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# The peculiarities of glass state formation and the role of random elastic fields in mixed crystals of the $\text{KH}_2\text{PO}_4$ family

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**Abstract.** The source of random static electrical fields, which is determined by both the piezoelectric coupling and the static elastic deformations induced by substitutional disorder of ions with different ionic radii has been considered for mixed crystals of the  $\text{KH}_2\text{PO}_4$  family. It is shown that the random electrical fields act mainly on the lattice polarization along the  $c$  axis and up–down proton configurations. The short-range interactions of four acid protons surrounding a  $\text{PO}_4$  group are represented as the random local uniaxial anisotropy for the mixed crystals provided the ice rule condition is fulfilled. It is also shown that the distinction of symmetry between the up–down and lateral proton configuration, and the peculiarities of proton–lattice interaction can lead to the coexistence of long-range order (for up–down/lateral configuration) with the glass or paraelectric (for lateral/up–down configuration) state.

## 1. Introduction

In study of the glass state, one frequently meets examples of glass states that are impossible to describe solely by random interaction [1–5]. This leads to the necessity to discuss alternative sources of disorder (such as random fields, random anisotropy, etc.) simultaneously with the random interaction. Disordered systems that cannot be described by taking into account only the random interaction between moments are mixed crystals of the potassium dihydrogenphosphate ( $\text{KH}_2\text{PO}_4$ , KDP) family, for example, rubidium ammonium dihydrogenphosphate,  $(\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ , RADP) [6–8]. The phase diagram of RADP [9–11] shows that, for  $0.0 < x < 0.22$ , a ferroelectric (FE) phase and, for  $0.74 < x < 1.0$ , an antiferroelectric (AF) phase are observed, while for the intermediate concentration,  $0.22 < x < 0.74$ , the crystals remain in a paraelectric (PE) phase and manifest glass-like properties on cooling [9–11]. This glass-like state is called a proton glass (PG). Initially, it was assumed that the type of order in RADP was determined by the  $\text{NH}_4$ -mediated interaction between acid protons belonging to different  $\text{PO}_4$  groups [12]. To describe the PG state, a random-bond Ising model was proposed [13]. However, the freezing of the acid protons occurs over an unusually large temperature interval far above the glass transition temperature  $T_g$  [2, 6, 8]. As a result, the necessity appeared for random local fields to be included in the description of the glass state. For this purpose, a random-bond Ising model with a random field was proposed [7]. The random local fields in RADP are assumed to be determined by the off-centre positions of  $\text{NH}_4$  groups, which induce a random tilt in the double-well potentials of the acid protons [6–8]. It is important to note that, although jumps of  $\text{NH}_4$  between the off-centre sites are much slower than interbond jumps of acid protons between the two possible equilibrium sites [14], the random local fields induced by the off-centre  $\text{NH}_4$  groups are not, in the strict sense, static fields. Brillouin-scattering investigations of RADP have

shown that a static central peak emerged in addition to a dynamic central peak [15–17]. The static central peak can be explained in terms of freezing of acid protons in the random static fields on the timescale of Brillouin scattering. The static local fields are also found by nuclear magnetic resonance (NMR) [8, 18] and electron paramagnetic resonance (EPR) [19] measurements at all temperatures. Consequently, it is necessary to study alternative sources of random local fields that generate the static fields and are not necessarily determined by the off-centre position of  $\text{NH}_4$  groups.

The special feature of the random local fields in RADP is an asymmetry of their influence on the freezing of acid protons. So, the onset of freezing of acid protons in the PE phase occurs at higher temperature for the range of  $x$  on the Rb-rich side than for the range of  $x$  on the  $\text{NH}_4$ -rich side [9–11]. Brillouin-scattering results also show that the range of the activation energy distribution on the Rb-rich side is wider than on the  $\text{NH}_4$ -rich side [16]. Therefore the feature of the random local fields mentioned above must be taken into account for an investigation of new sources of random local fields.

The polarization of KDP family crystals can interact both linearly (piezoelectric coupling) and quadratically (electrostriction) with the elastic deformation [15, 16]. The type of coupling of the polarization with elastic deformation depends on the content of  $\text{NH}_4$  groups. So, the piezoelectric coupling is the dominant coupling mechanism for  $x \rightarrow 0$ , whereas the electrostriction is the main coupling mechanism for  $x \rightarrow 1$  in mixed crystals of RADP type [16]. As a rule, for any mixed crystals, the substitutional disordered ions with different ionic radii generate static random elastic fields [3, 4]. The piezoelectric coupling and the random elastic fields can give rise to random electric fields. The importance of this mechanism for glass state formation was noted in a review [9]. These random fields enable us to understand not only the nature of the static central peak and asymmetric proton freezing mentioned above but also the nature of the dynamic central peak, which can be understood as the action of weak random electric fields via lattice anharmonic interaction [17] (e.g. electrostriction) as well. Hence, even weak random electric fields play an important role in glass state formation and need to be considered.

It should be pointed out that the random-bond Ising model with a random field [7] does not take into account an ice rule condition (two protons per  $\text{PO}_4$ ). In KDP family crystals, the configurations of acid protons follow the ice rule condition [20]. Although the investigation of the glass state in the KDP family under the ice rule is a more difficult problem than study of the glass state in, for example,  $\text{KBr}_{1-x}\text{CN}_x$  and  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ , it is clear that the ice rule condition must be taken into account in investigation of the PG state. The theoretical study of the PG state under the ice rule condition has been done elsewhere [12, 21–23], but they did not take into consideration the interactions between up–down proton configurations, the existence of random static fields, and the possibility of coexistence of long-range order with the glass state.

