \( K \) and \( r' = r - R \) connects an atom within the group with its centre of mass. In the present case, \( r' \) has only components perpendicular to the three-fold axis. The translational probability function for the centre of mass \( f_{\text{T}}^K(R) \) is taken, as usual, to be Gaussian. With uniaxial symmetry, it can be expressed as:

\[
\begin{equation}
f_{\text{T}}^K(R) = G \exp \left\{ \frac{X'^2 + Y'^2}{2 T_{11}^T} \right\} \exp \left\{ \frac{Z'^2}{2 T_{33}^T} \right\}
\end{equation}
\]

where \( R' = R - R_0^K = (X', Y', Z') \) is the displacement of the centre of mass with respect to its equilibrium position, \( T_{11}^T \) and \( T_{33}^T \) are the temperature factors for the group \( K \) perpendicular and parallel to the three-fold axis respectively; \( G \) is a normalization factor. In the present case, only the second term of \( f_{\text{T}}^K(R) \) interferes with the rotational part. Hence, the components along and perpendicular to the three fold axis can be separated in relation (2).

For small displacements of the centre of mass along \( Z \), a Taylor series of \( f_{\text{rot}}^K(r' | R) \) can be used:

\[
\begin{equation}
f_{\text{rot}}^K(r' | R) = f_{\text{rot}}^K(r' | Z') = f_{\text{rot}}^{K(0)}(r') + \sum_p \frac{1}{p!} f_{\text{rot}}^{K(p)}(r') Z'^p
\end{equation}
\]
with
\[ f_{rot}^{K(p)}(r') = \frac{\partial}{\partial z} \left[ f_{rot}^{K}(r' | R) \right]_{z = \rho} \]

The disorder being one-dimensional, the \( f_{rot}^{K(p)}(r') \), expressed in the cylindrical system \((r', \varphi', z')\), has the following form:
\[ f_{rot}^{K(p)}(r') = \frac{1}{r'} \delta(r' - \rho) \Delta^{K(p)}(\varphi') \]
\[ (5) \]

where \( \rho \) is the N-O bond distance.
\( f_{rot}^{K}(r' | R) \) has the full site symmetry, hence all terms in the expansion (4) have this symmetry as well. With the D\(_3\) symmetry for the N03 and with the \( \varphi \) angle origin along a two-fold axis direction, the \( \Delta^{K(p)}(\varphi') \) are described as:
\[ 2 \pi \Delta^{K(p)}(\varphi) = (T_{3a}^{1})^{-1/2} \left\{ \delta_{p,0} + \sum_{n=1}^{\infty} A_{3a}^{K(p)} \cos 3n\varphi \right\} \]
for \( p \) even
\[ (6) \]
\[ 2 \pi \Delta^{K(p)}(\varphi) = (T_{3a}^{1})^{-1/2} \left\{ \sum_{n=1}^{\infty} A_{3a}^{K(p)} \sin 3n\varphi \right\} \]
for \( p \) odd
\[ (6) \]

where \( \delta_{p,0} \) is the Kronecker symbol; the factor \( 2 \pi \) ensures normalization. The extra-coefficients \((T_{3a}^{1})^{-1/2}\) are such that the \( A_{3a}^{K(p)} \) parameters are dimensionless. In case of complete disorder, all the \( A_{3a}^{K(p)} \) parameters vanish and when the order becomes important, the number of \( A_{3a}^{K(p)} \) parameters having a significant value increases.

The inversion centre relates the positions of the two NO\(_3^-\) ions (for example (0, 0, 1/4) and (0, 0, -1/4)).

