

Theory of Phase Transitions in Mixed Crystals $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$

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Within the cluster approximation, phase transitions in the mixed crystals of hydrogen bonded ferroelectrics and antiferroelectrics $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ are discussed on the basis of a pseudospin model for the proton system. The phase diagram of this system in the temperature-composition plane is derived theoretically and compared with the experimental results in good agreement.

§ 1. Introduction

In recent years many experimental data on mixed dielectrics have been reported which remind us of the spin glass states in disordered magnetic systems. For instance, $(\text{KBr})_{1-x}(\text{KCN})_x$ ¹⁾ and $\text{K}_{1-x}\text{M}_x\text{TaO}_3$ ($\text{M}=\text{Li}, \text{Na}$)²⁾ seem to become at very low temperatures a "dipole glass" which is revealed by elastic, dielectric and neutron scattering experiments as a kind of collective effect among dipoles similar to in spin glass.

On the other hand, although there exist only a few experimental evidences, more interesting phenomena may be expected for mixed crystals of hydrogen bonded ferroelectrics (FE) and antiferroelectrics (AFE) with the same crystal structure: Frustration in the proton configuration under ice rule condition would produce a complicated random FE-AFE system.

Both RbH_2PO_4 (abbreviated as RDP) and $\text{NH}_4\text{H}_2\text{PO}_4$ (abbreviated as ADP) belong to the KDP-family and are called isomorphous tetragonal crystals which contain hydrogen bonds on the lines connecting two PO_4 radicals and undergo a structural transition from tetragonal to orthorhombic at low temperature triggered by an order-disorder rearrangement in the proton configuration. RDP becomes ferroelectric below $T_c=146\text{K}$ with a second order transition while ADP makes a first order antiferroelectric transition at $T_c=147\text{K}$. Since both crystals have nearly the same lattice constant, they can be mixed at any composition into a mixed crystal $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ ($0 \leq x \leq 1$).

The phase diagram of this mixed crystals is investigated by Courtens³⁾ for ferroelectric side ($x \geq 0$) by means of birefringence and dielectric measurements, and by Iida-Terauchi⁴⁾ for antiferroelectric side ($x \leq 1$) from dielectric constants and X-ray diffraction profiles. The obtained phase diagram for all range of x (see Fig. 3 of Ref. 4) or Fig. 1 of Ref. 5)) resembles that of random magnetic mixture of ferro and antiferromagnetics (see for instance Fig. 1 of Ref. 6)). A theoretical consideration on this system has been given by Prelovšek and Blinc,⁷⁾ but they describe each of ferroelectric, antiferroelectric and glass transitions by each different formula to obtain a result which is far from experimental one.

Therefore in this paper we try to describe the various phase transitions in the mixed crystals on the basis of single free energy expression. In order to retain a clear correspondence with the spin glass, we adopt the Ising pseudospin model for hydrogen bond system, and under the strict constraint of the ice rule we discuss theoretically possible phase transitions in this mixed system within the cluster approximation.

The organization of this paper is as follows. In §2 a cluster theory is formulated to derive a general expression of free energy for a cluster composed of four protons. In §3 it is shown that the derived free energy can be used to describe two pure limits RDP and ADP in complete agreement with the previous theories of ferroelectric transition for RDP (or KDP)⁸⁾ and antiferroelectric transition for ADP.⁹⁾ In §4 the free energy of mixed crystal is constructed to discuss the phase transitions. A model to account for short range fluctuation in mixed crystals is proposed, and numerical calculation is performed to produce a theoretical phase diagram which is compared with the observed one. The last section is devoted to discussion.

§ 2. Formulation of cluster theory

We adopt the pseudospin model to describe the proton configurations in the hydrogen bond system in the same way as our previous theory on squaric acid,¹⁰⁾ and introduce spin variable S_i which takes +1 or -1 according as the i -th proton occupies one site or the other of two possible positions. Total configurational energy of the proton system is given by

$$H = - \sum_{i>j} J_{ij} S_i S_j. \quad (2.1)$$

Assuming inter-proton interaction of short range, we choose two parameters U and V such that (see Fig. 1 and also Ref. 10))