In this work we will propose to use the pseudovector representation for the lowest Slater proton configurations instead of the pseudospins of acid protons. Within this representation, we will present the short-range interaction of acid protons surrounding a  $\text{PO}_4$  group as a random local anisotropy for mixed crystals of RADP type, provided that the ice rule condition is fulfilled. Then we will investigate the source of the static random electric fields based on both the piezoelectric coupling and the static random deformation induced by the difference in ionic radii between the substitutional ions in the mixed crystals. It will also be shown that the piezoelectric coupling decreases as  $x \rightarrow 1$  in mixed crystals of RADP type. From the distinction of symmetry between the up–down and the lateral proton configuration, and from the peculiarities of proton-lattice interaction, we will show that the

coexistence of long-range order (for up-down/lateral configuration) with the glass state (for lateral/up-down configuration) can take place in mixed crystals of RADP type.

## 2. Ice rule and model Hamiltonian

Before proceeding to a consideration of proton-lattice interactions, we have modified the representation for the lowest Slater configurations of acid protons and short-range interaction of four protons associated with a  $PO_4$  group given in [12, 22, 23]. In order to describe the proton configurations in the KDP family, pseudospins  $\sigma_i(\mathbf{r})$ , which take value +1 or -1 for the two possible positions of  $i$ th proton, are introduced. The Hamiltonian of short-range interaction in clusters of four spins  $\sigma_1(\mathbf{r})$  ( $\mathbf{r}$  is the position of the  $PO_4$  groups, and  $i, j = 1-4$  are the indexes of protons surrounding the  $PO_4$  group) is given by

$$H_s = - \sum_{\mathbf{r}} H_4(\mathbf{r}) = - \sum_{\mathbf{r}, j>i} J_{ij}(\mathbf{r}) \sigma_i(\mathbf{r}) \sigma_j(\mathbf{r})$$

$$J_{12}(\mathbf{r}) = J_{23}(\mathbf{r}) = J_{34}(\mathbf{r}) = J_{41}(\mathbf{r}) = -V$$

$$J_{13}(\mathbf{r}) = J_{24}(\mathbf{r}) = -U. \quad (1)$$

In RADP it is assumed that each  $H_2PO_4$  cluster has a random set of parameters ( $U, V$ ) that is determined according to RDP-like ( $\epsilon_0 = 4(V - U) > 0$ ) or ADP-like ( $\epsilon_0 < 0$ ) surrounding [22, 23]. Among the 16 possible states of protons surrounding a  $PO_4$ , only the six lowest Slater configurations of protons (up-down and lateral) have two protons near  $PO_4$  group ( $H_2PO_4$ ) [20]. Following [22, 23], the condition

$$\sigma_1(\mathbf{r}) + \sigma_2(\mathbf{r}) + \sigma_3(\mathbf{r}) + \sigma_4(\mathbf{r}) = 0 \quad (2)$$

is realized for the lowest Slater configurations of protons. Equation (2) is the ice rule condition.

Let us introduce the components of pseudovector  $S$  in the form

$$S_x(\mathbf{r}) = \frac{1}{4}[\sigma_1(\mathbf{r}) + \sigma_2(\mathbf{r}) - \sigma_3(\mathbf{r}) - \sigma_4(\mathbf{r})] \quad (3a)$$

$$S_y(\mathbf{r}) = \frac{1}{4}[\sigma_1(\mathbf{r}) - \sigma_2(\mathbf{r}) - \sigma_3(\mathbf{r}) + \sigma_4(\mathbf{r})] \quad (3b)$$

$$S_z(\mathbf{r}) = \frac{1}{4}[\sigma_1(\mathbf{r}) - \sigma_2(\mathbf{r}) + \sigma_3(\mathbf{r}) - \sigma_4(\mathbf{r})]. \quad (3c)$$

The components  $S_\alpha(\mathbf{r})$  ( $\alpha = x, y, z$ ) can be represented as a unit vector that points along  $\langle 100 \rangle$  directions

$$S(\mathbf{r}) = e_x S_x(\mathbf{r}) + e_y S_y(\mathbf{r}) + e_z S_z(\mathbf{r}) \quad (4)$$

$$(e_\alpha e_\beta) = \delta_{\alpha\beta} \quad \sum_{\alpha} S_\alpha^2 = 1$$

where  $\delta_{\alpha\beta}$  is the Kronecker symbol ( $\alpha, \beta, \gamma = x, y, z$ ).

Expressing  $\sigma_i(\mathbf{r})$  in terms of components  $S_\alpha$  (equations (3a)–(3c)) under the ice rule condition (2) and substituting in  $H_4(\mathbf{r})$ , we have

$$H_4(\mathbf{r}) = -\epsilon_0(\mathbf{r}) S_z^2(\mathbf{r}) \quad \text{for } \epsilon_0 > 0 \quad (5)$$

$$H_4(\mathbf{r}) = \epsilon_0(\mathbf{r}) [S_x^2(\mathbf{r}) + S_y^2(\mathbf{r})] \quad \text{for } \epsilon_0 < 0. \quad (6)$$

Close inspection of equations (5) and (6) shows that  $H_s$  can be represented in the form

$$H_s = - \sum_{\mathbf{r}} |\epsilon_0(\mathbf{r})| [L(\mathbf{r})S(\mathbf{r})]^2 \quad L^2(\mathbf{r}) = 1 \quad (7)$$

where vector  $L$  points along one of  $\{100\}$  directions ( $L(\mathbf{r})\|e_z$  for  $\epsilon_0(\mathbf{r}) > 0$  and  $L(\mathbf{r})\|e_x, e_y$  for  $\epsilon_0(\mathbf{r}) < 0$ ).

