

Unified model for the transverse electric susceptibility in KH_2PO_4 - and $\text{NH}_4\text{H}_2\text{PO}_4$ -type crystals

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(Received 12 January 1976)

The dielectric properties of $\text{NH}_4\text{H}_2\text{PO}_4$ -type crystals are investigated using an antiferroelectric version of an extended pseudospin model previously applied to ferroelectric KH_2PO_4 -type crystals. The model takes into account the transverse polarization induced by the proton displacements along the hydrogen bonds. The Hamiltonian is based on a four-sublattice version of the Slater-Takagi protonic configurations around the PO_4 groups and includes also a long-range antiferroelectric interaction energy. The temperature dependence of the susceptibilities along the a and c directions is calculated by applying a four-cluster approximation to the model. The theoretical results are compared to the available data for the dielectric constants along the a and c directions of $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{ND}_4\text{D}_2\text{PO}_4$, and $\text{NH}_4\text{H}_2\text{AsO}_4$. An excellent fit to the data for both the a and c directions is achieved by taking a single set of energy parameters for each crystal. It is found that both the long-range antiferroelectric interaction and the Slater short-range energy play an important role in the antiferroelectric ordering. We also present a detailed comparison of our model for antiferroelectric $\text{NH}_4\text{H}_2\text{PO}_4$ -type crystals with that of Ishibashi *et al.* and we find that our results for the transverse susceptibility differ from theirs. This difference arises from our inclusion of the direct contribution of the proton displacements to the transverse polarization.

I. INTRODUCTION

Among the isomorphs of KH_2PO_4 (KDP) crystals, the $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) type are known to undergo a first-order antiferroelectric phase transformation.^{1,2} The transition is characterized by a change in the crystal structure which is tetragonal $D_2 - 42m$ above and orthorhombic $D_2 - 222$ below the transition point T_c , as well as by latent heat and thermal hysteresis in the dielectric constant at T_c .^{1,2} Despite the availability of extensive experimental data, there has been much less theoretical work done on ADP than on KDP. The object of this paper is to present a theoretical model for ADP which will bring it into conformity with KDP. It is based on an antiferroelectric version of an extended model previously presented by the authors to explain the properties of KH_2PO_4 -type crystals along the a axis.^{3,4} The model includes, in addition to the usual Blinc-de Gennes Hamiltonian,^{5,6} the transverse polarization induced by the protonic displacements along the hydrogen bonds. We show here that this model, which successfully explained the dielectric properties in KDP along both the a and c directions, is also capable of consistently explaining the dielectric properties of ADP-type crystals.

Measurements of the longitudinal and transverse dielectric constant, ϵ_c and ϵ_a of $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP), $\text{ND}_4\text{D}_2\text{PO}_4$ (dADP), and $\text{NH}_4\text{H}_2\text{AsO}_4$ (ADA) were carried out by Mason and Matthias⁷ and others.^{8,9} These experiments have shown that the above

crystals undergo a sharp first-order antiferroelectric transition manifested by large discontinuities in ϵ_c and ϵ_a . In addition, ϵ_a has a much higher value and stronger temperature dependence than ϵ_c , indicating the importance of the transverse dielectric properties in the antiferroelectric ADP-type crystals.

The extension of our model, from the ferroelectric to the antiferroelectric case, is based on the four-sublattice version of the Slater¹⁰ description of the proton configurations around the PO_4 groups and on the inclusion of antiferroelectric long-range interaction between the different sublattices.¹¹ Solution of the problem for this model is carried out by applying a four-cluster approximation which is capable of explaining the onset of the first-order antiferroelectric transition.

Recently, Ishibashi, Ohya, and Takagi (IOT) have presented a theory for the phase transition of ADP.¹¹ Although their theory does explain the essence of the antiferroelectric transition, the dielectric properties along the a and c direction were not consistently explained. Our model as well as that of IOT is based on the four-sublattice version of the Slater model. However, we differ essentially in our basic assumption about the origin of the transverse polarization of the H_2PO_4 groups. In the model of IOT, the dipole moments in both the longitudinal and transverse directions are tied directly to the proton configurations around the PO_4 groups. In contrast, the dipole moments in our model are directly related

to changes in order parameter of individual hydrogen bonds which are induced by crystalline and applied fields. Thus, as will be shown later in detail, our model leads to a completely different microscopic description of the transverse dielectric properties in ADP than that of IOT, and in particular is successful in explaining the dielectric-constant data. Finally, it is our model that the transverse polarization is directly related to the individual proton displacements, which enables us to present for the first time a pseudospin model for antiferroelectric ADP-type crystals.

II. THEORY

Our theoretical treatment of antiferroelectric ADP-type crystals is based on a pseudospin Hamiltonian which incorporates both a transverse long-range dipole-dipole antiferroelectric interaction and an interaction between the transverse dipoles and an external transverse field.