$$J_{12} = J_{23} = J_{34} = J_{41} = -V, \quad (2.2)$$

$$J_{13} = J_{24} = -U. \quad (2.3)$$

In order to fulfil a requirement imposed by the ice rule, it is necessary to take account of short range correlation in a proton cluster at least composed of four protons surrounding one PO_4 radical. Thus the analysis of present cluster theory goes almost parallel to the cluster theory of squaric acid.¹⁰⁾ We start with the cluster Hamiltonian

$$H_4 = V(S_1 S_2 + S_2 S_3 + S_3 S_4 + S_4 S_1) + U(S_1 S_3 + S_2 S_4) - \sum_{i=1}^4 h_i S_i, \quad (2.4)$$

where the mean field at the i -th site h_i is given by

$$h_i = m_i + W \langle S_i \rangle. \quad (2.5)$$

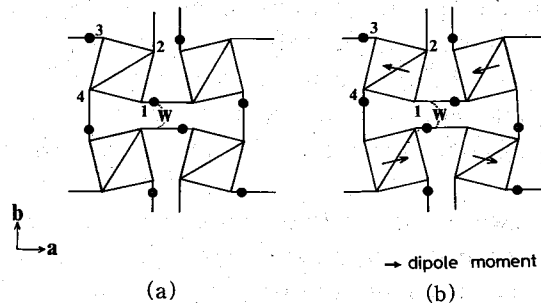


Fig. 1. Ordered proton configurations.

(a) Ferroelectric RDP. (b) Antiferroelectric ADP.

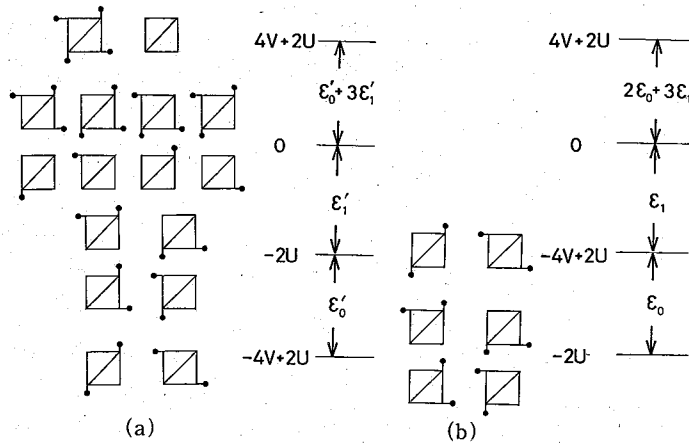


Fig. 2. Configurational energies of a 4-proton cluster without mean field. (a) RDP, (b) ADP.

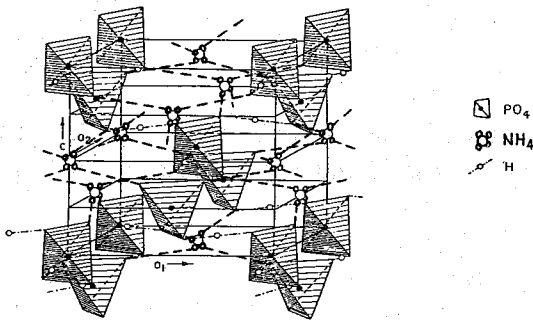


Fig. 3. Crystal structure of ADP. Hydrogen bonds connecting PO_4-NH_4 exist in addition to usual hydrogen bonds on the lines connecting two PO_4 similar to RDP.

m_i is the same function of U, V and thermal average of $S_j, \langle S_j \rangle$, defined in Ref. 10), whereas W is an antiferroelectric coupling parameter between neighbouring two clusters as shown in Fig. 1. The necessity of this W -type term is first noted by Ishibashi et al.⁹⁾ who show that in order to single out the observed antiferroelectric proton configuration in ADP from similar states having otherwise the same free energy, certain antiferroelectric coupling among PO_4 -dipoles is needed to stabilize the observed ordered state against other configurations. It should be

noted that the same inter-cluster coupling does not prevent RDP from tending to the ferroelectric configuration.

