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REVIEW OF ORDER–DISORDER MODELS FOR KDP-FAMILY CRYSTALS

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The various order–disorder-type models for crystals in the KDP (potassium dihydrogen phosphate) family are reviewed, beginning with the Slater–Takagi–Senko model, continuing with tunneling additions by Blinc and Svetina, and analyzing the pressure-induced tricritical point in the Slater–Takagi–Senko model. The possibility of a deuteration-induced tricritical point at atmospheric pressure in RDP (rubidium dihydrogen phosphate) is explored. The Ishibashi model for ADP (ammonium dihydrogen phosphate) is reviewed, and finally various theories and computer simulations for the mixed RDP–ADP crystal system are discussed in terms of their prediction of the observed ferroelectric and antiferroelectric transitions and proton glass behavior.

INTRODUCTION

Potassium dihydrogen phosphate (KDP), formula KH_2PO_4, is the prototype of order–disorder-type ferroelectrics. Although Busch and Scherrer[1] discovered the ferroelectric (FE) nature of this crystal in 1935, only in 1941 did Slater[2] publish his famous order–disorder theory of its FE transition. In those days before neutron diffraction the hydrogen positions were unknown, but he boldly assumed that the hydrogens are in off-center positions in O—H· · ·O bonds linking the closest oxygens in neighboring phosphate ions. By analogy with Pauling's[3] treatment of ice, he assumed that above the Curie temperature T_c the protons are disordered in the off-center positions subject to the Pauling "ice rules" modified by substituting "phosphate" for "oxygen":

1) One and only one proton per hydrogen bond, and

2) Two protons close to a given phosphate, while the other two bonds linking the phosphate to its neighbors have their protons close to the neighboring phosphates.

With additional assumptions described below, he was able to predict a ferroelectric transition, but of a unique type in which all polarization values could occur at T_c. Also, his theory provides no mechanism for proton rearrangements as required at the transition or in response to changing electric fields.

Takagi[4] improved the theory in both regards in 1948 by allowing four each HPO_4 and H_3PO_4 groups in addition to the six types of Slater H_2PO_4 groups. This predicted a second-order transition with a rounded curve for variation of spontaneous polarization with temperature, and provided a mechanism for dynamic response of the crystal to changing temperature or electric field.

Further improvements to the theory were made by Senko[5] who introduced a long-range interaction, by Blinc and Svetina[6] who introduced tunneling and showed that the assumption of tunneling for undeuterated crystals but no tunneling for deuterated crystals can explain some observed isotope effects, and by Torstveit[7] who included electrostrictive effects.

Silsbee, Uehling, and Schmidt (SUS)[8] showed that the Slater–Takagi–Senko model can predict either first or second order transitions. Later it was found experimentally[9] that the KDP transition is first order, showing a small jump in spontaneous polarization at T_c, followed by a rounded increase with decreasing temperature. When interest in higher-order critical points awoke in the early 1970's, Schmidt[10] considered parameters which could produce such a change from a first- to a second-order transition in KDP, and predicted that hydrostatic pressure could bring the crystal to such a tricritical point. He and his group discovered this tricritical point shortly thereafter.[11,12]

Nagamiya[13] in 1952 correctly postulated that the ordered antiferroelectric (AFE) phases in ADP (ammonium dihydrogen phosphate, $NH_4H_2PO_4$) are composed of the four Slater H_2PO_4 groups which in the Slater theory of KDP-type FE crystals have higher energy and do not form FE domains. Ishibashi *et al.*[14] developed a theory for the AFE transition in ADP based on reversing the sign of the Slater energy parameter and introducing a dipolar interaction.

After the "proton glass" behavior of mixed crystals of RDP (rubidium dihydrogen phosphate) and ADP was discovered by Courtens,[15] various theories to explain this behavior were proposed by Prevlovsek and Blinc,[16] Schmidt *et al.*,[17,18], Ishibashi and Suzuki,[19] and Matsushita and Matsubara.[20,21] Monte Carlo tests of these theories are being made by Selke and Courtens[22] and by Schnackenberg and Schmidt.[23]

Finally, we mention but do not discuss further the chemically related crystals CsH_2PO_4[24] and TlH_2PO_4[25] which are not isostructural with KDP.

We discuss first the FE pure crystals, then the AFE crystals, followed by the mixed crystals with frustrated FE and AFE interactions.

FERROELECTRIC CRYSTALS

We consider in this paper the crystals and mixed crystals having the characterisitc KDP three-dimensional hydrogen-bonded network shown in Figure 1. These crystals can have K, Rb and Cs as cations giving a FE transition, whereas NH_4 causes an AFE transition. Substitution of D for H tends to double the transition temperatures. All of the transitions are of first order, except for RbH_2PO_4(RDP) which has a second-order transition. Both PO_4 and AsO_4 can serve as anions, with the latter enhancing the first-order nature of the FE transitions, as does deuteration. Hydrostatic pressure reduces the transition temperatures, to 0 K in some cases.[26,27] CsH_2PO_4, CsD_2PO_4, and fully deuterated RbD_2PO_4 do not have the KDP structure but instead crystallize in the monoclinic system.