Thus the relation between the rotational probability functions of the two NO\(_3^-\) ions of the unit cell is:
\[ f_{rot}^{K}(r' | Z') = f_{rot}^{K}(r', \varphi', z' | Z') = f_{rot}^{K}(r', \varphi' + \pi, -z' | -Z') \]
\[ (7) \]

This relation involves for the \( A_{3a}^{K(p)} \) coefficients:
\[ A_{3a}^{K(p)} = (-1)^{p+n} A_{3a}^{K(p)} \]
\[ (8) \]

The structure factor is then calculated using:
\[ F(Q) = \sum_{K} b_{K}(Q) f_{K}(Q) \]
\[ (9) \]

where the sum runs over all the \( k \) atoms of the \( K \) groups of the unit cell; \( b_{K}(Q) \) is the scattering length of the \( k \) atom for neutron diffraction and the scattering form factor for X-ray diffraction. \( f_{K}(Q) \) is defined as:
\[ f_{K}(Q) = \int f(r) e^{iQr} dr \]
\[ (10) \]

Using the relation:
\[ \exp \{ iQr \} = \exp \{ iQ_{z} z' \} \{ J_{0}(Q_{z}, r') + \sum_{m} (i)^{m} J_{m}(Q_{z}, r') \cos (m(\varphi - \varphi')) \} \]

where the \( Q \) vector is expressed in cylindrical coordinates: \( Q = (Q_{z}, Q_{\varphi}, Q_{r}) \) and \( J_{m}(Q_{z}, r') \) is the cylindrical Bessel function of order \( m \), the structure factor, for sodium nitrate, is given by the following relation:

\[ F(Q) = F(h, k, l) = [1 + (-1)^{l}] b_{Na} e^{-w_{Na}} + 2 \cos \frac{n \pi}{2} [b_{N} e^{-w_{N}} + 3 b_{O} e^{-w_{O}} J_{0}(Q_{z}, \rho)] + \]
\[ + 6 b_{O} e^{-w_{O}} \sum_{n=1}^{\infty} \left[ A_{3a}^{(0)} + \frac{A_{3a}^{(2)}}{2} (1 - Q_{z}^{2} T_{33}) \right] \cos \frac{n \pi}{2} (l - n) J_{3a}(Q_{z}, \rho) \cos 3n\varphi_{Q} \]
\[ - 6 Q_{z} \sqrt{T_{33}} b_{O} e^{-w_{O}} \sum_{n=1}^{\infty} \left[ \frac{A_{3a}^{(1)}}{2} + \frac{A_{3a}^{(3)}}{6} (3 - Q_{z}^{2} T_{33}) \right] \sin \frac{n \pi}{2} (l - n) J_{3a}(Q_{z}, \rho) \sin 3n\varphi_{Q} \]
\[ (11) \]

The expansion over \( p \) has been limited to 3; \( b_{Na}, b_{N} \) and \( b_{O} \) are the neutron scattering lengths (or scattering form factors for X-rays) of sodium, nitrogen and oxygen atoms respectively; \( w_{Na}, w_{N} \) and \( w_{O} \) are the Debye-Waller exponents for these atoms. Note that \( w_{N} \) simply corresponds to the translational displacements of the NO\(_3^-\) groups. For \( w_{O} \), a term taking into account the librational motion perpendicular to the three fold axis has been added. In the high temperature phase, the structure factors with \( l \) odd vanish, which implies the value zero for the \( A_{3a}^{(2p)} \) and \( A_{3a}^{(2p+1)} \) coefficients at the transition temperature.

5. Relation between the two models.

5.1. Probability function coefficients in the harmonic approximation. — It is to be noted that model I can only be used in the case where the NO\(_3^-\) ions are localized at their site. Then, taking into account the thermal motion, the atomic probability functions are assumed to be Gaussian. It is expressed
from the parameters of the harmonic model \((T_{33}, S_{33}, L_{33} \text{ and } \eta)\) with the following relation [13] :

\[
j^k(\varphi, Z') = \frac{c}{2 \pi} \left\{ T_{33}^k L_{33}^k - S_{33}^k \right\}^{1/2} \sum_{i=1}^{6} p_i \exp \left\{ - \frac{L_{33}^k Z'^2 - 2 S_{33}^k Z' \left( \varphi - \varphi_0 \right) + T_{33}^k \left( \varphi - \varphi_0 \right)^2}{2(T_{33}^k L_{33}^k - S_{33}^k)} \right\}
\]

where the sum runs over the six possible equilibrium positions of the NO\(_3\) ions. For the three « ordered » positions \(\varphi_0 = 0, \pm \frac{2 \pi}{3}\) for the first ions of the unit cell,

\[
p' = \frac{1}{6} (1 + \eta) \quad \text{and} \quad S_{33}^k = S_{33}^k
\]

and for the three « disordered » positions

\[
p' = \frac{1}{6} (1 - \eta) \quad \text{and} \quad S_{33}^k = - S_{33}^k \text{ (see § 3)}.
\]

