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Short-Range Interaction Explanation of Ferroelectric, Antiferroelectric and Proton Glass Behavior in Pure RDP, ADP, and Mixed RDP-ADP Crystals Respectively

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A unified model is presented for $Rb_{1-x}(NH_4)_xH_2PO_4$ crystals over the whole range $x=0$ (RDP) to $x=1$ (ADP). Two short-range interactions are postulated. One is the Slater energy ε_0 which is kept at the value for RDP for all x. The other is an interaction ε_a between two hydrogens in O-H$\cdots$O bonds across an NH_4^+ ion from each other. It is responsible for the off-center positions observed for ammonium ions in the antiferroelectric phase of ADP. Its strength is assumed proportional to x. By minimizing the free energy, one finds a range of x for which no transition occurs, but instead proton glass behavior sets in. Fox x near 0 and 1 respectively, first-order ferroelectric and antiferroelectric transitions are predicted. Both phase boundaries are close to those observed experimentally.

§1. Introduction

We present here a unified model employing only short-range interactions which reproduces quite accurately the $Rb_{1-x}(NH_4)_xH_2PO_4$ phase diagram. This is the first model employing only short-range interactions which explains the following three features:

1) Ferroelectric (FE) transition in RbH_2PO_4 (RDP),
2) Antiferroelectric (AFE) transition in $NH_4H_2PO_4$ (ADP), and
3) Proton glass behavior in $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP).

However, Matsushita and Matsubara have presented two cluster theories closely related to each other, one[1] which explains the FE and AFE transitions and the other[2] which explains proton glass behavior. Also, Prelovsek and Blinc[3] developed a cluster theory which treats all three features above.

In the $x=0$ limit our model reduces to the Slater[4] model for KH_2PO_4 (KDP) and its isomorphs such as RDP. For ADP ($x=1$) it differs from the Ishibashi[5] model in that it requires no longrange interaction to predict the AFE transition. For RADP it predicts accurately the range of x for which Courtens[6] and Terauchi *et al.*[7] found frozen-in disorder at low temperature.

§2. Model Description

We deviate in two ways from Ishibashi's treatment of ADP. First, we keep the Slater energy ε_0 unchanged as x goes from 0 to 1, instead of changing its sign. Second, instead of introducing the long-range Coulomb interactions which Ishibashi *et al.* needed even with negative ε_0 to obtain the AFE transition at nonzero temperature, we introduce a new short-range energy ε_a.

Our basis for introducing e_a was the observation by Hewat[8] that in the AFE phase of ADP, the NH_4^+ ions sit near one side of the puckered square of four oxygens to which they are H-bonded (upper right side in Fig. 1). They form two adjacent shorter H-bonds to two oxygens which have their acid protons at the far ends of their O-H$\cdots$O bonds, and form longer (weaker) bonds to the other two oxygens which have close acid protons. To account for this off-center NH_4^+ position, we assign energy $-\varepsilon_a/2$ to a pair of oxygens with one close and one far acid hydrogen (O_a and O_b, or O_c and O_d, in Fig. 1), and assign energy $+\varepsilon_a/2$ if both protons are close, or both far. We assume in this paper that ε_a is proportional to the ammonium concentration x.

The numbers of down and up polarized Slater groups are labelled N_d and N_u respectively. The number of groups which constitute the four types of AFE domains are labelled N_r, N_g, N_f, and N_b. The N_i and fractional populations $n_i=N_i/N$ obey the relations $\Sigma N_i=N$ and $\Sigma n_i=1$, where N is the number of phosphate ions.

In calculating the internal energy we find, for example, that the probability that in the configuration shown in Fig. 1 there is an acid hydrogen near (as shown) to the oxygen H-bonded on the left side of the ammonium ion is $n_u+n_r+n_b$.

