

# Influence of inter-chain correlations on proton ordering in $\text{MeHXO}_4$ protonic conductors

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## Abstract

Energy spectrum and thermodynamics of the proton subsystem of the crystal with chains of hydrogen bonds are investigated. The consideration is based on the orientational-tunneling model, which includes two types of proton transfer. The strong short-range interactions and the influence of the internal ordering field arising due to the inter-chain correlations are taken into account. It is shown that under certain conditions the uniform proton distribution along the chain becomes unstable. A possible explanation of the precursor effect observed in the  $\text{CsDSO}_4$  crystal at temperatures below the superionic transition point is proposed. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Due to the intensive experimental investigations of the proton conductivity in the crystalline and molecular systems and the discovery of the new materials (superionic crystals with hydrogen bonds, quasi-one-dimensional proton conductors), the problem of the importance of the proton transfer in the thermodynamics and energy spectrum of such objects as well as in phase transitions in the proton subsystem becomes actual. In recent years, the approaches explicitly taking into account the dynamics of the proton jumps besides the short-range and

long-range interactions between protons are developed. Direct inclusion of the proton transfer into the Hamiltonian of the system has an essential influence on the proton energy spectrum that possesses in this case a band structure. On the other hand, proton–proton interactions can lead to the superionic phase transitions, which are connected usually with the order–disorder transformation in the subsystem of the virtual hydrogen bonds. Moreover, in this case, protons change their states from the localized to delocalized ones.

An interesting feature of the superionic phase transitions in the  $\text{MeHXO}_4$  system ( $\text{Me}=\text{Cs}, \text{Rb}, \text{NH}_4$ ;  $\text{X}=\text{S}, \text{Se}$ ) is the precursor effect reported recently for  $\text{CsDSO}_4$ . A considerable deviation from the ordered hydrogen bond structure was observed far below the temperature of the superionic phase transition  $T_s$  (in the temperature range of 40 K). The

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ideal zigzag chain structure of the hydrogen bonds (A-positions), which is a characteristic of the low-temperature phase II [1], is transformed into a partially disordered one. Some deuterons become redistributed and occupy the inter-chain B-positions [2] (see also Ref. [3]). The evidences of such behaviour of protons were obtained by the 2-D NMR deuteron spectroscopy [2,3]. This effect is also visible as a broadening of the half-width of the DSO Raman bands [4].

In the present work, the so-called orientational-tunneling model (which is the generalization of the lattice gas model) is used for consideration of the abovementioned effect. The model is based on the two-stage Grotthuss mechanism of the proton transfer; the short-range proton correlations (of the Slater–Takagi interaction type) are taken into account. Investigation of the proton energy spectrum and thermodynamics of model is performed at different proton concentrations in the quasi-one-dimensional case, when one considers the molecular chains of the ionic groups consecutively connected by the hydrogen bonds. The influence of the internal field (appearing due to the inter-chain interactions) on the stability of the chain structure of hydrogen bonds is studied. On the basis of the obtained results, the possible mechanism of the precursor effect in the CsDSO<sub>4</sub> crystal is discussed.

## 2. Orientational-tunneling model

Investigation of the energy spectrum and thermodynamics of the proton (deuteron) subsystem of the hydrogen-bonded chain of ionic groups is based in this work on the orientational-tunneling model. The

model was introduced in Ref. [5] (see also Ref. [6]) to describe the linear molecular complexes with hydrogen bonds (Fig. 1). It includes two types of transfer: the tunneling-like hopping between two equilibrium  $a$  and  $b$  positions of proton (deuteron) on the bond ( $\Omega_0$ ) and reorientational jumps between bonds ( $\Omega_R$ ). The short-range interactions caused by the differences between the energies of the proton configurations near ionic groups (see Fig. 2) as well as the energies of the creation of D- and L-defects are taken into account. The role of the internal ordering field is considered (in the case of the CsDSO<sub>4</sub> crystal deuterons occupy only  $a$  (or  $b$ ) positions along the given...SO<sub>4</sub>–O–SO<sub>4</sub>–O–SO<sub>4</sub>...chain in the low-temperature phase; that is the consequence of the inter-chain interaction).

