

# STATISTICAL THEORY FOR DISORDERED QUASI-ONE-DIMENSIONAL FERROELECTRICS WITH HYDROGEN BONDS

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Thermodynamics and dynamics of the quasi-one-dimensional disordered ferroelectrics with hydrogen bonds are studied within the framework of disordered Ising model. We obtain thermodynamic potentials, polarization, static and dynamic  $\mathbf{q}$ -dependent susceptibilities within the two-site cluster approximation for short-range interactions. Theoretical results are compared to dielectric measurements in pure and partially deuterated ferroelectrics  $Cs(H_{1-x}D_x)_2PO_4$  and  $PbH(D)PO_4$ . The model predicts the sort ordering in the former crystal: protons and deuterons tend to occupy the nearest neighbour H-bonds.

## 1. Introduction

Ferroelectrics of *KDP* family compels much attention due to their simple structure and interesting properties. Many investigations have been devoted to low-symmetric ferroelectrics, i.e.  $CsH_2PO_4$  (CDP),  $PbHPO_4$  (LHP) and their deuterated isomorphs.

The structure of the cesium dihydrogen phosphate crystal is shown in figure 1. In the high-temperature paraelectric phase CDP crystal and its deuterated isomorph  $CsD_2PO_4$  (DCDP) are monoclinic and belong to space group  $P2_1/m$  [1–3]. The elementary cell has parameters  $a=7.906\text{\AA}$ ,  $b=6.372\text{\AA}$ ,  $c=4.883\text{\AA}$ ,  $\beta = 107.73^\circ$  and contains two formula units. There are hydrogen bonds  $O - H \cdots O$  of two types in this crystals [4–6]. The shorter bonds  $O3 - H1 \cdots O3$  ( $R_{O \cdots O} = 2.48\text{\AA}$ ) connect  $PO_4$  groups in zig-zag chains along the  $b$ -axis. The longer bonds  $O2 - H2 \cdots O2$  ( $R_{O \cdots O} = 2.56\text{\AA}$ ) are almost parallel to the  $c$ -axis and connect  $b$ -chains of  $PO_4$  groups in the  $(b, c)$ -plane. Between  $(b, c)$ -planes of  $PO_4$  groups the  $Cs^+$  ions are situated.

In the paraelectric phase the protons of the shorter  $H$ -bonds occupy one of two equilibrium positions with equal probability. The cooling to  $T_c = 156\text{K}$  brings CDP crystal in the ferroelectric phase [5,6] with the  $P2_1$  symmetry. In this phase the  $H1$  protons localize in the acentric ordered positions in  $H$ -bonds and the  $PO_4$  tetrahedra slightly turn around the  $P - O2$  bonds [7]. Such ordering of the shorter  $H$ -bonds also takes place in the antiferroelectric phase of the CDP crystal, that replaces the ferroelectric one

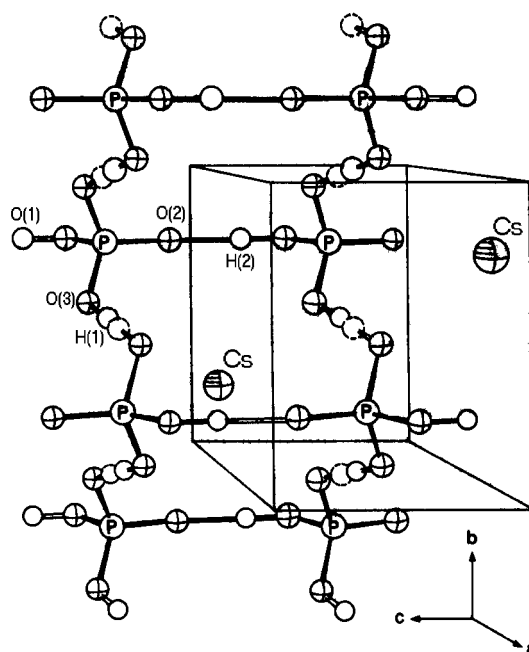


Figure 1. The structure of the  $CsH_2PO_4$  crystal.

under hydrostatic pressure ( $P \geq 330 \text{ MPa}$ ). The protons  $H2$  of the longer  $H$ -bonds are ordered at any temperature and hydrostatic pressure. An important role of protons in the phase transition is justified by the isotopic effect: Curie temperature in the deuterated CDP raises to 268K [3,4].

It is possible to achieve the perfect  $(b, c)$ -plane chips of this crystal that shows a weakness of the interplane forces. Since during the phase transition into the ferroelectric phase the ordering of protons takes place only on the shorter  $H$ -bonds with the appearance of the polarization along chains, the CDP-type crystals are described as the quasi-one-dimensional in contrast to the three-dimensional tetragonal crystals of the  $KH_2PO_4$  group.

$PbHPO_4$  (LHP) and  $PbDPO_4$  (DLHP) are also monoclinic crystals, which possess the ferroelectric phase transition of the second kind at temperatures 310K and 452K, respectively [8]. At room temperature they belong to the space group  $Pc$ , whereas in the paraelectric phase their symmetry is  $P2_1/c$ . Both LHP and DLHP contain two formula units in the elementary cell. These crystals have only short hydrogen bonds  $O - H \cdots O$  ( $R_{O \cdots O} = 2.52 \text{ \AA}$ ), which connect  $PO_4$  groups in the chains along the  $c$ -axis. The hydrogen bonds direction in these crystals is almost parallel to the direction of the spontaneous polarization [8]. The papers [9–12] show that protons (deuterons) in the LHP (DLHP) hydrogen bonds move in the double-well potential and their behaviour is similar to that of the protons in the shorter  $H$ -bonds of CDP. The large change of  $T_c$  with deuteration shows that the phase transitions in these crystals are also closely related to the proton or deuteron ordering.

Thus at this moment the notion has been established about the quasi-one-dimensional character of proton (deuteron) ordering in CDP and LHP crystals with strong intrachain and weak interchain interactions. It brings the idea to describe the phase transition in these crystals on the basis of

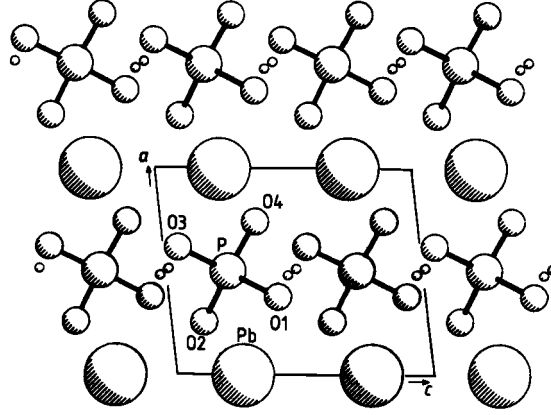


Figure 2. The structure of the  $PbHPO_4$  crystal in projection on the  $(a, c)$  plane. Two formula units in the primitive cell are related by the symmetry with respect to  $c$ -glide plane perpendicular to  $b$ -axis. Parameters of the elementary cell are  $a = 4.688\text{\AA}$ ,  $b = 6.649\text{\AA}$ ,  $c = 5.781\text{\AA}$ ,  $\beta = 97.11^\circ$ . In  $PbDPO_4$   $a = 4.6855\text{\AA}$ ,  $b = 6.6911\text{\AA}$ ,  $c = 5.7867\text{\AA}$ ,  $\beta = 97.10^\circ$ .

the quasi-one-dimensional Ising model. This idea was realized in the papers [5,9,13–23] (CDP) and [9,24,25] (LHP) where the phase transition, static and dynamic properties of the mentioned ferroelectrics was discussed in the framework of the microscopic theories [13,23,24,26,27]) based on the quasi-one-dimensional Ising model. It has been shown that this model provide a good description of polarization, dielectric permittivity, specific heat and dynamic susceptibility of CDP and LHP crystals as well as of their deuterated analogs.

Some authors [15,16,28,29] came to the conclusion that Ising model can not describe the isotopic effect in CDP. They experienced the following problems.

According to Ising model, the dielectric permittivity in paraelectric phase is

$$\varepsilon = 1 + \frac{A}{\theta \exp(-2K/\theta) - J}, \quad (1.1)$$

where  $\theta = k_B T$ ,  $k_B$  is a Boltzman constant,  $K$  and  $J$  are the nearest neighbour coupling and  $\mathbf{q} = 0$  Fourier-transform of long-range interaction, respectively. Authors of the papers [9,15] found values of the parameters  $A$ ,  $K$  and  $J$  that gave the best fit of the permittivity (1.1) to their experimental data. They got that the Curie constant  $A = 4\pi n\mu^2$  ( $n$  is a number of quasispins in the unit volume,  $\mu$  being a dipole moment of the quasispin along the ferroelectric axis) is less in the deuterated crystal than in the ordinary CDP (see table 1.). Then Ising model suggests that saturated value of the spontaneous polarization  $P^s = \mu n$  lowers with deuteration. The experiment instead shows that  $P^s$  increases. Weakening of the long-range interaction  $J$  also contradicts to the  $P^s$  rise, because the main contribution to  $J$  is given by the dipole-dipole interaction, which is proportional to  $\mu^2$ .

These inconsistencies are weakened within the transverse field Ising

Table 1. Parameters of Ising model that describe the experimental data on CDP/DCDP. CDP parameter is in the nominator, denominator contains DCDP parameter.

	[9]	[25]	[15]	[30]
$K/k_B, K$	305/682.5	350/540	265.5/611	300/491
$J/k_B, K$	3.6/0.8	1.76/4.79	6/2.1	6/6
$A, K$	4650/2361	4825/7326	6780/2980	6597/6469
$\Omega/k_B, K$	0/0	0/0	0/0	105/83.5

model. The papers [30,31] attribute the isotopic effect to changes in a tunnelling parameter  $\Omega$  instead of changes in  $K$  and  $J$ . Nevertheless inconsistency related to Curie constant remains.

The authors of the papers [30,31] have also shown that if the tunnelling frequency is small ( $2\Omega \ll K$ ) then the dynamic susceptibility of the transverse field Ising model is of the relaxational type and model describes the dynamic dielectric permittivity of CDP and DCDP. But recently Sorokov and Levitskii [32] have displayed the incorrectness of the approximations used in [30,31] for the temperatures  $\theta > \Omega$ . On the basis of an improved approximation they show that this model does not describe the high-frequency behaviour of  $\varepsilon(\omega)$  in CDP and can not describe Debye-type relaxation at all.