The internal energy U then is given by

$$U=-N\mu E(n_d-n_u)+N\varepsilon_0(n_r+n_g+n_f+n_b)$$

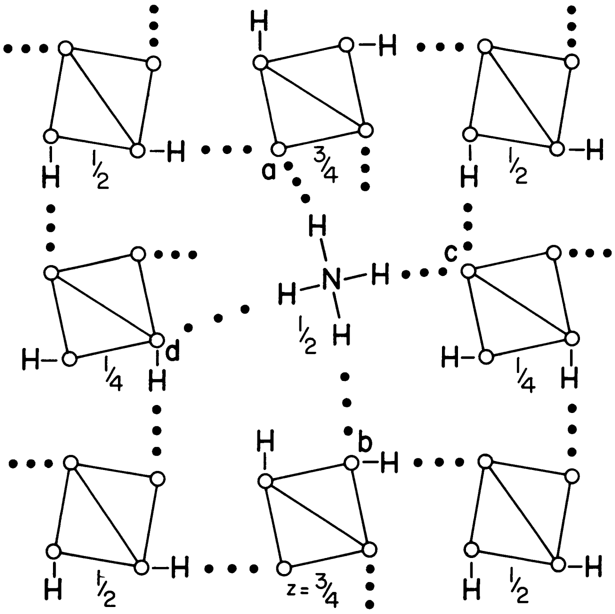

Fig. 1. Projection along c of ADP structure in AFE state. An ammonium ion is shown in its off-center position relative to neighboring phosphate ions.

$$+N\varepsilon_a[(n_d-n_u)^2-(n_r-n_g)^2-(n_f-n_b)^2]/2, \tag{1}$$

where E is electric field along c.

The equilibrium state is found by minimizing the Helmholtz free energy $U\text{-}TS=U\text{-}kT\ln W$. Here W is the number of ways of achieving a particular set of populations N_i. It is given by $W=N!C/\Pi_i N_i!$, where $C=\Pi_i C_i^{N_i/2}$, and C_i is the probability that an ith type H_2PO_4 group is compatible with its four neighbors. The C_i are given by

$$C_u=(n_u+n_r+n_f)(n_u+n_r+n_b)(n_u+n_g+n_f)(n_u+n_g+n_b), \tag{2}$$

$$C_d=(n_d+n_r+n_f)(n_d+n_r+n_b)(n_d+n_g+n_f)(n_d+n_g+n_b), \tag{3}$$

$$C_r=(n_u+n_r+n_f)(n_u+n_r+n_b)(n_d+n_r+n_f)(n_d+n_r+n_b), \tag{4}$$

$$C_g=(n_u+n_g+n_f)(n_u+n_g+n_b)(n_d+n_g+n_f)(n_d+n_g+n_b), \tag{5}$$

$$C_f=(n_u+n_r+n_f)(n_u+n_g+n_f)(n_d+n_r+n_f)(n_d+n_g+n_f), \tag{6}$$

$$C_b=(n_u+n_r+n_b)(n_u+n_g+n_b)(n_d+n_r+n_b)(n_d+n_g+n_b). \tag{7}$$

Each C_i is the product of 4 factors for the 4 H-bonds linking each phosphate to its neighbors, and each factor is the sum of the n_i for the compatible group types.

Upon making the Stirling approximation, the free energy can be written as

$$\begin{aligned} F&=U-kT\ln(W)\\ &=N\{-\mu E(n_d-n_u)+\varepsilon_0(n_r+n_g+n_f+n_b)\\ &\quad+\varepsilon_a[(n_d-n_u)^2-(n_r-n_g)^2-(n_f-n_b)^2]/2\\ &\quad-kT\sum_i[n_i\ln(C_i^{0.5}/n_i)]\}. \end{aligned} \tag{8}$$

We will rewrite F in different ways to predict behavior in different parts of the x-T phase diagram.

§3. Model Predictions for Proton Glass Behavior

To determine the x-T phase diagram we first find the region in which proton glass behavior occurs. We begin by finding the ground state at $T=0$ from eq. (8). For a FE state, $n_d=1$ for example and the other $n_i=0$, so if $E=0$ we have $F=N\varepsilon_a/2$. For an AFE state, $n_r=1$ for example, we have $F=N\varepsilon_0-N\varepsilon_a/2$. A hypothetical paraelectric (PE) state with $n_d=n_u=0.5$ would have $F=0$. This is lower than F for the FE and AFE states for $0<\varepsilon_a<2\varepsilon_0$. However, u and d groups are incompatible as neighbors. Accordingly, we must find the maximum $n_d=n_u=f/2$ as limited by this incompatibility. Here f is the fraction of FE groups.

