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PROTON ORDERING MODEL OF SUPERIONIC PHASE TRANSITION IN $(NH_4)_3H(SeO_4)_2$ CRYSTAL

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Модель протонного впорядкування для опису суперіонного фазового переходу у кристалі $(NH_4)_3H(SeO_4)_2$

І.В.Стасюк, Н.Павленко, Б.Хільчер

Анотація. Для опису послідовності фазових переходів з суперіонної фази II до сегнетоеластичних фаз III і IV в кристалі $(NH_4)_3H(SeO_4)_2$розвинена мікроскопічна модель протонного впорядкування. Використовуючи структурні дані проведений симетрійний аналіз протонного впорядкування в фазах III і IV. В рамках наближення середнього поля досліджений рівноважний стан протонної підсистеми і побудована фазова діаграма,яка визначає необхідні умови для існування різних типів протонних впорядкувань. Чисельно проведено дослідження термодинамічних функцій,а також температурних залежностей середніх протонних чисел заповнення. Отримані результати порівнюються з висновками, які випливають з розкладу Ландау.

Proton Ordering Model of Superionic Phase Transition in $(NH_4)_3H(SeO_4)_2$ crystal

I.V. Stasyuk, N. Pavlenko, B. Hilczer

Abstract. The microscopic proton ordering model is developed for the description of phase transitions sequence from superionic phase II to ferroelastic phases III and IV in the $(NH_4)_3H(SeO_4)_2$ crystal. Symmetry analysis of proton orderings in phases III and IV is performed using the structural data. The equilibrium states of proton subsystem are studied and the corresponding phase diagram determining the necessary conditions for the existence of different proton orderings is constructed within the frame of mean field approximation taking into account the long-range proton interactions. Investigations of thermodynamical functions as well as the temperature dependences of proton average occupation numbers are performed numerically. The obtained results are compared with the conclusions which follow from the phenomenological approach based on Landau expansion.

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1. Introduction

The investigation of crystals which belong to $M_3H(XO_4)_2$-class (M=K, Rb, Cs; X=Se, S) has received much attention in recent years. Such an active studies are caused by the existence of structural and ferroelectric phase transitions in these crystals, connected with the rearrangements of hydrogen bonds network, proton ordering and ionic groups reorientation processes, accompanied by the crystal lattice deformation. The essential feature of this class of materials is their high-temperature transitions to the so-called superionic (superprotonic) phases, in which the conductivity is accomplished by the fast proton transport. In these phases the specific type of proton disorder is realized when protons are distributed randomly in the sublattice of structurally equivalent positions and the available positions number exceeds the number of protons. As charge carriers, protons are transferred through the crystal with low activation energy.

The characteristic feature of crystals of the $M_3H(XO_4)_2$ family is that the tetrahedra $SeO_4(SO_4)$ are linked by hydrogen bonds $O(2)\text{-}H\cdots O(2')$ into pairs (dimers) [1,2,4–7] in the low symmetry (nonsuperionic) phases. There exist three possible dimer configurations connected with their orientations in lattice. The transition to superionic phases involves the destruction of dimer structure, reorientation of XO_4 groups between three equilibrium positions as well as dynamic disordering of protons between three structural equivalent positions in the (001) plane with the probability of occupation of each position equal to 1/3 [8–10].

For the majority of crystals of this type the similar sequence of phase transitions is observed. The superionic phase with decreasing of temperature is replaced by two ferroelastic phases generally, and for low temperatures the transitions to states with ferroelectric ordering are often noted. Despite some discrepancies among existing structural data [2,4,8,9], it is generally accepted, that superionic phase transitions in most cases are accompanied by the structural transformations from monoclinic ferroelastic phase with space group A2/a ($Z = 2$) to trigonal paraelastic with space symmetry $R\bar{3}m$($Z = 1$). In particular, for the crystals $Rb_3H(XO_4)_2$ and $Cs_3H(XO_4)_2$ [4,10–12] the transformation outlined above takes place. The situation is more complicated for the crystals $(NH_4)_3H(SeO_4)_2$ with ammonium groups. Structural investigations performed in works [6–8] revealed that in contradiction to accepted previously concepts [2,9], in crystal $(NH_4)_3H(SeO_4)_2$ more complex phase sequence is realized: trigonal phase I (space group $R\bar{3}m$); trigonal phase II ($R\bar{3}$); triclinic phase III ($C\bar{1}$ or $P\bar{1}$, with small deviations

from monoclinic C2/c); monoclinic phase IV (C2/c); monoclinic phase V (Cc) and monoclinic phase VI (Cc) (the transition temperatures are 332K, 302K, 275K, 181K and 101K respectively). The results of recent structural analysis [3] do not exclude the possibility of existence of intermediate phase between the structures $R\bar{3}m$ and A2/a (or C2/c) in the crystal $(NH_4)_3H(SO_4)_2$ as well.

Beside the structural X-ray studies of $M_3H(XO_4)_2$ type crystals, the calorimetric measurements, investigations of vibrational spectra by Raman and IR spectroscopy, dielectric susceptibility, elastic and lattice constants, NMR-spectra, static and dynamic conductivity (impedances $Z'(\omega)$, $Z''(\omega)$) have been performed [3,13–23]. Considerable attention has been paid also to studies of external stress effect [13] and influence of deuteration [1] on the phase transitions in these compounds. In patricular, the entropy change ΔS at superionic phase transition, obtained from calorimetric studies [11,17], is equal to $1.1R$, $1.2R$ and $1.0R$ for the crystals $Cs_3H(SeO_4)_2$, $(NH_4)_3H(SeO_4)_2$ and $Rb_3H(SeO_4)_2$ respectively, that is in consistent with configurational entropy value $\Delta S_{cf} = R\ln 3 = 1.1R$. Thereby these results support the assumption concerning proton disordering between three positions in the unit cell of the superionic phase. Raman and NMR spectroscopy measurements [1,10,20] indicate in turn the fast dynamics and reorientations of XO_4 groups, which accompany the phase transitions and become significantly intensive in the superionic phase. These movements together with the drastically increased amplitudes of thermal vibrations (measured by Debye-Waller factor) assist the proton transport and thereby are responsible in great degree for the appearance of superprotonic conductivity [8].