In order to remove the Curie constant inconsistency Kojyo and Onodera [28,29] suggested quasispin model which attaches dipole moment to the  $PO_4$  groups. In this model  $H$ -bonds, since they are oriented almost perpendicularly to the ferroelectric axis, induce polarization indirectly, influencing deformation of the  $PO_4$  tetrahedra. Parameters of this model suggested by the authors are free of the mentioned above inconsistencies, but the advantages of the model remain doubtful, because the Curie constant found from the permittivity data is one and half times larger than that obtained from  $P^s$ .

The authors of the papers [22,23] insist on the applicability of the Ising model to the description of thermodynamic and dynamic properties of CDP and DCDP. They have found the model parameters which are free of the mentioned above inconsistencies and provide a satisfactory description for a large set of experimental data within the wide range of temperatures and frequencies. In the same papers a good description of the partially deuterated crystals  $Cs(H_{1-x}D_x)_2PO_4$  is achieved on the basis of an assumption that the parameters of Ising model are linear functions of the deuterium concentration  $x$  (mean crystal approximation). This latter result is quite strange because in the systems with strong short-range correlations a disorder brought with deuteration should produce more pronounced effects.

In this paper we aim to describe both the thermodynamics and the dynamic properties of disordered Ising model on the basis of the same consistent approach. This approach allows us to study the effect of disorder in quasi-one-dimensional ferroelectrics with hydrogen bonds.

## 2. The Hamiltonian. Formulation of the problem

Following the ideas of the papers [22,23,25] we try to describe the properties of the quasi-one-dimensional ferroelectrics on the basis of Ising model with strong nearest neighbour interaction in chains  $K_{ij}$  and weak long-range interaction  $J_{ij}$

$$H = - \sum_{(ij)} K_{ij} S_i S_j - \frac{1}{2} \sum_{ij} J_{ij} S_i S_j - \sum_i \kappa_i S_i. \quad (2.1)$$

Here  $S_i = \pm 1$  is an operator of the  $z$ -component of quasispin, that corresponds to the two possible equilibrium positions of proton (deuteron) in  $H$ -bond;  $K_{ij}$  is a coupling between the nearest neighbours in chains;  $J_{ij}$  denotes an effective long-range interaction between quasispins that contains indirect interaction of protons (deuterons) via lattice vibrations;  $\kappa_i = \mathbf{E} \mathbf{d}_i$ , where  $\mathbf{E}$  is an external electric field, and  $\mathbf{d}_i$  is an effective dipole moment that accounts also a contribution of the other elements of the lattice. Partial deuteration brings chaos into the system and requires to consider the disordered Ising model. We assume the interaction parameters to be locally dependent on the sort configuration

$$\begin{aligned} K_{ij} &= \sum_{\alpha\beta} K_{i\alpha,j\beta} X_{i\alpha} X_{j\beta}; \quad J_{ij} = \sum_{\alpha\beta} J_{i\alpha,j\beta} X_{i\alpha} X_{j\beta}; \\ \kappa_i &= \sum_{\alpha} \kappa_{i\alpha} X_{i\alpha}. \end{aligned} \quad (2.2)$$

Operators  $X_{i\alpha}$  describe the sort configuration:  $X_{i\alpha} = 1$  if site  $i$  contains the quasispin of sort  $\alpha$ , otherwise  $X_{i\alpha} = 0$ . In the partially deuterated ferroelectric the hydrogen bond may contain proton or deuteron, therefore the sort indices (greek letters) take two values:  $\alpha = 1(D)$  or  $2(H)$ . A site index is two-component:  $i = \frac{l}{a}$ , in the nominator we write the index of elementary cell ( $l = 1 \dots N$ ), denominator contains sublattice index (the elementary cells of CDP and LHP contain two quasispins (short H-bonds):  $a = A, B$ ).

The model can be considered in the two limiting cases. In the case of annealed system the equilibrium sort configuration is realized and the thermodynamic averaging implies going over all spin and sort configurations:

$$\begin{aligned} \langle \dots \rangle_{eq} &= Z^{-1} \text{Sp}_{\{S, X\}} \exp(-H/\theta) (\dots), \\ Z &= \text{Sp}_{\{S, X\}} \exp(-H/\theta). \end{aligned} \quad (2.3)$$

In the case of quenched system the sort configuration is fixed, and the thermodynamic averaging  $\langle \dots \rangle_H$  contains a trace over spin configurations

$$\langle \dots \rangle_H = \text{Sp}_{\{S\}} [\rho_x(\{S\})(\dots)] \quad (2.4)$$

$$\rho_x(\{S\}) = Z_x^{-1} \exp(-H/\theta) \quad (2.5)$$

$$Z_x = \text{Sp}_{\{S\}} \exp(-H/\theta) \quad (2.6)$$

In order to calculate the observable quantities in quenched system one has to perform also an averaging over the sort configurations

$$\langle \dots \rangle_x = \text{Sp}_{\{X\}} \rho(\{X\})(\dots), \quad (2.7)$$

where distribution  $\rho_x(\{S\})$  is determined by the conditions of the system freezing. For example, if the system was prepared at very high temperatures and then quickly cooled then there is no correlations in sort distribution

$$\langle X_{i\alpha} X_{j\beta} \rangle_x = \langle X_{i\alpha} \rangle_x \langle X_{j\beta} \rangle_x = c_\alpha c_\beta, \quad (2.8)$$

where  $c_\alpha$  is a fraction of the sort  $\alpha$  quasispins in the mixture.

In the case of the equilibrium disorder the properties of the system are affected by the “nonexchange” interaction between quasispins

$$\begin{aligned} -\sum_{(ij)} V_{ij} &= -\sum_{(ij)} \sum_{\alpha\beta} V_{i\alpha,j\beta} X_{i\alpha} X_{j\beta}, \\ -\frac{1}{2} \sum_{ij} I_{ij} &= -\frac{1}{2} \sum_{i\alpha,j\beta} I_{i\alpha,j\beta} X_{i\alpha} X_{j\beta}, \end{aligned} \quad (2.9)$$

that should be included in the Hamiltonian ( $V_{ij}$  denotes the nearest neighbour interaction,  $I_{ij}$  is the long-range interaction). In the case of deuterated ferroelectrics such terms in the Hamiltonian may describe the elastic energy of the lattice deformation that appears after the replacement of proton to deuteron.

The annealed model within the grand canonical ensemble is described by the density matrix

$$\rho(\{S, X\}) = \mathcal{Z}^{-1} \exp(-\mathcal{H}/\theta); \mathcal{H} = H - \sum_{\alpha} \mu_{\alpha} \hat{N}_{\alpha}; \quad (2.10)$$

$$\mathcal{Z} = \text{Sp}_{\{S, X\}} \exp(-\mathcal{H}/\theta); \hat{N}_{\alpha} = \sum_i X_{i\alpha} \quad (2.11)$$

$$\begin{aligned} \mathcal{H} &= -\sum_{(ij)} K_{ij} S_i S_j - \frac{1}{2} \sum_{ij} J_{ij} S_i S_j - \sum_i \kappa_i S_i \\ &\quad - \sum_{(ij)} V_{ij} - \frac{1}{2} \sum_{ij} I_{ij} - \sum_i \mu_i \end{aligned} \quad (2.12)$$

$$\mu_i = \sum_{\alpha} \mu_{i\alpha} X_{i\alpha} \quad (2.13)$$

Chemical potentials have to be found from the conditions

$$\langle X_{i\alpha} \rangle_{\mathcal{H}} = c_{\alpha}, \quad (2.14)$$

where

$$\langle (\dots) \rangle_{\mathcal{H}} = \text{Sp}_{\{S, X\}} [\rho(\{S, X\}) (\dots)]. \quad (2.15)$$

The sort configuration relaxation time in the considered compounds is unknown at this time, therefore we do not know what type of disorder is observed in the dielectric [15,16] and calorimetric [20,21] experiments. This situation requires both types of disorder to be considered theoretically and compared with experimental data.

Ising models with the annealed or quenched disorder compel attention of theoreticians for many years, because they are simple and nontrivial microscopic models for the processes of chemical, ferroelectric or magnetic ordering in alloys of magnets, magnets with nonmagnetic impurities, solid solutions of ferroelectrics, etc. For the one-dimensional model with the

nearest-neighbour interactions some exact results are obtained: for both annealed and quenched systems the thermodynamic potentials and correlation functions have been calculated [33] (for quenched system only the zero field results have been found), for the ideal (one-sort) system without field Glauber's kinetic equation has been solved (dynamic pair correlation function has been calculated [34]). Percolation phenomena and universality problems inspire new Monte-Carlo experiments with the diluted (noninteracting impurities) quenched system. When the couplings  $K_{i\alpha,j\beta}$  can take values of different signs, one faces the problems of frustration and spin glass, which we do not consider in this paper, because herein we assume  $K_{i\alpha,j\beta} > 0$ . In the annealed model the coupling between sort and spin ordering is of great interest [35,36]. The model provides also a test for the approximate approaches of statistical physics. For example, the mean field approximation (MFA) does not distinguish between the properties of the annealed and quenched ferroelectrics, does not retrieve percolation phenomena, does not describe the influence of sort ordering on the quasispin alignment [35,37]. The main reason for this result is that MFA neglect fluctuations of the concentration and spin moment. Therefore, the most straightforward way to improve the theory that is based on an effective field can be reached by the account of local spin and sort moments fluctuations within the cluster approach. Different cluster approximations suggested in papers [36,38,39] give qualitatively correct results, which can be systematically improved in the higher order approximations. The papers [38] (AS) and [36] (QS) have presented phase diagrams of the model in some cluster approximations, which are quite close to Monte-Carlo results. An Effective Field Approximation of Kaneyoshi et. al. provides good results for average value of spin, static susceptibility and critical temperature of the diluted quenched system [40]. In this paper we shall use the previously developed cluster approach [41–43], that gives us the analytical expressions for the thermodynamic potentials,  $\mathbf{q}$ -dependent static and dynamic correlation functions of the model. We shall briefly mention the main points of the method and generalize it on the two-sublattice model appropriate for the CDP-type ferroelectrics.