The structure shown in Figure 1 is that of one of the two types of FE domains, characterized by having two protons close to the upper ends of phosphate groups, as postulated by Slater[2] and confirmed by neutron scattering.[28] Slater further assumed that this H_2PO_4 arrangement has zero energy and dipole moment $-\mu$, while one with both protons near the bottom of a phosphate group has zero energy and dipole moment $+\mu$. The other 4 arrangements, with one proton near

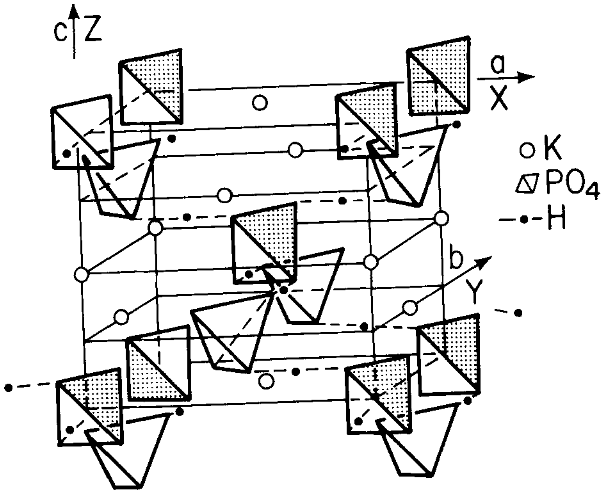

FIGURE 1 Structure of KH_2PO_4. (Reference 52).

the top and one near the bottom, have positive energy ε_0 and no dipole moment along c. This led to a spontaneous polarization curve as shown in Figure 2(a), where all polarizations from $-P_s$ to $+P_s$ are possible at $T_c = \varepsilon_0/k \ln 2$. This occurs because the free energy is flat for all order parameter values from -1 to 1. In present terminology, his transition was locked into a tricritical point of a special type.

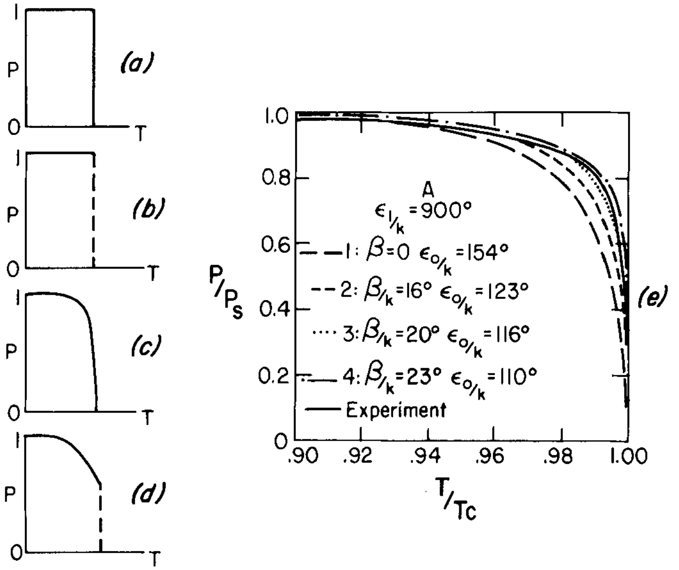

FIGURE 2 Spontaneous polarization *vs*. temperature for a KDP-type ferroelectric. Curves (a) through (d) are qualitative plots for (a) Slater model, (b) Slater model plus long-range interaction or cross-cation interaction, (c) Slater–Takagi model, (d) Slater–Takagi–Senko model with long-range interaction sufficiently strong to put transition into first-order range, (e) comparison of KD_2PO_4 polarization with Slater–Takagi–Senko model predictions. (Reference 8).

A serious defect of the Slater model is its lack of a mechanism for dynamic behavior. If one proton moves, Pauling's second rule above is broken for two phosphates. Six or more protons can move simultaneously within their bonds without breaking that rule under certain circumstances, but no change in dipole moment along the FE c axis can result.

Takagi[4] in 1948 removed the restriction of two protons near each phosphate group, allowing HPO_4 and H_3PO_4 groups having energy ε_1, relative to the polar H_2PO_4 configurations, and dipole moment $\pm\mu/2$. This made the transition definitely second order, with a continuous spontaneous polarization curve as shown in Figure 2(c) and curve 1 of Figure 2(e) in better agreement with the experimental curve. He found that breaking the other ice rule, of one and only one proton per bond, gave similar results.[29] Both rules must be broken to allow the observed[30,31] protonic conductivity in KDP-type crystals, or in ice for that matter.

Experimental verification of the existence of Takagi groups and their importance for static and dynamic properties was provided by Schmidt and Uehling.[31] From deuteron NMR experiments on mostly deuterated KDP, they found that the activation energy for creation of Takagi groups was much lower than that for removing deuterons from bonds. This latter energy, as determined by both NMR and electrical conductivity measurements, is too high to have a significant effect on FE behavior.

Schmidt[32] showed that Takagi groups govern dynamical phenomena such as domain wall motion and dielectric and NMR relaxation in KD_2PO_4, and presumably in related crystals. The Takagi groups are created in DPO_4–D_3PO_4 pairs which *in effect* migrate through the crystal by switching a deuteron to the other end of its bond with each migration step.

For completeness, one should also consider the last two of the 16 phosphate configuration, PO_4 and H_4PO_4, having no dipole moment. Their energy is high enough so that they will have little effect on physical properties. This energy could be assigned arbitrarily, but it seems more reasonable to determine it, as was done by Tokunaga and Matsubara,[33] from a pseudospin model. Their model has two nearest-neighbor proton–proton interactions, one of strength U across the top or bottom of a phosphate (diagonal directions in Figure 3) and the other from top to bottom (horizontal or vertical direction in Figure 3). The interaction energies are compared with the Slater, Takagi and PO_4 and H_4PO_4 energies in Figure 3. The pseudospin model is not useful for analytic predictions because of the complex "lattice" arrangement of the spins, but it is useful in Monte Carlo simulations.