Figure 2 shows various energy levels of the four proton system which are organized so as to easily take into account the ice rule condition. Figure 2(a) corresponds to the case of RDP where the level differences are related to U and V as

$$U = \epsilon_1' / 2, \quad V = \frac{1}{4}(\epsilon_0' + 2\epsilon_1'). \tag{2.6}$$

ADP has the same crystal structure as RDP.¹¹⁾ In the case of ADP, however, as shown in Fig. 3, it is characterized by the presence of extra hydrogen bonds between PO_4 and NH_4 ¹²⁾ which would modify the interaction parameter given in (2.2), (2.3) as

$$-V \rightarrow -V + g_1, \tag{2.7}$$

$$-U \rightarrow -U - g_2. \tag{2.8}$$

For simplicity we take $g_1 = g_2 = g$, and if we assume that

$$\epsilon_0' / 8 < g < (\epsilon_0' + \epsilon_1') / 6, \tag{2.9}$$

Table I.

	S_1	S_2	S_3	S_4	Energy E_i	Boltzmann Factor
(a)	+	+	+	+	$4V+2U-\sum h_i$	$a^3 b^4 f_1^{-1} f_2^{-1} f_3^{-1} f_4^{-1}$
	-	-	-	-	$4V+2U+\sum h_i$	$a^3 b^4 f_1 f_2 f_3 f_4$
(b)	+	+	+	-	$-h_1-h_2-h_3+h_4$	$ab f_1^{-1} f_2^{-1} f_3^{-1} f_4$
	+	+	-	+	$-h_1-h_2+h_3-h_4$	$ab f_1^{-1} f_2^{-1} f_3 f_4^{-1}$
	+	-	+	+	$-h_1+h_2-h_3-h_4$	$ab f_1^{-1} f_2 f_3^{-1} f_4^{-1}$
	-	+	+	+	$h_1-h_2-h_3-h_4$	$ab f_1 f_2^{-1} f_3^{-1} f_4^{-1}$
	-	-	-	+	$h_1+h_2+h_3-h_4$	$ab f_1 f_2 f_3 f_4^{-1}$
	-	-	+	-	$h_1+h_2-h_3+h_4$	$ab f_1 f_2 f_3^{-1} f_4$
	-	+	-	-	$h_1-h_2+h_3+h_4$	$ab f_1 f_2^{-1} f_3 f_4$
	+	-	-	-	$-h_1+h_2+h_3+h_4$	$ab f_1^{-1} f_2 f_3 f_4$
(c)	+	-	+	-	$-4V+2U-h_1+h_2-h_3+h_4$	$af_1^{-1} f_2 f_3^{-1} f_4$
	-	+	-	+	$-4V+2U+h_1-h_2+h_3-h_4$	$af_1 f_2^{-1} f_3 f_4^{-1}$
(d)	+	+	-	-	$-2U-h_1-h_2+h_3+h_4$	$f_1^{-1} f_2^{-1} f_3 f_4$
	+	-	-	+	$-2U-h_1+h_2+h_3-h_4$	$f_1^{-1} f_2 f_3 f_4^{-1}$
	-	-	+	+	$-2U+h_1+h_2-h_3-h_4$	$f_1 f_2 f_3^{-1} f_4^{-1}$
	-	+	+	-	$-2U+h_1-h_2-h_3+h_4$	$f_1 f_2^{-1} f_3^{-1} f_4$

it is shown that the lowest two levels in Fig. 2(a) are reversed in their order as in Fig. 2(b) which corresponds to the case of ADP. In the latter case U and V are related to the level scheme as

$$U = \frac{1}{2}(\epsilon_0 + \epsilon_1), \quad V = \frac{1}{4}(\epsilon_0 + 2\epsilon_1). \quad (2.10)$$

ϵ_0' is now a negative quantity. In a mixed crystal of RDP and ADP, we may assume that each cluster has a set of parameters (U , V) given by (2.7) and (2.8) in which $g=0$ or $g \neq 0$ depending on environment, and random distribution of g is reflected into the fluctuation in ϵ_0 .

To facilitate further statistical mechanical analysis, the energies E_i and Boltzmann factor $\exp[-(E_i+2U)/k_B T]$ of 2^4 proton configurations are listed in Table I with abbreviation

$$\begin{aligned} a &= \exp(-\epsilon_0/k_B T), & b &= \exp(-\epsilon_1/k_B T) \\ f_i &= \exp(-h_i/k_B T). \quad (i=1, 2, 3, 4) \end{aligned} \quad (2.11)$$