### 3. Thermodynamics and correlation functions of the model

As well as by the density matrices (2.5) and (2.10) the complete statistical description of a system is provided by the generating functions

$$QS: \quad F(\{\kappa\}) = \langle \ln Z_x \rangle_x, \quad (3.1)$$

$$AS: \quad \mathcal{F}(\{\kappa, \mu\}) = \ln \mathcal{Z}.$$

Nonuniform fields  $\kappa_{i\alpha}$ ,  $\mu_{i\alpha}$  allow us to calculate the correlation functions of the model with the use of the differentiation of the generating functions

$$QS: \quad \langle \langle S_{i_1\alpha_1} \cdots S_{i_n\alpha_n} \rangle_H^c \rangle_x = \theta^n \frac{\partial}{\partial \kappa_{i_1\alpha_1}} \cdots \frac{\partial}{\partial \kappa_{i_n\alpha_n}} F(\{\kappa\}) \quad (3.2)$$

$$AS: \quad \langle X_{i_1\alpha_1} \cdots X_{i_n\alpha_n} S_{j_1\beta_1} \cdots S_{j_l\beta_l} \rangle^c = \theta^{n+l} \frac{\partial}{\partial \mu_{i_1\alpha_1}} \cdots \frac{\partial}{\partial \mu_{i_n\alpha_n}} \cdot \frac{\partial}{\partial \kappa_{j_1\beta_1}} \cdots \frac{\partial}{\partial \kappa_{j_l\beta_l}} \mathcal{F}(\{\kappa, \mu\}), \quad (3.3)$$

where the superscript  $c$  denotes the cumulant averaging, and  $S_{i\alpha} = S_i X_{i\alpha}$ . Let us introduce the short notations for these correlation functions

$$QS : m_{i_1\alpha_1 \dots i_n\alpha_n}^{(n)} = \langle \langle S_{i_1\alpha_1} \dots S_{i_n\alpha_n} \rangle_H^c \rangle_x, \quad (3.4)$$

$$AS : M_{i_1\alpha_1 \dots i_n\alpha_n}^{(n)} = \langle \mathcal{S}_{i_1\alpha_1} \dots \mathcal{S}_{i_n\alpha_n} \rangle_{\mathcal{H}}^c, \quad (3.5)$$

sort index in the case of AS takes three values:

$$\mathcal{S}_{i\alpha} = \begin{cases} S_{i\alpha}, & \alpha = 1, 2 \\ X_{i1}, & \alpha = 3 \end{cases} \quad (3.6)$$

In the final expressions one should account the translational invariance of the system in uniform field (UF) and assume the fields and chemical potentials to be independent of elementary cell index:

$$\kappa_{\frac{1}{a}\alpha} \stackrel{UF}{=} \kappa_{\bar{a}\alpha}, \quad \mu_{\frac{1}{a}\alpha} \stackrel{UF}{=} \mu_{\bar{a}\alpha}.$$

Having found the generating functions, one obtains the free energy (QS)  $F = -\theta F(\{\kappa\})$  and the grand thermodynamic potential (AS)  $G = -\theta \mathcal{F}(\{\kappa, \mu\})$ .

For long-range interactions the mean field approximation yield satisfactory results. Therefore we adopt MFA for interactions  $V_{i\alpha,j\beta}$ ,  $I_{i\alpha,j\beta}$  and the problem reduces to the calculation of the thermodynamic potentials of the model with short-range interactions in some self-consistent field [41] (the reference system). The static and dynamic correlation functions of the model can be analytically expressed via the corresponding values for the reference system. For the system with short-range interactions the approach of cluster expansions is natural [43]. Having performed the cluster expansion [44] of the free energy (two-site cluster) and restricting that expansion to the first term [41,43] one obtains the result of the first order cluster approximation. Thus obtained generating functions contain only one- and two-site contributions

$$QS : F(\{\kappa\}) = -z' \sum_i \langle F_i \rangle_x + \sum_{(ij)} \langle F_{ij} \rangle_x, \quad (3.7)$$

$$AS : \mathcal{F}(\{\kappa, \mu\}) = -z' \sum_i \mathcal{F}_i + \sum_{(ij)} \mathcal{F}_{ij}, \quad (3.8)$$

where  $z' = z - 1$ ,  $z$  is the first coordination number,  $\sum_{(ij)}$  denotes the sum over pairs of the nearest neighbour sites. The one-site contributions

$$F_i = \ln Z_i, \quad Z_i = \text{Sp}_{S_i} e^{-H_i/\theta}, \quad H_i = -\bar{\kappa}_i S_i, \quad (3.9)$$

$$\bar{\kappa}_i = \kappa_i + \sum_j \bar{\varphi}_{ij};$$

$$\mathcal{F}_i = \ln \mathcal{Z}_i, \quad \mathcal{Z}_i = \text{Sp}_{S_i X_i} e^{-\mathcal{H}_i/\theta}, \quad \mathcal{H}_i = -\bar{\kappa}_i S_i - \bar{\mu}_i, \quad (3.10)$$

$$\bar{\mu}_i = \mu_i + \sum_j \bar{\psi}_{ij};$$

and the two-site ones

$$\begin{aligned} F_{ij} &= \ln Z_{ij}, \quad Z_{ij} = \text{Sp}_{S_i S_j} e^{-H_{ij}/\theta}, \\ H_{ij} &= -{}_j \bar{\kappa}_i S_i - {}_i \bar{\kappa}_j S_j - K_{ij} S_i S_j, \end{aligned} \quad (3.11)$$



$$\begin{aligned}
{}_j\bar{\kappa}_i &= \kappa_i + \sum_{r \neq j} {}_r\bar{\varphi}_i; \\
\mathcal{F}_{ij} &= \ln \mathcal{Z}_{ij}, \quad \mathcal{Z}_{ij} = \text{Sp}_{S_i X_i S_j X_j} e^{-\mathcal{H}_{ij}/\theta}, \\
\mathcal{H}_{ij} &= -{}_j\bar{\kappa}_i S_i - {}_i\bar{\kappa}_j S_j - K_{ij} S_i S_j - {}_j\bar{\mu}_i - {}_i\bar{\mu}_j - V_{ij}, \\
{}_j\bar{\mu}_i &= \mu_i + \sum_{r \neq j} {}_r\bar{\psi}_i
\end{aligned} \tag{3.12}$$

contain effective fields  ${}_j\bar{\varphi}_i, {}_j\bar{\psi}_i$ , that describe the influence of the site  $j$  on its nearest neighbour  $i$ . We assume these fields to be locally sort dependent

$${}_j\bar{\varphi}_i = \sum_{\alpha} {}_j\bar{\varphi}_{i\alpha} X_{i\alpha}, \quad {}_j\bar{\psi}_i = \sum_{\alpha} {}_j\bar{\psi}_{i\alpha} X_{i\alpha}. \tag{3.13}$$

In the uniform field limit they lose their dependence on the elementary cell index

$${}_i\bar{\varphi}_{\frac{1}{b}\alpha} \stackrel{UF}{=} \bar{\varphi}_{\frac{1}{b}\alpha}, \quad {}_i\bar{\psi}_{\frac{1}{b}\alpha} \stackrel{UF}{=} \bar{\psi}_{\frac{1}{b}\alpha}. \tag{3.14}$$

The quantities  $\bar{\varphi}$  and  $\bar{\psi}$  are variational parameters that must provide extremum of the generating functions

$$QS : \quad \frac{\partial F(\{\kappa\})}{\partial {}_r\bar{\varphi}_{i\alpha}} = 0; \tag{3.15}$$

$$AS : \quad \frac{\partial \mathcal{F}(\{\kappa, \mu\})}{\partial {}_r\bar{\varphi}_{i\alpha}} = 0, \quad \frac{\partial \mathcal{F}(\{\kappa, \mu\})}{\partial {}_r\bar{\psi}_{i\alpha}} = 0. \tag{3.16}$$

These conditions lead to the following expressions for the first moments

$$QS : \quad m_{i\alpha}^{(1)} = \langle \langle S_{i\alpha} \rangle_{H_i} \rangle_x = \langle \langle S_{i\alpha} \rangle_{H_{ij}} \rangle_x, \tag{3.17}$$

$$\rho_i = Z_i^{-1} e^{-H_i/\theta}; \quad \rho_{ij} = Z_{ij}^{-1} e^{-H_{ij}/\theta},$$

$$AS : \quad M_{i\alpha}^{(1)} = \langle \mathcal{S}_{i\alpha} \rangle_{\mathcal{H}_i} = \langle \mathcal{S}_{i\alpha} \rangle_{\mathcal{H}_{ij}}, \tag{3.18}$$

$$\rho_i = \mathcal{Z}_i^{-1} e^{-\mathcal{H}_i/\theta}; \quad \rho_{ij} = \mathcal{Z}_{ij}^{-1} e^{-\mathcal{H}_{ij}/\theta}$$

The equations (3.17) and (3.18) for the fields  $\bar{\varphi}, \bar{\psi}$  give the selfconsistency conditions, that require equality of the first moments found with the one-site  $\rho_i$  and cluster  $\rho_{ij}$  density matrices. In the case of the simple lattice and uniform field we obtain the generally known results of the Bethe approximation and the first-order cluster variation method [37,39]. Nonuniform fields allows us to obtain the correlation functions by the differentiation of the generating functions, and it is the advantage of our approach. For example, after differentiation of the equation (3.17) with respect to  $\kappa_{j\beta}$  we obtain the Ornstein-Zernike type equation for the pair correlation function. This equation can be written in the matrix form

$$QS : \quad \hat{U}_{ii} \hat{m}_{ij}^{(2)} = \delta_{ij} + \sum_r \hat{G}_{ir} \hat{m}_{rj}^{(2)}, \tag{3.19}$$

where

$$\begin{aligned}\hat{U}_{ii} &= -z'(\hat{F}_i^{(2)})^{-1} - \sum_r \left[ \hat{F}_{ir}^{(11)}(\hat{F}_{ri}^{(20)})^{-1}\hat{F}_{ri}^{(11)} - \hat{F}_{ir}^{(20)} \right]^{-1}, \\ G_{ir} &= \left[ \hat{F}_{ri}^{(20)}(\hat{F}_{ir}^{(11)})^{-1}\hat{F}_{ir}^{(20)} - \hat{F}_{ri}^{(11)} \right]^{-1},\end{aligned}\quad (3.20)$$

$r$  is the nearest neighbour of the site  $i$  (and therefore belong to the other sublattice), matrices  $F$  are the one-site and intracluster correlation functions

$$\begin{aligned}(\hat{F}_{ij}^{(20)})_{\alpha\beta} &= \langle \langle S_{i\alpha} S_{j\beta} \rangle_{H_{ij}}^c \rangle_x, \\ (\hat{F}_{ij}^{(11)})_{\alpha\beta} &= \langle \langle S_{i\alpha} S_{j\beta} \rangle_{H_{ij}}^c \rangle_x, \\ (\hat{F}_i^{(2)})_{\alpha\beta} &= \langle \langle S_{i\alpha} S_{i\beta} \rangle_{H_i}^c \rangle_x.\end{aligned}\quad (3.21)$$

In the uniform field the pair correlation function become invariant with respect to the translation on a lattice vector

$$m_{\frac{i}{a}\alpha\frac{j}{b}\beta}^{(2)} = m_{\frac{a}{a}\alpha\frac{b}{b}\beta}^{(2)}(\mathbf{R}_i, \mathbf{R}_j) \stackrel{UF}{=} m_{\frac{a}{a}\alpha\frac{b}{b}\beta}^{(2)}(\mathbf{R}_i - \mathbf{R}_j), \quad (3.22)$$

and the equation (3.19) can be solved in the Fourier representation

$$m_{\frac{a}{a}\alpha\frac{b}{b}\beta}^{(2)}(\mathbf{R}_i - \mathbf{R}_j) = \frac{V_e}{(2\pi)^3} \int d^3q e^{-i\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j)} m_{\frac{a}{a}\alpha\frac{b}{b}\beta}^{(2)}(\mathbf{q}), \quad (3.23)$$

where  $V_e$  is a volume of the elementary cell,  $\mathbf{R}_i$  is a coordinate of the  $i$ th elementary cell.