One can see from  $H_s$  in (7) that the random sign of  $\epsilon_0(\mathbf{r})$  is similar to the random local uniaxial anisotropy [1].

In view of the fact that the short-range interaction characterized by the parameter  $\epsilon_0$  is greater than other interactions in crystals of the KDP family, the random local uniaxial anisotropy (7) has to be strong. In this case vector  $S$  can be written in the form

$$S(\mathbf{r}) = \sum_i^{N_i} e_z s_z \delta_{r r_i} + \sum_{\substack{\alpha=x,y \\ j \neq i}}^{N_j} e_\alpha s_\alpha \delta_{r r_j}. \quad (8)$$

Here  $s_z$  takes value  $+1$  and  $-1$  for the up-down configurations;  $s_x$  and  $s_y$  are components of a vector that points along one of  $[100]$ ,  $[\bar{1}00]$ ,  $[010]$ ,  $[0\bar{1}0]$  directions and describes the lateral configurations;  $r_i$  are sites for  $\epsilon_0 > 0$  and  $N_i$  ( $1-x = N_i/N$ ) is the number of sites;  $r_j$  are sites for  $\epsilon_0 < 0$  and  $N_j$  ( $x = N_j/N$ ) is the number of sites; and  $N$  is the number of  $PO_4$  groups.

### 3. Piezoelectric coupling and random fields

Let us now turn to a consideration of the interactions of acid protons with acoustic and low-frequency optical phonons. The vibrations of displacements of the centre of mass of a unit cell  $u'(\mathbf{r})$  are known to define the acoustic phonons. The Hamiltonian of acoustic phonons has the well known form

$$H_a = K + U_a = \frac{1}{2} \sum_k \left[ M \dot{u}'(k) \dot{u}'(-k) + \sum_{\alpha\beta} u'_\alpha(k) A'_{\alpha\beta}(k) u'_\beta(-k) \right] \quad (9)$$

where  $u'(k)$  is the Fourier transform of  $u'(\mathbf{r})$ :

$$u'(\mathbf{r}) = \frac{1}{N^{1/2}} \sum_k e^{ikr} u'(k).$$

Hereafter we will use the notations  $u(k) = u'(k)M^{1/2}$  and  $A(k) = A'(k)/M$ .

Let us consider the effect of substitutional disorder of ions with different ionic radii in the lattice. Substitutional disorder can be the reason for static displacements of the centres of mass. The distinctive property of the disorder discussed above is the concentration dependence of the lattice constants [24]. So, the concentration dependence of lattice constants is observed in RADP [11] also. Hence it is necessary to discuss these effects of disorder to understand the type of order in RADP. It is convenient to present the density of local forces with the help of an elastic dipole moment tensor,  $\Omega_{\alpha\beta}$ . The tensor  $\Omega_{\alpha\beta}$  is defined by the relation [25].

$$H_{\text{imp}} = - \sum_{\mathbf{r}, \alpha\beta} \Omega_{\alpha\beta}(\mathbf{r}) u_{\alpha\beta}(\mathbf{r}) = -i \sum_{\mathbf{k}, \alpha\beta} \Omega_{\alpha\beta}(\mathbf{k}) k_\alpha u_\beta(\mathbf{k}) \quad (10a)$$

$$u_{\alpha\beta} = \frac{1}{2} [\partial u_\alpha(\mathbf{r}) / \partial r_\beta + \partial u_\beta(\mathbf{r}) / \partial r_\alpha] \quad (10b)$$

$$\Omega_{\alpha\beta}(\mathbf{r}) = (\Omega_{\alpha\beta} / M^{1/2}) \Delta \rho(\mathbf{r}) \quad \Delta \rho(\mathbf{r}) = \delta_{rr}, -x \quad (10c)$$

where  $r_i$  are the positions of ions with concentration  $x$ , and  $M$  is the average mass per unit cell. In this paper it is assumed that only the dilatational part  $\Omega_{\alpha\beta} = \Omega_1 \delta_{\alpha\beta}$  determines the size of the elastic dipole tensor, whereas the quadrupole part is negligibly small.

The new equilibrium positions induced by the substitutional disorder are determined by minimizing the elastic energy  $H_1 = U_a + H_{imp}$ . Results of minimization determine the contribution to the new displacements of the centres of mass of unit cells

$$y_\beta(\mathbf{k}) = u_\beta(\mathbf{k}) - u_\beta^{st}(\mathbf{k}) = u_\beta(\mathbf{k}) + i \sum_\gamma k_\gamma [\Omega(\mathbf{k}) A^{-1}(\mathbf{k})]_{\beta\gamma} \quad (11)$$

where  $u_\beta^{st}(\mathbf{k})$  is the Fourier transform of the static displacement induced by the substitutional disorder in the approximation of isotropic elastic medium [24]. Taking into account equation (11), Hamiltonian (6) can be written in the form

$$H_a = \frac{1}{2} \sum_{\mathbf{k}} [\dot{y}(\mathbf{k}) \dot{y}(-\mathbf{k}) + \sum_{\alpha\beta} y_\alpha(\mathbf{k}) A_{\alpha\beta}(\mathbf{k}) y_\beta(\mathbf{k})] - \frac{1}{2} \sum_{\gamma\gamma'k} k_\gamma k_{\gamma'} [\Omega(\mathbf{k}) A^{-1}(\mathbf{k}) \Omega(\mathbf{k})]_{\gamma\gamma'} \quad (12)$$

The last term of Hamiltonian (12) is the indirect interaction of elastic dipoles via acoustic phonons. In this work it is assumed that the indirect interaction is negligible and can be ignored. It should be noted that a similar indirect interaction was considered for  $KBr_{1-x}CN_x$  [3] and  $K_{1-x}Li_xTaO_3$  [4, 26].