With the use of Table I it is straightforward to evaluate the partition function of the four proton cluster

$$\begin{aligned} Z_4 &= \text{Tr}[\exp(-H_4/k_B T)] \\ &= a^3 b^4 (f_1 f_2 f_3 f_4 + f_1^{-1} f_2^{-1} f_3^{-1} f_4^{-1}) \\ &\quad + ab (f_1 f_2 f_3 f_4^{-1} + f_1^{-1} f_2^{-1} f_3^{-1} f_4 + f_1 f_2 f_3^{-1} f_4 + f_1^{-1} f_2^{-1} f_3 f_4^{-1}) \\ &\quad + f_1 f_2^{-1} f_3 f_4 + f_1^{-1} f_2 f_3^{-1} f_4^{-1} + f_1^{-1} f_2 f_3 f_4 + f_1 f_2^{-1} f_3^{-1} f_4^{-1}) \\ &\quad + a (f_1^{-1} f_2 f_3^{-1} f_4 + f_1 f_2^{-1} f_3 f_4^{-1}) + f_1 f_2 f_3^{-1} f_4^{-1} + f_1^{-1} f_2^{-1} f_3 f_4 \\ &\quad + f_1 f_2^{-1} f_3^{-1} f_4 + f_1^{-1} f_2 f_3 f_4^{-1} \end{aligned} \quad (2.12)$$

from which the thermal average of S_1 is calculated as

$$\begin{aligned} \langle S_1 \rangle = & Z_4^{-1} [a^3 b^4 (f_1^{-1} f_2^{-1} f_3^{-1} f_4^{-1} - f_1 f_2 f_3 f_4) \\ & + ab (f_1^{-1} f_2^{-1} f_3^{-1} f_4 - f_1 f_2 f_3 f_4^{-1} + f_1^{-1} f_2^{-1} f_3 f_4^{-1} - f_1 f_2 f_3^{-1} f_4 \\ & + f_1^{-1} f_2 f_3^{-1} f_4^{-1} - f_1 f_2^{-1} f_3 f_4 + f_1^{-1} f_2 f_3 f_4 - f_1 f_2^{-1} f_3^{-1} f_4^{-1}) \\ & + a (f_1^{-1} f_2 f_3^{-1} f_4 - f_1 f_2^{-1} f_3 f_4^{-1}) + f_1^{-1} f_2^{-1} f_3 f_4 - f_1 f_2 f_3^{-1} f_4^{-1} \\ & + f_1^{-1} f_2 f_3 f_4^{-1} - f_1 f_2^{-1} f_3^{-1} f_4]. \end{aligned} \quad (2.13)$$

As discussed in detail in the previous paper,¹⁰ Eq. (2.13) is not adequate to determine the order parameter $\langle S \rangle$. The right way to determine $\langle S \rangle$ is to combine Eq. (2.13) with a corresponding formula derived from single proton system embedded in the same mean field, which turns out to be given by

$$\langle S_1 \rangle = (f_1^{-2} - f_1^2) / (f_1^{-2} + f_1^2). \quad (2.14)$$

Upon eliminating $\langle S_1 \rangle$ from (2.13) and (2.14), one obtains an equation which is also to be derived from

$$f_1 \frac{d}{df_1} \left[\ln Z_4 - \frac{1}{2} \ln Z_1(1) \right] = 0 \quad (2.15)$$

with

$$Z_1(i) = f_i^{-2} + f_i^2. \quad (2.16)$$

The self-consistent equation (2.15) does not contain U and V explicitly and hence remains finite even in the ice rule limit $\epsilon_1 \rightarrow \infty$.

In later section it becomes useful to construct an effective free energy such that minimization of free energy gives us Eq. (2.15). It is an easy task to check that

$$F = -\frac{1}{2} k_B T \ln [Z_4^2 / \prod_{i=1}^4 Z_1(i)] + \frac{1}{4} W \sum_{i=1}^4 \langle S_i \rangle^2 \quad (2.17)$$

with

$$Z_1(i) = 2 \cosh[(2h_i - W \langle S_i \rangle) / k_B T], \quad (i=1, 2, 3, 4) \quad (2.18)$$

has such a property.

§ 3. Relation to previous theories

In §2 we have constructed the free energy for a 4-proton cluster in random environment characterized by a set of interaction parameters (U , V , W). This free energy is applicable to mixed crystal $(RDP)_{1-x}(ADP)_x$ if suitable average over U , V and W is taken. Before entering such analysis of mixed crystal, however, it is important to examine that the expression for free energy (2.17) can describe correctly both pure limits of $RDP(x=0)$ and $ADP(x=1)$.