The information obtained from available experiments, indicates the essentially important role of proton subsystem, first of all in the superionic phase transitions. Proton ordering and changes of its character after transitions to the low-temperature phases is the factor which should be considered primarily in the developing of theory of such transitions. Although more complete and consistent theory must take into account the orientation motions of ionic groups, the proton ordering model can be usable as the basic. Such approach was developed in [24,25], where by the treatment of protons interactions in the mean field approximation within the framework of lattice gas model the consideration of proton ordering in crystal $Rb_3H(SeO_4)_2$ at the transition from superionic phase $R\bar{3}m$ to low-temperature phase A2/a has been carried out. It should be noted, that thermodynamical description of such transition based on Landau expansion, with taking into account the interaction of formally introduced order parameters with lattice strain, has been proposed in

[26].

The aim of this work is the further development of the approach used in [24,25]. We will consider first of all the specific sequence of phase transitions from the superionic phase II to ferroelastic phases III and IV, which was observed in the $(NH_4)_3H(SeO_4)_2$ crystal. Using the structural data, the symmetry analysis of proton orderings in phases III and IV will be performed. On the basis of the model including the long-range proton interactions, the equilibrium states of proton system will be studied and the corresponding phase diagram determining the necessary conditions for theexistence of different proton orderings will be constructed. The investigations of thermodynamical functions, calculated in the mean field approximation, as well as the solving of equations for order parameters and calculation of their temperature dependences will be performed numerically. The obtained results will be compared with the conclusions resulting from the phenomenological theory based on Landau expansion.

2. Mean Field Approximation

The transitions from superionic to ferroelastic phases are primarily related to the changes of statistical distribution of protons over the lattice. In phases III, IV protons are placed within the hydrogen bonds with well defined positions. On the contrary, in superionic phase the number of available for protons positions increases considerably. The virtual hydrogen bonds network arises with the occupation probability 1/3 for each bond.

The characteristic features of proton arrangement in crystal structures of phases II, III and IV are illustrated in Figs.1-4 (we have used in this case the results of X-ray studies obtained by Pietraszko, Lukaszewicz, Augustyniak [6–8]). Rhombohedral coordinate system with lattice vectors $\vec{a}_1 = (-a\frac{\sqrt{3}}{2}, \frac{a}{2}, \frac{c}{3})$, $\vec{a}_2 = (a\frac{\sqrt{3}}{2}, \frac{a}{2}, \frac{c}{3})$, $\vec{a}_3 = (0, -a, \frac{c}{3})$ ($a = 8.399\AA$, $c = 22.904\AA$) was chosen as a basis (Fig.1). There are two SeO_4 groups and three possible proton positions (three virtual bonds) in primitive unit cell of phase II(Z=1, space group R$\bar{3}$ (C^2_{3i})). It is assumed that three virtual bonds $f = 1, 2, 3$ adjacent to the upper $(SeO_4)''$ group ($(SeO_4)''$ group lies at a distance $c/3$ along c-axis above the lower $(SeO_4)'$ group) belong to primitive unit cell with coordinate, given by vector $\vec{R}_m$ ($\vec{R}_m = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$). Hydrogen bonds, adjacent to $(SeO_4)'$, belong to the neighbouring unit cells with vectors $\vec{R}_m - \vec{a}_f$ (see Fig.2).

The transition from phase II to phase III (Z=2, space group C$\bar{1}$ (C^1_i)) is accompanied by doubling of elementary unit cell volume as well as the crystal lattice period along one of the directions given by vectors $\vec{a}_i$. Three possible orientation states are characterized by wave vectors $\{\frac{1}{2}\vec{b}_1, \frac{1}{2}\vec{b}_2, \frac{1}{2}\vec{b}_3\}$ which belong to $\{\vec{k}_4\}$ star (in Kovalev notations [27]). At every such state the proton positions are occupied in a definite manner. As an example, for the case $\vec{k}_4 = \frac{1}{2}\vec{b}_3$, the positions $f = 1$ or $f = 2$ are occupied in unit cell, with alternately change of these occupation numbers at translation along the $\vec{a}_3$ direction. The occupation of proton positions with the same indices f ($\vec{R}_{mf}$ and $\vec{R}_{mf} - \vec{a}_f$) is the characteristic feature of the pair $(SeO_4)'$ and $(SeO_4)''$ groups, which are the nearest neighbours along c-axis. As the result, the sequences of $(SeO_4)'$ and $(SeO_4)''$ dimers aligned along $\vec{a}_1$ and $\vec{a}_2$ directions arise (Fig.3).

The character of proton arrangement in phase IV is different. Now the same proton position in each lattice cell is occupied (see Fig.4). The three different orientation states of the crystal correspond to three possible directions of occupied hydrogen bonds as well as to sequences of hydrogen-bonded SeO_4 dimers. The hydrogen bonds along each sequence of dimers are shifted alteratively from it axis on the distance $\pm\delta$ ($\delta = 0.025b$) in the (a, b) plane. This is correlated with the rotations of neighbouring SeO_4 groups in opposite directions. The resulting structure modulation (in comparison with phase II) is characterized by $\{\vec{k}_8\}$ star, which consists of one vector $\vec{k}_8 = \frac{1}{2}(\vec{b}_1 + \vec{b}_2 + \vec{b}_3)$.

Orientation degrees of freedom, describing the SeO_4 groups motion, manifest themselves in the phase transition between superionic phases II and I. It is precisely to these rotations the ionic groups disordering and lattice symmetry increasing due to mirror planes appearance are related (the space group of phase I is R$\bar{3}$m (D^5_{3d}); $Z = 1$).

Restricting ourselves to the analysis of proton ordering only in sublattice of positions $\vec{R}_{mf}$, that provides a possibility to consider the phase transitions from phase II to III and IV, we will use in this work the mean field approximation taking into account the proton interactions.

As was done by [24,25], let's present this interaction in a bilinear form:

$$H_{int} = \frac{1}{2} \sum_{\substack{mm' \\ ff'}} \Phi_{ff'}(mm') n_{mf} n_{m'f'}, \tag{2.1}$$

where $n_{mf} = 0$ or 1 is the occupation number of proton in position f of unit cell m; $\Phi_{ff'}(mm')$ denotes the energy of pair interaction. The Hamiltonian of the protons system includes besides (2.1) the sum of single particle energies:

$$H_0 = \sum_{mf}(E-\mu)n_{mf}. \tag{2.2}$$

The proton chemical potential μ at the given average number of protons should be determined from the condition:

$$\sum_{mf}\bar{n}_{mf} = \bar{n}, \tag{2.3}$$

where $\bar{n}$ is the average protons number per unit cell. For the case of the $(NH_4)_3H(SeO_4)_2$-type crystals, which is considered here, $\bar{n}=1$.