To find this limit we hypothesize that W (in the Stirling approximation) cannot be less than 1. Because $n_d=n_u=f/2$ and $n_r=n_g=n_f=n_b=(1-f)/4$ in the PE phase, $C_i=1/16$ in eqs. (2-7). Then, using the Stirling approximation,

$$W=N^N\prod_i(C_i^{0.5}/N_i)^{N_i}=[2f^{-f}(1-f)^{-(1-f)}]^N=1, \tag{9}$$

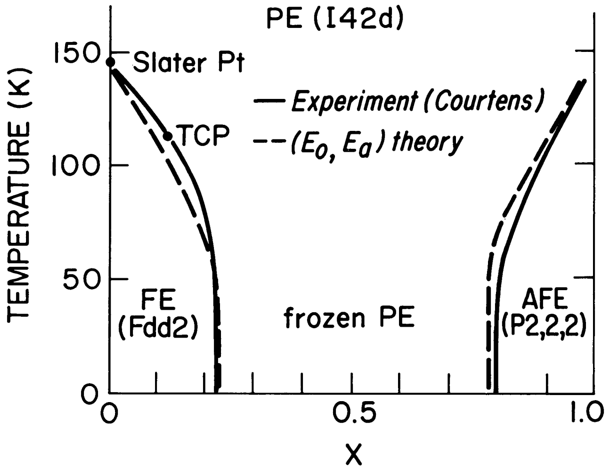

Fig. 2. Phase diagram for mixed RDP-ADP system showing model predictions and experimental results for PE, PG, FE, and AFE regions.

which yields $f_g=0.77291$ for the value of f at which proton glass behavior sets in.

To find the temperature T_g where the PG region of the PE phase begins, we note that in the PE phase the free energy reduces to the Slater expression, for which f is given by

$$f=[1+2\exp(-\varepsilon_0/kT)]^{-1}. \tag{10}$$

Solving for the temperature T_g at which $f=f_g$, we find

$$T_g=\varepsilon_0/\{k\ln[2f_g/1-f_g)]\}=0.52139\varepsilon_0/k. \tag{11}$$

As shown in Fig. 2, T_g is independent of x (and ε_a). Given that the Slater transition temperature $T_c=\varepsilon_0/[k\ln(2)]=147$ K for RDP, the proton glass temperature T_g is predicted to be 53 K.

Once W reaches 1 at T_g, by our hypothesis no further proton rearrangements can occur as temperature drops further, so the boundaries of both the FE and AFE phases with the PG region of the PE phase are vertical as shown in Fig. 2.

§4. Model Predictions for Ferroelectric Transition

For small x for which a FE transition occurs, all AFE type groups have equal population and $n_r=n_g=n_f=n_b$. We define $2a=n_r+n_g+n_f+n_b$ as the fraction of AFE groups. Then $n_u=(1+p-2a)/2$ and $n_d=(1-p-2a)/2$, and the free energy in eq. (8) becomes

$$\begin{aligned} F=N\{&-\mu Ep+2\varepsilon_0 a+\varepsilon_a p^2/2-kT[(1+p)\ln(1+p)\\ &+(1-p)\ln(1-p)-(1-2a)\ln(2)-2a\ln(2a)\\ &-0.5(1+p-2a)\ln(1+p-2a)\\ &-0.5(1-p-2a)\ln(1-p-2a)]\}. \end{aligned} \tag{12}$$

At equilibrium,

$$\begin{aligned} N^{-1}\partial F/\partial p=-\mu E+\varepsilon_a p-0.5kT\ln&[(1+p)^2(1-p-2a)\\ &/(1-p)^2(1+p-2a)]=0, \end{aligned} \tag{13}$$

$$\begin{aligned} N^{-1}\partial F/\partial a=2\varepsilon_0-kT\ln&[(1+p-2a)(1-p-2a)/a^2]\\ &=0. \end{aligned} \tag{14}$$

From *eq.* (11) we obtain

$$p^2=(1-2a)^2-a^2\exp(2\varepsilon_0/kT), \tag{15}$$

while eq. (10) yields

$$(1+p)^2(1-p-2a)=(1-p)^2(1+p-2a) \times \exp\,[2(\varepsilon_a p-\mu E)/kT]. \tag{16}$$

Simultaneous solution of eqs. (15) and (16) yields $p=0$ and $p=\pm 1$. By setting the free energies at these p values equal, we find the FE transition temperature T_c at which a first-order transition from a PE to a fully ordered FE state is predicted. The T_c curve is vertical at T_g and thus is tangent to the FE-PG boundary.