For this purpose, first consider the case of RDP which is similar to KH_2PO_4 (KDP) where at low temperature the ordered state may be characterized by single order parameter

$$f \equiv f_1 = f_3 = f_2^{-1} = f_4^{-1}. \quad (3.1)$$

Then the coupled equations (2.13) and (2.14) become

$$\langle S \rangle = \frac{2 \sinh(2h/k_B T) [ab + a \cosh(2h/k_B T)]}{2 + a^3 b^4 + 4ab \cosh(2h/k_B T) + a \cosh(4h/k_B T)}, \quad (3.2)$$

$$\langle S \rangle = \tanh[(2h - W \langle S \rangle) / k_B T]. \quad (3.3)$$

To simplify the analysis, we shall confine ourselves within the case in which the ice rule is strictly fulfilled, that is, we take $b=0$ in what follows. Noting that as $T \rightarrow T_c$, $\langle S \rangle \rightarrow 0$ and $h \rightarrow 0$, and expanding (3.2) and (3.3) in power of h and $\langle S \rangle$, we obtain ferroelectric transition temperature T_c^F as a solution of an equation

$$W/k_B T = \exp(-|\varepsilon_0|/k_B T) - \frac{1}{2}. \quad (3.4)$$

When $W=0$, (3.4) yields

$$k_B T_c^F = |\varepsilon_0| / \ln 2, \quad (3.5)$$

which is precisely the same as Slater's result for KDP.¹³⁾ $W=0$ means that "dipole interaction" is unnecessary to attain the ferroelectric phase in contrast to antiferroelectric phase we are going to discuss next.

In the case of ADP, antiferroelectric ordered phase at low temperature can be described by an order parameter

$$f \equiv f_1 = f_2 = f_3^{-1} = f_4^{-1}. \quad (3.6)$$

Then the coupled equations are (3.3) and

$$\langle S \rangle = \frac{2 \sinh(2h/k_B T) [ab + \cosh(2h/k_B T)]}{1 + a + a^3 b^4 + 4ab \cosh(2h/k_B T) + \cosh(4h/k_B T)} \quad (3.7)$$

in place of (3.2), and when $b=0$ antiferroelectric transition temperature T_c^{AF} is determined from

$$(k_B T_c^{AF} / W) = 2 \exp(\varepsilon_0 / k_B T_c^{AF}) \quad (3.8)$$

which may be transcribed as

$$1 - W/k_B T_c^{AF} = 1 - \frac{1}{2} \exp(-\varepsilon_0 / k_B T_c^{AF}). \quad (3.9)$$

It is interesting to observe that (3.9) is an expansion form of

$$\exp(-W/k_B T_c^{AF}) = \left[1 + \frac{1}{2} \exp(-\varepsilon_0 / k_B T_c^{AF}) \right]^{-1}, \quad (3.10)$$

which is exactly the same as an equation to determine the antiferroelectric transition temperature of ADP derived by Ishibashi et al.,⁹⁾ if W is read as

$$W \rightarrow \mu_a^2. \quad (3.11)$$

They interpreted μ_a^2 as dipole-dipole interaction along the a -axis necessary to make the ordered state depicted in Fig. 1(b) the lowest energy configuration. Although the physical

meaning of the W -term may be different, it is concluded that our free energy of cluster can describe the phase transitions of both pure limits for RDP ($x=0$) and ADP ($x=1$). The formal difference between (3·8) and (3·10) will stem from a fact that the inter-cluster coupling W cannot be treated in the present 4-proton cluster theory better than in a crude mean field approximation.

§ 4. Free energy of mixed crystals

From the argument given in §3, it is observed that both ferroelectric and antiferroelectric order in the present model are described respectively by

$$\text{FE:} \quad \langle S_1 \rangle = -\langle S_2 \rangle = \langle S_3 \rangle = -\langle S_4 \rangle, \quad (4\cdot1)$$

$$\text{AFE:} \quad \langle S_1 \rangle = \langle S_2 \rangle = -\langle S_3 \rangle = -\langle S_4 \rangle. \quad (4\cdot2)$$