Senko[5] added a long-range interaction parameter β to the Slater–Takagi model, having interaction energy $-\beta P^2$ proportional to the square of the order parameter. It has been attributed to the dipole–dipole interaction, but because the latter depends on sample shape and boundary conditions (shorted or open electrodes or no electrodes) it seems more reasonable to consider it as a mechanical energy associated with the shear strain which accompanies the polarization.

Silsbee, Uehling and Schmidt[8] in 1964 examined in detail the predictions of the Slater–Takagi–Senko model, and showed that for a strong enough long-range

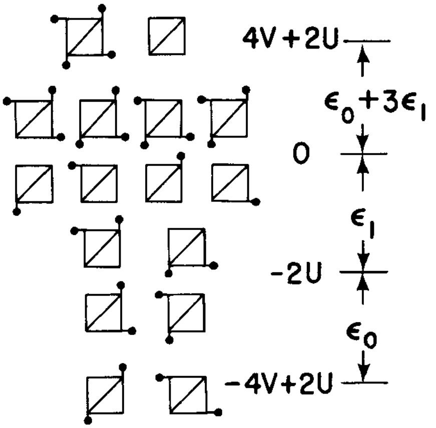

FIGURE 3 Configurational energies of the 16 types of phosphate groups, represented in the pseudospin formalism and in terms of the Slater energy ε_0 and the Takagi energy ε_1. (Reference 20).

interaction a first-order transition should occur, with a spontaneous polarization as shown in Figure 2(d) or curve 3 of Figure 2(e). At that time the transition was still thought to be of second order, but shortly thereafter it was found[9] to be of first order. With the rise in interest in higher-order critical points in the 1970's, Schmidt[10] proposed that a tricritical point might occur in temperature–pressure–electric field parameter space. This point was discovered soon after, by Western, Baker and Schmidt,[11,12] and occurs where two lines of field-induced critical points meet a zero-field line of critical points as shown in Figure 4. They found the mean-field tricritical value of 5 for the critical exponent δ relating polarization to field at the tricritical point. Bastie *et al.*[34] corroborated

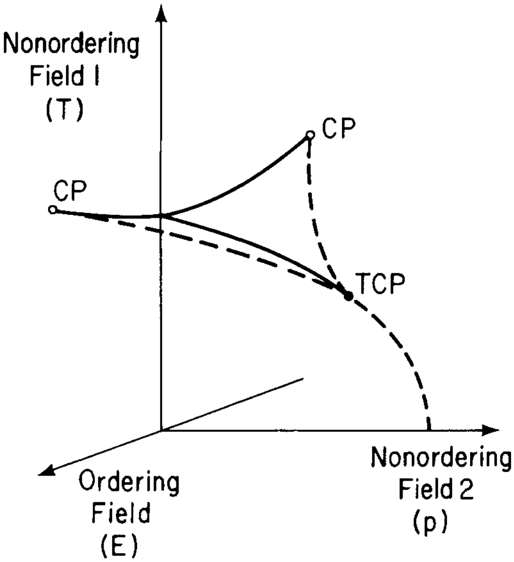

FIGURE 4 Topology of the KDP tricritical point. First-order transition lines are solid, second-order dashed. The tricritical point (TCP) occurs where the three lines of critical points (CP) meet.

the existence of the tricritical point, and found the mean-field tricritical value of 1/4 for the exponent β relating polarization to T_c-T.

A tricritical point at atmospheric pressure and high level of deuteration may exist in the mixed crystal system $Rb(H_{1-x}D_x)_2PO_4$. Schnackenberg *et al.*[35] found a second-order transition for $x = 0$, 0.3, and 0.97. Nelmes[36] pointed out that T_c for pure RbD_2PO_4 may be higher than was generally believed, and that T_c for the above supposedly $x = 0.97$ crystal is consistent with $x = 0.7$.[37] A subsequent proton NMR determination of the deuteration confirmed this 70% figure. Based on this value, the mixed crystal measurements[35] predict a tricritical deuteration of 75 to 80% in the $Rb(H_{1-x}D_x)PO_4$ system.

Recent data[38] on a more highly deuterated sample (85% based on T_c) appear to show a first-order transition, again indicating the existence of a tricritical deuteration. Other workers had previously predicted a second-order transition at full deuteration based on dynamic measurements on samples for which 80% was the highest deuteration level.[39] Their most deuterated sample showed no discontinuities at the transition, probably because it was so close to the tricritical point.

Blinc and Svetina[6] in 1966 added a proton tunneling parameter Γ to the SUS model and obtained better agreement with experiment for KH_2PO_4, while for KD_2PO_4 the tunneling parameter was near zero for best fit. Fairall and Reese[40] tabulated Slatert, Takagi, long-range and tunneling parameters for a number of KDP-crystals, as shown in Table I.

Torstveit[7] considered pressure, deuteration, and electrostrictive effects and fit them to the Blinc–Svetina[6] model. He obtained a good fit if the Senko[5] long-range energy parameter was chosen to be negative. This implies that the long-range interaction is antipolar, and that the short-range interactions cause the FE ordered state.

Pawley and Tibballs[41] performed the first Monte Carlo calculation for the KDP structure. They used a slightly modified Slater and Takagi energy scheme and introduced electric fields as well. Their "crystal" consisted of 8 × 8 × 8 unit cells. Their transition temperature approached the Slater value as the Takagi energy tended toward infinity.