The solution has the form

$$\begin{pmatrix} \hat{m}_{AA}^{(2)}(\mathbf{q}) & \hat{m}_{AB}^{(2)}(\mathbf{q}) \\ \hat{m}_{BA}^{(2)}(\mathbf{q}) & \hat{m}_{BB}^{(2)}(\mathbf{q}) \end{pmatrix} = \begin{pmatrix} \hat{U}_{AA} & \hat{Y}_{\mathbf{q}} \\ \hat{Y}_{\mathbf{q}}^* & \hat{U}_{BB} \end{pmatrix}^{-1} \quad (3.24)$$

where

$$\begin{aligned}\hat{U}_{AA} &= -(\hat{F}_A^{(2)})^{-1} - \hat{E}_{AB} - \hat{E}_{BA}; \\ \hat{U}_{BB} &= -(\hat{F}_B^{(2)})^{-1} - \hat{E}_{AB} - \hat{E}_{BA} \\ \hat{Y}_{\mathbf{q}} &= -\hat{G}_{AB}e^{i\mathbf{q}\mathbf{R}_f} - \hat{G}_{BA}e^{-i\mathbf{q}\mathbf{R}_f} \\ \hat{E}_{AB} &= (\hat{F}_{AB}^{(11)}(\hat{F}_{BA}^{(20)})^{-1}\hat{F}_{BA}^{(11)} - \hat{F}_{AB}^{(20)})^{-1} \\ \hat{G}_{AB} &= (\hat{F}_{BA}^{(20)}(\hat{F}_{AB}^{(11)})^{-1}\hat{F}_{AB}^{(20)} - \hat{F}_{BA}^{(11)})^{-1},\end{aligned}\quad (3.25)$$

$\mathbf{R}_f$  is a base vector of the elementary cell along the chain. We have expressed the correlation functions

$$\left( \hat{m}_{ab}^{(2)}(\mathbf{q}) \right)_{\alpha\beta} = m_{\frac{a}{a}\alpha\frac{b}{b}\beta}^{(2)}(\mathbf{q}) \quad (3.26)$$

via the one-site and intracluster correlation functions

$$\begin{aligned}
\left(\hat{F}_{AB}^{(20)}\right)_{\alpha\beta} &= \left\langle \left\langle S_{\frac{i}{A}\alpha} S_{\frac{i}{A}\beta} \right\rangle_{H_{\frac{i}{A}\frac{i}{B}}}^c \right\rangle_x ; \\
\left(\hat{F}_{AB}^{(11)}\right)_{\alpha\beta} &= \left\langle \left\langle S_{\frac{i}{A}\alpha} S_{\frac{i}{B}\beta} \right\rangle_{H_{\frac{i}{A}\frac{i}{B}}}^c \right\rangle_x ; \\
\left(\hat{F}_A^{(2)}\right)_{\alpha\beta} &= \left\langle \left\langle S_{\frac{i}{A}\alpha} S_{\frac{i}{A}\beta} \right\rangle_{H_{\frac{i}{A}}}^c \right\rangle_x .
\end{aligned} \tag{3.27}$$

This “partial” correlation functions contain trace over small number of spin and sort configurations and can be easily calculated. We can go on with the differentiation procedure and obtain the three-site and higher correlation functions [41,43]. The same can be done for the annealed system. We come to the similar form

$$\begin{pmatrix} \hat{M}_{AA}^{(2)}(\mathbf{q}) & \hat{M}_{AB}^{(2)}(\mathbf{q}) \\ \hat{M}_{BA}^{(2)}(\mathbf{q}) & \hat{M}_{BB}^{(2)}(\mathbf{q}) \end{pmatrix} = \begin{pmatrix} \hat{U}_{AA} & \hat{Y}_{\mathbf{q}} \\ \hat{Y}_{\mathbf{q}}^* & \hat{U}_{BB} \end{pmatrix}^{-1} \tag{3.28}$$

where  $\hat{M}_{ab}^{(2)}(\mathbf{q})$  are  $3 \times 3$  matrices whose elements are the Fourier-transforms of the pair correlation functions

$$M_{\frac{i}{a}\alpha\frac{j}{b}\beta}^{(2)} = \frac{V_e}{(2\pi)^3} \int d^3q e^{-i\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j)} \left(\hat{M}_{ab}^{(2)}(\mathbf{q})\right)_{\alpha\beta} . \tag{3.29}$$

Again our approach has expressed the model correlation functions via the “partial” ones

$$\begin{aligned}
\left(\hat{\mathcal{F}}_{AB}^{(20)}\right)_{\alpha\beta} &= \left\langle \mathcal{S}_{\frac{i}{A}\alpha} \mathcal{S}_{\frac{i}{A}\beta} \right\rangle_{\mathcal{H}_{\frac{i}{A}\frac{i}{B}}}^c , \\
\left(\hat{\mathcal{F}}_{AB}^{(11)}\right)_{\alpha\beta} &= \left\langle \mathcal{S}_{\frac{i}{A}\alpha} \mathcal{S}_{\frac{i}{B}\beta} \right\rangle_{\mathcal{H}_{\frac{i}{A}\frac{i}{B}}}^c , \\
\left(\hat{\mathcal{F}}_A^{(2)}\right)_{\alpha\beta} &= \left\langle \mathcal{S}_{\frac{i}{A}\alpha} \mathcal{S}_{\frac{i}{A}\beta} \right\rangle_{\mathcal{H}_{\frac{i}{A}}}^c .
\end{aligned} \tag{3.30}$$

#### 4. Dynamic properties

The cluster approach of the previous sections can be applied to the description of the system’s dynamics. Within the master equation approach the density matrix  $\rho(\{S\}, t)$  is governed by the equation that describes some stationary Markov process

$$\frac{d}{dt} \rho(\{S\}, t) = \sum_{\{S\}'} \hat{W} \rho(\{S\}, t) \tag{4.1}$$

Kinetics of the system is determined by the transition matrix  $\hat{W}$ . Within the Glauber’s [45] approach the spin system interacts with a heat bath which induces spin flips ( $S_i \rightarrow -S_i$ ). The state of the heat bath is assumed to be constant, therefore a probability of the spin flip per unit time  $W_i(\{S\})$

depends only on the spin configuration and is independent of time. Thus the master equation takes the form

$$\begin{aligned} \frac{d}{dt}\rho_x(\{S\}, t) &= \sum_i W_i(\dots - S_i \dots) \rho_x(\dots - S_i \dots, t) \\ &- \sum_i W_i(\dots S_i \dots) \rho_x(\dots S_i \dots, t) \end{aligned} \quad (4.2)$$

A detail balance condition for the equilibrium density matrix of the system leads to the following relations for the transition matrix

$$\frac{W_i(\dots S_i \dots)}{W_i(\dots - S_i \dots)} = \frac{\rho_x(\dots - S_i \dots)}{\rho_x(\dots S_i \dots)} = \frac{\exp(-\varepsilon_i S_i / \theta)}{\exp(\varepsilon_i S_i / \theta)} = \frac{1 - S_i \tanh \varepsilon_i / \theta}{1 + S_i \tanh \varepsilon_i / \theta}, \quad (4.3)$$

where  $\varepsilon_i$  is a local field acting on the  $i$ th spin

$$\varepsilon_i = \kappa_i + \sum_j K_{ij} S_j. \quad (4.4)$$

Suzuki and Kubo [34] suggested the following form of the transition probability, which is compatible with (4.3)

$$W_i(\dots S_i \dots) = \frac{1}{2\tau_i} (1 - S_i \tanh \varepsilon_i / \theta), \quad (4.5)$$

where  $\tau_i$  is a constant which characterize an interaction of the  $i$ th spin with the heat bath and define the time scale of the relaxation processes.

Expressions (4.2) and (4.5) lead to the following equation for an average value of spin

$$D_{i,t} \langle S_i \rangle_{H,t} = \langle \tanh \varepsilon_i / \theta \rangle_{H,t}, \quad (4.6)$$

where

$$\langle (\dots) \rangle_{H,t} = \text{Sp}_{\{S\}} \rho(\{S\}, t) (\dots); \quad D_{i,t} = 1 + \tau_i \frac{d}{dt}. \quad (4.7)$$

This equation can also be derived more rigirously from the Liouville equation with spin-phonon Hamiltonian. Nonequilibrium statistical operator method with an assumption that the phonon-phonon correlation functions are independent of frequency near  $\omega \approx 1/\tau_i$  [47] gives the same results as the Glauber's approach yields and provides microscopic expressions for the phenomenological constant  $\tau_i$ . The same can be done within the perturbation theory [46] on the basis of the quantum equation of motion for the spin moment.

In the case of the equilibrium disorder the sort configuration changes as well as the spin configuration during the observation time, thus in this case one should consider the sort kinetics also. This kinetics can also be formulated in terms of spin operators:  $\sigma_i = X_{i1} - X_{i2}$  ( $\sigma_i = \pm 1$ ), but the equation of Glauber type is invalid in this case, because the spin flip ( $\sigma_i \rightarrow -\sigma_i$ ), which is the basic process of equation (4.2), means the transformation of  $H$  ion to  $D$  ion (and vice versa) at  $i$ th hydrogen bond. It is obvious that the sort configuration changes due to another processes. For the annealed

system the Kawasaki equation [48,49] is relevant, which considers elementary processes  $\{\dots\sigma_i\dots\sigma_j\dots\} \rightarrow \{\dots\sigma_j\dots\sigma_i\dots\}$  (an exchange between the nearest neighbour sites).