The vibrations of the displacements  $x_\alpha^m(\mathbf{r})$  ( $m$  is the index of displacement of ions relative to the position of the centre of mass) are known to determine optical phonons in the lattice. The Hamiltonian of the optical phonons has the usual form

$$\begin{aligned} H_O &= \frac{1}{2} \sum_{m,\mathbf{k}} \left( \mu_m \dot{x}^m(\mathbf{k}) \dot{x}^m(-\mathbf{k}) + \sum_{\alpha\beta} x_\alpha^m(\mathbf{k}) \Phi_{\alpha\beta}^m(\mathbf{k}) x_\beta^m(-\mathbf{k}) \right) \\ &= \frac{1}{2} \sum_{\mathbf{k},\nu} [\dot{x}_\nu(\mathbf{k}) \dot{x}_\nu(-\mathbf{k}) + \omega_\nu^2(\mathbf{k}) x_\nu(\mathbf{k}) x_\nu(-\mathbf{k})] \end{aligned} \quad (13)$$

where  $x_\alpha^m(\mathbf{k})$  is the Fourier transform of  $x_\alpha^m(\mathbf{r})$ , i.e.

$$x_\alpha^m(\mathbf{k}) = \frac{1}{\mu_m^{1/2}} \sum_\nu e_\alpha^{\nu m}(\mathbf{k}) x_\nu(\mathbf{k}).$$

Here  $x_\nu(\mathbf{k})$  is the normal-mode coordinate for the  $\nu$ th optical branch of frequency  $\omega_\nu(\mathbf{k})$ ,  $e_\alpha^{\nu m}$  are components of the polarization vector and  $\mu_m$  is the reduced mass.

In the following we shall restrict our consideration only to cases of low-frequency optical phonons of  $B_2$  ( $\nu = 1$ ) and  $E$  ( $\nu = 2$ ) symmetries. The optical modes of  $B_2$  symmetry are determined by  $Rb-H_2PO_4$  vibrations.  $Rb-H_2PO_4$  groups form the lattice polarizations along the  $c$  axis [27]. The optical  $E$  modes are determined by  $NH_4-H_2PO_4$  vibrations.  $NH_4-H_2PO_4$  groups form the lattice polarization in the plane  $a-b$  [27].

In the KDP family elastic deformation can interact with polarization via linear piezoelectric coupling as well as quadratic electrostriction coupling [28]. Here we shall restrict ourselves only to the case of linear piezoelectric coupling, which can be written in the form

$$H_{ao} = \sum_{\substack{r,r' \\ \alpha\beta m}} D_{\alpha\beta}(\mathbf{r} - \mathbf{r}') u_\alpha(\mathbf{r}) x_\beta^m(\mathbf{r}) = \sum_{\mathbf{k},\nu\alpha} D_\alpha^\nu(\mathbf{k}) u_\alpha'(\mathbf{k}) x_\nu(-\mathbf{k}). \quad (14)$$

In the long-wave limit the coupling coefficients  $D_\alpha^y(k)$  are [29]

$$D_\alpha^y(k) = D_{\alpha\beta}^y k_\beta \quad D_{\alpha\beta}^y = D_{\beta\alpha}^y \quad (15)$$

where  $D_{\alpha\beta}^y$  are the components of a piezoelectric tensor  $D_{\alpha\beta}^y$  ( $D_{xy}^1 = D_{xy}^z$ ,  $D_{yz}^2 = D_{yz}^x$ ,  $D_{xz}^2 = D_{xz}^y$  and the other  $D_{\alpha\beta}^y = 0$ ).

The conditions

$$D_{xy}^z \gg D_{yz}^x = D_{xz}^y \quad (16)$$

are realized in the KDP family [28]. From conditions (16) it follows that we can restrict our consideration to piezoelectric coupling  $D_{xy}^z$  for  $B_2$  symmetry polarization along the  $c$  axis with the shift deformation  $u_{xy}$ . The piezoelectric coupling  $H_{a0}$  in (14) is represented for pure crystals of the KDP family. In mixed crystals, as is seen from equation (11), the substitutional disorder induces random elastic fields. As a consequence,  $H_{a0}$  needs to be represented with the help of  $y_\beta(k)$ . So, one obtains

$$H_{a0} = i \sum_{\substack{k, \alpha\beta \\ \alpha, \beta = x, y}} \frac{D_{\alpha\beta}^z}{M^{1/2}} k_\alpha y_\beta(k) x_1(-k) - \sum_k E_{RF}(k) x_1(-k) \quad (17)$$

$$E_{RF}(k) = i \sum_{\substack{k, \alpha\beta \\ \alpha, \beta = x, y}} \frac{D_{\alpha\beta}^z}{M^{1/2}} k_\alpha u_\beta^{st}(k).$$

From equation (17) it follows that  $E_{RF}(k)$  acts as the static random electric field on polarization along the  $c$  axis. For the random electric field, we have

$$\overline{E_{RF}(k)} = 0, \quad \overline{E_{RF}(k) E_{RF}(-k')} \sim \delta_{kk'} x(1-x) (D_{xy}^z)^2 (\Omega_1)^2 \quad (18)$$

where an overbar represents configurational averaging.