TABLE I

Results of fitting the small-tunneling version of the hydrogen-bond occupation model to the polarization of materials isomorphic to KDP. In this table experimental values are in parentheses and parameters fixed by the fitting procedure are underlined. (Ref. 40)

Property	KH_2AsO_4	RbH_2AsO_4	CsH_2AsO_4	KH_2PO_4	RbH_2PO_4	KD_2AsO_4	CsD_2AsO_4	KD_2PO_4
$T_c(K)$	$\underline{(96.15)}$	$\underline{(109.75)}$	$\underline{(146.23)}$	$\underline{(122.)}$	$\underline{(146.8)}$	$\underline{(161.04)}$	$\underline{(190.2)}$	$\underline{(220)}$
ε_0/K_BT_c	0.361	0.405	0.455	0.494	0.510	0.345	0.440	0.513
ε_1/K_BT_c	4.34	4.20	3.97	5.80	4.43	4.26	3.90	4.90
β/K_BT_c	0.205	0.185	0.154	0.160	0.135	0.208	0.158	0.102
Γ/K_BT_c	0.25	0.30	0.20	0.90	0.50	0	0	0
$\Delta S/R$	0.501	0.513	0.533	0.400	0.489	0.507	0.546	0.520
	$\underline{(0.506)}$	$\underline{(0.502)}$	$\underline{(0.530)}$	$\underline{(0.40)}$	$\underline{(0.488)}$	(0.500)	(0.521)	(0.46, 0.504)
$P^2(0)V\alpha/2R$	0.528	0.530	0.526	0.498	0.513	0.522	0.526	0.513
$T_c - \theta(K)$	1.55	0.75	0.25	0.21	−0.08	3.63	1.13	0.70
	(1.90)	(1.75)		(0.02)		(8.04)		(1.5)
$P(T_c)/P(0)$	$\underline{0.862}$	$\underline{0.755}$	$\underline{0.625}$	$\underline{0.365}$	$\underline{0.300}$	$\underline{0.922}$	$\underline{0.701}$	$\underline{0.724}$

ANTIFERROELECTRIC CRYSTALS

Turning to ammonium dihydrogen phosphate, Nagamiya[13] proposed in 1952 that the nonpolar Slater groups form four types of ordered AFE domains below the phase transition which experiment had shown to be nonferroelectric. This conjecture was borne out by neutron scattering.[42] There are two AFE order parameters, each allowing two domain types which transform one into the other upon reversal of H positions in the O—H· · ·O bonds. At a given phosphate site, each of the four zero-moment Slater groups of energy ε_0 corresponds to one of these four domains. A projection of one of these domains along *c* is shown in Figure 5.

Ishibashi *et al.*[14] proposed what seemed the most reasonable explanation for this ordering, namely that the Slater parameter ε_0 becomes negative. This change alone in the Slater model is not sufficient to cause an AFE transition, so they also introduced a dipolar interaction which predicts the observed first-order AFE transition and precludes the formation of other ordered phases not observed experimentally. The nature of this dipolar interaction is discussed below in connection with proton glasses, together with details of the ammonium ordering and its implications.

MIXED FERROELECTRIC-ANTIFERROELECTRIC CRYSTALS

Recently there has been considerable interest in proton glasses, which have the basic KDP structure but are mixtures of a ferroelectric, generally RDP, and of an antiferroelectric such as ADP. The formula for this mixed crystal is

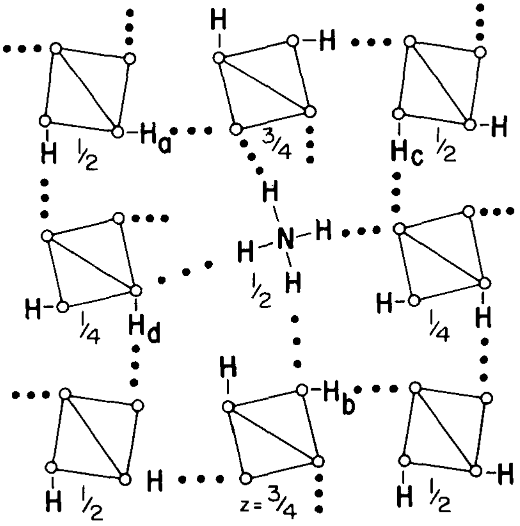

FIGURE 5 Projection along *c* of ADP structure in AFE state. An ammonium ion is shown in its off-center position relative to neighboring phosphate ions. The cross-cation interaction of Reference 18 occurs between acid (O—H· · ·O) hydrogens H_a and H_b, and between H_c and H_d. Fractions indicate phosphate and ammonium heights in terms of *c* lattice spacing.

$Rb_{1-x}(NH_4)_xH_2PO_4$, abbreviated RADP. Pioneering studies of this mixed crystal system were made by Courtens.[15] in the Rb-rich region and by Iida and Terauchi[43] on the NH_4-rich side. To interpret the results, it is helpful to have good models both for RDP and for ADP, and to introduce an additional parameter which takes into account the randomness of the structure. The work in this area has followed two lines—mean-field models and Monte Carlo calculations.

Prelovsek and Blinc[16] presented the first theory for proton glasses, based on Slater groups with both positive and negative Slater energies ε_0 for the nonpolar groups to take into account the presence of both Rb and NH_4 ions. They also included dipolar interactions. Their agreement with the observed FE and AFE phase boundaries was poor, and they predicted a proton glass transition which has not been observed.

Courtens[44] was able to obtain very good agreement with measured dielectric susceptibility data from 2 to 33 K and 106 to 33,700 Hz, using a Vogel–Fulcher law with seven adjustable parameters which he did not relate to any microscopic model.

