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NON-LINEARITY EFFECTS IN MIXED HYDROGEN BONDED FERROELECTRICS. PHASE DIAGRAMS, PHASE TRANSITIONS, THERMODYNAMIC FUNCTIONS

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Abstract. The temperature and concentration dependencies of thermodynamic functions for ferroelectric-antiferroelectric mixed systems are discussed. The model Hamiltonian describe both ferroelectric (site dipole momentum oriented in *z*-direction in crystal) and antiferroelectric (site dipole momentum oriented in *x*-direction) subsytems of mixed hydrogen bonded ferroelectrics of KDP type. In the second order of replicas expansion, the free energy and others thermodynamic functions are calculated. The conditions for different phases (para-, ferro-, antiferroelectric, dipole glass, and some mixed combinations of them) realization has been founded. The critical behaviour of thermodynamic functions and the crossover problem are discussed.

1. INTRODUCTION

The most of existing crystalline materials, as it is well known, are not perfect structurally. The presence of impurities, defects, dislocations in them are usually observed. The great interest is now turned to the investigation of systems with magnetic or electric charged impurities inserted into a neutral matrix. Due to the competition of interaction among randomly distributed different particles there arises a new possibilities for ordering processes in the system. The most interesting of them are a long range ferromagnetic or ferroelectric states and a short range correlations, so called frozen spin disorder - the glassy state, which take place at low temperatures. The long range ordering is always observed for sufficient density of 'active' particles and is connected with the percolation problem, but a glassy state is present for intermediate concentration. Historically, the magnetic diluted systems were investigated for the first time in [1-4].

The process of preparation of the sample from solution or melt determine a two possible different types of disorder states. The slow cooling gives a statistically equilibrium distribution of impurities everywhere in the crystal. But rapid cooling leads to non equilibrium distribution of impurities, or quenched state. The first case is usually called the liquid-like state but the second one is called the amorphous state of the material. So, a great theoretical problem arises how to use the equilibrium statistic mechanics and to obtain a real physical properties of

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the second type investigated systems. The most effective method to solve this problem was done by Edwards and Anderson their famous 'replica method' [5]. In this method, the configuration averaging of randomly distributed impurities is performed not in a partition function, as it is usually done for equilibrium distribution, but in a free energy function (in the logarithm of partition function). Due to this approach, a thermodynamic functions of a system are obtained by two stage averaging procedure: local equilibrium thermal averaging for a given distribution of interparticle interactions and a stochastic averaging over choosen form of distribution (depending on the type of disorder in a simple) of this interactions.

The object of this paper is a ferroelectric-antiferroelectric mixed system of KDP type. A main feature of this type of materials is the presence of strong hydrogen bonds, which connect a neighboring oxygen in O_4 tetrahedra; the bonds connect also these tetrahedra. We should also note a fact that compounds containing potassium, rubidium, and cesium possess a ferroelectric properties with the polarization along *z*-axis of the crystal, but compounds containing ammonium group NH_4 instead them are antiferroelectrics with the axis of antipolarization in the perpendicular *x* or *z* directions. The typical representative of this class of compounds is a mixed Rubidium Ammonium Dihydrogen Arsenate $Rb_n(NH_4)_{1-n}H_2AsO_4$ (RADA), which was intensively studied by experimental methods in [6-11]. Those investigations were directed to found a phase diagram and the behaviour of thermodynamic functions. The existence of para-, ferro-, antiferroelectric, dipole glass, and several mixed phases in this complex compound was shown. The collected material confirm the ferroelectric properties of RADA at concentration $n \to 1$ and antiferroelectric properties at $n \to 0$. But only a dipole glass phase remains for intermediate concentration $0.35 \le n \le 0.85$ below the "freezing" temperature (50-80K).