In order to include these transverse properties we take into account changes in the transverse dipole moments induced by the fields acting on the protonic displacements along the hydrogen bonds, similar to our previous treatment of the transverse properties of KDP-type crystals.^{3,4} Thus we distinguish between two kinds of hydrogen bonds. A bond is labeled plus (minus) when the displacement of its proton towards its spin-up position contributes positively (negatively) to the polarization along the a or b direction. Accordingly the polarization along the a and b directions are given by $P_a \propto \sum_i Z_i^{+a} - \sum_i Z_i^{-a}$ and $P_b \propto \sum_i Z_i^{+b} - \sum_i Z_i^{-b}$, respectively, where $Z_i^{\pm\alpha}$ is the pseudo-spin operator associated with a plus or minus bond aligned in the α direction, and α is a or b .

The inclusion of a transverse long-range dipole-dipole interaction is accomplished by introducing four pseudospin sublattices similar to the four sublattices of the Slater PO_4 groups considered by IOT.¹¹

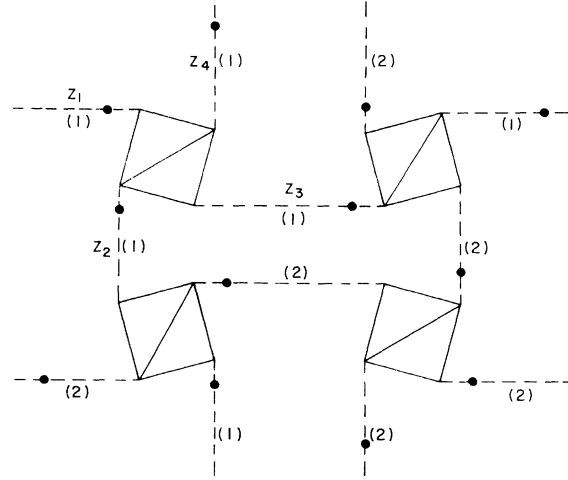


FIG. 1. Four-sublattice model of ADP. The hydrogen bonds along each transverse direction are divided into two sublattices, designated by (1) and (2).

The bonds in a unit cell of ADP lie in four parallel planes perpendicular to the c axis, whereby each plane constitutes one of the four sublattices as shown in Fig. 1. In this figure the bonds along each transverse direction are divided into two sublattices designated by (1) and (2), so that alternating layers belong to different sublattices. Thus, the plane containing the Z_1 and Z_3 bonds consists of the sublattice (1) of the bonds in the a direction. The higher plane, containing the Z_2 and Z_4 bonds, forms the sublattice (1) of the bonds in the b direction. Similarly, the third and fourth planes consist of the sublattices (2) of the bonds in the a and b directions, respectively. Accordingly, we include in this Hamiltonian an antiferroelectric long-range interaction between the transverse dipoles of the two different sublattices in each direction. Thus our pseudospin Hamiltonian gets the following form:

$$\begin{aligned}
 H = & -\frac{1}{2} \sum_{i,j} J_{ij} Z_i Z_j - (\mu_1 E_c + \gamma \langle Z \rangle) \sum_i Z_i \\
 & - \sum_{\alpha=a,b} [\mu_2 E_\alpha - \frac{1}{2} \lambda \langle Z^{+\alpha}(2) - Z^{-\alpha}(2) \rangle] \left(\sum_i Z_i^{+\alpha}(1) - \sum_i Z_i^{-\alpha}(1) \right) \\
 & - \sum_{\alpha=a,b} [\mu_2 E_\alpha - \frac{1}{2} \lambda \langle Z^{+\alpha}(1) - Z^{-\alpha}(1) \rangle] \left(\sum_i Z_i^{+\alpha}(2) - \sum_i Z_i^{-\alpha}(2) \right). \quad (1)
 \end{aligned}$$

The first term represents the effective short-range proton-proton interaction and is the same as the usual Blinc-de Gennes Hamiltonian for KDP-type crystals with zero tunneling. The reason for neglecting

the tunneling term will be given later in Sec. III. The second term represents the interaction of the spins with an external electric field along the c direction and their interaction with the average longitudinal polarization $\langle Z \rangle$ via the long-range dipole-dipole interaction γ . Here $\langle Z \rangle$ is defined by

$$\langle Z \rangle = \frac{1}{2N} \left\langle \sum_{i=1}^{2N} Z_i \right\rangle,$$

where N is the number of PO_4 groups. The last terms represent the interaction of the transverse polarization of the four sublattices with an external transverse field and also the long-range transverse dipole-dipole antiferroelectric interaction between transverse dipole moments of different sublattices aligned in the same transverse direction. The quantity λ is the long-range antiferroelectric interaction constant, and the symbols $Z^{*\alpha}(1)$ and $Z^{*\alpha}(2)$ stand for pseudospins in sublattices (1) and (2), respectively, associated with the direction α (see Fig. 1).