Thus it holds for both cases that

$$\langle S_1 \rangle = -\langle S_4 \rangle, \quad \langle S_2 \rangle = -\langle S_3 \rangle \quad (4\cdot3)$$

and discrimination between ferro and antiferroelectric orders can be made by the difference in

$$\begin{aligned} \langle S_1 \rangle = \langle S_3 \rangle & \quad \text{for ferroelectric phase,} \\ \langle S_1 \rangle = -\langle S_3 \rangle & \quad \text{for antiferroelectric phase.} \end{aligned} \quad (4\cdot4)$$

Using this fact, we may simplify the expressions for the free energy of the cluster by reducing the number of variables as:

$$F = \frac{1}{2} W (\langle S_1 \rangle^2 + \langle S_3 \rangle^2) - k_B T \ln [Z_4 / Z_1(1) Z_1(3)], \quad (4\cdot5)$$

$$Z_4 = 2[a \cosh(2(h_1 + h_3)/k_B T) + \cosh(2(h_1 - h_3)/k_B T) + 1], \quad (4\cdot6)$$

$$Z_1(1) = 2 \cosh[(2h_1 - W \langle S_1 \rangle) / k_B T], \quad (4\cdot7)$$

$$Z_1(3) = 2 \cosh[(2h_3 - W \langle S_3 \rangle) / k_B T]. \quad (4\cdot8)$$

Now it is convenient to put all the quantities in dimensionless forms by making use of

$$\begin{aligned} \langle S_1 \rangle = y_1, \quad \langle S_3 \rangle = y_3, \\ 2h_1/k_B T = x_1, \quad 2h_3/k_B T = x_3, \quad W/k_B T = \lambda. \end{aligned} \quad (4\cdot9)$$

Then (4·5) may be put in the following form:

$$\mathcal{F} \equiv F/k_B T = \frac{1}{2} \lambda (y_1^2 + y_3^2) - \ln \left[\frac{a \cosh(x_1 + x_3) + \cosh(x_1 - x_3) + 1}{2 \cosh(x_1 - \lambda y_1) \cosh(x_3 - \lambda y_3)} \right]. \quad (4\cdot10)$$

Equation (4·10) represents the free energy of a cluster in an environment characterized by (ϵ_0, W) . In the mixed crystal, coupling parameters should vary from cluster to cluster and hence we have to consider some distribution of coupling parameters and take average of the free energy over this distribution. Let F_j be the free energy of a cluster having $(\epsilon_0(j), W_j)$ and P_j be the probability of its occurrence. Then the free energy of mixed crystal can be evaluated from the averaged cluster free energy

$$F = \sum_j P_j F_j \quad (4.11)$$

with

$$\sum_j P_j = 1. \quad (4.12)$$

It is not easy to guess the distribution of coupling parameters: Large fluctuation is expected to exist due to the frustration enforced by severe ice rule imposed on proton arrangement. Therefore we shall content ourselves with a simplified treatment based upon an assumption on P_j and F_j such that only three types of cluster are allowed to exist: ferroelectric, antiferroelectric and neutral clusters. They are assumed to be specified by interaction parameters and probabilities such that

$$\text{Ferro:} \quad F_+ = F(\epsilon_0 < 0, W = 0); \quad P_+, \quad (4.13)$$

$$\text{Neutral:} \quad F_0 = F(\epsilon_0 = 0, W = 0); \quad P_0, \quad (4.14)$$

$$\text{Antiferro:} \quad F_- = F(\epsilon_0 > 0, W \neq 0); \quad P_-. \quad (4.15)$$

Thus we adopt the following free energy for mixed crystal:

$$\begin{aligned} \mathcal{F} = & \ln 2 + P - \frac{1}{2} \lambda (y_1^2 + y_3^2) + P \ln [\cosh(x_1 - \lambda y_1) \cosh(x_3 - \lambda y_3)] \\ & + (P_+ + P_0) \ln [\cosh x_1 \cosh x_3] - \sum_{j=+,0,-} P_j \ln [1 + \cosh(x_1 - x_3) + a_j \cosh(x_1 + x_3)], \end{aligned} \quad (4.16)$$

where

$$a_j = \exp(\epsilon_j / k_B T), \quad \epsilon_j = \begin{cases} \epsilon_0 & \text{for } j = +, \\ 0 & \text{for } j = 0, \\ -\epsilon_0 & \text{for } j = -. \end{cases} \quad (4.17)$$