We shall consider the dynamics of model near the frequencies of the ferroelectric dispersion. It seems obvious that the sort configuration can not change during the time  $10^{-6}s$ . This implies that the sort distribution is frozen with respect to quick changes of the external field (but can feel the slow changes of temperature and the quasistatic changes of the field). Therefore in the frequency region  $\nu > 1MHz$  the spin kinetics of both annealed and quenched models is governed by the equations (4.2), (4.6). Their dynamic correlation functions, however, differ due to the differences in the sort distribution.

When one expands  $\tanh \varepsilon_i/\theta$  in a power serie, he obtains moments  $\langle S_{i_1} \dots S_{i_n} \rangle_{H,t}$  in the right-hand side of (4.6), where sites  $i_1 \dots i_n$  are the nearest neighbours of the site  $i$ . Expressions (4.2) – (4.6) yield an equation for these moments that in turn involves the second coordination sphere, therefore equation (4.6) is accurately solvable only for the one-dimensional models in zero field (ideal chain [45,34,50], chain with impurity on one site [51]). For models with field or chaos or in the lattice of higher dimensions the closures are used, which express the higher moments via lower. For example, the random phase approximation  $\langle S_{i_1} \dots S_{i_n} \rangle_{H,t} \approx \langle S_{i_1} \rangle_{H,t} \dots \langle S_{i_n} \rangle_{H,t}$  provides a closure to equation (4.6) and lead to the results of MFA in statics. We can not restrict our consideration to MFA, because, as we mention before, it yield some qualitatively incorrect results for the disordered system with short-range interactions. The better results can be achieved in the two-site cluster approximation. This approximation with the long-range interactions accounted in MFA provides good agreement between the theory and the experimental data on the crystals  $CsD_2PO_4$ ,  $CsH_2PO_4$  [23,22] and  $PbDPO_4$ ,  $PbHPO_4$  [25] for spontaneous polarization, specific heat, static and dynamic permittivity.

In our previous papers [41,42,52] the two-site cluster approximation was developed for disordered Ising model and improved in order to obtain the  $\mathbf{q}$ -dependent dynamic pair correlation function of the model. The exact results for one-dimensional lattice (dynamic pair correlator of ideal chain without field [34], static correlation functions (3.24)) are partial cases of the obtained formula. In this paper we apply the same method for the two-sublattice model, which are appropriate for the CDP-type ferroelectrics.

We construct the self-consistency equation, similar to the equation (3.17). Within a one-site approximation we replace in  $\varepsilon_i$  the contributions of all spins by the effective fields

$$\varepsilon_i \rightarrow \varepsilon_i^{[1]} = \sum_r \bar{\varphi}_{it} + \kappa_{it} \equiv \bar{\kappa}_{it}, \quad (4.8)$$

whereas in a two-site approximation the contribution of the one spin is considered explicitly

$$\varepsilon_i \rightarrow \varepsilon_i^{[2]} = \sum_{r \neq j} \bar{\varphi}_{it} + K_{ij} S_j + \kappa_{it} \equiv {}_j \bar{\kappa}_{it} + K_{ij} S_j. \quad (4.9)$$

In the case of the ideal system no more assumptions are needed in order to obtain the closed set of kinetic equations:

$$D_{it} \langle S_i \rangle_{H,t} = \langle \tanh \varepsilon_i^{[1]} / \theta \rangle_{H,t} = \tanh \varepsilon_i^{[1]} / \theta, \quad (4.10)$$

$$D_{it}\langle S_i \rangle_{H,t} = \langle \tanh \varepsilon_i^{[2]}/\theta \rangle_{H,t} = P_{it}\langle S_i \rangle_{H,t} + L_{it},$$

where

$$\begin{aligned} P_{it} &= \frac{1}{2} \left[ \tanh({}_j\bar{\kappa}_{it} + K_{ij})/\theta - \tanh({}_j\bar{\kappa}_{it} - K_{ij})/\theta \right] \\ L_{it} &= \frac{1}{2} \left[ \tanh({}_j\bar{\kappa}_{it} + K_{ij})/\theta + \tanh({}_j\bar{\kappa}_{it} - K_{ij})/\theta \right]. \end{aligned} \quad (4.11)$$

For the disordered system one should point out the dependence of the effective fields  ${}_r\bar{\varphi}_{it}$  on the sort configuration. We shall consider the fields  ${}_r\bar{\varphi}_{it}$  to be different in the one-site and two-site approximations until the sort averaging is carried out. For the sort averaging procedure both the “one-site” and “two-site” fields will be assumed to be locally sort-dependent

$${}_r\bar{\varphi}_{it} = \sum_{\alpha} {}_r\bar{\varphi}_{i\alpha,t} X_{i\alpha}. \quad (4.12)$$

We also consider the relaxation times  $\tau_i$  to be different for deuteron and proton

$$\tau_i = \sum_{\alpha} \tau_{\alpha}^0 X_{i\alpha}. \quad (4.13)$$

The technique, similar to those used in the static case, yields us the dynamic pair correlation function of the model, as a response of the spin moment to weak perturbation of external field with the frequency  $\omega$  and wavevector  $\mathbf{q}$ :

$$m_{\frac{a}{\alpha}\frac{b}{\beta}}^{(2)}(\mathbf{q}, \omega) = \theta \frac{\delta m_{\frac{a}{\alpha}}^{(1)}(\mathbf{q}, \omega)}{\delta \kappa_{\frac{b}{\beta}}(\mathbf{q}, \omega)}. \quad (4.14)$$

We obtain

$$\begin{pmatrix} \hat{m}_{AA}^{(2)}(\mathbf{q}, \omega) & \hat{m}_{AB}^{(2)}(\mathbf{q}, \omega) \\ \hat{m}_{BA}^{(2)}(\mathbf{q}, \omega) & \hat{m}_{BB}^{(2)}(\mathbf{q}, \omega) \end{pmatrix} = \begin{pmatrix} \hat{U}_{AA}(\mathbf{q}, \omega) & \hat{Y}_{\mathbf{q}, \omega} \\ \hat{Y}_{\mathbf{q}, \omega}^* & \hat{U}_{BB}(\mathbf{q}, \omega) \end{pmatrix}^{-1}, \quad (4.15)$$

where the matrices  $\hat{U}$ ,  $\hat{Y}$  have the form (3.20) with the  $\omega$ -dependent cluster correlators in place of the matrices  $\hat{F}$ . This correlators depend on the lowest moments of sort distribution  $\langle X_{i\alpha} \rangle_x = c_{\alpha}$  and  $\langle X_{i\alpha} X_{j\beta} \rangle_x = w_{i\alpha, j\beta}$ . The former is the fraction of the sort  $\alpha$  quasispins, the latter is a probability to find the quasispins of sorts  $\alpha$  and  $\beta$  at sites  $i, j$  respectively.  $c_{\alpha}$  is defined by the chemical content of the sample; in the quenched system  $w_{i\alpha, j\beta}$  is a constant defined by the conditions of the sample freezing, in the case of the annealed system  $w_{i\alpha, j\beta}$  can be found from the static theory

$$w_{i\alpha, j\beta} = \langle X_{i\alpha} X_{j\beta} \rangle_{\mathcal{H}_{ij}} \quad (4.16)$$

and depends on the temperature and static external field.

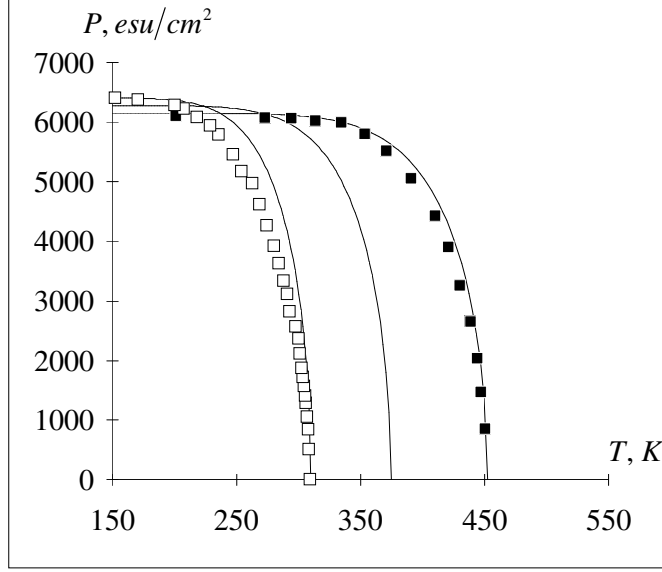


Figure 3. Temperature dependence of the spontaneous polarization in LHP and DLHP crystals. Lines present theoretical results for concentrations 0, 0.5, 1 with parameters  $K_{HH} = 500K$ ,  $K_{DD} = 785.3K$ ,  $K_{HD} = \sqrt{K_{HH}K_{DD}}$ ,  $J_{HH} = 12.3K$ ,  $J_{DD} = 14K$ ,  $J_{HD} = \sqrt{J_{HH}J_{DD}}$ ,  $\mu_H = 0.573D$ ,  $\mu_D = 0.55D$ ,  $\tau_H^0 = \tau_D^0 = 2.4 * 10^{-15}s$ . Symbols show experimental data [8].