Strong non-linear dependencies of all physical characteristics of investigated system on concentration and temperature were also observed. From the physical point of view, those non-linearities are a consequence of correlation between particles belonging to the same and to the different subsystems. Mathematically, all observed physical characteristics of the mixed system satisfy a set of non-linear equations and therefore demonstrate a non-linear behaviour. The problem of consequential description of physical properties for ferroelectric-antiferroelectric mixed RADA-type compounds will be considered below.

2. THE HAMILTONIAN

We regard a regular crystalline lattice of KDP-type system each site of which is occupied (quite randomly) by rubidium or ammonium groups, so by Rb or NH_4. Interaction between dipole momenta of Rb-AsO_4 groups from the same (short range forces) and from different (long range forces) sites leads to possibility of ferroelectric ordering along *z*-axis of the crystal. But the intercation between dipole momenta of NH_4-AsO_4 groups is responsible for antiferroelectric ordering in *x* direction.

The corresponding Hamiltonian has a form [12]:

$$\begin{aligned} H = -\frac{1}{2}\sum_{i,j}\sum_{mm'}\Big\{ & V_{ij}^{mm'}\hat{n}_i\hat{n}_j S_{mi}^{z} S_{m'j}^{z} \\ & + U_{ij}^{mm'}(1-\hat{n}_i)(1-\hat{n}_j) S_{mi}^{x} S_{m'j}^{x} \Big\}. \end{aligned} \tag{1}$$

Here both $V_{ij}^{mm'}$ and $U_{ij}^{mm'}$ are the intensities of interaction between *m*-th dipole particle in *i*-th site with m'-th dipole particle in *j*-th site for ferroelectric ordering subsystem (*z*-direction in the crystalline lattice) and for antiferroelectric ordering subsystem (*x*-direction) correspondingly; S^x, S^z are projections of the unit classical vector $\vec{S}$ on *x* and *z* axis respectively; the site occupation operators $\hat{n}_i$ have the next eigenvalues

$$n_i = \begin{cases} 1, \text{ when } i - \text{th site is occupied} \\ \text{by } z - \text{oriented particles} \\ 0, \text{ when } i - \text{th site is occupied} \\ \text{by } x - \text{oriented particles.} \end{cases}$$

Due to the competition between ferroelectric and antiferroelectric types of ordering at certain values of temperature and concentration of one component (for example rubidium containing sites) the crystal undergoes frustration: any long range order cannot exist and only short range correlations, which form a dipole-glass phase, remains. It is quite evidently that such situation take place for two different points in a phase diagram concentration - temperature (n,T). The first point corresponds to ferroelectric phase disappearance and the second one to antiferroelectric phase disappearance. So, we have a possibility to describe all experimentally detected thermodynamic phases and different types of ordering in the investigated mixed system.

Since the unit cell for KDP-type crystal contains two formula units (there are two sublatticies below a phase transition point) [13], the numbers *m, m′* run from 1 to 2. So, we will use the two-particle cluster approximation in which the interaction of particles belonging to the some site is taking exactly, but belonging to a different sites is taking with the help of self-consistent field [14]. In this approach we have:
for short range (intrasite) interactions

$$V_{ii}^{11} = V_{ii}^{22} = U_{ii}^{11} = U_{ii}^{22} = 0, \qquad V_{ii}^{12} = V_{ii}^{21} = V,\, U_{ii}^{12} = U_{ii}^{21} = U \tag{2}$$

and for symmetrized long-range (intersites) interactions

$$V_f = \frac{1}{2}\sum_j \left(V_{ij}^{11} + V_{ij}^{12}\right),\; U_f = \frac{1}{2}\sum_j \left(U_{ij}^{11} + U_{ij}^{12}\right), \qquad V_{\alpha f} = \frac{1}{2}\sum_j \left(V_{ij}^{11} - V_{ij}^{12}\right),\; U_{\alpha f} = \frac{1}{2}\sum_j \left(U_{ij}^{11} - U_{ij}^{12}\right). \tag{3}$$

Introduction of a self-consistent field is based on the assumption about negligible role of a square fluctuations:

$$\left(S_{mi}^{\alpha} - \left\langle S_{mi}^{\alpha}\right\rangle\right)\left(S_{m'i}^{\alpha} - \left\langle S_{m'i}^{\alpha}\right\rangle\right) = 0 \quad \text{for } i \neq j \;(\alpha = x, z) \tag{4}$$

outside of the second order phase transition point neighborhood.