Let us introduce the interaction of pseudospins  $\sigma_i(\mathbf{r})$  with acoustic phonons by means of piezoelectric coupling, as was done in [29] for pure KDP. This interaction can be written in the form

$$H_{sa} = \sum_{i, \mathbf{r}\mathbf{r}'} d_\alpha^i(\mathbf{r} - \mathbf{r}') \sigma_i(\mathbf{r}) u_\alpha(\mathbf{r}). \quad (19)$$

It should be pointed out that the coefficients  $d_\alpha^i(\mathbf{r} - \mathbf{r}')$  must possess properties identical with  $D_{\alpha\beta}(\mathbf{r} - \mathbf{r}')$ . So, the conditions

$$d_{xy}^z \gg d_{xz}^y = d_{yz}^x \quad (20)$$

are realized for the components of piezoelectric tensor  $d_{\alpha\beta}^y$ . Individual pseudospins  $\sigma_i(\mathbf{r})$  or their combination have to satisfy the necessary symmetrical properties. The Slater configurations  $s_x$ ,  $s_y$  and  $s_z$  possess the required symmetries, whereas the individual pseudospins have not. The  $s_z$  configurations have  $B_2$  symmetry [27]. The configurations  $s_x$  and  $s_y$  have E symmetry [27] and can interact with  $u_{yz}$  and  $u_{xz}$  via  $d_{yz}^x$  and  $d_{xz}^y$  respectively.

Based on the symmetry properties of piezoelectric coupling and conditions (20),  $H_{sa}$  can be represented in the form

$$H_{sa} = i \sum_{\alpha, \beta=x, y} \frac{d_{\alpha\beta}^z}{M^{1/2}} k_\alpha u_\beta(\mathbf{k}) s_z(-\mathbf{k}). \quad (21)$$

Here the strong uniaxial anisotropy (7) is taken into account.

In view of the fact that the substitutional disorder generates the random displacements (11),  $H_{sa}$  in (21) can be written in the form

$$H_{sa}^m = i \sum_{\alpha, \beta=x, y} \frac{d_{\alpha\beta}^z}{M^{1/2}} k_\alpha y_\beta(\mathbf{k}) s_z(-\mathbf{k}) - \sum_{\mathbf{k}} \mathcal{E}_{RF}(\mathbf{k}) s_z(-\mathbf{k}) \quad (22)$$

$$\mathcal{E}_{RF}(\mathbf{k}) = i \sum_{\alpha, \beta=x, y} \frac{d_{\alpha\beta}^z}{M^{1/2}} k_\alpha u_\beta^{st}(\mathbf{k}).$$

Analogously to equation (18), the random fields  $\mathcal{E}_{RF}$  satisfy conditions

$$\overline{\mathcal{E}_{RF}(\mathbf{k})} = 0 \quad |\overline{\mathcal{E}_{RF}(\mathbf{k}) \mathcal{E}_{RF}(-\mathbf{k})}| \sim x(1-x)(d_{xy}^z)^2 (\Omega_1)^2. \quad (23)$$

As is seen from equations (18) and (22), the random electric fields associated with piezoelectric coupling mainly act on the lattice polarization along the  $c$  axis and proton configurations  $s_z$ . Because the polarization along the  $c$  axis and up-down configurations are determined by the ions with concentration  $1-x$  in mixed crystals of  $Rb_{1-x}(NH_4)_xH_2PO_4$  type, this leads to a decrease in the piezoelectric coupling with  $x \rightarrow 1$ .

#### 4. Coexistence of ordering with glass or paraelectric state

In the KDP family the acid protons can interact with the low-frequency optical phonons by means of linear coupling [30]. So, the  $B_2$  optical mode interacts with  $s_z$  proton configurations, whereas  $E$  optical modes interact with  $s_x$  and  $s_y$  [27]. The Hamiltonian of the interaction of the polarization and acid protons is

$$H_{so} = \sum_{\mathbf{k}} f_1^z x_1(\mathbf{k}) s_z(-\mathbf{k}) - \sum_{\alpha=x, y} \sum_{\mathbf{k}} f_2^\alpha x_2(\mathbf{k}) s_\alpha(-\mathbf{k}). \quad (24)$$

For mixed crystals of the KDP family, the Hamiltonian of the total proton-lattice coupling without considering electrostriction and tunnelling is given by

$$H_{tot} = H_F + H_{AF} + H_s \quad (25)$$

with

$$\begin{aligned} H_F = & \frac{1}{2} \sum_{\mathbf{k}} (\dot{x}_1(\mathbf{k}) \dot{x}_1(-\mathbf{k}) + \omega_1^2(\mathbf{k}) x_1(\mathbf{k}) x_1(-\mathbf{k})) \\ & + \frac{1}{2} \sum_{\mathbf{k}} \left( \dot{y}(\mathbf{k}) \dot{y}(-\mathbf{k}) + \sum_{\lambda} y_\lambda(\mathbf{k}) C_{\lambda\lambda}(\mathbf{k}) y_\lambda(-\mathbf{k}) \right) + \sum_{\mathbf{k}} D y_6(\mathbf{k}) x_1(-\mathbf{k}) \\ & + \sum_{\mathbf{k}} [d y_6(\mathbf{k}) s_z(-\mathbf{k}) + \mathcal{E}_{RF}(\mathbf{k}) s_z(-\mathbf{k}) + E_{RF}(\mathbf{k}) x_1(-\mathbf{k}) + f_1^z x_1(\mathbf{k}) s_z(-\mathbf{k})] \end{aligned} \quad (26)$$