Since the solution of the pseudospin model for KH_2PO_4 -type crystal by a four-cluster approximation describes adequately most of the static properties of these crystals,^{3,12-16} we apply the same approximation to the Hamiltonian in Eq. (1) for ADP. The four-particle Hamiltonian describing the energy of four pseudospins which surround a PO_4 group and in which all the spins belong to sublattices (1), can be shown to be

$$\begin{aligned} H_4(1) = & -V[Z_1(1)Z_2(1) + Z_2(1)Z_3(1) + Z_3(1)Z_4(1) + Z_4(1)Z_1(1)] \\ & -U[Z_1(1)Z_3(1) + Z_2(1)Z_4(1)] - (\mu_1 E_c + \gamma \langle Z \rangle + \frac{1}{2} \Delta_c) \sum_{i=1}^4 Z_i(1) \\ & -[\mu_2 E_a - \frac{1}{2} \lambda \langle Z^{*a}(2) - Z^{-a}(2) \rangle + \frac{1}{2} \Delta_a][Z_3(1) - Z_1(1)] \\ & -[\mu_2 E_b - \frac{1}{2} \lambda \langle Z^{*b}(2) - Z^{-b}(2) \rangle + \frac{1}{2} \Delta_b][Z_2(1) - Z_4(1)], \end{aligned} \quad (2)$$

where U and V are the short-range interaction energies and are related to the Slater-Takagi parameters by $4U = -2\epsilon_1 + 2\epsilon_0$; $4V = 2\epsilon_1 - \epsilon_0$.¹² The quantities Z_1 and Z_3 are the Ising pseudospins representing the minus and plus hydrogen bonds along the a direction, and Z_2 and Z_4 are those for the b direction (see Fig. 1). The quantities Δ_a , Δ_b , and Δ_c are the energies due to effective fields along the a , b , and c directions, respectively, produced by the adjacent bonds outside the cluster. The quantities μ_1 and μ_2 are the dipole moments along the a (b) and c directions, respectively.

The one-particle Hamiltonian for the plus and minus bonds aligned along the a direction is given by

$$\begin{aligned} H^{*a}(1) = & -[\mu_1 E_c + \gamma \langle Z \rangle + \Delta_c + \mu_2 E_a \\ & - \frac{1}{2} \lambda \langle Z_3(2) - Z_1(2) \rangle + \Delta_a] Z_3(1), \\ H^{-a}(1) = & -[\mu_1 E_c + \gamma \langle Z \rangle + \Delta_c - \mu_2 E_a \\ & + \frac{1}{2} \lambda \langle Z_3(2) - Z_1(2) \rangle - \Delta_a] Z_1(1). \end{aligned} \quad (3)$$

Similar expressions exist for the one-particle Hamiltonian for the bonds along the b direction.

In order to calculate the averages $\langle Z^{*\alpha}(1) \rangle$ and $\langle Z^{*\alpha}(2) \rangle$ one has to take into account also the Hamiltonians of the pseudospins belonging to the second sublattices, $H_4(2)$ and $H^{*\alpha}(2)$ which are of a similar form as $H_4(1)$ and $H^{*\alpha}(1)$ in Eqs. (2) and (3). The effective cluster fields Δ_a , Δ_b , and Δ_c

are determined with the aid of the cluster equilibrium condition

$$\frac{\partial F}{\partial \Delta_a} = \frac{\partial F}{\partial \Delta_b} = \frac{\partial F}{\partial \Delta_c} = 0, \quad (4)$$

where F is the approximate Helmholtz free energy given by

$$\begin{aligned} F = & -\frac{k_B T}{2} \left(\ln \mathfrak{z}_4(1) + \ln \mathfrak{z}_4(2) - \frac{1}{4} \sum_{i=1,2} [\ln \mathfrak{z}_{(i)}^{*\alpha} + \ln \mathfrak{z}_{(i)}^{-\alpha}] \right) \\ & + \gamma \langle Z \rangle^2 + \frac{\lambda}{4} \sum_{\alpha=a,b} \langle Z^{*\alpha}(1) - Z^{-\alpha}(1) \rangle \langle Z^{*\alpha}(2) - Z^{-\alpha}(2) \rangle, \end{aligned} \quad (5)$$

where $\mathfrak{z}_4(i)$ and $\mathfrak{z}^{*\alpha}(i)$ are the partition functions of the four- and one-particle Hamiltonians $H_4(i)$ and $H^{*\alpha}(i)$, respectively. Following the usual procedure for obtaining the antiferroelectric transition temperature T_a from the free energy, we obtain the following result:

$$\exp(-\lambda/k_B T_a) = 2/[2 + \exp(\epsilon_0/k_B T_a)]. \quad (6)$$

In obtaining Eq. (6), it was assumed that the three-proton configuration energy parameter ϵ_1 is infinitely large. This is reasonable in view of the large discontinuities of χ_a and χ_c in ADP-type crystals at the transition temperature.⁷⁻⁹