3. REPLICA EXPANSION

The replica method is used for configuration averaging of thermodynamic functions over randomly distributed particles (groups) with *z*- and *x*-oriented dipole momenta all over the sites of crystalline lattice. This method [5,15] is based on the introduction of replicas istead original variables. In the present problem we must introduce *n* replicas σ_{mi}^{k} for S_{mi}^{z} and *n* replicas ξ_{ml}^{k} for S_{mi}^{x}.

We will use the next property of a binomial random variable χ_c. If the probability of χ_c $\Pr\{\chi_c = r\} = \binom{c}{r} p^r q^{c-r}$, then the expected value of $\exp\{a\chi_c\}$ is

$$E\left[\exp\{a\chi_c\}\right] = \left(pe^{a} + q\right)^{c}, \tag{5}$$

which behaves like 1+*c*ln(*pe*^{a} +*q*) when the analytic continuation for c→0 is taken out. The presence in the investigated system of two binomial random variables (σ and ξ) and a natural notation *p*=*n*, *q*=1-*n*, where *n* is a density (concentration) of groups with *z*-oriented dipole momentum in crystal, gives a possibility to obtain a systematic expansion for -β*H*:

$$\begin{aligned} -\beta H = \sum_{ij} \Big\{ & \sum_{k} J_1 \left[H_{ij}(\sigma^{k}) - H_{ij}(\xi^{k})\right] \\ & + \tanh(\beta V) H_{ij}(\xi^{k}) + \sum_{k,k'} J_2 \left[H_{ij}(\sigma^{k}) - H_{ij}(\xi^{k})\right] \\ & \times \left[H_{ij}(\sigma^{k'}) - H_{ij}(\xi^{k'})\right] + \ldots \\ & + \sum_{k_1, k_2, \ldots k_l} J_l \left[H_{ij}(\sigma^{k_1}) - H_{ij}(\xi^{k_1})\right] \\ & \left[H_{ij}(\sigma^{k_2}) - H_{ij}(\xi^{k_2})\right] \ldots \left[H_{ij}(\sigma^{k_l}) - H_{ij}(\xi^{k_l})\right] + \ldots \Big\}. \end{aligned} \tag{6}$$

Here

$$H_{ij}(\sigma^{k}) = \frac{1}{V}\sum_{m,m'} V_{ij}^{mm'} \sigma_{mi}^{k} \sigma_{m'j}^{k}, \qquad H_{ij}(\xi^{k}) = \frac{1}{V}\sum_{m,m'} U_{ij}^{mm'} \xi_{mi}^{k} \xi_{m'j}^{k}, \tag{7}$$

$$\begin{aligned} J_1 &= \sum_{t=1}^{\infty} (-1)^{t}\, 2 \ln\left(1 - n + ne^{-2\beta V_t}\right), \\ J_l &= \sum_{t=1}^{\infty} (-1)^{t}\, 4 \ln\left(1 - n + ne^{-2\beta V_t}\right), \\ &\;\;\vdots \\ J_l &= \sum_{t=1}^{\infty} (-1)^{t} P_{l-1} \ln\left(1 - n + ne^{-2\beta V_t}\right), \end{aligned} \tag{8}$$

$P_{l\text{-}1}$(t) is a polynomial in *t* with degree *l*-1, β=1/*kT*, *k* is the Boltzman constant, *T* is the absolute temperature.