§5. Model Predictions for Antiferroelectric Phase Transition

We consider the case that the crystal orders into an r-type domain, so the relevant AFE order parameter is $q=n_r-n_g$. We assume zero field, so that $n_u=n_d$, and define $f=n_u+n_d$. By symmetry $n_f=n_b$, and we define $a=n_f+n_b$. Then $n_r=(1-f-a+q)/2$ and $n_g=(1-f-a-q)/2$, and the free energy after some manipulation is

$$F=N\{\varepsilon_0(1-f)-\varepsilon_a q^2/2\}-NkT\{f\ln\,[(1-q^2)/2f] +a\ln\,[(1-q^2)/2a]+0.5(1-f-a+q)\ln\,[(1+q)^2 /2(1-f-a+q)]+0.5(1-f-a-q)\ln\,[(1-q)^2 /2(1-f-a-q)]\}. \tag{17}$$

From $\partial F/\partial f=0$ we obtain after some simplification

$$(1-f-a)^2-q^2=f^2\exp\,(-2\varepsilon_0/kT), \tag{18}$$

while $\partial F/\partial a$ yields

$$(1-f)^2-2a(1-f)=q^2. \tag{19}$$

Substitution of q^2 from eq. (19) into eq. (18) gives

$$a=f\exp\,(-\varepsilon_0/kT), \tag{20}$$

so the non-ordering group populations are related by their Boltzmann factors. Combining eqs. (19) and (20) provides

$$(1-f)[1-f-2f\exp\,(-\varepsilon_0/kT)]=q^2. \tag{21}$$

Setting $\partial F/\partial q=0$ yields, after substituting for a from eq. (20),

$$(1+q^2)\{1-q-f[1+\exp\,(-\varepsilon_0/kT)]\} =(1-q)^2\{1+q-f[1+\exp\,(-\varepsilon_0/kT)]\} \times\exp\,(-2\varepsilon_a q/kT). \tag{22}$$

Now, f can be eliminated by solving eqs. (21) and (22) simultaneously. The valid solutions are $q=0$ and $q=\pm 1$. The PE-AFE transition temperature T_N occurs at the temperature T_N where the free energies for the $q=0$ and $q=\pm 1$ solutions are equal. Accordingly, the transition is of first order and the order parameter jumps from 0 to 1 at T_N. The shape of this phase boundary is the mirror image of the PE-FE boundary, as seen in Fig. 1. From eqs. (12) and (17), because $T_N=T_c$ for the RADP system, $\varepsilon_a=2\varepsilon_0 x$ for this system.

§6. Discussion

This model accounts quite well for the shape of the RDP-ADP system phase diagram. It extends the Slater model to deal with proton glass behavior and the AFE transition in this system.

Several modifications would improve agreement with experiment. First, Takagi groups[9] would allow dynamic behavior to be studied and should eliminate the abrupt boundary between the ordinary PE and the PG regions and the unphysical jump from zero to maximum order parameter for the FE and AFE transitions.

In the $x=0$ or RDP limit Takagi groups are known to predict a second-order FE transition. This agrees with experiment for RDP. As x increases the tendency of the ε_a interaction to cause a first-order FE transition will predict the tricritical point observed by Courtens.[10] However, KDP and all its other isomorphs have first-order transitions. This can be predicted by this model if ε_a is allowed to have a positive value at $x=0$ large enough to overcome the tendency of the Takagi groups to produce a second-order transition.

Incorporation of tunneling into this model might explain differences in dielectric behavior of deuterated and undeuterated mixed crystals in the glass region. The deuterated crystal has a sharper dielectric peak and its susceptibility becomes flat as 0 K is approached, while the undeuterated crystal shows finite slope there.[11] Also, from more recent measurements the lossy component goes to zero at finite temperature for the deuterated but not the undeuterated crystal as temperature decreases.

We are presently employing the ε_0, ε_a, and Takagi interactions in a Monte Carlo simulation. This eliminates approximations such as compatibility factors and by placing ammonium ions randomly allows introduction of a bond asymmetry energy.[11]

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