In the mean field approximation

$$\hat{H}_{MF} = U_0 + \sum_{mf}\gamma_f(m)n_{mf} + \sum_{mf}(E-\mu)n_{mf}; \tag{2.4}$$

where

$$\begin{aligned} \gamma_f(m) &= \sum_{m'f'}\Phi_{ff'}(mm')\bar{n}_{m'f'}, \\ U_0 &= -\frac{1}{2}\sum_{\substack{mm'\\ ff'}}\Phi_{ff'}(mm')\bar{n}_{mf}\bar{n}_{m'f'}. \end{aligned} \tag{2.5}$$

The partition function Z and thermodynamical potential Ω for the system with Hamiltonian (2.4) are determined in an ordinary way:

$$\begin{aligned} Z &= \mathrm{Sp}\, e^{-\beta\hat{H}_{MF}} = \prod_{mf}\sum_{n_f=0,1} e^{-\beta(\gamma_f(m)+E-\mu)n_{mf}}e^{-\beta U_0} && (2.6)\\ \Omega &= -\Theta\ln Z = U_0 - \Theta\sum_{mf}\ln(1+e^{-\beta(\gamma_f(m)+E-\mu)}). && (2.7) \end{aligned}$$

Consequently

$$\bar{n}_{mf} = [e^{\beta(\gamma_f(m)+E-\mu)}+1]^{-1}, \tag{2.8}$$

whence follows the system of the selfconsistent equations for average occupation numbers $\bar{n}_{mf}$. It is easy to verify that solutions of system (2.8) satisfy on one side, the extremum conditions of thermodynamical potential Ω

$$\frac{\partial\Omega}{\partial\bar{n}_{m'f'}} = 0 \tag{2.9}$$

for the given value of chemical potential μ and, on other side, the conditions of extremum of free energy $F=\Omega+\mu\bar{n}N$ for the given average proton concentration $\bar{n}$:

$$\frac{\partial F}{\partial\bar{n}_{m'f'}} = 0 \tag{2.10}$$

(in the latter case it is necessary to take into account the dependence of μ on the average occupation number $\bar{n}_{m'f'}$, which follows from the condition (2.8)).

Let us express the average values $\bar{n}_{mf}$ as:

$$\bar{n}_{mf} = \frac{1}{3}\bar{n} + \delta\bar{n}_{mf}. \tag{2.11}$$

The deviations $\delta\bar{n}_{mf}$ of the proton occupation numbers from their average values become nonzero with the proton ordering.

Similarly to [24,25], for the description of ordering in phase III, we use the expansion in terms of the wave vector stars, which include star $\{\vec{k}_7=0\}$ in addition to the star $\{\vec{k}_4\}$. For the transition to the orientation state with vector $\vec{k}_3=\frac{1}{2}\vec{b}_3$, the representation

$$\begin{aligned} \delta\bar{n}_{1f} &= \frac{1}{\sqrt{2}}ue^{i\vec{k}_3\vec{R}_m} + \frac{1}{\sqrt{6}}v, \\ \delta\bar{n}_{2f} &= -\frac{1}{\sqrt{2}}ue^{i\vec{k}_3\vec{R}_m} + \frac{1}{\sqrt{6}}v, \\ \delta\bar{n}_{3f} &= -\frac{2}{\sqrt{6}}v \end{aligned} \tag{2.12}$$

makes possible to obtain the observed occupations of proton positions ($\bar{n}_{1m}=1$, $\bar{n}_{2m}=0$, $\bar{n}_{3m}=0$ or $\bar{n}_{1m}=0$, $\bar{n}_{2m}=1$, $\bar{n}_{3m}=0$) for the saturation values of order parameters u and v: $u=\pm\frac{1}{\sqrt{2}}$, $v=\frac{1}{\sqrt{6}}$. Here

$$u = \pm\frac{1}{\sqrt{2}}\langle n_{m1}-n_{m2}\rangle; \qquad v = \frac{1}{\sqrt{6}}\langle n_{m1}+n_{m2}-2n_{m3}\rangle. \tag{2.13}$$

Analogously, for the transitions corresponding to vectors $\vec{k}_1=\frac{1}{2}\vec{b}_1$ and $\vec{k}_2=\frac{1}{2}\vec{b}_2$

$$\begin{aligned} \delta\bar{n}_{1f} &= -\frac{2}{\sqrt{6}}v \\ \delta\bar{n}_{2f} &= \frac{1}{\sqrt{2}}ue^{i\vec{k}_1\vec{R}_m} + \frac{1}{\sqrt{6}}v, \\ \delta\bar{n}_{3f} &= -\frac{1}{\sqrt{2}}ue^{i\vec{k}_1\vec{R}_m} + \frac{1}{\sqrt{6}}v, \end{aligned} \tag{2.14}$$

and

$$
\begin{aligned}
\delta\bar{n}_{1f} &= \frac{1}{\sqrt{2}} u e^{i\vec{k}_2\vec{R}_m} + \frac{1}{\sqrt{6}} v, \\
\delta\bar{n}_{2f} &= -\frac{2}{\sqrt{6}} v \\
\delta\bar{n}_{3f} &= -\frac{1}{\sqrt{2}} u e^{i\vec{k}_2\vec{R}_m} + \frac{1}{\sqrt{6}} v.
\end{aligned}
\tag{2.15}
$$

The resulting orderings are induced by the irreducible representation $A_g(\tau_1)$ of the wave vector group $G_{\vec{k}_i}$ as well as by the representation $E_g(\tau_3+\tau_5)$ of the point group $G_{\vec{k}_7=0}$. In fact, in a general case the deviation can be written as

$$
\begin{aligned}
\delta\bar{n}_1 &= \frac{1}{\sqrt{2}}[u_3 e^{i\vec{k}_3\vec{R}_m} - u_2 e^{i\vec{k}_2\vec{R}_m}] + \frac{1}{3}(\eta+\zeta), \\
\delta\bar{n}_2 &= \frac{1}{\sqrt{2}}[u_1 e^{i\vec{k}_1\vec{R}_m} - u_3 e^{i\vec{k}_3\vec{R}_m}] + \frac{1}{3}(\varepsilon^2\eta+\varepsilon\zeta), \\
\delta\bar{n}_3 &= \frac{1}{\sqrt{2}}[u_2 e^{i\vec{k}_2\vec{R}_m} - u_1 e^{i\vec{k}_1\vec{R}_m}] + \frac{1}{3}(\varepsilon\eta+\varepsilon^2\zeta),
\end{aligned}
\tag{2.16}
$$