Matsushita and Matsubara[20] developed a theory in which the Slater energy is positive, negative, or zero, depending on the type of H_2PO_4 cluster. The clusters are considered FE, AFE, or mixed if the cations immediately above (along c) or below are respectively both Rb, both NH_4, or one of each. To obtain the correct type of AFE phase, they used the parallel-bond interaction first proposed by Ishibashi *et al.*[14] They obtained FE and AFE phase boundaries in the $T - x$ plane in good agreement with experiment. In this paper they did not consider the glassy region, other than to include it in the PE phase.

In a subsequent paper,[21] they treated the glassy behavior with a cluster theory employing the replica method. They obtain a definite glass transition in the 20 to 30 K range, as shown in Figure 6. However, no experimental evidence for a definite phase transition to a proton glass state has been presented for the proton glasses.

Ishibashi and Suzuki[19] adapted the previous model of Ishibashi *et al.*[14] to the RADP mixed crystal system and obtained moderately good agreement with experiment. They pointed out that if the dipolar interaction changes sign, a (non-observed) FE phase with polarization in the ab plane would result.

Schmidt *et al.*[17] in a paper presenting dielectric susceptibility results for a mostly deuterated RADP crystal, pointed out that an interaction energy hierarchy will tend to determine the hydrogen ordering. They assumed that the energy required to remove a proton from its bond is effectively infinite, the next largest energy is the Takagi group energy, followed by the bond asymmetry energy for O—H· · ·O bonds having one Rb and one NH_4 neighbor, with the Slater energy being the smallest. In this paper they followed the then-universal belief than the Slater energy changes sign in going from RDP to ADP. They presented a table illustrating the rather small degree of freedom allowed if the above energies are to be minimized for each H_2PO_4 ion, even when interactions with neighboring groups are ignored. They presented a very simple noninteracting-asymmetric-bond model which gives qualitative agreement with susceptibility results in the proton glass region.

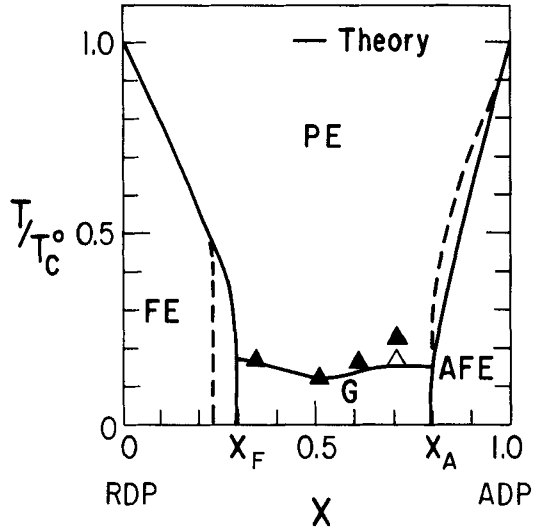

FIGURE 6 Phase diagram for RADP mixed crystals, according to Matsushita and Matsubara (References 20 and 21). Dashed lines and triangles show experimental results.

The following year, a mean field calculation of RADP in the spirit of the Slater model was presented by Schmidt *et al.*[18] They made the new assumption that the Slater parameter ε_0 is independent of the ammonium fractional concentration x, rather than changing its sign for ADP as in previous theories. The justification for this assumption is that the Slater energy represents interactions among protons around a given phosphate ion, and to a first approximation this interaction should be independent of whether the cation is Rb or NH_4. The value of ε_0 is thus fixed for all x at

$$\varepsilon_0 = kT_c(\text{RDP}) \ln 2,$$

which is the value required by the Slater theory to give the correct FE transition temperature for pure RDP.

This new assumption of cation-independent ε_0 was adopted for the Monte Carlo simulations described below. Some evidence in its favor is the report by Lamotte *et al.*[45] in 1972 that, based on EPR studies of $(AsO_4)^{4-}$ radicals in irradiated normal and deuterated ammonium dihydrogen arsenate in the PE phase, the polar Slater groups become more numerous with decreasing temperature. However, with EPR measurements there is always the possibility that the radical is distorting its environment and not giving results characteristic of the undisturbed crystal.

With ε_0 fixed, another parameter is required to explain the AFE transition of ADP. This parameter is based on Hewat's[42] determination by powder-sample neutron diffraction of the AFE phase structure for ADP. There are six important points:

1) Except for the cations, the structure is basically the same as for RDP.
2) Each ammonium is connected by four intrinsically asymmetric N—H· · ·O

hydrogen bonds to four different oxygens, and each oxygen is a member of one and only one such bond, as well as being part of an O—H· · ·O bond.

3) The N—H· · ·O bonds run to corners of a compressed oxygen tetrahedron, which in the c-axis projection form an approximate cross.

4) Two N—H· · ·O bonds adjacent in this cross are short (strong) and the other two are long (weak).

5) For each O—H· · ·O bond, one oxygen participates in a short (N—H· · ·O) bond to the ammonium ion while the other participates in a long (N—H· · ·O) bond. The O—H· · ·O proton is close to the oxygen participating in the long N—H· · ·O bond, as shown in Figure 5 and in the schematic representation below:

N—H· · ·O· · ·H—O· · ·H—N

6) The requirement that two *adjacent* N—H· · ·O bonds be short is incompatible with FE ordering of protons around the phosphates, but is compatible with AFE ordering. The ammonium's desire to be in an off-center position of this type must be stronger than the phosphate's desire to be surrounded by a FE proton arrangement, because the observed structure is AFE.