$$H_{AF} = \frac{1}{2} \sum_{\mathbf{k}} \left( \dot{x}_2(\mathbf{k}) \dot{x}_2(-\mathbf{k}) + \omega_2^2(\mathbf{k}) x_2(\mathbf{k}) x_2(-\mathbf{k}) \right) + \sum_{\gamma=x, y} f_2^\gamma x_2(\mathbf{k}) s_\gamma(-\mathbf{k}) \quad (27)$$



where  $y_\alpha(\mathbf{k})$  and  $A(\mathbf{k})$  are represented in more suitable forms by means of a deformation tensor  $y_\lambda$  and elastic constants  $C_{\lambda\lambda} = c_{\lambda\lambda}v$  ( $v$  is the volume of the unit cell); for  $\lambda = 6$ ,  $2y_6(\mathbf{k}) = y_{xy}(\mathbf{k})$  ( $y_{\alpha\beta} = (1/M^{1/2})[k_\alpha y_\beta(\mathbf{k}) + k_\beta y_\alpha(\mathbf{k})]$ ),  $d_{xy}^z = d$  and  $D_{xy}^z = D$ . The Hamiltonian  $H_s$  in (25) is given by (7).

As seen from Hamiltonian (25), the protons are divided into two independent systems. (i) The acid protons from one system are associated with  $s_z$  configurations placed in the sites with local uniaxial anisotropy along the  $c$  axis (5). These protons interact with both low-frequency  $B_2$  modes and acoustic modes. The piezoelectric coupling ( $D_{xy}^z$  and  $d_{xy}^z$ ) and random elastic deformations induced by substitutional disorder generate random static electrical fields  $E_{RF}$  (17) and  $\mathcal{E}_{RF}$  (22), which act on the lattice polarization along the  $c$  axis and  $s_z$  configurations, respectively. (ii) The other system of protons associated with  $s_x, s_y$  configurations and arranged in positions with local uniaxial anisotropy perpendicular to the  $c$  axis has negligibly small piezoelectric coupling. Consequently, the main source of the random electrical fields for  $s_x$  and  $s_y$  may take place due to the off-centre position of  $NH_4^+$  ions [6–8].

In addition, as follows from  $H_{tot}$ , the cooperative properties of  $s_z$  configurations are mainly defined by indirect interaction via the low-frequency optical  $B_2$  mode, while the cooperative properties of  $s_x, s_y$  configurations are due to indirect interaction via the low-frequency optical E mode. As a consequence of disordered positions of  $s_z$  and  $s_x, s_y$  configurations in systems of RADP type, random-sign indirect interaction terms appear in addition to terms of constant-sign indirect interaction. The terms of random-sign interaction are known to give rise to the PG state. Hence the partitioning of  $H_{tot}$  (25) into  $H_F$  and  $H_{AF}$  can lead to a mixed phase that is characterized by the coexistence of the ordered state with glass or PE state, which was in fact observed recently [31]. So, if  $x \rightarrow 0$ , FE ordering occurs for  $s_z$  configurations, whereas the PG state independently takes place for  $s_x$  and  $s_y$  configurations. If  $x \rightarrow 1$ , the PG state takes place for  $s_z$ , while AF ordering occurs for  $s_x$  and  $s_y$ . For  $x \sim 0.5$ , the PG state appears for  $s_z$  as well as  $s_x, s_y$  configurations. Up to now, when studying the PG state in RADP, particular attention has been given to  $NH_4$ -mediated indirect interactions of pseudospins  $\sigma_i(\mathbf{r})$  [6, 8, 12, 32] and non-identity of  $s_x$  and  $s_y$  configurations [12]. This interaction can be derived from  $H_{AF}$ , and non-identity of  $s_x$  and  $s_y$  may be obtained by means of the different coefficients of linear coupling with the low-frequency optical E mode.

However, the understanding of ordering of acid protons in mixed crystals of KDP type is not possible without a theoretical consideration of Hamiltonian  $H_F$ . Unlike  $H_{AF}$ , terms of linear coupling  $s_z$  configurations with the optical  $B_2$  mode result in the indirect interaction via  $Rb-PO_4$  groups. In addition, linear piezoelectric coupling (21) leads to electrical fields  $\mathcal{E}_{RF}$  that act on  $s_z$  configurations. As a result, the effect of  $\mathcal{E}_{RF}$  gives rise to the onset of freezing of the acid protons at higher temperature for  $s_z$  configurations than for  $s_x, s_y$  configurations.

It should be pointed out that the peculiarities of the phase transitions in mixed ferroelectrics  $KH_2P_{1-x}As_xO_4$  (for  $x = 0$ ,  $T_{c1} = 122$  K; and for  $x = 1$ ,  $T_{c2} = 96$  K) [33, 34] can be described with the help of  $H_F$  only, because in this case all the acid protons are in the form of  $s_z$  configurations. Hence the investigation of cooperative behaviour of  $s_z$  configurations is the urgent problem.

## 5. Cooperative behaviour of $s_z$ configurations

The study of the cooperative properties of  $s_z$  configurations in RADP on the basis of  $H_F$  is a complicated task, which requires taking into account the disorder effects both for the

system of acid protons and for the low-frequency optical  $B_2$  mode simultaneously. Let us restrict ourselves to the simplest case of site disorder of  $s_z$  configurations. The optical  $B_2$  mode will be assumed to have no dependence on  $x$  and  $E_{RF}$ . We shall suppose also that the effective lattice-mediated interaction between  $s_z$  configurations is mainly defined by the constant-sign interaction for the considered concentration range.