Multiplying relation (12) by \(\cos 3 n \varphi\) or \(\sin 3 n \varphi\) and after integration over \(Z'\) and \(\varphi\) (1'), the \(A_{43}^{(p)}\) coefficients can be expressed from coefficients of the harmonic approximation as : (thermal coefficients without upper script are relative to the first NO\(_3\) ion of the cell).

\[
A_{3n}^{(0)} = \alpha_n \left[ 1 + \frac{1}{2} \left( \frac{3 n S_{33}}{\sqrt{T_{33}}} \right)^2 \right] \exp \left\{ - \frac{9}{2} n^2 L_{33} \right\}
\]

\[
A_{3n}^{(1)} = \beta_n \left[ \frac{3 n S_{33}}{\sqrt{T_{33}}} \right] \left[ 1 + \frac{1}{2} \left( \frac{3 n S_{33}}{\sqrt{T_{33}}} \right)^2 \right] \times \exp \left\{ - \frac{9}{2} n^2 L_{33} \right\}
\]

\[
A_{3n}^{(2)} = - \alpha_n \left( \frac{3 n S_{33}}{T_{33}} \right)^2 \exp \left\{ - \frac{9}{2} n^2 L_{33} \right\}
\]

\[
A_{3n}^{(3)} = - \beta_n \left( \frac{3 n S_{33}}{T_{33}} \right)^3 \exp \left\{ - \frac{9}{2} n^2 L_{33} \right\}
\]

with

\[
\alpha_n = (1 + \eta) + (-1)^n (1 - \eta)
\]

\[
\beta_n = (1 + \eta) + (-1)^n+1 (1 - \eta)
\]

As for the structure factor, the expansion has been limited to \(p = 3\). The convergence in \(n\) is assumed by the exponential term \(\exp \left\{ - \frac{9}{2} n^2 L_{33} \right\}\) : a large value of \(L_{33}\) limits the number of \(A_{3n}^{(p)}\) coefficients with significant value. The last relations show unambiguously the effect of the translation-rotation coupling : if \(S_{33}\) equals zero, all the \(A_{3n}^{(p)}\) coefficients (with \(p \neq 0\)) vanish. Finally, the conditions for the phase transition (§ 3) are contained in the \(\alpha_n\) and \(\beta_n\) terms.

5.2. ORDER PARAMETER : LIMIT OF THE HARMONIC HYPOTHESIS. — With an orientational probability function for a given NO\(_3\) group, it is easy to determine if this group is on an « ordered » or on a « disordered » position. For example, the first group of the unit cell will be on an « ordered » position when \(\varphi\) is on one of the three following sextants :

\[
- \frac{\pi}{6} \leq \varphi \leq \frac{\pi}{6}; \quad \frac{\pi}{2} \leq \varphi \leq \frac{5 \pi}{6}; \quad \frac{5 \pi}{6} \leq \varphi \leq \frac{\pi}{2}
\]

it will be on a « disordered » position on the other three sextants. Owing to its definition, the order parameter can be expressed from the \(A_{43}^{(p)}\) coefficients after suitable integrations of relation (4) over \(\varphi\) and \(Z'\) :

\[
\eta = \frac{2}{\pi} \sum_{q=0}^{\infty} \frac{(-1)^q}{2 q + 1} \left[ A_{4q+3}^{(0)} + A_{4q+3}^{(2)} \right].
\]