To approximate these ammonium-induced interactions, it was postulated that two protons directly opposite each other across an ammonium (in the c-axis projection shown in Figure 5) have negative interaction energy if one is close to, and the other far from, their respective oxygens bonded to that ammonium. If both are close or both far, the interaction energy is positive. In a mean-field calculation for ADP, this leads to a first-order transition (as observed) at the correct Neel temperature T_N if the interaction energy ε_a obeys the relation

$$\varepsilon_a(\mathrm{ADP}) = 2\varepsilon_0$$

which has this simple form because T_c and T_N are practically equal, near 147 K. Thus the two energy parameters ε_0 and ε_a are chosen from the transition temperatures T_c and T_N of the two pure constituents RDP and APD. For the mixed crystal of fractional ammonium concentration x, the simplest possible mean-field assumption is made, that

$$\varepsilon_a = x\varepsilon_a(\mathrm{ADP}),$$

which means that the AFE interaction energy ε_a is linearly proportional to the concentration of ammonium ions which cause the AFE ordering tendency.

This Slater-type model predicts a FE transition temperature T_c decreasing with increasing x on the small-x (RDP) side of the phase diagram in $T - x$ space, while an AFE transition temperature T_N increasing with increasing x is found on the ADP side where x approaches 1. However, at lower temperatures a self-inconsistent result is predicted. The phase diagram becomes reentrant at both ends, so that for $T = 0$ and $0 < x < 1$ the ground state is predicted to be one containing a random mixture of Slater up- and down-polarized (FE) groups, with no (AFE) groups of energy ε_0. Such a mixture is impossible, because no polar Slater group can have as its neighbor a polar group of opposite polarity. Further, this mixture has a negative entropy. To eliminate this inconsistency, it was assumed that as temperature decreases and the concentration of polar Slater groups increases, at the temperature at which the entropy reaches zero the relative populations of the up-, down-, and zero-polarized groups are frozen and not allowed to change as temperature decreases further. In a crude sense, this could be considered as a limiting temperature T_g for glassy behavior. It does not denote a phase transition in the usual sense, in accord with experimental results which show no phase transition to a proton glass for this system, but rather a continuous variation from ordinary paraelectric (PE) to proton glass (PG) behavior.

The comparison of the predicted and observed $T - x$ phase diagrams appears in Figure 7. The agreement is surprisingly good, considering that the two parameters ε_0 and ε_a are fixed by the two endpoints T_c and T_N of the phase boundaries. The FE and AFE transition temperatures have very nearly the x-dependences determined experimentally. The temperature T_g is in the correct range. The AFE transition is predicted to be first-order, as observed. However, the FE transition is also predicted to be first-order, except for RDP ($x = 0$) where it has the peculiar "tricritical" behavior predicted by Slater, whereas RDP has a second-order transition and the changeover to first-order behavior according to Courtens[46] occurs at nonzero x. Also, in the PE phase the energy ε_a does not appear in the free energy, which remains in the Slater form in this phase, so that the specific heat is predicted to be independent of x in the PE phase above T_g. This prediction is difficult to compare with experiment, because the proton system specific heat in this region is small compared with the specific heat of the phonon system. It is, however, consistent with the EPR result of Lamotte *et al.*[45] discussed above, because the Slater model predicts the polar Slater group concentration to increase from 1/3 at infinite temperature to 1/2 at T_c.

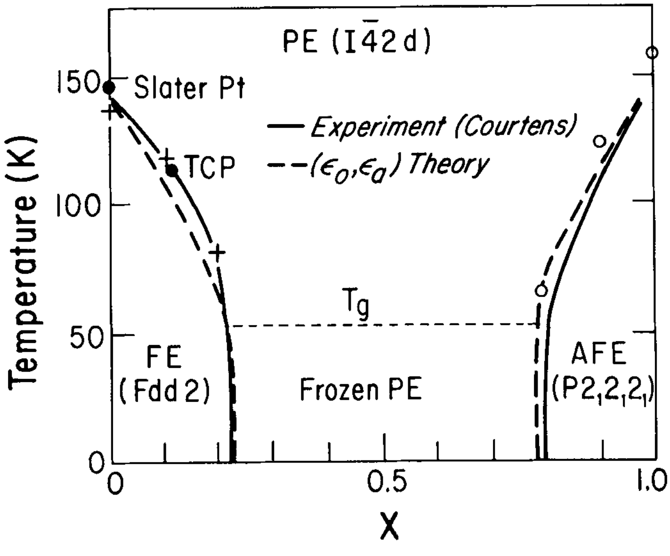

FIGURE 7 Phase diagram for RADP showing boundaries determined by experiment (Reference 46), from mean field theory (Reference 18), and from Monte Carlo heating (crosses) and cooling (circles) runs (Reference 23).

Other discrepancies between predictions of this theory and experiment are of the nature expected from a Slater-type theroy. The FE and AFE order immediately become complete below the transition temperatures. For intermediate x, the transition from PE behavior to completely frozen glass behavior is abrupt. The most serious defect of this theory (shared of course by the Slater theory) is its complete inability to predict any dynamic behavior, because of the exclusion of Takagi groups which are the vehicle for such behavior.