($\varepsilon = e^{i2\pi/3}$); the variables

$$
\begin{aligned}
\eta &= \bar{n}_1 + \varepsilon\bar{n}_2 + \varepsilon^2\bar{n}_3, \\
\zeta &= \bar{n}_1 + \varepsilon^2\bar{n}_2 + \varepsilon\bar{n}_3
\end{aligned}
\tag{2.17}
$$

are transformed according to the E_g representation under point group operations. Setting

$$
\eta = |\eta|e^{i\psi}; \qquad \zeta = |\eta|e^{-i\psi}, \tag{2.18}
$$

we have

$$
\begin{gathered}
\eta+\zeta = 2|\eta|\cos\psi; \\
\varepsilon^2\eta+\varepsilon\zeta = 2|\eta|\cos(\psi-\frac{2\pi}{3}); \qquad \varepsilon\eta+\varepsilon^2\zeta = 2|\eta|\cos(\psi-\frac{4\pi}{3}).
\end{gathered}
\tag{2.19}
$$

The choice $|\eta| = \sqrt{\frac{3}{2}}v$; $\psi = \{\frac{\pi}{3}; \pi; -\frac{\pi}{3}\}$ (and in addition $u_f = \{u\delta_{f3}, u\delta_{f1}, u\delta_{f2}\}$) corresponds to the presented above orientation states (2.12)-(2.15).

The identical character of proton positions occupation in each unit cell is an inherent feature of the proton ordering in phase IV in spite of the appearance of superstructure with vector $\vec{k}_8$ due to the space modulation of the SeO$_4$ groups rotation angles. Therefore, the change in symmetry of proton distribution in phase IV, in comparison with phase II, may be formally connected with one of the irreducible representations of group $G_{\vec{k}=0}$, with taking into consideration only the proton subsystem (the results obtained on this assumption remain valid after including of orientation degrees of freedom into model since the wave vector groups $G_{\vec{k}=0}$ and $G_{\vec{k}_8}$ are the same). For the basis (n_1, n_2, n_3) only two-dimensional irreducible representation E_g is suitable.

In this case the expressions for deviations $\delta\bar{n}_f$ can be deduced from (2.16) with restriction to uniform terms only:

$$
\begin{aligned}
\delta\bar{n}_1 &= \frac{1}{3}(\eta+\zeta) = \frac{2}{3}|\eta|\cos\psi, \\
\delta\bar{n}_2 &= \frac{1}{3}(\varepsilon^2\eta+\varepsilon\zeta) = \frac{2}{3}|\eta|\cos(\psi-\frac{2\pi}{3}), \\
\delta\bar{n}_3 &= \frac{1}{3}(\varepsilon\eta+\varepsilon^2\zeta) = \frac{2}{3}|\eta|\cos(\psi-\frac{4\pi}{3}).
\end{aligned}
\tag{2.20}
$$

The values $|\eta| = 1$ and $\psi = 0, \frac{2\pi}{3}, \frac{4\pi}{3}$ correspond to three orientation states with $\bar{n}_{mf} = (1,0,0), (0,1,0)$ and $(0,0,1)$ respectively.

Thus, the expressions (2.16) for the deviations of proton occupation numbers include the cases of all three phases (II, III and IV). In particular, the representation of $\delta\bar{n}_{mf}$ in the form (2.12) gives the possibility to describe beside the ordering corresponding to orientation state with vector $\vec{k}_3$ of phase III (for $u \neq 0$, $v \neq 0$), also the ordering with $\bar{n}_{mf} = (0,0,1)$ for phase IV (with $u = 0$, $v \neq 0$ and saturation value $v = -\frac{2}{\sqrt{6}}$).

Our further consideration will be devoted to more elaborate investigation of orderings given by expressions (2.12). We will use this representation for deriving in explicit form the equations for proton average occupation numbers and thermodynamic functions in the mean field approximation.

After substitution (2.12) in (2.4) and (2.5), we obtain:

$$
\begin{aligned}
\gamma_1(m) &= \gamma_0 + av + b e^{i\vec{k}_3\vec{R}_m} u \\
\gamma_2(m) &= \gamma_0 + av - b e^{i\vec{k}_3\vec{R}_m} u \\
\gamma_3(m) &= \gamma_0 - 2av.
\end{aligned}
\tag{2.21}
$$

Here

$$\begin{aligned}
\gamma_0 &= \frac{1}{3}\bar{n}\sum_{f'}\Phi_{ff'}(0),\\
a &= \frac{1}{\sqrt{6}}[\varphi_{11}(0)-\varphi_{12}(0)], \qquad (2.22)\\
b &= \frac{1}{\sqrt{2}}[\varphi_{11}(\vec{k}_3)-\varphi_{12}(\vec{k}_3)],
\end{aligned}$$

where

$$\varphi_{ff'}(\vec{k}) = \sum_{m'}\Phi_{ff'}(mm')e^{-i\vec{k}(\vec{R}_m-\vec{R}_{m'})},$$

is the Fourier transform of proton interaction matrix. In this case

$$U_0 = -\frac{N}{2}\gamma_0 - \frac{N}{2}\sqrt{6}av^2 - \frac{N}{2}\sqrt{2}bu^2. \tag{2.23}$$

The quantities u and v play here a role of the order parameters. The thermodynamic equilibrium conditions (2.9) or (2.10) can be written here as minimum conditions with respect to parameters u and v:

$$\frac{\partial}{\partial u}\Big(\frac{1}{N}F\Big)= 0; \qquad \frac{\partial}{\partial v}\Big(\frac{1}{N}F\Big)= 0, \tag{2.24}$$

and

$$\lambda_\mu > 0,$$

where λ_μ are the eigenvalues of matrix

$$\Delta_2 F = \begin{pmatrix} \dfrac{\partial^2 F}{\partial u^2} & \dfrac{\partial^2 F}{\partial u \partial v}\\ \dfrac{\partial^2 F}{\partial v \partial u} & \dfrac{\partial^2 F}{\partial v^2}\end{pmatrix}$$