With the accuracy up to the second order of replicas expansion in (6) and using the two-particle cluster approximation we have:

$$\begin{aligned} -\beta H = \sum_{i} \big\{ & A_1 \sigma_{1i} \sigma_{2i} + B_1 \left(\sigma_{1i} + \sigma_{2i}\right) \\ & + A_2 \xi_{1i} \xi_{2i} + B_2 \left(\xi_{1i} - \xi_{2i}\right) \big\} - C. \end{aligned} \tag{9}$$

Here

$$C=\left\{J_1\frac{V_f}{V}P^2+\left(\tanh\beta V-J_1\right)\frac{U_{af}}{V}q^2\right.$$
$$+\frac{J_2}{2}\left[-2+\left(g_z-\frac{U}{V}g_x\right)^2+\left(\frac{V_f+V_{af}}{V}\right.\right.$$
$$\left.+\frac{V_f+V_{af}}{V}g_z\right)^2+\left(\frac{U_f+U_{af}}{V}+\frac{U_f+U_{af}}{V}g_x\right)^2 \qquad (10)$$
$$\left.\left.+24\left(\frac{V_f}{V}P^2-\frac{U_{af}}{V}q^2\right)^2\right]\right\};$$

$$A_1=J_1+J_2\left[\frac{V_f^2-V_{af}^2}{V^2}+\left(1+\left(\frac{V_f-V_{af}}{V}\right)\right)g_z\right.$$
$$\left.-\frac{U}{V}g_x\right],$$
$$B_1=J_1\frac{V_f}{V}P+4J_2\left[\left(\frac{V_f}{V}\right)^2P^3-\frac{V_f}{V}\frac{U_{af}}{V}Pq^2\right],$$
$$A_2=\left(\tanh\beta V-J_1\right)\frac{U}{V}$$
$$+J_2\left[\frac{U_f^2-U_{af}^2}{V^2}+\left(\left(\frac{U}{V}\right)^2+\left(\frac{U_f-U_{af}}{V}\right)^2\right)g_x\right.$$
$$\left.-\frac{U}{V}g_z\right], \qquad (11)$$
$$B_2=\left(\tanh\beta V-J_1\right)\frac{U_{af}}{V}q$$
$$+4J_2\left[\left(\frac{U_{af}}{V}\right)^2q^3-\frac{V_f}{V}\frac{U_{af}}{V}P^2q\right];$$

$P=\overline{\langle\sigma_{1i}\rangle}, q=\overline{\langle\xi_{1i}\rangle}$ are ferroelectric and antiferroelectric order parameters respectively; $g_z=\overline{\langle\sigma_{1i}\sigma_{2i}\rangle}$, $g_x=\overline{\langle\xi_{1i}\xi_{2i}\rangle}$ are dipole glass parameters, $\langle\ldots\rangle$ denotes thermal averaging for a given distribution of *z*- and *x*-oriented dipole momentum of Rb-AsO$_4$ or NH$_4$-AsO$_4$ groups respectively, whereas a bar denotes a stochastic averaging over different distributions.

4. PHASE DIAGRAM. THERMODYNAMIC FUNCTIONS

Performing the trace operation in the expression for free energy

$$F=-\frac{1}{\beta}\ln Tr\left\{e^{-\beta H}\right\} \qquad (12)$$

over cluster states of spin-like variables σ and ξ one can obtain:

$$F=-\frac{1}{\beta\ln}\left\{4\left(e^{-A_1}+e^{A_1}\cosh 2B_1\right)\right.$$
$$\left.\times\left(e^{-A_2}+e^{A_2}\cosh 2B_2\right)\right\}+\frac{1}{\beta}C. \qquad (13)$$

Minimization procedure of (13) under all introduced order parameters *P*, *q*, g_z, g_x gives a set of equations for their determination:

$$P=Z^{-1}e^{A_1}\sinh 2B_1\left(e^{A_2}+e^{-A_1}\cosh 2B_2\right),$$
$$q=Z^{-1}e^{A_2}\sinh 2B_2\left(e^{-A_1}+e^{A_2}\cosh 2B_1\right),$$
$$g_z=Z^{-1}\left(e^{-A_1}-e^{A_1}\cosh 2B_1\right)$$
$$\times\left(e^{A2}+e^{-A_2}\cosh 2B_2\right),$$
$$g_x=Z^{-1}\left(e^{-A_1}+e^{A_1}\cosh 2B_1\right)$$
$$\times\left(e^{A2}-e^{-A_2}\cosh 2B_2\right), \qquad (14)$$
$$Z=\left(e^{-A_1}+e^{A_1}\cosh 2B_1\right)$$
$$\times\left(e^{A2}+e^{-A_2}\cosh 2B_2\right).$$