We shall include the electrical fields  $\mathcal{E}_{RF}$  in the simple mean-field model by means of standard statistical-mechanical procedures [35, 36] for random-field systems. The mean-field approximation for Hamiltonian  $H_F$  has the form

$$\begin{aligned}
 H_F^{mf} = & Nf_1^z \langle x_1 \rangle \overline{\langle s_z \rangle} - Nd \langle y_6 \rangle \overline{\langle s_z \rangle} - \sum_{\mathbf{r}_i} [f_1^z \langle x_1 \rangle - d \langle y_6 \rangle + \mathcal{E}_{RF}(\mathbf{r})] s_z(\mathbf{r}_i) \\
 & - N^{1/2} (Z_1 E - f_1^z \overline{\langle s_z \rangle}) x_1(0) + \frac{1}{2} [\dot{x}_1(0)^2 + \omega_1(0)^2 x_1(0)^2] \\
 & + \frac{1}{2} [\dot{y}_6(0) \dot{y}_6(0) + y_6(0) C_{66}(0) y_6(0)] + D y_6(0) x_1(0) + N^{1/2} d \overline{\langle s_z \rangle} y_6(0) \\
 & + \frac{1}{2} \sum_{\mathbf{k} \neq 0} \{ [\dot{x}_1(\mathbf{k}) \dot{x}_1(-\mathbf{k}) + \omega_1(\mathbf{k})^2 x_1(\mathbf{k}) x_1(-\mathbf{k})] + y_6(\mathbf{k}) C_{66}(\mathbf{k}) y_6(-\mathbf{k}) \} \\
 & + \frac{1}{2} \sum_{\mathbf{k}} \left( \dot{y}_6(\mathbf{k}) \dot{y}_6(-\mathbf{k}) + \sum_{\lambda \neq 6} y_\lambda(\mathbf{k}) C_{\lambda\lambda}(\mathbf{k}) y_\lambda(-\mathbf{k}) \right). \quad (28)
 \end{aligned}$$

Here  $\langle x_1 \rangle$  is the thermal average of displacement associated with the polarization along the  $c$  axis,  $\langle y_6 \rangle$  is the thermal average of elastic deformation  $y_{xy}$ ,  $x_1(0)$  and  $y_6(0)$  are  $x_1(\mathbf{k})$  and  $y_6(\mathbf{k})$  for  $\mathbf{k} = 0$ ,  $E$  is the external electric field, and  $z_1$  is the charge of the optic mode ( $\nu = 1$ ). For the case of 'free' crystal  $X_6 = 0$  ( $X_6$  is a shift strain  $X_{xy}$ ) [28], the thermal averages  $\langle x_1(0) \rangle$  and  $\langle y_6(0) \rangle$  are found from the conditions [29]

$$\begin{aligned}
 \partial H_F^{mf} / \partial x_1(0) = 0 & = \omega_1^2 \langle x_1(0) \rangle - N^{1/2} [z_1 E + f_1^z \langle y_6(0) \rangle] + D \langle y_6(0) \rangle \\
 \partial H_F^{mf} / \partial y_6(0) = 0 & = C_{66} \langle y_6(0) \rangle + N^{1/2} d \overline{\langle s_z \rangle} + D \langle x_1(0) \rangle. \quad (29)
 \end{aligned}$$

Here  $\langle x_1(0) \rangle = N^{1/2} \langle x_1 \rangle$  and  $\langle y_6(0) \rangle = N^{1/2} \langle y_6 \rangle$ ,  $\omega_1 = \omega_1(0)$ . In the following discussion we shall restrict our consideration to the case of weak piezoelectric coupling ( $D^2 \ll C_{66} \omega_1^2$  and  $d^2 < (f_1^z)^2 C_{66} / \omega_1^2$ ). Expressing  $\langle y_6(0) \rangle$  and  $\langle x_1(0) \rangle$  in terms of  $\overline{\langle s_z \rangle}$  and substituting them into Hamiltonian (28), one obtains

$$\begin{aligned}
 H_{\text{eff}} = & \frac{1}{2} N J_0 \overline{\langle s_z \rangle}^2 - (N z_1^2 / 2 \omega_1^2) (1 + D^2 / C_{66} \omega_1^2) E^2 \\
 & - \sum_{\mathbf{r}_i} (J_0 \overline{\langle s_z \rangle} + \mu_{\text{eff}} E + \mathcal{E}_{RF}) s_z(\mathbf{r}_i) + \frac{1}{2} \omega_1^2 (1 - D^2 / C_{66} \omega_1^2) [x_1(0) - \langle x_1(0) \rangle]^2 \\
 & + \frac{1}{2} C_{66} [y_6(0) - \langle y_6(0) \rangle]^2 + \frac{1}{2} \sum_{\mathbf{k} \neq 0} [\dot{x}_1(\mathbf{k}) \dot{x}_1(-\mathbf{k}) + \omega_1(\mathbf{k})^2 x_1(\mathbf{k}) x_1(-\mathbf{k})] \\
 & + \frac{1}{2} \left[ \sum_{\mathbf{k}} \left( \dot{y}_6(\mathbf{k}) \dot{y}_6(-\mathbf{k}) + \sum_{\lambda=1}^5 y_\lambda(\mathbf{k}) C_{\lambda\lambda}(\mathbf{k}) y_\lambda(-\mathbf{k}) \right) + \sum_{\mathbf{k} \neq 0} y_6(\mathbf{k}) C_{66}(\mathbf{k}) y_6(-\mathbf{k}) \right] \quad (30)
 \end{aligned}$$

with

$$\begin{aligned}
 J_0 & = (f_1^z)^2 / \omega_1^2 + (1 / C_{66}) (d + D f_1^z / \omega_1^2)^2 \\
 \mu_{\text{eff}} & = f_1^z z_1 / \omega_1^2 + (D z_1 / C_{66} \omega_1^2) (d + D f_1^z / \omega_1^2)
 \end{aligned}$$

where  $J_0$  is the sign-constant indirect interaction between  $s_z$  configurations, and  $\mu_{\text{eff}}$  is an effective dipole moment.