With the explicit form of the free energy F as a function of order parameters u and v:

$$\begin{aligned}
\frac{1}{N}F &= \frac{1}{N}U_0 - \Theta\Big[\ln(1+\frac{1}{y}e^{-\beta(av+bu)}) + \qquad (2.25)\\
&\ln(1+\frac{1}{y}e^{-\beta(av-bu)}) + \ln(1+\frac{1}{y}e^{2\beta av})\Big] + \mu\bar{n},
\end{aligned}$$

where $y = e^{\beta(E-\mu+\gamma_0)}$, the following system of equations for u and v parameters is derived:

$$\begin{aligned}
u &= \frac{1}{\sqrt{2}}\Big[\frac{1}{ye^{\beta(av+bu)}+1} - \frac{1}{ye^{\beta(av-bu)}+1}\Big], \qquad (2.26)\\
v &= \frac{1}{\sqrt{6}}\Big[\frac{1}{ye^{\beta(av+bu)}+1} + \frac{1}{ye^{\beta(av-bu)}+1} - \frac{y}{ye^{-2\beta av}+1}\Big].
\end{aligned}$$

The parameter y can be obtained from the equation

$$\frac{1}{ye^{\beta(av+bu)}+1} + \frac{1}{ye^{\beta(av-bu)}+1} + \frac{1}{ye^{-2\beta av}+1} = \bar{n}, \tag{2.27}$$

which follows from (2.8).

The equations (2.26) and (2.27) give the possibility to investigate the equilibrium distributions of protons for arbitrary average proton number $\bar{n}$. Further we shall pay our attention to the case $\bar{n} = 1$, restricting only to the case of ideal crystals.

The solving of the systen of equations(2.26), (2.27), the analysis of extremums and search for the minima as well as selection of absolute minima of the function F was performed numerically.

Examinations of function $F(u,v)$ profiles for different values of ratio $\tilde{b} = b/a$ revealed that for $\tilde{b} < \tilde{b}^* = \sqrt{3}$ the transition to phase IV with $u = 0, v \neq 0$ occurs and for $\tilde{b} > \tilde{b}^*$ the transition to the ordered state corresponding to phase III $u \neq 0, v \neq 0$ takes place. In the first case the free energy surface have one absolute minimum for saturation value $u = 0, v = -\frac{2}{\sqrt{6}}$ besides the local minimum at a point $u = 0, v = 0$ (see Fig.5). With the temperature increase the depths of minima $u = 0, v \neq 0$ and $u = 0, v = 0$ are redistributed, becoming equal in a point of phase transition, which thereby is of the first order. In the latter case two absolute symmetrical minima with coordinates $u = \pm\frac{1}{\sqrt{2}}$, $v = \frac{1}{\sqrt{6}}$ in saturation state exist (Fig.6). The order of transition to phase III changes from first for $\tilde{b}^* < \tilde{b} < \tilde{b}_c$ to second for $\tilde{b} > \tilde{b}_c$, which points up the existence of three-critical point with coordinates $(\tilde{b}_c \simeq 2.07, \tau_c = \frac{T_c}{|a|} \simeq 0.65)$. For $\tilde{b} = \tilde{b}^*$ all three absolute minima of free energy for $T < T_c$ coexist with equal depth (Fig.7).

All these results can be shown in the form of phase diagram $(\tau, \tilde{b})$ (see Fig.8), where $\tau = \frac{T}{|a|}$, with the indication of coexistence curves for different phases and critical points. The line of coexistence of phases III and IV $\tilde{b} = \tilde{b}^*$ is in this case parallel to the ordinate axis.

Results of the temperature dependences calculation of parameters u and v(performed with the elimination of chemical potential with the help of (2.27)) are presented in Fig.10 and 11 for various values of $\tilde{b}$.

In the same figures one can see the temperature dependences of the proton positions average occupation numbers $\bar{n}_1$, $\bar{n}_2$ and $\bar{n}_3$. As may be seen, after transition to phases III or IV these occupancies approach corresponding saturation values ($\bar{n}_{1(2)} = 1$, $\bar{n}_{2(1)} = 0$, $\bar{n}_3 = 0$ or $\bar{n}_1 = \bar{n}_2 = 0$, $\bar{n}_3 = 1$).

The temperature dependences of the entropy $S = -\frac{\partial F}{\partial t}$ are illustrated in Fig.9 for the cases of transitions to phase III or IV. The resulting entropy change after transition from disordered phase II to phase III amounts to 1.9R, which exceeds the above mentioned value of configurational entropy for transitions with ordering in one of three possible positions. This discrepancy is connected with using of the mean field approximation and consequent averaging procedure in our calculations.

3. Landau expansion

It is reasonable to compare the results obtained in the mean field approximation, with the general thermodynamic criterions, which can be deduced from the Landau expansion of thermodynamical potential or free energy in terms of parameters u and v. Such an expansion is a special case of more general expansion in terms of u_1, u_2, u_3 components and variables η, ζ (or $|\eta|$ and ψ).

The form of the latter can be determined from the symmetry analysis:

$$\begin{aligned}
&\frac{1}{N}F = f_0 + \alpha(u_1^2+u_2^2+u_3^2) + \beta|\eta|^2 + \\
&\gamma[u_1^2\cos\psi + u_2^2\cos(\psi-\frac{2\pi}{3}) + \\
&u_3^2\cos(\psi-\frac{4\pi}{3})]|\eta| + \delta|\eta|^3\cos(3\psi) + \chi(u_1^4+u_2^4+u_3^4) + \\
&\rho(u_2^2u_3^2+u_3^2u_1^2+u_1^2u_2^2) + \mu[u_1^2(\cos^2(\psi-\frac{4\pi}{3})+\cos^2(\psi-\frac{2\pi}{3})) \\
&+u_2^2(\cos^2\psi+\cos^2(\psi-\frac{4\pi}{3})) + u_3^2(\cos^2(\psi-\frac{2\pi}{3})+\cos^2\psi)]|\eta|^2 \\
&+\nu|\eta|^4.
\end{aligned} \tag{3.1}$$

The order parameters can be evaluated from the equilibrium conditions

$$\frac{\partial}{\partial u_i}\Big(\frac{1}{N}F\Big) = 0; \quad \frac{\partial}{\partial|\eta|}\Big(\frac{1}{N}F\Big) = 0; \quad \frac{\partial}{\partial\psi}\Big(\frac{1}{N}F\Big) = 0 \tag{3.2}$$

Among the possible solutions of this system of equations there are following:

$$\begin{aligned}
&1)\quad u_1 \neq 0, u_2 = u_3 = 0; \quad \sin\psi = 0 \\
&2)\quad u_2 \neq 0, u_1 = u_3 = 0; \quad \sin(\psi-\frac{2\pi}{3}) = 0 \\
&3)\quad u_3 \neq 0, u_1 = u_2 = 0; \quad \sin(\psi-\frac{4\pi}{3}) = 0 \\
&4)\quad u_1 = u_2 = u_3 = 0; \quad \sin 3\psi = 0
\end{aligned} \tag{3.3}$$

The first three of them correspond to the phase ψ values π, $-\frac{\pi}{3}$ and $\frac{\pi}{3}$,respectively, and are concerned to the three different orientation states of the phase III (see equation (2.17)). The last solution includes the possible orientation states of the phase IV with $\psi = 0, \frac{2\pi}{3}, \frac{4\pi}{3}$.