The Hamiltonian of the model in the second quantization representation has the following form:

$$H = H_c + H_t + H_d + H' - \mu N, \quad (1)$$

where

$$\begin{aligned} \hat{H}_c &= \sum_i [\varepsilon(1 - n_{ib})n_{i+1,a} + \varepsilon n_{ib}(1 - n_{i+1,a}) \\ &\quad + wn_{ib}n_{i+1,a} + w'(1 - n_{ib})(1 - n_{i+1,a})] \\ \hat{H}_t &= \sum_i [\Omega_0(c_{ia}^+c_{ib} + c_{ib}^+c_{ia}) \\ &\quad + \Omega_R(c_{ib}^+c_{i+1,a} + c_{i+1,a}^+c_{ib})] \\ \hat{H}_d &= \sum_i [Un_{ia}n_{ib} + V(1 - n_{ia})(1 - n_{ib})] \\ H' &= h \sum_i (n_{ia} - n_{ib}) \\ \hat{N} &= \sum_i (n_{ia} + n_{ib}). \end{aligned} \quad (2)$$

Here,  $n_{i\alpha}$  ( $\alpha = a, b$ ) is the proton occupation number in the  $\alpha$  position on the  $i$  bond;  $c_{i,\alpha}$  ( $c_{i,\alpha}^+$ )

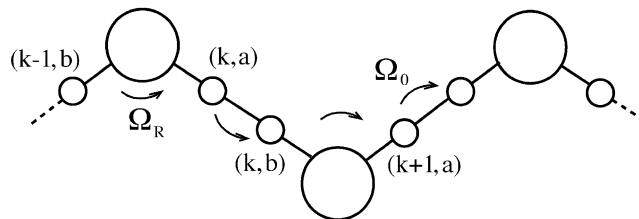


Fig. 1. Proton conductor model. Large circles correspond to the ionic groups (A), small ones to the possible positions of protons.

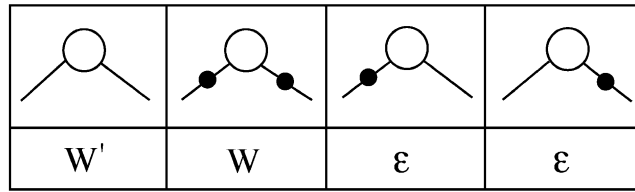


Fig. 2. Energies of the proton configurations with the different number of protons in the equilibrium positions near the ionic group.

are the proton annihilation (creation) operators;  $U$  and  $V$  are energies of the D- (two protons on the bond) and L- (a broken bond) defects, respectively;  $w$ ,  $\varepsilon$  and  $w'$  are energies of the configurations with two, one and without protons near the ionic groups (see Fig. 2).

Model (1) (without the proton transfer) was used for the description of the superionic phase transitions [7,8]. On its basis, a calculation of the conductivity coefficients for the  $(\text{NH}_4)_2\text{H}(\text{XO}_4)_3$  ( $\text{X}=\text{S}, \text{Se}$ ) family of the superionic crystals was performed [9,10].

The energy spectrum of the orientational-tunneling model (similar to other fermionic lattice models [11]) has a band character and its structure is determined by the ratio of the effective transfer parameter  $\Omega_{\text{ef}}$  ( $\Omega_{\text{ef}} = \Omega_0, \Omega_R$ ) to the characteristic energy of the short-range interaction  $\bar{W}_s$ , which is determined by the interaction constants  $w, w', U, V$  and is of the order of proton energies  $\varepsilon_\alpha$  (see below).

In the case when  $\Omega_{\text{ef}} \gg \bar{W}_s$ , the interaction between protons can be taken into account in the mean field approximation (MFA). It shifts the proton energy bands and can also lead to the splitting of the bands at the transition to the low-temperature ordered phases. Such approach was utilized in Ref. [9] for the calculation of the dispersion curves  $E(\vec{k})$  for the proton bands, which describes the motion of protons in the quasi-two-dimensional layers of the hydrogen bonds in  $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$  crystal.

Otherwise (when  $\Omega_{\text{ef}} \ll \bar{W}_s$ ), the proton correlation leads to the additional splitting in spectra. This result is well known for the Hubbard model and the similar ones [12]. Corresponding theoretical investigations cannot be performed in the MFA; it has to be based on the allowance for the short-range interactions in the zero approximation. The cluster approximation and its generalization are used for this purpose in the present work.

### 3. Proton energy spectrum in cluster approximation

We use the thermodynamical perturbation theory performing the expansion in terms of the transfer parameters  $\Omega_0$  and  $\Omega_R$ . Calculation of the proton energy spectrum at the different proton concentrations is performed using the Green's function method. The cluster expansion approach is utilized.