## 5. Comparison with the experiment

The theory developed above provides the analytic expressions for such observable quantities as the specific heat, polarization

$$P = \frac{1}{V} \sum_{i\alpha} d_\alpha \langle S_{i\alpha} \rangle \quad (5.1)$$

(here  $\langle \dots \rangle$  denotes the averaging that corresponds to the type of disorder), static susceptibility

$$\chi(\mathbf{q}) = \frac{N}{k_B T} \cdot \frac{1}{V} \sum_{\alpha\beta} d_\alpha d_\beta \langle S_{i\alpha} S_{j\beta} \rangle^c e^{i\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j)}, \quad (5.2)$$

$$\overset{QS}{=} \frac{N}{k_B T} \cdot \frac{1}{V} \sum_{\alpha\beta} d_\alpha d_\beta \exp(i\mathbf{q}(\mathbf{r}_a - \mathbf{r}_b)) m_{\bar{a}\alpha, \bar{b}\beta}^{(2)}(\mathbf{q}), \quad (5.3)$$

$$\overset{AS}{=} \frac{1}{k_B T} \cdot \frac{1}{V} \sum_{\alpha\beta} d_\alpha d_\beta \exp(i\mathbf{q}(\mathbf{r}_a - \mathbf{r}_b)) M_{\bar{a}\alpha, \bar{b}\beta}^{(2)}(\mathbf{q}), \quad (5.4)$$

dynamic susceptibility (AS:  $\omega > 1MHz$ , QS: any  $\omega$ )

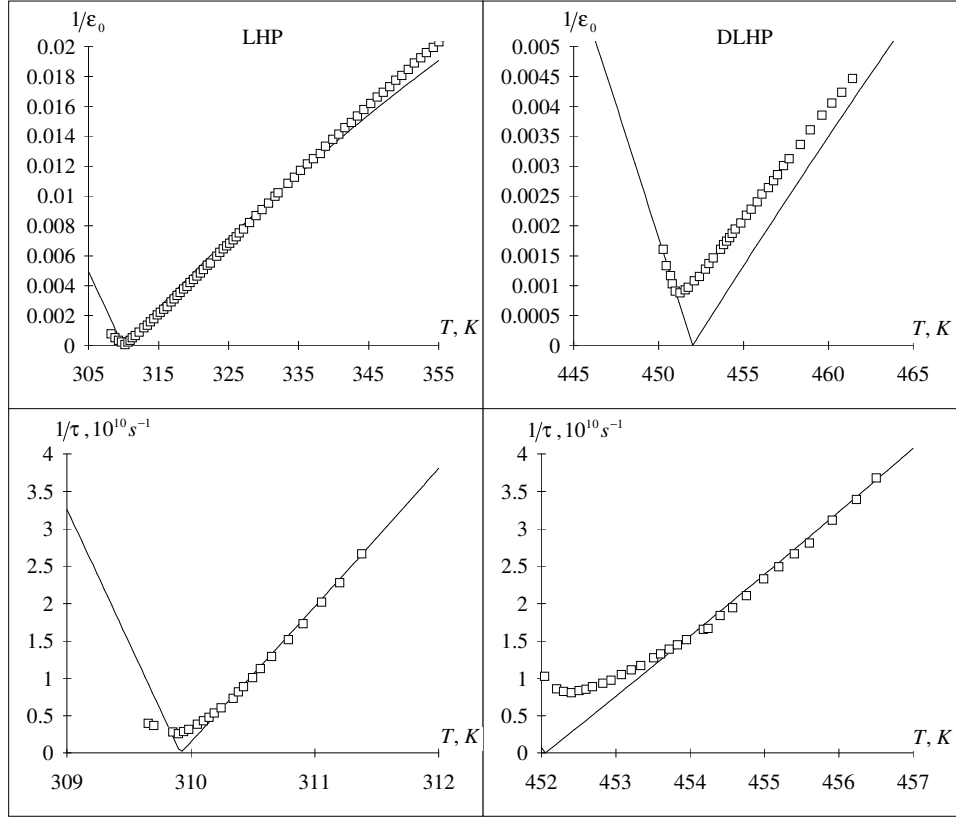


Figure 4. Inverse dielectric permittivity and relaxation time of the crystals LHP and DLHP. Lines present the theory, symbols are experimental data [17]. There is no good fit for deuterated crystal near  $T_c$  due to smearing of the phase transition in DLHP. The reason for such smearing out may be defects of crystal. Small spontaneous polarization in DLHP (see figure 3) is the evidence of these defects.

$$\chi(\mathbf{q}, \omega) = \frac{N}{k_B T} \cdot \frac{1}{V} \sum_{\substack{\alpha\beta \\ ab}} d_\alpha d_\beta \exp(i\mathbf{q}(\mathbf{r}_a - \mathbf{r}_b)) m_{\frac{a}{\alpha}, \frac{b}{\beta}}^{(2)}(\mathbf{q}, \omega), \quad (5.5)$$

where  $\mathbf{r}_a$  is a position of the quasispin that belong to sublattice  $a$  in the elementary cell,  $d_\alpha$  is a dipole moment of the sort  $\alpha$  quasispins along the ferroelectric axis.

The dielectric permittivity of a ferroelectric crystal is  $\varepsilon = \varepsilon^\infty + 4\pi\chi$ ,  $\varepsilon^\infty$  is greater than 1 due to the contribution of the electron and other subsystems of the crystal. It does not depend on temperature or frequency in the region of the ferroelectric dispersion and can be easily estimated from the experimental data  $\varepsilon^\infty = \varepsilon(\infty)$ .

It should be noted that in the annealed model formulae (5.2) and (5.5) yield different results for the static susceptibility in the ferroelectric phase:  $\chi(\mathbf{q}) \neq \chi(\mathbf{q}, 0)$ . The reason for this is that in the dynamic theory we suppose sort configuration to be frozen with respect to the changes of the field. Doing



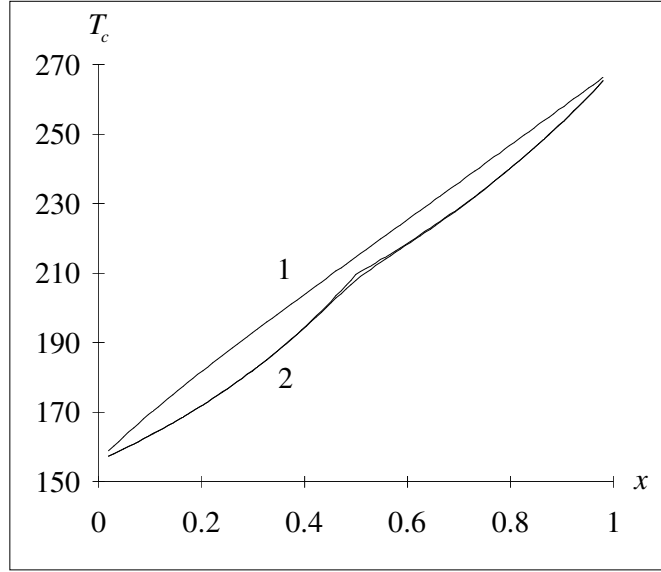


Figure 5. The dependence of the ferroelectric transition temperature  $T_c$  on the degree of deuteration for CDP crystal (parameters are given in table 2). The line 1 corresponds to the quenched system with the complete sort chaos. The lines for the annealed system and the quenched system with ordering almost coincide and are denoted by number 2.

so, we exclude from  $\chi(\mathbf{q}, \omega)$  the corresponding contribution. This is correct at the frequencies of ferroelectric dispersion, but wrong at  $\omega \rightarrow 0$ .

The one-dimensional model without a long-range interaction does not possess a phase transition. With the interchain interaction being accounted this model predicts the ferroelectric phase transition of the second kind. In the case of annealed system the sort ordering or segregation transition also appears. Description of the ordered or segregated phase does not introduce significant difficulties into the theory, but we restrict our consideration to the uniform mixture.

Having accounted the symmetry of the CDP and LHP crystals, one obtains that the nearest neighbour interactions  $K_{i\alpha,j\beta}$ ,  $V_{i\alpha,j\beta}$  do not depend on position in chain,  $\mathbf{q} = 0$  Fourier-transforms of the long-range interactions do not depend on the sublattice indices ( $\sum_j J_{i\alpha,j\beta} = J_{\alpha\beta}$ ,  $\sum_j I_{i\alpha,j\beta} = I_{\alpha\beta}$ ) therefore without the transverse electric field sublattices A and B are equivalent and constitute one simple lattice. In this case the correlation functions do not depend on the sublattice indices, final expressions become much simpler, and we present them below. The free energy of the system takes the form

$$QS: \quad F/N = \theta z' \sum_{\alpha} c_{\alpha} \ln Z_{\alpha} - \theta \frac{z}{2} \sum_{\alpha\beta} w_{\alpha\beta} \ln Z_{\alpha\beta} + \frac{1}{2} \sum_{\alpha\beta} J_{\alpha\beta} m_{\alpha}^{(1)} m_{\beta}^{(1)};$$

$$Z_{\alpha\beta} = 2 \exp(K_{\alpha\beta} + V_{\alpha\beta}) / \theta \left[ \cosh(\bar{\kappa}'_{\alpha} + \bar{\kappa}'_{\beta}) + a_{\alpha\beta} \cosh(\bar{\kappa}'_{\alpha} - \bar{\kappa}'_{\beta}) \right];$$

Table 2. The model parameters that describe experimental data on  $Cs(\bar{H}_{1-x}D_x)_2PO_4$ : the nearest neighbour coupling  $K_{\alpha\beta}$ ; the long-range interaction  $J_{\alpha\beta}$ ; the effective dipole moment of proton (deuteron) on a hydrogen bond  $d_\alpha$ ; the parameter of kinetic equation — relaxation time of noninteracting proton (deuteron)  $\tau_\alpha^0$ . The parameters  $\tilde{V} = V_{DD} + V_{HH} - 2V_{HD}$ ,  $I_{\alpha\beta}$  describe nonexchange interaction of quasispins.

	AS	QS	
		$w_{HD} = c_H c_D$	$w_{HD} = \min(c_H, c_D)$
$K_{HD}/k_B, K$	500	500	500
$J_{HD}/k_B, K$	1.6	3.2	1.6
$\tilde{V}/k_B, K$	-1000	—	—
$I_{\alpha\beta}/k_B, K$	0	—	—
$K_{DD}/k_B, K$		610	
$K_{HH}/k_B, K$		390	
$J_{DD}/k_B, K$		2.85	
$J_{HH}/k_B, K$		1.05	
$d_D, e.s.u.$		$2.18 \times 10^{-18}$	
$d_H, e.s.u.$		$1.87 \times 10^{-18}$	
$\tau_D^0, s$		$3 \times 10^{-14}$	
$\tau_H^0, s$		$6.2 \times 10^{-15}$	

$$Z_\alpha = 2 \left( 1 - (m_\alpha^{(1)}/c_\alpha)^{-2} \right), \quad a_{\alpha\beta} = \exp(-2K_{\alpha\beta}/\theta),$$

$$\bar{\kappa}'_\alpha = \left( \kappa_\alpha/\theta + \sum_\beta J_{\alpha\beta} m_\beta^{(1)}/\theta + z' \ln \frac{c_\alpha + m_\alpha^{(1)}}{c_\alpha - m_\alpha^{(1)}} \right) / z; \quad (5.6)$$

$$AS : \quad F/N = \theta z' \ln \frac{Z_2}{c_2} - \theta \frac{z}{2} \ln \left( \frac{R Z_{22}}{2c_1 c_2 x} \left[ \frac{R}{2c_2} + 1 \right] \right)$$

$$+ \frac{1}{2} \sum_{\alpha\beta} J_{\alpha\beta} m_\alpha^{(1)} m_\beta^{(1)} - \frac{1}{2} \sum_{\alpha\beta} I_{\alpha\beta} c_\alpha c_\beta; \quad (5.7)$$

$$x = \frac{Z_{11} Z_{22}}{Z_{12}^2}, R = \alpha + \sqrt{\alpha^2 + x(1 - \alpha^2)}, \alpha = c_1 - c_2.$$