The free energy expansion in terms of u and v parameters

$$\frac{1}{N}F = f = \frac{1}{2}\alpha_1 v^2 + \frac{1}{2}\alpha_2 u^2 + \gamma_1 v^3 + \gamma_2 v u^2 + \delta_1 v^4 + \delta_2 v^2u^2 + \delta_3 u^4 \tag{3.4}$$

corresponds to the orderings described by expressions (2.12). This expansion can be derived from (3.1) with the constraint $u_1 = u_2 = 0; u_3 = u$ and with the use of relations (2.17). The expression (3.4) is the general form of Landau expansion describing the transitions into the given orientation state. Formulae (2.25) and (2.27) provides the possibility of determination of microscopic expressions for Landau expansion coefficients in the mean field approximation:

$$\begin{aligned}
&\alpha_1 = -\sqrt{6}a - \frac{4}{3}\beta a^2; \quad \alpha_2 = -\sqrt{2}b - \frac{4}{9}\beta b^2 \\
&\gamma_1 = \frac{2}{27}\beta^2|a|^3; \quad \gamma_2 = -\frac{2}{27}\beta^2|a|b^2 \\
&\delta_1 = \frac{5}{54}\beta^3a^4; \quad \delta_2 = \frac{5}{81}\beta^3a^2b^2; \quad \delta_3 = \frac{5}{6\cdot 81}\beta^3b^4.
\end{aligned} \tag{3.5}$$

Standard thermodynamical analysis of expansion (3.4) with the help of equilibrium conditions:

$$\frac{\partial f}{\partial u} = 0; \qquad \frac{\partial f}{\partial v} = 0 \tag{3.6}$$

and corresponding stability criterions determines the areas of existence of different orderings and, therefore, possible phases of system.

The solution $u = 0, v = 0$ (phase II) is stable in the region of the temperature and the interaction parameters values a and b determined from inequalities:

$$\alpha_1 > 0, \qquad \alpha_2 > 0. \tag{3.7}$$

Equation $\alpha_2 = 0$ gives the temperature of transition into the state with $u \neq 0, v \neq 0$ (phase III) in the case of second order phase transition ($\Theta_c^{(2)} = \frac{4}{9\sqrt{2}}|b|$). This takes place for $\tilde{b} > \tilde{b}_c$. When $\Theta \leq \Theta_c^{(2)}$

$$\begin{aligned} \alpha_2 &\sim |\Theta_c^{(2)} - \Theta_c| \\ v &\approx \frac{\gamma_2\alpha_2}{4\delta_3\alpha_1 - 2\gamma_2^2} \sim |\Theta_c^{(2)} - \Theta_c| \\ u &\approx \left[-\frac{\alpha_2}{4\delta_3} - \frac{2\gamma_2}{4\delta_3}v\right]^{\frac{1}{2}} \sim |\Theta_c^{(2)} - \Theta_c|^{\frac{1}{2}} \end{aligned} \tag{3.8}$$

The transition from disordered phase to the state with $u = 0, v \neq 0$ (phase IV) is of the first order. Temperature of transition $\Theta_c^{(1)}$ is determined from the condition:

$$2\alpha_1\delta_1 = \gamma_1^2,$$

and a jump of the order parameter v in this case is equal to

$$v_0 = -\frac{\gamma_1}{2\delta_1}.$$

Using the relations (3.5) we get

$$\Theta_c^{(1)} = 1.022\Theta_{c0}^{(1)}; \qquad v_0 = -\frac{8}{15\sqrt{6}}, \tag{3.9}$$

where $\Theta_{c0}^{(1)} = \frac{4}{3\sqrt{6}}|a|$.

On cooling a phase transition from disordered phase to the states ($u \neq 0, v \neq 0$) and ($u = 0, v \neq 0$) occurs when $b/a > \sqrt{3}$ and $b/a < \sqrt{3}$ respectively. The equation

$$b/a = \sqrt{3} \tag{3.10}$$

determines the coexistence curve of phases III and IV, along which the first order phase transition takes place.

In phase diagram $(\frac{T}{|a|}, \frac{b}{a})$ this curve is parallel to the temperature axis for the considered model. Thus it is evident that the considering of only the long-range proton interactions for the proton orderings investigation can not be sufficient for the description of phase transition between the phases III and IV, which occurs with temperature change.

4. Final Conclusions

There exists an agreement of the results obtained using Landau expansion of free energy and presented above data of numerical calculations. Phenomenological approach with the using of the microscopic expressions for expansion coefficients in the mean field approximation, gives confirmation of the form of phase diagram presented in Fig.8 as well as the character of phase transitions. The qualitative changes in the form of phase diagram and phase transition sequence may appear in the case of going beyond the framework of the mean field approximation through the including of short range proton correlations. The considering of the proton interaction with other (for example, orientation) degrees of freedom and lattice deformation also extends the possibilities of applications of proton ordering model.

In general, however the proposed proton ordering model covers the main features of transitions from superionic phase II to ferroelastic phases III and IV in $(NH_4)_3H(SeO_4)_2$ crystal and similar compounds, giving the explanation of the principal changes of proton arrangements. This model can be basic for further consideration of proton dynamics as well as for investigation of the mechanism of proton transport through lattice in different phases.

Acknowledgements

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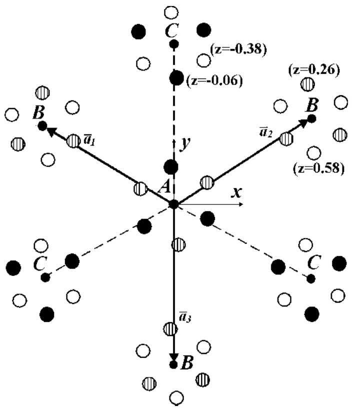

Figure 1: Projection of the rhombohedric primitive cell of the crystal $(NH_4)_3H(SeO_4)_2$ with lattice vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ on the (001) plane in the hexagonal coordinate system in phase II. The big circles correspond to the possible positions of O(2) oxygens; A ($z = 0$), B ($z = 1/3$) and C ($z = -1/3$) denote the positions of Se atoms in SeO_4' groups.