With the expressions (13) of \(A_{4q+3}^{(0)}\) and \(A_{4q+3}^{(2)}\) (these expressions are true only in the case of the harmonic approximation), an \(\eta\)-independent relation is obtained characterizing the limit validity of the harmonic approximation :

\[
4 \sum_{q=0}^{\infty} \frac{(-1)^q}{2 q + 1} \exp \left\{ - \frac{9}{2} (2 q + 1)^2 L_{33} \right\} = 1.
\]

On figure 2, the value of this series is plotted versus the square root of the librational temperature factor \(\{L_{33}\}^{1/2}\). It appears that for values higher than 12° for \(\{L_{33}\}^{1/2}\) (\(L_{33} \gtrsim 0.045 \text{ rd}^2\)) the value of the first term of (15) becomes different from 1 : beyond this value of \(L_{33}\), the harmonic approximation assumption cannot be applied.

6. Results and discussion.

For the five temperatures studied (22, 228, 245, 257 and 266 °C = \(T_c - 10 °C\)) several fits have been performed using either the harmonic model (§ 3, model I) or the one-dimensional orientational probability function (§ 4, model II). For the latter, different adjustments were attempted according to the \(p\) limiting value for the \(A_{3n}^{(p)}\) coefficients. First, with only
the $A_{3}(P)$ coefficients (Model II), the agreement between calculated and measured structure factors is very poor. This point confirms a large translation-rotation coupling for the NO$_3$ ions. The adjustments up to $p = 1$ and 2 are reported in the following (hereafter named II and I,2). Finally the introduction of the $A_{3n}(P)$ coefficients (113) do not give a better agreement than the I,2 calculation and the corresponding new coefficients are not very well determined by the fitting procedure.

The values of the parameters corresponding to the best adjustments are reported in tables I and II for the five studied temperatures and for the I, II, and I,2 models. For the $A_{3}(P)$ coefficients, the limited value of $n$ is obtained (for a given value of $p$) when the standard deviation becomes of the order of the coefficient itself.

At room temperature, the reliability index $R$ (2) is approximately the same for the three reported adjustments : 5.5, 5.6 and 5.3 % for models I, II, and I,2 respectively when the number of parameters increases from 9 to 19 and 24. From these results it can be concluded that :

(i) The nitrate ions are very well localized around their equilibrium positions at room temperature (cf. model I);
(ii) The model using a one-dimensional orientational probability function (model II) seems to be able to describe a structure such as sodium nitrate. In particular, when the atom groups are ordered, such as in this case, it is necessary to introduce a large number of parameters in the fitting procedure.

With increasing temperature, the reliability index decreases systematically for model I to model II, and then to model I,2. For example, at 266°C ($T_c - 10°C$), $R_I = 7.7 %$ and $R_{I,2} = 5.4 %$ while the number of parameters increases from 10 to 15.

### 6.1. Temperature Factors.

For the temperature factors, the three models give, for each of the five studied temperatures, the same values for the four translational terms ($T_1$, $T_3$, $T_6$ and $T_9$) (table I and Fig. 3). Note the rapid increase of the 4 translational temperature factors above 245°C ($T_c - 30°C$). $T_3$ flattens out near the transition temperature ($T_c - 20°C$), this point will be discussed later.