In the Hubbard-I type approximation [13], we obtain

$$E_\alpha^\pm(k) = \varepsilon_\alpha \pm \sqrt{h^2 + C_\alpha^a C_\alpha^b |t_{ab}(k)|^2} - \mu \quad (3)$$

$$|t_{ab}(k)| = [\Omega_0^2 + \Omega_R^2 + 2\Omega_0\Omega_R \cos ka]^{1/2}, \quad (4)$$

( $a$  is a lattice constant of a chain;  $\vec{k}$  is a wave vector). Energy spectrum consists of eight subbands (in the approach we use, they are independent). The splitting of spectrum is caused by the dependence of the proton energy at the given site on the occupancy of the neighbouring positions (there are four possible configurations). Proton site energies

$$\begin{aligned} \varepsilon_1 &= \varepsilon - w' - V, \\ \varepsilon_2 &= \varepsilon - w' + U, \\ \varepsilon_3 &= -\varepsilon + w - V, \\ \varepsilon_4 &= -\varepsilon + w + U, \end{aligned} \quad (5)$$

are calculated on clusters  $[(k-1, b), (ka), (kb)]$  and  $[(ka), (kb), (k+1, a)]$ . Coefficients  $C_\alpha^p$  ( $p = a, b$ ) are expressed in terms of the pair correlation functions

$$\begin{aligned} C_1^a &= \langle (1 - n_{k-1,b})(1 - n_{kb}) \rangle, \\ C_2^a &= \langle (1 - n_{k-1,b})n_{kb} \rangle, \\ C_3^a &= \langle n_{k-1,b}(1 - n_{kb}) \rangle, \\ C_4^a &= \langle n_{k-1,b}n_{kb} \rangle, \end{aligned} \quad (6)$$

for an  $a$  sublattice, and, respectively, for a  $b$  sublattice.

Chemical potential  $\mu$  as a function of the proton concentration  $n = \langle n_{ka} + n_{kb} \rangle$  is determined from the equation

$$n = \sum_{\alpha=1}^4 \frac{1}{N} \left[ \frac{P_{\alpha}^{+}}{e^{\beta E_{\alpha}^{+}(k)} + 1} + \frac{P_{\alpha}^{-}}{e^{\beta E_{\alpha}^{-}(k)} + 1} \right], \quad (7)$$

where

$$P_{\alpha}^{\pm} = S_{\alpha}^{a,\mp} + S_{\alpha}^{b,\pm}$$

$$S_{\alpha}^{p,\pm} = \left( 1 \pm \frac{h}{\sqrt{h^2 + C_{\alpha}^a C_{\alpha}^b |t_{ab}|^2}} \right) C_{\alpha}^p, \quad (8)$$

are statistical weights of the energy subbands.

Eq. (7) should be supplemented by the functional dependence of parameters  $C_{\alpha}^p$  on  $T$  and  $n$ . The calculation of correlators (6) was performed by the transfer matrix method in the zero approximation

with respect to the proton hopping parameters (described by the part  $H_t$  of the Hamiltonian).

The analysis of energy spectrum and numerical calculations were performed using the available estimates for the model parameter values. The interaction constants were taken equal to:  $U = 3280 \text{ cm}^{-1}$ ,  $V = 3130 \text{ cm}^{-1}$  [13];  $w - \varepsilon = 10000 \text{ cm}^{-1}$ ,  $J = w + w' - 2\varepsilon = 9400 \text{ cm}^{-1}$  [14]. The values of the proton hopping constants were obtained using the data on the average intrabond- (interbond-) hopping time parameters (see for example, Ref. [15]):  $\Omega_0 = 40\text{--}100 \text{ cm}^{-1}$ ;  $\Omega_R = 500\text{--}2500 \text{ cm}^{-1}$ .

Proton bands  $E_{\alpha}^{\pm}(k)$  are grouped into four pairs. The distance  $\Delta E_{\alpha}$  between the subbands in the pair ( $\Delta E_{\alpha} = 2C_{\alpha}|\Omega_R - \Omega_0|$  at  $h = 0$ ) is small compared with the distance between pairs (Fig. 3). The latter is of the same order as the transition energy  $\varepsilon_a$  in the cluster. At small values of  $h$ , the width of each subband in the pair is of the order of  $2C_{\alpha}\Omega_0$  when  $\Omega_R > \Omega_0$  or  $2C_{\alpha}\Omega_R$  when  $\Omega_0 > \Omega_R$ , respectively.