Obvious improvements to this theory would be incorporation of Takagi groups and/or tunneling, but this has not yet been done. Takagi groups would make the RDP transition second-order as observed,[35] and by adjusting the Takagi energy ε_1 it would be possible to obtain a tricritical point at some desired non-zero value of ammonium concentration x, as was reported by Courtens.[46]

Another interesting modification would be assuming that the cross-cation interaction ε_a has a small positive value even for $x = 0$. If Takagi groups are not allowed, this would predict a first-order transition as observed for instance with KDP. By having the correct ratio of ε_a to the Takagi energy ε_1 it might be possible to come close to the observed spontaneous polarization curve *vs.* temperature for KDP,[47] which consists of a jump at T_c followed by a rounded curve increasing to a saturation value at low temperature. In this way, the need for the long-range interaction introduced by Senko[5] and studied by SUS[8] might be eliminated. This assumption of non-zero ε_a for $x = 0$ is reasonable because there must be some interaction between protons separated by an alkali ion, even though it should be much weaker than across an ammonium ion because of lack of the N—H· · ·O bonds.

Such improved mean-field theories would be one way to approach the truth about these mixed crystals. A second method, being pursued by Selke and Courtens[22] and our group,[23] is Monte Carlo calculations using short-range-interaction models on finite "crystals". Such calculations have the advantage that the (assumed) random placing of the ammoniums on cation sites in the mixed crystals goes directly into the simulation, and other mean-field approximations are also avoided. Also, the dynamical behavior of the crystal can be studied without adding greatly to the complexity of the Monte Carlo calculation. The drawbacks of this method are the large amount of computer time required, especially in the proton glass region, and the necessity of working with very small crystals from which results for infinite crystals must be extrapolated. Also, additional parameters must be introduced as described below.

The first such parameter originates in the need to obtain only the four types of observed AFE domains. Mere introduction of ε_a will lead with equal probability to such domains and to the types of non-observed ordering described by Ishibashi.[14] A structural feature that exists for the observed FE and AFE domains but not for the non-observed ordering is a particular hydrogen arrangement in parallel hydrogen bonds. Specifically, all the O—H· · ·O bonds can be arranged in staggered chains running along c, with the O—O vectors in each chain being essentially parallel. In, and only in, the observed ordered phases the proton arrangement in each chain is as would be expected from electrostatic repulsion, with protons in adjacent bonds being at opposite ends of the bonds, as shown in Figure 8. The interaction energy of adjacent protons can be estimated electro-

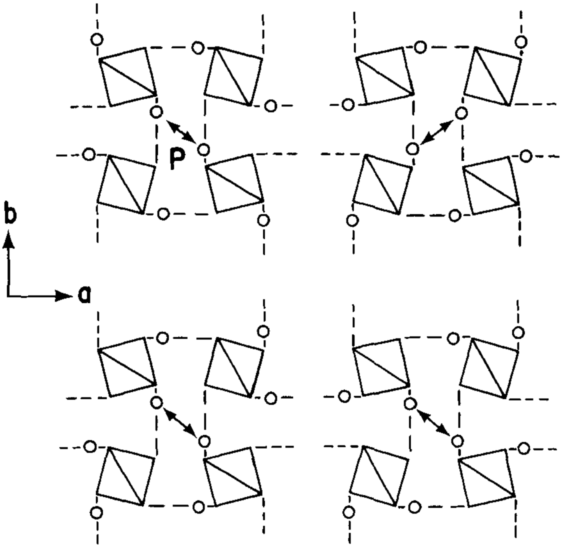

FIGURE 8 Atomic arrangements of H_2PO_4 groups in the two types of FE domains in KDP or RDP (top), and in one of the two types of AFE domains for each of the two AFE order parameters in ADP (bottom). The parallel-bond dipolar interaction is designated by arrows. (Reference 53).

statically or can be used as a free parameter. Electrostatic estimation is reasonable (much more so than for estimation of Slater or Takagi energies) because such bonds are separated by two intervening phosphates instead of one, which should make chemical effects small in the interaction. Because this interaction tends to stabilize both the FE and AFE phases, its presence reduces the magnitudes of ε_0 and ε_a necessary to predict the correct transition temperatures T_c and T_N.

Another interaction which can be introduced here, but not into mean field theories in any direct way, is one which gives a permanent "tilt" to certain O—H· · ·O bonds in a mixed crystal.[17,44] It will occur in those bonds in which one oxygen is H-bonded to an ammonium ion, while the other oxygen in the O—H· · ·O bond neighbors on a Rb ion. A fraction $2x(1-x)$ of the bonds will be tilted. This fraction has a rounded maximum of 0.5 for $x=0.5$. If this tilt is considered strong enough so no proton transfer can occur along these bonds at sufficiently low temperature, then the Takagi groups must migrate along the remaining fraction $1+2x^2-2x$ of the bonds. Near $x=0.5$ it is not certain whether infinite-distance Takagi group percolation can occur along such bonds. Cayley-tree calculations indicate that the system is near the percolation limit. The rejoining of percolation paths ignored in the Cayley tree calculation makes percolation more difficult than indicated by this calculation.

Another effect of these biased bonds is to favor given positions for that fraction $2x(1-x)$ of the protons. These positions depend on the random ammonium arrangement, and will not favor any particular FE or AFE ordered state. Combined with the Takagi interaction, for x near 0.5 this interaction will determine most of the proton positions at low temperature.[17] If all were determined, one could speak of a unique ground state with no *macroscopically observable* order parameter. This situation has some similarities with the Edwards–Anderson model[48] ground state(s), but there is an important difference. In the Edwards–Anderson model for a spin glass, the spins only interact with each other via random short-range interactions, leading to a *phase transition* to an ordered state with no observable order parameter. In our case, for x near 0.5 the pseudospins interact with the lattice (randomly placed Rb and NH_4 ions) about as strongly as with each other. The interaction with the lattice can be viewed as a random field, which is likely to be strong enough to determine the order and override the order that the pseudo-spin interactions alone would achieve, thus explaining the lack of a distinct glass transition temperature in the proton glass system.