Spin moments  $m_\alpha^{(1)} = \langle S_{i\alpha} \rangle$  should be found by minimization of the free energy. The cluster dynamic correlation functions read

$$\left( \hat{F}^{(2)}(\omega) \right)_{\alpha\beta} = \delta_{\alpha\beta} c_\alpha \frac{1 - (m_\alpha^{(1)}/c_\alpha)^2}{D_\alpha},$$

$$\left( \hat{F}^{(20)}(\omega) \right)_{\alpha\beta} = \delta_{\alpha\beta} \sum_\gamma w_{\alpha\gamma} \frac{R_{\alpha\gamma} D_\gamma}{D_\alpha D_\gamma - P_{\alpha\gamma} P_{\gamma\alpha}}, \quad (5.8)$$

$$\left( \hat{F}^{(11)}(\omega) \right)_{\alpha\beta} = w_{\alpha\beta} \frac{R_{\beta\alpha} P_{\alpha\beta}}{D_\alpha D_\beta - P_{\alpha\beta} P_{\beta\alpha}},$$

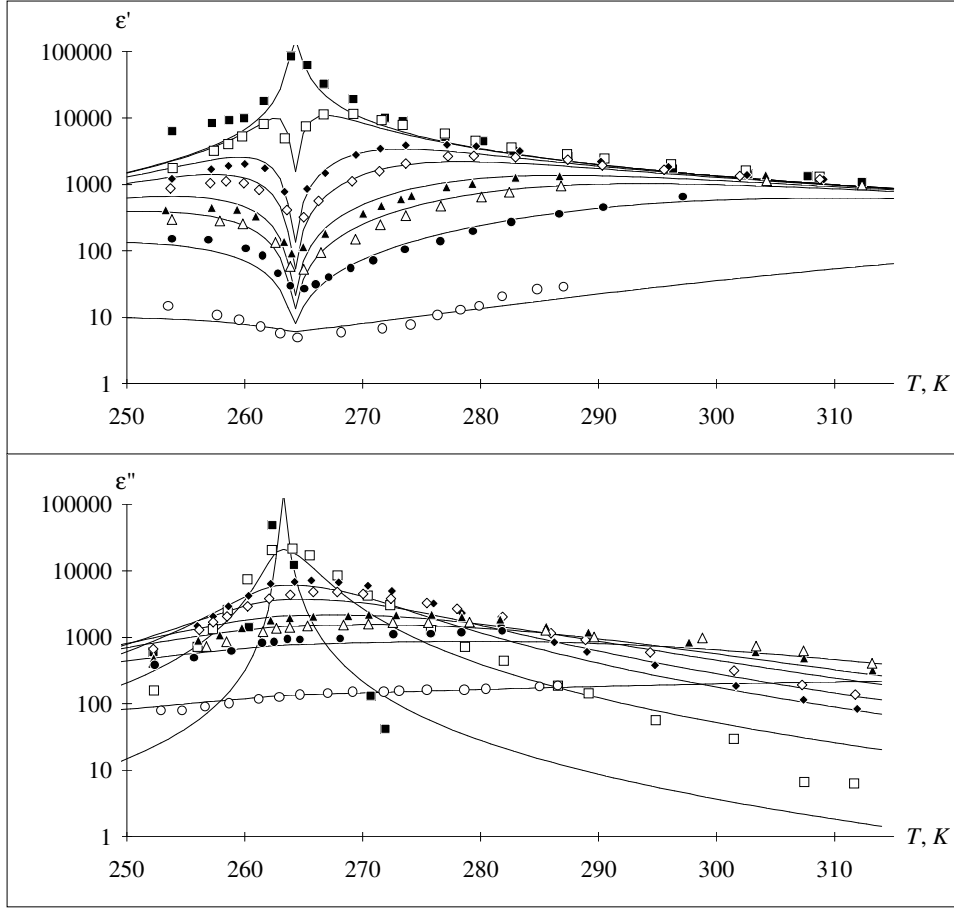


Figure 6. The dynamic dielectric permittivity  $\varepsilon = \varepsilon' - i\varepsilon''$  of the crystal  $CsD_2PO_4$  at the frequencies  $\nu = 5.1, 72.4, 251, 423, 730, 1044, 2000, 1150$  MHz: theoretical lines correspond to the model parameters of the table 2, symbols present the experimental data [9,16,22].

and

$$D_\alpha = 1 + i\omega\tau_\alpha^0; \quad P_{\alpha\beta} = \frac{1}{2} [\tanh(\bar{\kappa}'_\alpha + K_{\alpha\beta}) - \tanh(\bar{\kappa}'_\alpha - K_{\alpha\beta})] \quad (5.9)$$

$$R_{\alpha\beta} = 2a_{\alpha\beta} \frac{2a_{\alpha\beta}(1 + \cosh 2\bar{\kappa}'_\alpha \cosh 2\bar{\kappa}'_\beta) + (1 + a_{\alpha\beta}^2)(\cosh 2\bar{\kappa}'_\alpha + \cosh 2\bar{\kappa}'_\beta)}{\left[ \cosh(\bar{\kappa}'_\alpha + \bar{\kappa}'_\beta) + a_{\alpha\beta} \cosh(\bar{\kappa}'_\alpha - \bar{\kappa}'_\beta) \right]^2 (1 + a_{\alpha\beta}^2 + 2a_{\alpha\beta} \cosh 2\bar{\kappa}'_\alpha)}$$

Parameters of the theory are: the short-range interaction in chains  $K_{DD}$ ,  $K_{DH} = K_{HD}$ ,  $K_{HH}$ ; the  $\mathbf{q} = 0$  Fourier-transform of the long-range interaction  $J_{DD}$ ,  $J_{DH} = J_{HD}$ ,  $J_{HH}$ ; the effective dipole moments of deuteron and proton in hydrogen bond  $d_D$ ,  $d_H$ ; the relaxation times of noninteracting proton and deuteron  $\tau_D^0$ ,  $\tau_H^0$ . In the case of quenched disorder the probability  $w_{DH}$  to find proton and deuteron at the nearest neighbour  $H$ -bonds is another parameter, for the annealed system the parameter is a quantity  $\tilde{V} = V_{DD} + V_{HH} - 2V_{DH}$  that defines energetical advantage ( $\tilde{V} < 0$ ) or dis-

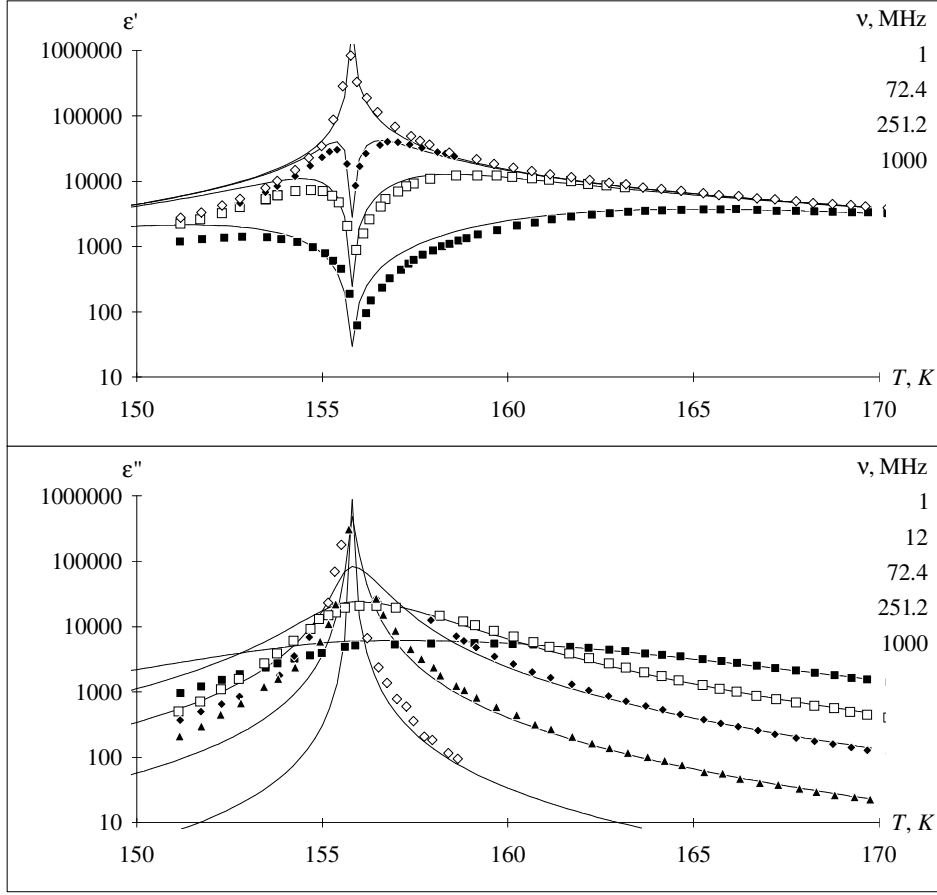


Figure 7. The dynamic dielectric permittivity of the crystal  $CsH_2PO_4$ . Lines present theoretical results (parameters in table. 2), symbols show experimental data [16].

advantage ( $\tilde{V} > 0$ ) of the sort configurations, when the nearest neighbour  $H$ -bonds contain proton and deuteron.

The figures 3, 4 and 6, 7 show that the theory provides good description for the crystals without chaos: CDP, LHP and their completely deuterated analogs (model parameters are given in table 2). For the better description of the permittivity and relaxation time in the ferroelectric phase one should take somewhat different values for the quasispin dipole moment  $d_\alpha$  and the bare relaxation time  $\tau_\alpha^0$  as it was in the papers [22,23,25].

For CDP there exist also dielectric measurements of partially deuterated crystals [15,16]. It should be noted that deuteron concentration  $x$  has not been measured in this experiments and dependence of the Curie temperature  $T_c$  on the degree of deuteration is unknown. Such information is highly desirable, because it raises requirements to the model parameters. Theoretical  $T_c(x)$  dependence for CDP is shown in the figure 5. Another drawback of the mentioned above experiments is that permittivity and relaxation time were not measured in the ferroelectric phase, where multidispersive relaxation and greater differences between annealed and quenched systems may take place.