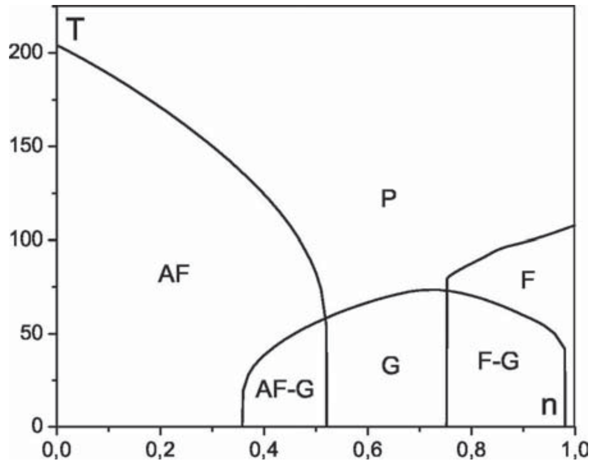

Fig. 1. Phase diagram of RADA (phase transition temperature versus concentration *n* of Rb containing groups in the crystal) built for the model Hamiltonian parameters: V_f=70K, V_{af}=-80K, U_f=-40K, U_{af}=120K, *V*=65K, *U*=-210K.

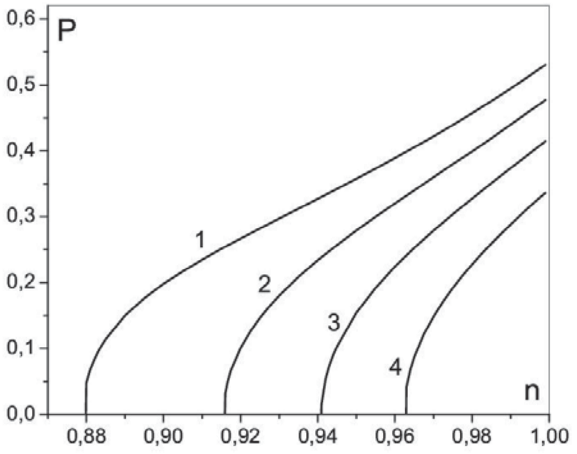

Fig. 2. Ferroelectric order parameters versus concentration n for some fixed temperatures; curves: 1-T=98K, 2-T=100K, 3-T=102K, 4-T=104K. The model Hamiltonian parameters are the same as in Fig. 1.

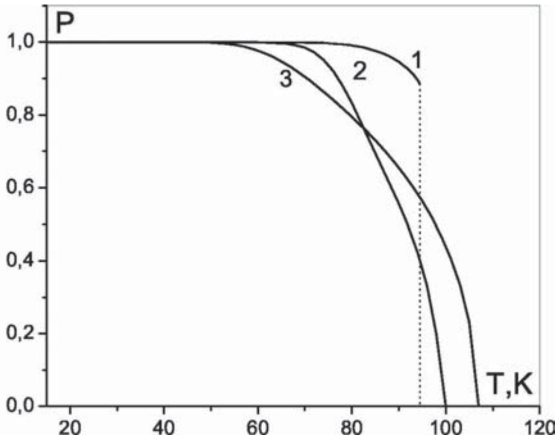

Fig. 3. Ferroelectric order parameters versus temperature for some fixed concentrations n; curves: 1-n=0,80, 2-n=0,90, 3-n=0,99. The model Hamiltonian parameters are the same as in Fig. 1.