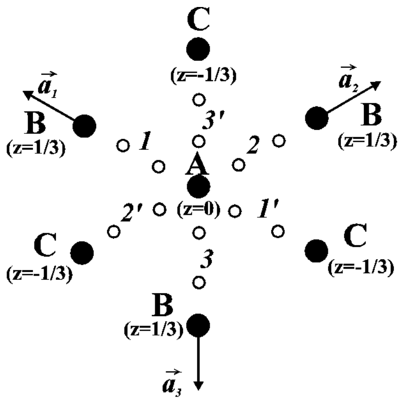

Figure 2: Network of the virtual hydrogen bonds in the phase II. 1, 2 and 3 ($z = 0.27$) denote the hydrogen bonds in the unit cell $\vec{R}_m$, the bonds marked by $1'$, $2'$ and $3'$ ($z = -0.07$) belong to the neighbouring unit cells $\vec{R}_m - \vec{a}_1$, $\vec{R}_m - \vec{a}_2$ and $\vec{R}_m - \vec{a}_3$ respectively.

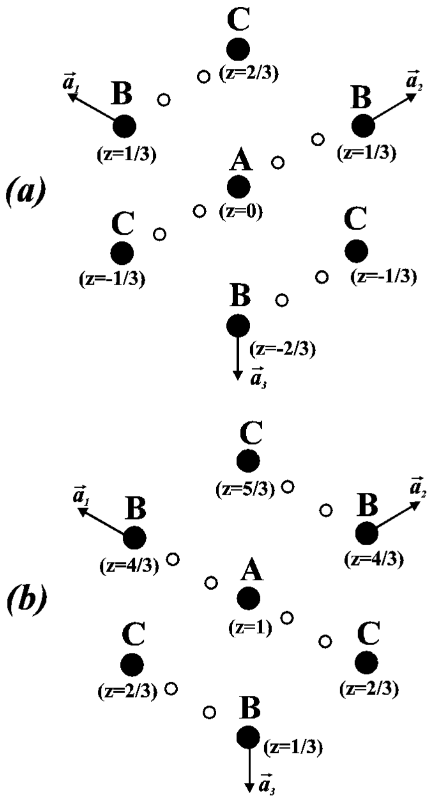

Figure 3: Projection of the hydrogen bonds network structure of $(NH_4)_3H(SeO_4)_2$ crystal on the (001) plane in the hexagonal coordinate system in phase III; the hydrogen bonds form the sequences along $\vec{a}_1$ and $\vec{a}_2$ directions with the step height $c/3$. Cases (a) and (b) are distinguished by the translation on c along hexagonal axis; the structural modulation corresponds to doubling of lattice period along $\vec{a}_3$ direction.

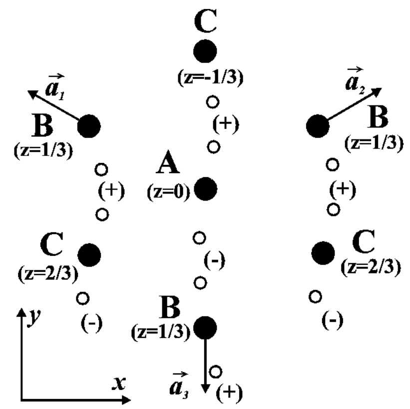

Figure 4: Projection of the hydrogen bonds network structure of $(NH_4)_3H(SeO_4)_2$ crystal on the (001) plane in the hexagonal coordinate system in phase IV; the hydrogen bonds $\{+,-,+,...\}$ form the sequences along $\vec{a}_3$ direction with the step height $c/3$; $x(+)-x(-)=0.05$.

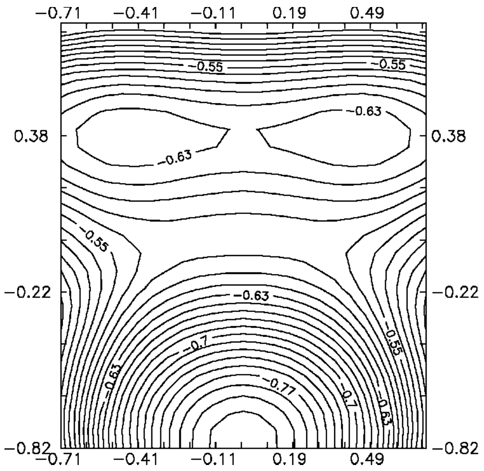

Figure 5: Free energy as a function of u and v for $\tilde{b}=1$, $\tau=0.3$.

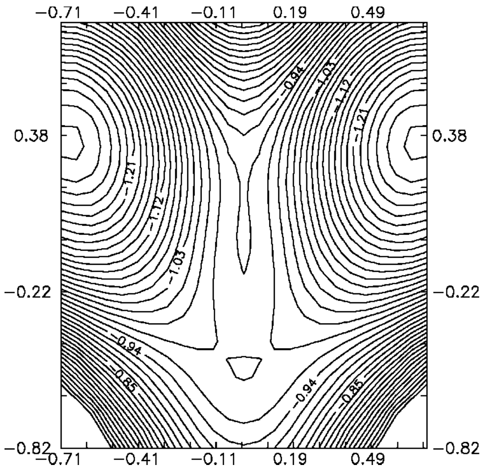

Figure 6: Free energy as a function of u and v for $\tilde{b}=3$, $\tau=0.5$.

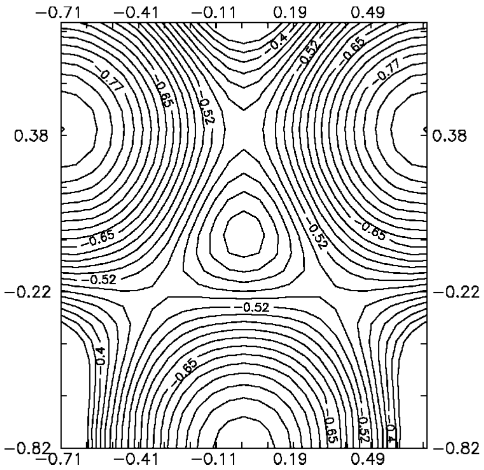

Figure 7: Free energy as a function of u and v for $\tilde{b}=1.9$, $\tau=0.2$.