#### 4. Conditions of thermodynamical stability

In the absence of the internal ordering field ( $h = 0$ ), the chemical potential, as a function of  $n$ , jumps three times: at  $n^* = 1$  between the  $E_4^{+}$  and  $E_1^{-}$  subbands and at  $n^* = 1 - 1/\sqrt{5}$  ( $n^* = 1 + 1/\sqrt{5}$ ) between  $E_1^{-}$  and  $E_1^{+}$  ( $E_4^{-}$  and  $E_4^{+}$ ) subbands (Fig. 3). At these critical concentrations, the proton subsystem behaves similarly to the electron gas in the dielectric crystal or semiconductor. An activation energy of the protonic conductivity is equal to  $E_a = U + V + J - (\Omega_0 + \Omega_R)$  for  $n^* = 1$ . The charge carriers in this case are the proton ‘pairs’ and ‘holes’ (D- and L-defects). At the intermediate values of  $n$  due to the partial occupation of the corresponding band, the conductivity is of the metallic type. Due to the formation of the protonic polarons (as a result of the proton–phonon interaction), the conductivity in this case is also of the activation nature [9,10].

The characteristic feature of the obtained dependence of the chemical potential  $\mu$  on  $n$  (see Fig. 3) is the existence of the regions with  $\partial\mu/\partial n < 0$ . This effect takes place at the certain proton concentrations (in the vicinity of the  $n = 1$  value) and when the values of the proton transfer parameters are considerably different ( $\Omega_0/\Omega_R \ll 1$  or  $\Omega_R/\Omega_0 \ll 1$ ) that

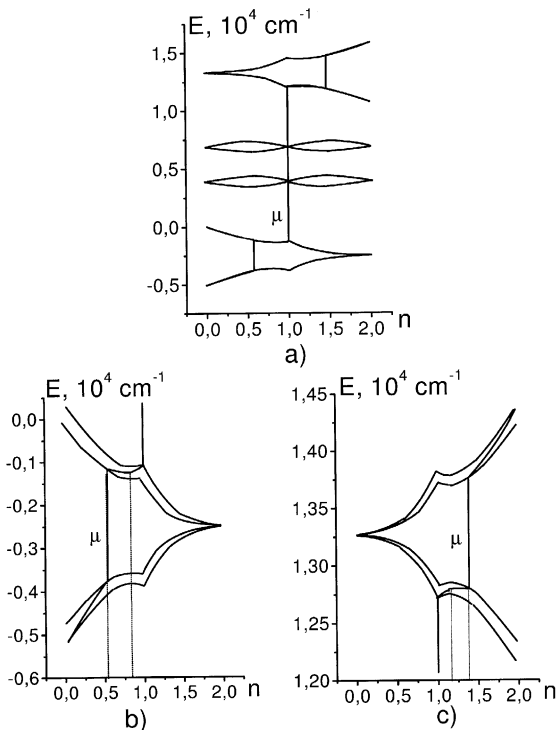


Fig. 3. Energy spectrum and chemical potential of the system as a function of  $n$  at  $h = 0$ : (a) the whole spectrum; (b) two lowest subbands; (c) two highest subbands.  $\Omega_0 = 100 \text{ cm}^{-1}$ ,  $\Omega_R = 2500 \text{ cm}^{-1}$ .

corresponds to the small widths of the bands. This fact points out to the instability of the ideal chain structure of the hydrogen bonds with the uniform distribution of protons. It can result in some kind of separation in the system and appearance of the regions with the different proton concentrations (that can be connected with the partial going out of protons (deuterons) into the positions placed outside the chains).

At small values of  $h$  ( $h \leq 20 \text{ cm}^{-1}$  at  $\Omega_0 = 100 \text{ cm}^{-1}$ ,  $\Omega_R = 250 \text{ cm}^{-1}$ ), the concentration range where  $\partial\mu/\partial n < 0$  broadens with the increase of  $h$  due to the change in the band shape (Fig. 4). Further increase of  $h$  leads to the situation when the statistical weight of the upper of the two lowest subbands becomes much smaller than the weight of the lower one. Accordingly, the region with  $\partial\mu/\partial n < 0$  starts to decrease and finally disappears (that take place at  $h \geq 40 \text{ cm}^{-1}$ ).

Thus, the concentrational instability exists only at small values of  $h$  (in the range from zero to some critical value). In the case  $\Omega_0 = 100 \text{ cm}^{-1}$ ,  $\Omega_R =$