The set (14) must be called the set equations of state, because it completely determine the state of investigated system with the Hamiltonian (1). It can be underline the complex non-linear dependencies of all order parameters on each other. So, the solution of (14) in a general form is a considerably complicated problem. But the most interesting in this situation is a phase diagram of investigated system. Such diagram can be obtained as lines dividing different possible phase regions in coordinates: concentration-temperature. Taking as fitting parameters of the theory the phase transition temperatures for pure compounds, namely for RbH_2AsO_4 T_c=110K, and for $NH_4H_2AsO_4$ T_N=216K, we had built a phase diagram of $Rb_n(NH_4)_{1-n}H_2AsO_4$ presented in Fig. 1. The lines dividing paraelectric (P) – ferroelectric (F) and paraelectric (P) – antiferroelectric (AF) phases are obtained from the conditions $P\to 0$ or $q\to 0$. But the line determined a dipole glass phase (G) (in lower part of the diagram) corresponds to the points of bifurcation the number of roots g_z, g_x for set (14). At low temperatures, below the mentioned line, there are several different values of g_z, g_x, but at high temperatures, upper this line, only one value of g_z and one value of g_x is realized. So, in our opinion, the dipole glass state is characterized by non-uniform short rang correlations of dipole momenta.

It is interesting to note the existence of mixed ferroelectric-dipole glass (F-G) and antiferroelectric-dipole glass (AF-G) phases, which take place in practically whole region of concentration for ferroelectric phase but only in rather small region of concentration for antiferroelectric phase. These results are in good coincidence with experiment [10,16]. But there are some quantitative discrepancy in the ciritical points of concentration where the ferroelectric phase appears. Namely, this calculated critical value is $n\approx 0,75\div 0,80$ whereas the experimental one is $n\approx 0,82\div 0,90$ [8-10]. As for the corresponding critical value of concentration for antiferroelectric branch of the phase diagram, the calculated and observed experimentally points are the same ($n\approx 0,50\div 0,52$).

The sharply asymmetric behaviour of $Rb_n(NH_4)_{1-n}H_2AsO_4$ phase diagram is usually explained by the large difference in the phase transition temperatures (approximately twice) for pure components. Our investigation shows an evident tendency of mixed system to prefer antiferroelectric type of ordering as compare with ferroelectric one. This assertion refers to corresponding values of concentration which are characteristic for both types of ordering (large and small n). As a result, the percolation phenomena for both types of ordering takes places at non-symmetric points.

The concentration dependence of ferroelectric order parameter (P) is presented in Fig. 2 for $n>0.78$. Each curve is built at fixed temperature from the region for which the ferroelectric phase exist. Similar behaviour demonstrate also curves for antiferroelectric order parameter (q), but for $n<0.5$ and in corresponding temperature region. Presented in Fig. 3 temperature dependence of P for different concentration shows an interesting peculiarity. When the concentration n increases, P behaves more smoothly, so a type of phase transition changes from the second order close to first order into strict second order one. We observe a cross-over of the phase transition order under concentration. Similar tendency, as it is well known, is typical when short range interaction becomes more and more weaker as compare with long range interparticle interaction. For antiferroelectric phase transition the same conclusion is true.

As for static dielectric susceptibility

$$\chi_f = \left(\frac{\partial P}{\partial E}\right)_{E=0}, \ \chi_{af} = \left(\frac{\partial q}{\partial E}\right)_{E=0} \tag{15}$$

one must remember that ferroelectric ordering reacts on uniform internal field E, but antiferroelectric ordering depend only on variable field $E(t)$ with a wave length multiple to a lattice period. So, in uniform field only $\chi_f \neq 0$. To calculate the first expression in (15) we had introduced in (9) a term

$$\sum_i \{\beta E(\sigma_{1i} + \sigma_{2i}) + \beta E(\xi_{1i} + \xi_{2i})\} \tag{16}$$

which gives an energy of investigated system in uniform external field E.