Using Hamiltonian (30), the free energy is determined by

$$F = -kT \int \prod_k \overline{dx_1(k) dx_1(-k) x_1(k) x_1(-k) \dots} \sum_{\{s_z(r_i)\}} \exp(-H_{\text{eff}}/kT). \quad (31)$$

From the condition  $\partial F / \partial \overline{\langle s_z \rangle} = 0$ , we have for RADP-type systems

$$\overline{\langle s_z \rangle} = (1-x) \overline{\{\tanh[(J_0 \overline{\langle s_z \rangle} + \mu_{\text{eff}} E + \mathcal{E}_{\text{RF}})/kT]\}}. \quad (32)$$

Taking into account (29) and (32), the polarization  $P$  per unit volume is  $P = z_1 \langle x_1 \rangle / v$  and the dielectric susceptibility has the conventional form

$$\epsilon = \epsilon_0 + [4\pi(1-x)(1-q)\mu_{\text{eff}}^2] / vk(T - T_c) \quad (33)$$

$$\epsilon_0 = \epsilon_\infty + (4\pi z_1^2 / v\omega_1^2)(1 + D^2 / C_{66}\omega_1^2) \quad (34)$$

$$T_c = (1-x)(1-q)J_0/k \quad (35)$$

$$q = \overline{\{\tanh[(J_0 \overline{\langle s_z \rangle} + \mu_{\text{eff}} E + \mathcal{E}_{\text{RF}})/kT]\}^2}. \quad (36)$$

Here  $\epsilon_\infty$  is the high-frequency dielectric susceptibility. It should be noted that the relation (35) is derived for mixed crystals of RADP type with low  $x$ . Equation (35) was initially obtained by Schneider and Pytte [35]. Using the high-temperature expansion, parameter  $q$  can be presented by

$$q \sim x(1-x)\Omega_1^2 (d_{xy}^z)^2. \quad (37)$$

In accordance with equations (35) and (37), the concentration dependence of  $T_c$  is defined not only by the multiplicative factor  $(1-x)$ , which characterizes the up-down proton configurations, but also by the concentration dependence of  $q$  as well.

From equations (23) and (37), it follows that the amplitude of the random elastic fields and  $q$  are described by the dilatational part of elastic dipole tensor  $\Omega_1$ , which is determined by the cell volume deformation due to the difference in ionic radii of substitutional ions. The ionic radii of  $\text{Rb}^+$ ,  $\text{NH}_4^+$  and  $\text{K}^+$  are 1.48, 1.42 and 1.33 Å respectively [9]. The closeness of ionic radii  $\text{Rb}^+$  and  $\text{NH}_4^+$  is the reason for the small relative change of volume of unit cells  $\Delta v/v \sim 0.005$  [9] of pure crystals (RDP and ADP) and the small value of  $\Omega_1$  in RADP, whereas the ionic radius  $\text{K}^+$  markedly differs from that of  $\text{NH}_4^+$ . This leads to the large relative change of volume of unit cells  $\Delta v/v \sim 0.09$  [9] for pure crystals (KDP and ADP) and large value of  $\Omega_1$  in  $\text{K}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ .

For mixed ferroelectric crystals  $\text{KH}_2\text{P}_{1-x}\text{As}_x\text{O}_4$ , the sign-constant lattice-mediated interaction of  $s_z$  proton configurations and random electrical fields are crucial in ordering of acid protons. Without counting the small difference in the dipole moments of  $\text{PO}_4$  and  $\text{AsO}_4$  groups ( $T_{c1} = T_{c2}$ ), the concentration dependences of  $\epsilon$  and  $T_c$  can be described by (33) and (35) in which the multiplicative factor  $(1-x)$  at  $J_0$  and  $\mu_{\text{eff}}^2$  is equal to 1. Then the concentration dependences of these parameters is defined by the random fields  $q$  (37). The relative change of volume of unit cells for  $\text{KH}_2\text{PO}_4$  and  $\text{KH}_2\text{AsO}_4$  is  $\Delta v/v \sim 0.08$  [9]. Hence the random electrical fields must be taken into account for the mixed ferroelectric crystals.

## 6. Conclusions

We have shown that the random electric fields that are connected with piezoelectric coupling and random elastic fields produced by difference in ionic radii must be taken into account in investigations of the glass state for mixed crystals of the  $KH_2PO_4$  family. It is also shown that the piezoelectric coupling decreases as  $x \rightarrow 1$  in mixed crystals of RADP type and the random electric fields associated with the piezoelectric coupling mainly act on the polarization along the  $c$  axis and up-down configurations. The random electric fields in mixed ferroelectric crystals of the  $KH_2P_{1-x}As_xO_4$  type are the chief cause of the disorder effects that are responsible for the glass state. It is demonstrated that the mixed crystals of RADP type have not only random-sign interaction between pseudospins and random fields but also random local anisotropy as well. The distinction of symmetry between the up-down and the lateral proton configurations together with the peculiarities of the proton-lattice interaction can give rise to the coexistence of long-range order (for the up-down/lateral configurations) with the glass state (for lateral/up-down configurations).

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