Minimization of \mathcal{F} with respect to y_1 and y_3 yields two equations

$$y_i = \tanh(x_i - \lambda y_i). \quad (i = 1 \text{ or } 3) \quad (4.18)$$

In the vicinity of transition point T_c , x and y are small and (4.18) may be expanded in power of x and y , obtaining x_i as a polynomial of y_i . Landau-type expansion of \mathcal{F} near T_c can be thus derived in power of y_i . However it is more convenient to use

$$Y = y_1 + y_3, \quad \bar{Y} = y_1 - y_3. \quad (4.19)$$

Then we have the following expansion of \mathcal{F} :

$$\begin{aligned} \mathcal{F} = & \sum_j P_j \ln [2 / (2 + a_j)] + A(T) \bar{Y}^2 + B(T) Y^2 + C(T) Y^2 \bar{Y}^2 \\ & + D(T) \bar{Y}^4 + E(T) Y^4 + G(T) \bar{Y}^6 + H(T) Y^6 + \dots \end{aligned} \quad (4.20)$$

The coefficients in (4.20) up to the 4-th order are

$$A(T) = \frac{1}{4} (1 + \lambda) P_- + (P_+ + P_0) \frac{1}{4} (1 + \lambda)^2 - \sum_j P_j (1 + \lambda)^2 / 2(2 + a_j),$$

$$\begin{aligned}
B(T) &= \frac{1}{4}(1+\lambda)P_- + (P_+ + P_0)\frac{1}{4}(1+\lambda)^2 - \sum_j P_j a_j (1+\lambda)^2 / 2(2+a_j), \\
C(T) &= \frac{3P_-}{16} + (P_+ + P_0)\frac{1}{4}(1+\lambda) - (P_+ + P_0)\frac{(1+\lambda)^4}{16} \\
&\quad - \sum_j P_j \frac{(1+\lambda)}{4(2+a_j)} \left[1 + a_j - \frac{a_j(1+\lambda)^3}{(2+a_j)} \right], \\
D(T) &= \frac{P_-}{32} + (P_+ + P_0)\frac{(1+\lambda)}{24} - (P_+ + P_0)\frac{(1+\lambda)^4}{96} \\
&\quad - \sum_j P_j \frac{(1+\lambda)}{24(2+a_j)} \left[2 + (1+\lambda)^3 \left(1 - \frac{3}{(2+a_j)} \right) \right], \\
E(T) &= \frac{P_-}{32} + (P_+ + P_0)\frac{(1+\lambda)}{24} - (P_+ + P_0)\frac{(1+\lambda)^4}{96} \\
&\quad - \sum_j P_j \frac{a_j(1+\lambda)}{24(2+a_j)} \left[2 + (1+\lambda)^3 \left(1 - \frac{3a_j}{(2+a_j)} \right) \right]. \tag{4.21}
\end{aligned}$$

It is evident from (4.4) that phase transitions to ferroelectric and antiferroelectric phases take place when

$$\begin{aligned}
\text{FE:} \quad & A(T) > 0 \quad \text{and} \quad B(T) \leq 0, \\
\text{AFE:} \quad & A(T) \leq 0 \quad \text{and} \quad B(T) > 0. \tag{4.22}
\end{aligned}$$

When $A(T) > 0$ and $B(T) > 0$, system remains in paraelectric phase.*)

Then the last but not least problem is how to relate the probabilities P_+ , P_0 and P_- with composition x of mixed crystal. Looking at the crystal structure depicted in Fig. 3, we observe that each PO_4 group has six neighbouring cation sites, two of which are located at straight up and down with shortest distance, about 0.6 \AA shorter than other four sites. Therefore we assume that when these two sites are occupied by NH_4 ion, the cluster belongs to antiferroelectric one (F_-) and when occupied by Rb -ion it belongs to

Table II.

x	No. of NH_4	P_+	P_0	P_-
0	0	1	0	0
1/6	1	2/3	1/3	0
1/3	2	6/15	8/15	1/15
1/2	3	1/5	3/5	1/5
2/3	4	1/15	8/15	6/15
5/6	5	0	1/3	2/3
1	6	0	0	1

*) Strictly speaking, the first order phase transition as in ADP takes place at

$$4A(T)G(T) = D(T)^2, \quad \text{when } D(T) < 0$$

or at

$$4B(T)H(T) = E(T)^2, \quad \text{when } E(T) < 0$$

instead of (4.22).