$$R = \frac{\Sigma |F_{obs} - |F_{calc}|}{\Sigma F_{obs}}.$$

| Table I. — Measured and calculated parameters for the three models and for the five temperatures studied for the sodium nitrate structure. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $T$ (°C) | 11 | 20 | 228 | 245 | 257 | 266 |
| $a$ | 5.000 | 5.000(2) | 5.000(2) | 5.000(2) | 5.000(2) | 5.000(2) |
| Number of reflections | 499 | 100 | 100 | 112 | 113 | 117 |
| Number of parameters | 9 | 19 | 20 | 30 | 35 | 44 |
| $R_{I,2}$ (10°C) | 100(2) | 183(1) | 100(1) | 473(10) | 499(12) | 499(12) | 543(12) |
| $R_{II}$ (10°C) | 287(1) | 287(1) | 287(1) | 543(12) | 543(12) | 543(12) | 543(12) |
| $R_{I,2}$ (10°C) | 295(1) | 295(1) | 295(1) | 543(12) | 543(12) | 543(12) | 543(12) |
| $R_{II}$ (10°C) | 151(1) | 151(1) | 151(1) | 379(8) | 379(8) | 379(8) | 379(8) |
| $R_{I,2}$ (10°C) | 234(1) | 234(1) | 234(1) | 520(8) | 520(8) | 520(8) | 520(8) |
| $R_{II}$ (10°C) | 100(1) | 100(1) | 100(1) | 320(17) | 320(17) | 320(17) | 320(17) |
| $R_{I,2}$ (10°C) | 129(3) | 129(3) | 129(3) | 320(17) | 320(17) | 320(17) | 320(17) |
| $R_{II}$ (10°C) | -112(3) | -112(3) | -112(3) | -112(3) | -112(3) | -112(3) | -112(3) |
| $R_{I,2}$ (10°C) | 1.244(1) | 1.244(1) | 1.244(1) | 1.244(1) | 1.244(1) | 1.244(1) | 1.244(1) |
| $R_{II}$ (10°C) | 1.770(7) | 1.770(7) | 1.770(7) | 1.770(7) | 1.770(7) | 1.770(7) | 1.770(7) |
| $R_{I,2}$ (10°C) | 114(5) | 114(5) | 114(5) | 114(5) | 114(5) | 114(5) | 114(5) |
| $R_{II}$ (10°C) | 100(4) | 100(4) | 100(4) | 100(4) | 100(4) | 100(4) | 100(4) |
| $R_{I,2}$ (10°C) | 9.3(5) | 9.3(5) | 9.3(5) | 9.3(5) | 9.3(5) | 9.3(5) | 9.3(5) |
| $R_{II}$ (10°C) | 10.0(5) | 10.0(5) | 10.0(5) | 10.0(5) | 10.0(5) | 10.0(5) | 10.0(5) |
| $R_{I,2}$ (10°C) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) |
| $R_{II}$ (10°C) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) |
| $R_{I,2}$ (10°C) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) |
| $R_{II}$ (10°C) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) |
| $R_{I,2}$ (10°C) | 10.0(4) | 10.0(4) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) |
| $R_{II}$ (10°C) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) |
| $R_{I,2}$ (10°C) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) |
| $R_{II}$ (10°C) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) |
| $R_{I,2}$ (10°C) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) | 10.0(4) |
| $R_{II}$ (10°C) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) | 11.0(9) |

---

**Fig. 2.** — First term of relation (15) versus the square root of the rotational temperature factor $L_{33}$.”
For the rotational term $L_{11}^{\text{NO}_3}$, corresponding to the rotation around an axis perpendicular to the three fold axis, there is a complete disagreement between the values calculated by the three models: those calculated using model II$_1$ are smaller than those of model II$_2$ which in turn are smaller than those of model I. According to relation (11) the $A_{3n}^{(2)}$ have, in the first order approximation, the same $Q_x$ dependence as $L_{11}$. Neglecting $A_{3n}^{(2)}$ (case of the model II$_1$) provides smaller values for $L_{11}$. For model I, it is well known [15] in case of large rotational temperature factors that the fitting procedure gives too small a value for the bond lengths. This is observed here for the N-O bond at higher temperature. As for the Debye Waller exponent $W_\phi$, it is the quantity $p^2 L_{11}$ which enters directly, the fitting procedure gives higher values of $L_{11}$ to compensate the shortening of the N-O bond. This is observed here for the N-O bond at higher temperature.

The order parameter, calculated from model I is plotted versus temperature in figure 5 together with values from the literature, by Paul and Pryor [4] from neutron diffraction and by Terauchi and Yamada [2] using X-ray diffraction. Our results seem to be in good agreement with those of Terauchi and Yamada, the values of Paul and Pryor tending to be higher.