Selke and Courtens[22] consider two statistical entities in their Monte Carlo model for the RADP system. One is the off-center position of the "acid" hydrogen in the O—H· · ·O bond, which can be in one of two positions. The other is the off-center position of the ammonium ion, which by their hypothesis must sit in one of four corners, as shown in Fig. 5. It then repels the two acid hydrogens close to that corner. They assume no interaction with the other two acid hydrogens near that ammonium, nor do they consider any Rb—NH_4-induced O—H· · ·O bond asymmetry other than that implied by repulsion of acid hydrogens by the short N—H· · ·O bonds. They alternately run Monte Carlo simulations on the acid proton and the ammonia systems, each for a certain number of steps. In effect, they have a system with three types of random entities: the ammonium *vs.* rubidium ion nominal locations, which stay fixed throughout a given run, the acid hydrogen positions, and the ammonium positions within a given ammonium "cavity". They have four interaction energies: Slater, Takagi, cross-cation, and parallel-bond. Their predicted phase diagram is compared with experiment in Figure 9.

Schmidt and Schnackenberg[23] independently developed another model which differs from the Selke–Courtens model in several respects. One difference is that the ammonium is assumed to adjust its position within its cavity adiabatically and almost instantaneously to any changes in adjacent acid hydrogen positions, and so the ammoniums are not considered as statistical entities. The rationale for this view is that the ammonium ion sits in a cavity having no apparent barriers to this position adjustment, whereas the acid hydrogens can move only when a Takagi group diffuses through its position, or at the cost of creating two Takagi groups of combined energy $2\varepsilon_1$.

Another difference is that Schmidt and Schnackenberg specifically put in an average O—H· · ·O bond asymmetry for bonds with one Rb and one NH_4 neighbor, while Selke and Courtens consider that a bond with Rb at one end and a "far" ammonium at the other is symmetric. Thus, Schmidt and Schnackenberg introduce one more energy parameter. Also, there ε_a is across the ammonium and independent of where the ammonium is actually sitting, while Selke and Courtens put the ammonium in a given position which is only statistically dependent on the local acid hydrogen configuration.

Comparison of Monte Carlo predictions by Schnackenberg and Schmidt with the observed phase diagram is presented in Figure 7. The agreement is quite

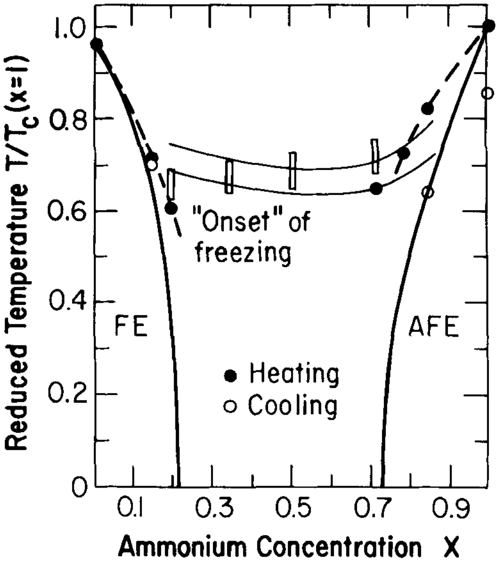

FIGURE 9 Phase diagram from Selke–Courtens (Reference 22) Monte Carlo simulation. Filled and open circles mark FE and AFE phase boundaries based on heating and cooling runs respectively, and rectangles indicate the onset of freezing obtained from the Edwards–Anderson (Reference 48) order parameter. Thin lines represent experimental results.

good, as is that of Selke and Courtens in Figure 9. This indicates that in spite of the differences in their models, both may represent the behavior of RADP quite well. The decision as to which (if either) is best may depend on how well each can fit dynamic results such as ac dielectric susceptibility, NMR relaxation, and Brillouin scattering.

Schnackenberg[23] has developed a histogram display of order parameter distribution for long runs, based on a method due to Mouritsen.[49] If with decreasing temperature the histogram goes smoothly from a single peak at zero order parameter to two peaks of equal and opposite order parameter, the transition is considered to be of second order. If two additional peaks appear at equal and opposite order parameter while the middle peak still exists, the transition is considered to be of first order. In results to date on "crystals" of 4 × 4 × 4 unit cells, this histogram method predicts a second-order phase diagram at the RDP end, as observed.

Schmidt[23] has found that above T_c at the RDP end of the phase diagram, the simulation of polarization decay upon removing an electric field gives a single time constant whose length obeys a Curie–Weiss law, as expected in the PE phase. At low temperature for intermediate x values, the decay exhibits a wide distribution of time constants, as found experimentally for normal and fully determined RADP[50] as well as for 71.4% deuterated RADP.[51]

CONCLUSIONS

In summary, order–disorder models for KDP-type crystals can explain most static phenomena and a wide range of dynamic behavior as well. Because they do not consider phonon modes, they are incapable of predicting soft mode behavior. Modification and merger of theories for ferroelectric KDP and antiferroelectric ADP provide mean-field theories and Monte Carlo simulations which are explaining a number of features of the RADP-type proton glasses.

For the future, one can expect that the current trend toward more complex mean-field order–disorder theories will not continue. Instead, a bifurcation is appearing: The more complex models are being studied in Monte-Carlo simulations which avoid mean-field approximations, while simpler mean-field theories are used to gain qualitative physical insights.

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