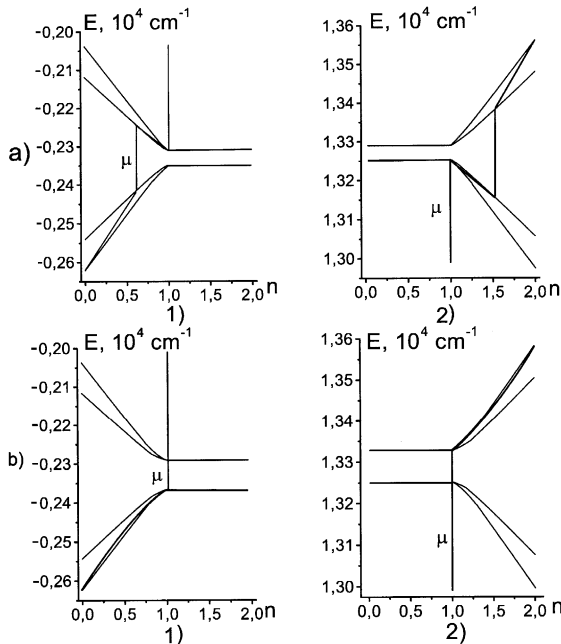


Fig. 4. Energy spectrum and chemical potential of the system as a function of  $n$  at  $h \neq 0$  ( $\Omega_0 = 100 \text{ cm}^{-1}$ ,  $\Omega_R = 250 \text{ cm}^{-1}$ ). (1) two lowest subbands, (2) two highest subbands; (a)  $h = 20 \text{ cm}^{-1}$ ; (b)  $h = 40 \text{ cm}^{-1}$ .

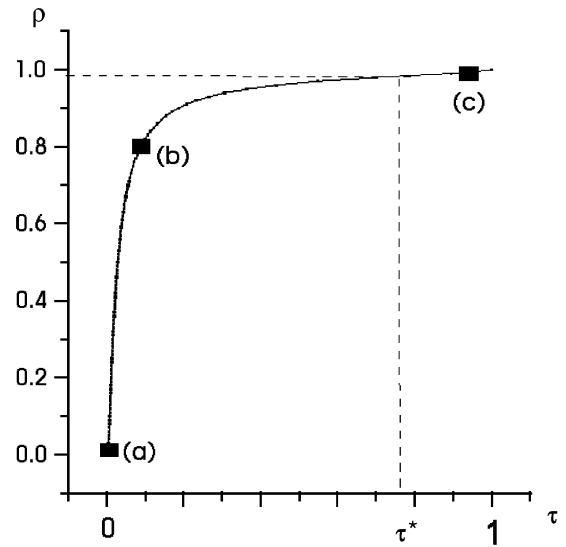


Fig. 5. Temperature dependence of  $\rho$  ( $\Omega_0 = 100 \text{ cm}^{-1}$ ,  $\Omega_R = 250 \text{ cm}^{-1}$ ). (a)  $h = \infty$  or  $\tau = 0$ ; (b) finite values of  $h$ ,  $\partial\mu/\partial n > 0$ ; (c) small values of  $h$ , the region of  $n$  with  $\partial\mu/\partial n < 0$  exists at  $\rho > \rho^* = 0.98$ .  $\tau = T/T_c$  is the dimensionless temperature.

$250 \text{ cm}^{-1}$ , the derivative  $\partial\mu/\partial n$  is negative when  $0.98 < \rho < 1$ , where  $\rho = e^{-2\beta h}$ .

The field  $h$ , which appears due to the inter-chain correlations, can be considered as proportional to the order parameter  $\langle n_{ka} - n_{kb} \rangle$  (describing the proton ordering in the chain) and in consequence should be determined in a self-consistent way in the spirit of the mean field approximation. The temperature dependence of the parameter  $\rho$  in this case is shown in Fig. 5. The value of  $\rho$  exceeds the critical one ( $\rho^* = 0.98$ ) at a certain temperature  $T^*$ , which is lower than the temperature  $T_c$  of the possible order–disorder phase transition in the chain (that could be realized in the absence of the transition into the superionic phase). In the case when  $T^* < T_s < T_c$ , the instability with respect to the separation into the regions with different proton concentrations exists within the temperature interval  $[T^*, T_s]$ .

## 5. Conclusions

- (1) Short-range proton correlations lead to the splitting in proton energy spectrum (which has a band character for the orientational-tunneling model).
- (2) The occupancy of the proton subbands can possess a quasimetallic (1) or dielectric (semi-con-

ductor) (2) character depending on the proton concentration. This determines the nature of the proton conductivity (quasipolaronic conductivity in case (1); defect one in case (2)).

(3) Possibility of the decrease of  $\mu$  with the increase of  $n$  ( $\partial\mu/\partial n < 0$ ) in the vicinity of the  $n = 1$  points out to the instability of the uniform proton distribution along the chain. This effect appears when the internal ordering field decreases with the increase of temperature.

(4) In the case of CsDSO<sub>4</sub> crystals, the abovementioned instability can be one of the reasons for transition of certain number of deuterons into B-positions (placed between the chains formed by the SO<sub>4</sub> groups and A-hydrogen positions). This effect can be considered as a possible explanation of the so-called precursor effect observed in the wide temperature range below  $T_s$  (the superionic phase transition point) [2–4].

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