### COEFFICIENTS OF THE ORIENTATIONAL PROBABILITY FUNCTION

The calculated $A_{3n}^{(2)}$ coefficients of the orientational probability function are reported in table II and their temperature dependence is shown in figure 6. On this figure, the lines correspond to the calculated values in the case of the harmonic approximation.
mation from relation (13). The two models (I and II) give similar values for $A_{3n}^{(0)}$ and $A_{3n}^{(2)}$, while the $A_{3n}^{(1)}$ values are very different. However, according to the value of $L_{33}$, the model is not valid for temperatures higher than 250 °C. It can be considered surprising to have such good an agreement between the two models. A possible reason is that there are six values of $A_{3n}^{(p)}$ for model II, and only three parameters ($L_{33}$, $S_{33}$ and $\eta$) for model I and the fit adjusts these three parameters to yield good values for the $A_{3n}^{(p)}$ coefficients. Naturally, these calculated values from model I have no physical background. Finally, it is to be noted that those calculated coefficients vanishing at the transition [$A_{6q}^{(3)}, A_{6q}^{(1)}, A_{6q}^{(2)}; \S 4$] decrease more rapidly with increasing temperature than the other ones.

In figure 7, the equiprobability curves, calculated from relation (4) and using the $A_{3n}^{(p)}$ coefficients obtained from the II fits, have been drawn in the ($p, z$) plane (development cylinder) for 22, 257 and 266 °C. At room temperature a very strong maximum appears on the « ordered » position ($\varphi = 0; z = 0$). The equiprobability curves have a very close to elliptical shape, the long axis forming an angle of about 45° with the $\varphi$ axis.
At 257 °C, the calculation takes into account a small probability of having the NO$_3^-$ ions in a « disordered » position ($\phi = 60^\circ$; $z = 0$). At this temperature the ellipses are somewhat distorted along their long axis. At 266 °C ($T_c - 10$ °C), the same 1.5 equiprobability curve, which corresponds to the tenth of the main maximum value, surrounds the two equilibrium positions. The shape of this curve shows clearly the jump mechanism of the NO$_3^-$ ions: when they go from an equilibrium position to another one, the jump is made with a translation along the Z axis (in the negative sense, if the ion located at $Z = \frac{c}{4}$ is considered). This translation avoids too close an approach of the Na$^+$ ion nearest neighbours (located at $R = \frac{a}{\sqrt{3}}$, $\phi = 30^\circ$ and $Z = \frac{c}{3}$ in cylindrical coordinates). At this temperature, the O-Na distance is 2.45 Å for the equilibrium position. During the reorientational motion with a translation along Z of the NO$_3^-$ ion, the O-Na distance for an angle of 30°, just corresponding to the middle of the jump is 2.49 ± 0.02 Å, while without translation along Z, the distance would be only 2.24 Å. A consequence of this process is the fact that $T_3$ cannot increase with temperature when reorientational motions appear. In our fitting values (table I, Fig. 3) $T_3$ becomes constant between 245 °C and 257 °C. This temperature range is to be compared with the value of 250 °C, which is the temperature above which the harmonic approximation is no longer valid.

Fig. 6. — Calculated $A_{3n}^{(3)}$ coefficients of the orientational probability function (from model II$_3$) versus temperature. Solid curves come from calculations with relation (13) using parameters found with model I.
7. Conclusion.

Two models have been proposed to describe the structure of sodium nitrate near the order-disorder phase transition. The first model corresponds to a static disorder for the NO$_3^-$ ions. In the second model, an orientational probability function has been introduced to take into account the disorder which is supposed as one-dimensional.

The second model seems to give a better description of the disorder at the approach of the transition temperature.

The formalism, introduced in this paper in case of a trigonal symmetry, is easily extended to crystals having a tetragonal or hexagonal symmetry.

Acknowledgments.

The authors wish to thank M. More and G. Odou for their help during the X-ray data collection.

Fig. 7. — Equiprobability curves in the ($\phi, z$) plane for the first NO$_3^-$ ion of the unit cell. Coefficients used are those calculated from model II$_2$. Maxima of probability are reported in the figure. Mixed curves correspond to the half height of the maximum. The same normalization factor has been applied for the three diagrams.
References

national Sommer School on Crystallographic Computing, Edited by F. R. Ahmed.