As a result, the expression (13) for the free energy changes into

$$F = -\frac{1}{\beta}\ln\Big\{4\Big[e^{-A_1} + e^{A_1}\cosh 2(B_1 + \beta E)\Big] \times\Big[e^{A_2}\cosh 2\beta E + e^{-A_2}\cosh 2B_2\Big]\Big\} + \frac{1}{\beta}C \tag{17}$$

and now we have a new expressions for P, q, g_z, g_x depending on E. For longitudinal dielectric susceptibility (along z-axis), one may obtained a formula

$$\chi(n,T) = \frac{2\beta\left(\cosh 2\tilde{B}_1 + e^{2A_1}\right)}{e^{2A_1}\left(\cosh 2\tilde{B}_1 + e^{-2A_1}\right)^2 - 2\left(\cosh 2\tilde{B}_1 + e^{2A_1}\right)\left(J_1\frac{V_f}{V} + 12J_2\left(\frac{V_f}{V}\right)^2 P^2\right)}, \tag{18}$$

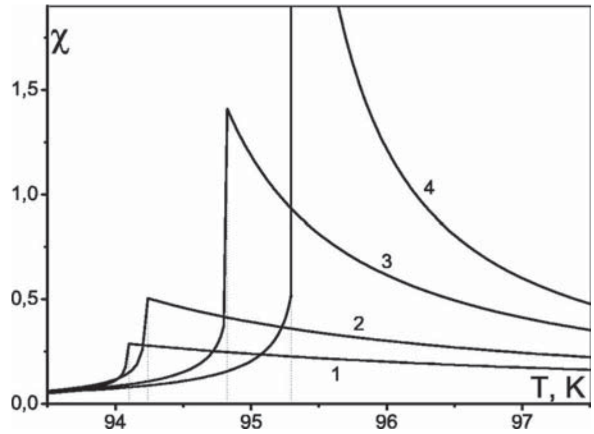

Fig. 4. The temperature dependencies of dielectric susceptibility (in arbitrary units) for some fixed concentrations n; curves: 1-n=0,81, 2-n=0,82, 3-n=0,83, 1-n=0,835. The model Hamiltonian parameters are the same as in Fig. 1.

where A_1 must be taken from (11), and

$$\tilde{B} = J_1\frac{V_f}{V}P + 4J_2\left(\frac{V_f}{V}\right)^2 P^3. \tag{19}$$

For four fixed concentrations the temperature dependence of $\chi(T)$ is presented in Fig.4. One can see a qualitative difference in the curves behaviour when a concentration is changed. For the frustration region of concentration their maximum becomes smaller and $\chi(T)$ possess the behaviour typical for the first order phase transition. The experimental confirmation of the $\chi(T)$ dependencies under concentration (Fig.4) one can found in [16], where for isomorphic $K_n(NH_4)_{1-n}H_2PO_4$ mixed system the dielectric permittivity is presented. A similar situation take place for transverse susceptibility (along x-axis) but at variable field only. Always one must remember that for dielectric susceptibility determination the external electric field must be conjugated to corresponding order parameter. As we observe the concentration and temperature behaviour of all thermodynamic functions for ferroelectric-antiferroelectric mixed system of KDP type is essentially non-linear.

5. SUMMARY

The model of ferroelectric-antiferroelectric mixed system has been applied for the description of thermodynamic properties of $Rb_n(NH_4)_{1-n}H_2PO_4$ (RADA) type crystals. The free energy of investigated system was obtained using the replica method for configuration averaging over randomly distributed particles with *z*- and *x*-oriented dipole momenta.

The existence of mixed ferroelectric-dipole glass and antiferroelectric-dipole glass phases was founded. The investigation shows a sharply asymmetric behaviour of RADA phase diagram under concentration of the one of the component, because the percolation phenomena for both types of ordering takes places at non-symmetric points. A crossover of the phase transition order under concentration is also observed.

The temperature and concentration dependencies of static dielectric susceptibility are calculated and analyzed. Their behaviour is in a good coincidence with the experimental data.

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