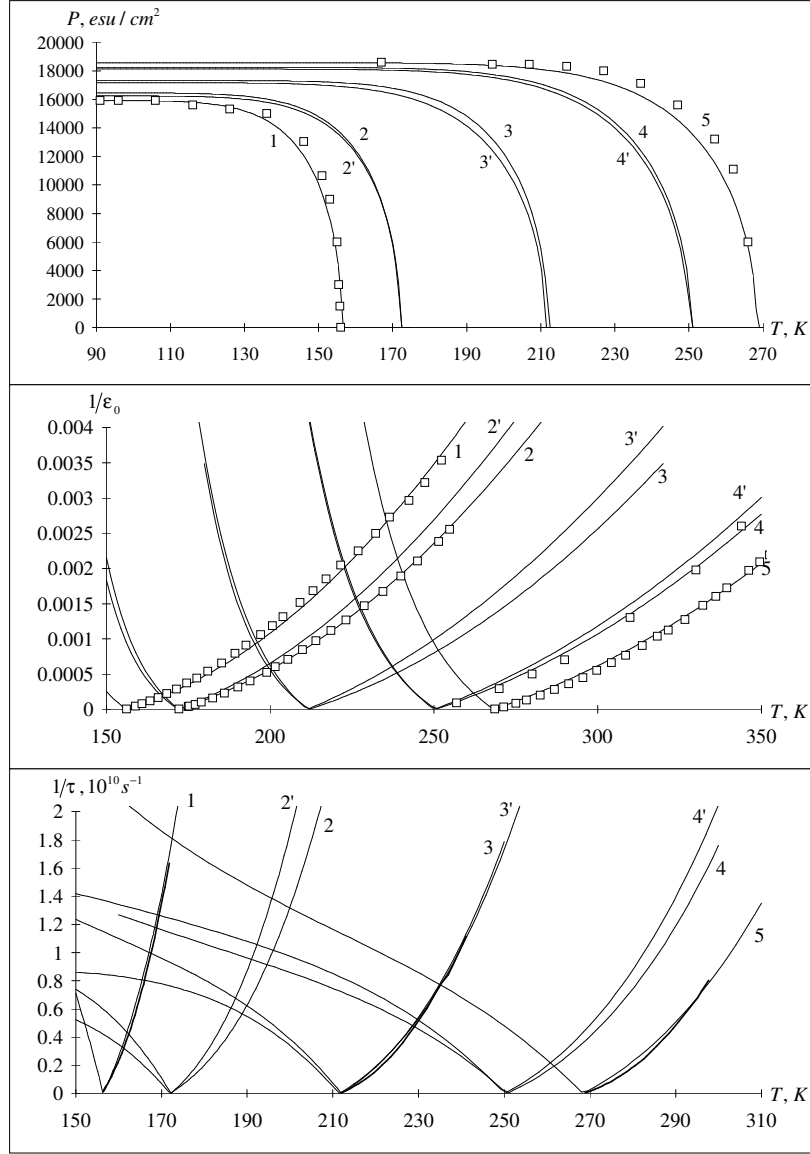


Figure 8. Comparison of the experiment (see also caption to figure 9) and the model with the nonequilibrium disorder. Thick lines show theoretical results for quenched model with parameters given in table 2. In the case of the complete sort chaos:  $w_{\alpha\beta} = c_\alpha c_\beta$  (lines 1, 2', 3', 4', 5 correspond to concentrations  $x = 0, 0.12, 0.47, 0.83, 1$ ) there is no satisfactory agreement between the theoretical and experimental values of  $1/\varepsilon_0$ . Good fit to experimental data can be reached, if we suppose that deuterons and protons tend to occupy the nearest  $H$ -bonds:  $w_{12} = \min(c_1, c_2) > c_1 c_2$  (the lines 1–5 describe concentrations  $x = 0, 0.2, 0.53, 0.88, 1$ ).

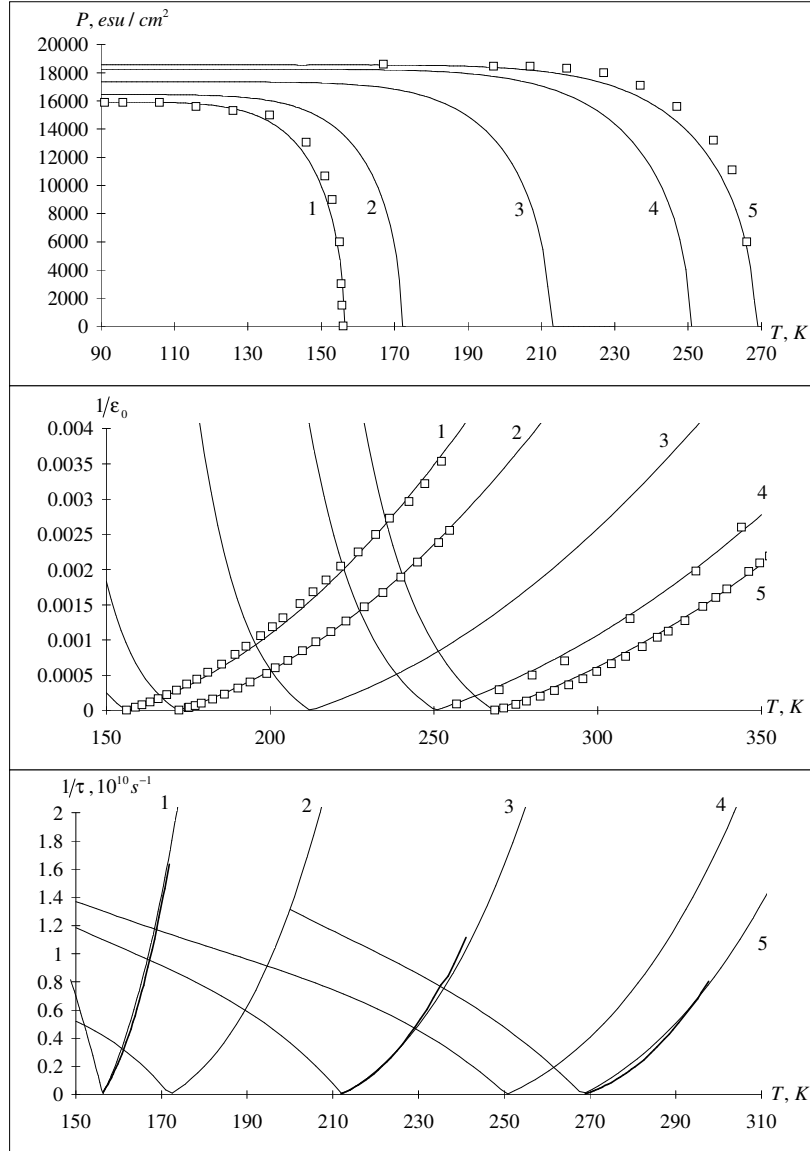


Figure 9. Spontaneous polarization  $P$ , inverse dielectric permittivity  $1/\epsilon_0$  and inverse relaxation time  $1/\tau$  of the ferroelectric  $\text{Cs}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$  at different degrees of deuteration. Squares correspond to experimental data [15], thin lines in the lower picture connect experimental points from the paper [16]. Thick lines, denoted by numbers 1–5 are theoretical results for equilibrium model with parameters given in table 2 for concentrations  $x = 0, 0.2, 0.54, 0.88, 1$ .

On the other hand, comparison of  $\mathbf{q}$ -dependent static and dynamic correlation functions with experimental data (e.g. neutron scattering experiments) might also be very interesting.

At given parameters the theory predicts almost monodispersive relaxation in paraphase for all  $x$ . Such behaviour actually takes place in the experiment for  $Cs(H_{1-x}D_x)_2PO_4$ . Figure 8 shows, that in the case of the quenched disorder with complete sort chaos ( $w_{\alpha\beta} = c_\alpha c_\beta$ ) the static permittivity differs from that of  $Cs(H_{1-x}D_x)_2PO_4$ . The annealed model with  $\tilde{V} = 0$  does not describe experiment also. Therefore we have rejected these (quite artificial) restrictions and obtained good fit to experiment within both annealed (figure 9) and quenched models (figure 8). Both models predict sort ordering in the system: great values of  $w_{12}$  signify that hydrogens and deuterons tend to situate at the nearest neighbour H-bonds. It means that the following ordering of  $H$  and  $D$  ions in chains takes place:  $DHDDDHDDHDDH$  at  $c_H < c_D$  (protons never meet together),  $HDHHDHHDHHDH$  at  $c_H > c_D$  (deuterons never situate at neighbouring hydrogen bonds) and  $DHDHDDH$  at  $c_H = c_D = \frac{1}{2}$ .

## 6. Conclusions

On the basis of disordered Ising model we develop the statistical theory for ferroelectric properties of pseudo-one-dimensional  $H$ -bonded ferroelectrics  $Cs(H_{1-x}D_x)_2PO_4$  and  $PbH_{1-x}D_xPO_4$ . We consider short-range intrachain interactions within two-site cluster approximation, long-range interactions are taken into account within mean field approximation. Dynamics of the system is considered on the basis of master equation approach. Thermodynamic potentials, order parameters, static and dynamic correlation functions of the model are calculated. We develop the theories for quenched and annealed systems and compare their predictions to experimental data. The model provides good description of dielectric measurements in the crystals of  $CsH_2PO_4$ ,  $PbHPO_4$  and their deuterated isomorphs. We have not determined a type of disorder in  $Cs(H_{1-x}D_x)_2PO_4$ , because both quenched and annealed theories match with available experimental data. The experimental determination of  $T_c(x)$ , dielectric measurements in the ferroelectric phase and the measurements, related with  $\mathbf{q}$ -dependent correlation functions, are desirable in this respect. The theory predicts a sort ordering in  $Cs(H_{1-x}D_x)_2PO_4$  crystals. This prediction as well as theoretical  $T_c$  on  $x$  dependence are the most interesting features for experimental verification.

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## СТАТИСТИЧНА ТЕОРІЯ КВАЗІОДНОВІМІРНИХ СЕГНЕТОЕЛЕКТРИКІВ З ВОДНЕВИМИ ЗВ'ЯЗКАМИ

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Термодинаміка і динаміка квазіодновимірних невідпорядкованих сегнетоелектриків з водневими зв'язками описується на основі невідпорядкованої моделі Ізінга. В наближенні двочастинкового кластера по короткосяжних взаємодіях розраховано термодинамічні потенціали, поляризацію, статичну і динамічну  $\mathbf{q}$ -залежні сприйнятливості. Теоретичні результати порівняно з результатами діелектричних вимірювань у чистих і частково дейтерованих сегнетоелектриках  $Cs(H_{1-x}D_x)_2PO_4$  та  $PbH(D)PO_4$ . Модель прогнозує наявність сортового впорядкування протонів і дейтеронів у  $Cs(H_{1-x}D_x)_2PO_4$ : протони і дейтерони мають тенденцію селитись на сусідніх водневих зв'язках.