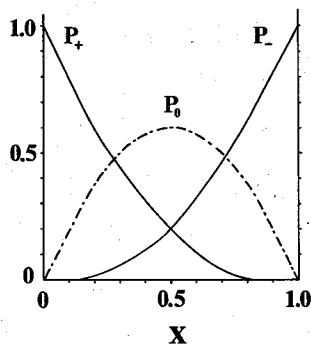


Fig. 4. Probabilities P_+ , P_0 , P_- as functions of x .

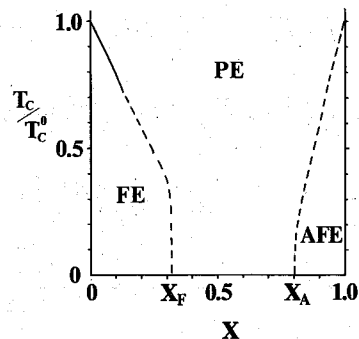


Fig. 5. T_c - x phase diagram with the parameter $\lambda=0.20$.

PE: Paraelectric phase.
 FE: Ferroelectric phase.
 AFE: Antiferroelectric phase.

ferroelectric cluster (F_+); for all other cases, large fluctuation cancels out the inter-proton interaction, leading the cluster to neutral one (F_0). With this prescription, possible configurations of Rb or NH_4 ions among six sites surrounding a PO_4 are examined and each arrangement is made belong to one of three types of clusters, assigning its probability. Table II shows the results of such calculation for possible seven cases, and Fig. 4 represents probability distribution functions $P_j(x)$ obtained by interpolating between the values listed in Table II.

Now we are ready to calculate theoretical phase diagram in which the boundaries of three phases, ferro, antiferro and paraelectric phases, are determined from the minimum principle of the free energy as function of temperature T and composition x . The result of numerical analysis is shown in Fig. 5. Since it holds that $T_c(x=0) \cong T_c(x=1) \equiv T_c^0$, the temperature axis is normalized by T_c^0 . By examining the sign of the fourth order coefficient we can discriminate the order of phase transitions. Solid line shows the boundary of the second order transition while dotted line that of the first order transition. The final theoretical results for the phase diagram are compared with the experimental one and it is found that the agreement between theory and experiments is quite good qualitatively. The ferroelectric phase disappears above a certain critical composition x_F and antiferroelectric phase does below x_A . The values for x_F and x_A theoretically predicted are near the observed values. In the intermediate range $x_F < x < x_A$ we have no solution except for the paraelectric phase. However there must exist a phase at low temperatures which exhibits some order. Whether this new phase is a glass phase or not will be an interesting problem and we will discuss it in a forthcoming paper.

§ 5. Discussion

Since RDP and ADP have competitive opposite tendencies toward ferro- and antiferroelectric orders, it is expected that the mixed crystal $(\text{RDP})_{1-x}(\text{ADP})_x$ will exhibit a complicated behaviour similar in some mixed magnetic crystals. However the mechanism of phase transition in the hydrogen bonded crystals is unique in that order-disorder arrangement of protons under strong constraint placed by the ice rule plays a central role, and frustration involved in the proton configurations in a mixed crystal seems to be of

different nature from that in disordered magnetic mixed crystals. So far we have discussed the phase transitions in $(RDP)_{1-x}(ADP)_x$ as a problem of phase transition in a proton system with random interactions and proposed a simple model to take account of short range fluctuation in frustrated interactions. The present treatment is in contrast to other published theory⁷⁾ which is based on a simple averaged free energy of the mixed crystal, obtaining a phase diagram in agreement with the observations much poorer than our theory.

In the intermediate range of x , the mixed crystals are supposed to reveal "glass-like" behaviours to be compared with spin glass in disordered magnets. Because our formulation is quite similar to the random Ising spin system, it would be expected that the spin glass properties predicted for the bond disorder Ising spin system are also to come out of our theory. However one should bear in mind the following characteristics of our system different from magnetic system: (1) The pseudospin represents two different positions of a proton. (2) Its occupancy is governed by tricky ice rule. (3) Fluctuation in ϵ_0 which looks primary origin of disorderness is the results from the complicated inter proton interactions. We have succeeded recently in transcribing the problem of disordered proton system with ice rule constraint into a disordered Ising spin system with special interactions. On the basis of our new formulation, we will generalize the present theory to a possible glass phase in the next paper.

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