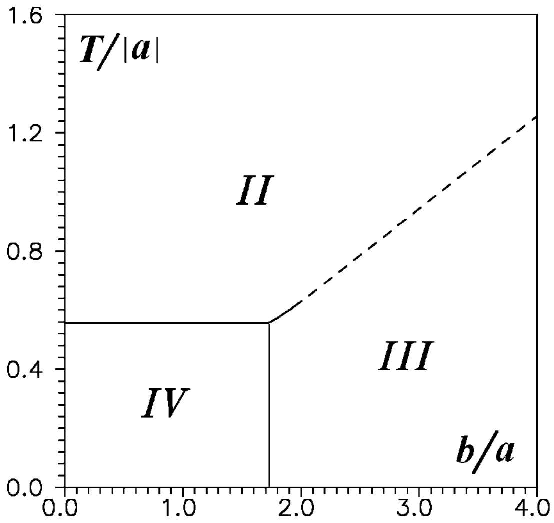

Figure 8: Phase diagram (τ, $\tilde{b}$), the solid and dashed lines indicate the first and second order phase transitions respectively.

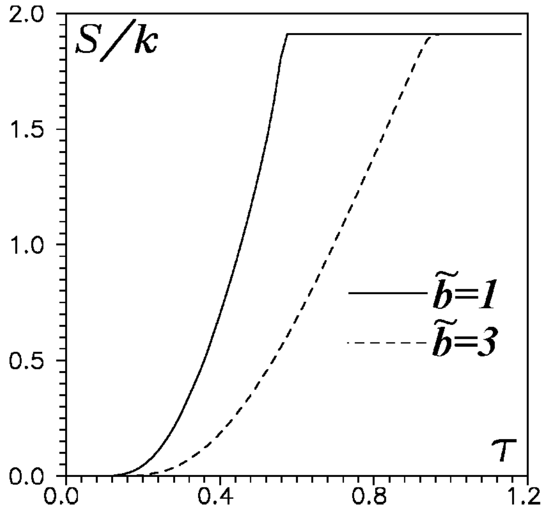

Figure 9: Temperature dependence of the entropy at the phase transitions from phase II to phase III ($\tilde{b} = 3$) and phase IV ($\tilde{b} = 1$).

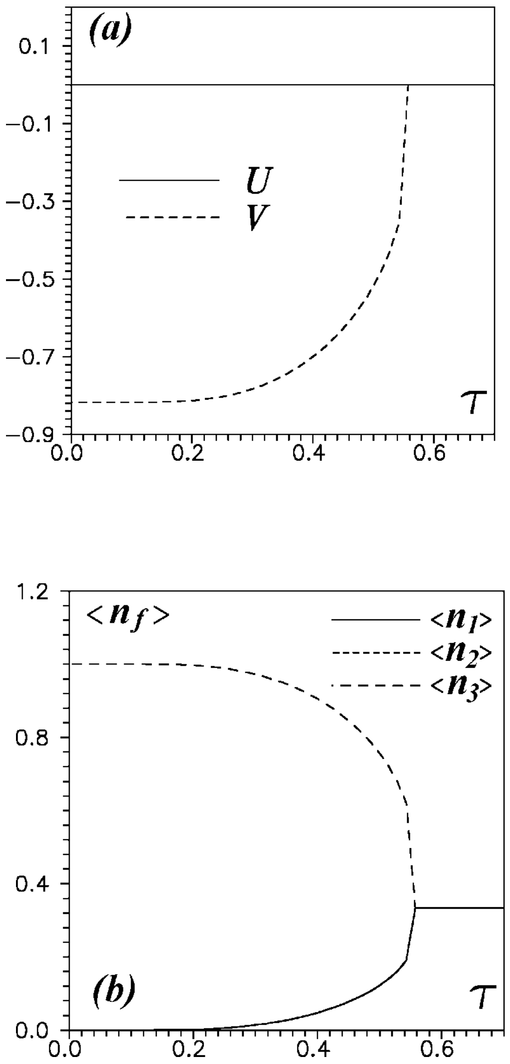

Figure 10: Dependence of (a) the order parameters and (b) the proton average occupation numbers on τ for $\tilde{b} = 1$ (the case of the first order phase transition from disordered phase II to phase IV).

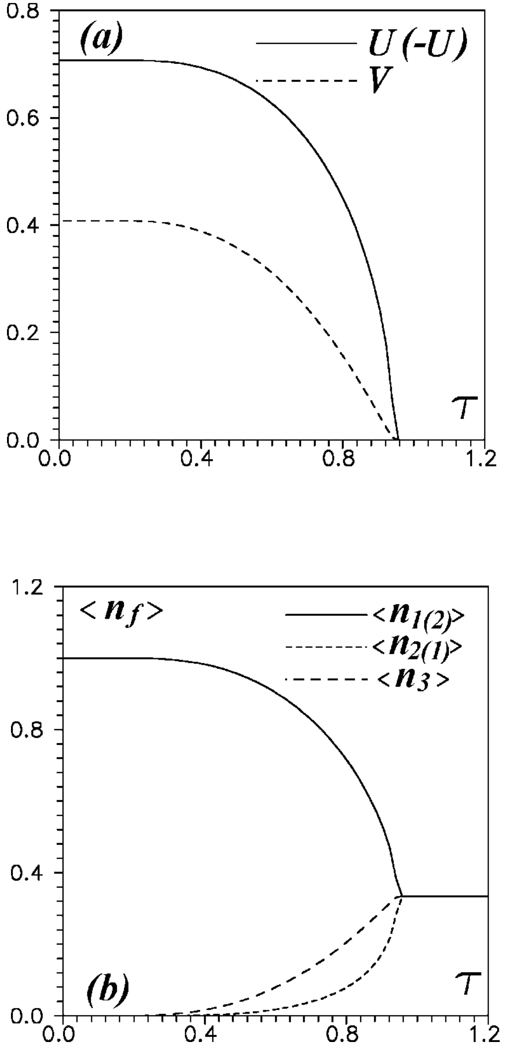

Figure 11: Dependence of (a) the order parameters and (b) the proton average occupation numbers on τ for $\tilde{b} = 3$ (the case of the second order phase transition from disordered phase II into phase III).

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Модель протонного впорядкування для опису суперіонного фазового переходу у кристалі $(NH_4)_3H(SeO_4)_2$

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