Equation (6) is the same condition for T_a as that

derived by IOT.¹¹ It should be noted that only when the antiferroelectric interaction constant λ is positive will an antiferroelectric phase transition occur. It should also be noted that solutions of Eq. (6) exist for both ϵ_0 positive and negative. However, as already discussed by IOT, the appearance of the antiferroelectric phase transition is further limited by the minimum free-energy condition which gives another restriction on the values of ϵ_0 and λ . In fact comparison of the values of the free energy, Eq. (5), in the ferroelectric phase ($\langle Z \rangle = 1$) and the antiferroelectric phase [$\langle Z^{+\alpha}(1) - Z^{-\alpha}(1) \rangle = -\langle Z^{+\alpha}(2) - Z^{-\alpha}(2) \rangle = 2$] yields the following further condition for the occurrence of the antiferroelectric phase transition

$$\epsilon_0 \leq \lambda - \gamma. \quad (7)$$

The susceptibilities χ_a and χ_c are defined in our model as

$$\chi_a = \frac{N\mu_2}{4} \frac{d}{dE_a} \langle Z^{+\alpha}(1) + Z^{+\alpha}(2) - Z^{-\alpha}(1) - Z^{-\alpha}(2) \rangle, \quad (8)$$

$$\chi_c = N\mu_1 \frac{d}{dE_c} \langle Z \rangle.$$

Calculation of the averages appearing in Eq. (8) with the aid of the relation $\langle A \rangle = \text{Tr}[Ae^{-\beta H_A}] / \text{Tr}[e^{-\beta H_A}]$ and Eq. (4) yields for $T > T_a$

$$\chi_a = \frac{2N\mu_2^2}{k_B T \exp(\epsilon_0/k_B T) + 2\lambda}, \quad (9)$$

$$\chi_c = \frac{4N\mu_1^2}{k_B T [2 \exp(-\epsilon_0/k_B T) - 1] - 2\gamma}. \quad (10)$$

The above expression for χ_c is the same as the one derived by Silsbee, Uehling, and Schmidt for KDP.¹³ However, the expression for χ_a is new and different from that given by IOT for ADP-type crystals. The origin of this difference will be discussed below.

III. COMPARISON WITH EXPERIMENT

The predictions of Eqs. (9) and (10) are compared to the available susceptibility data on ADP, dADP, and ADA⁷⁻⁹ as shown in Fig. 2. The cor-

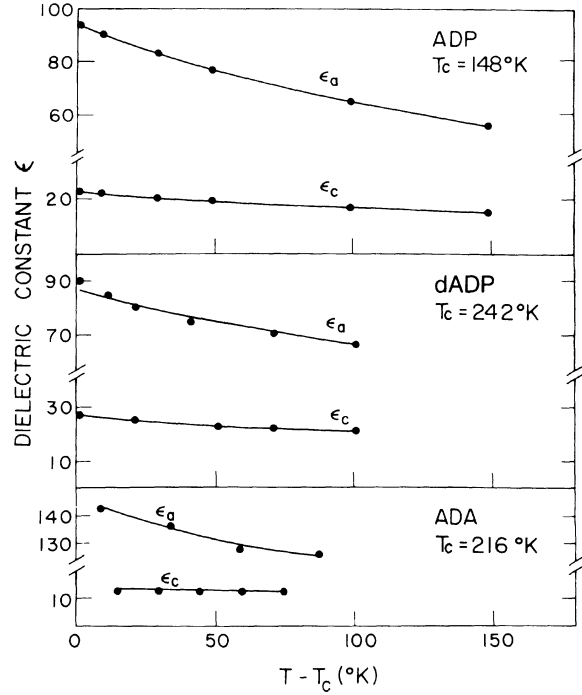


FIG. 2. Comparison of the theoretical dielectric constant ϵ_a and ϵ_c with experiment. The points are the experimental data taken from Refs. 7-9. The solid curves are the theoretical results calculated from Eqs. (6), (9), and (10). In order to fit the theory to the experimental results we used the relations between the clamped and the free susceptibilities given by Nagamya (Ref. 2).

responding Slater energy ϵ_0 , the long-range antiferroelectric interaction λ , and the dipole moments μ_1 and μ_2 which give the best fit to the data are listed in Table I. It is noted that, for each crystal, an excellent fit to the data for χ_a and χ_c is achieved by a single set of energies ϵ_0 and λ , which are related through Eq. (6). It is also seen from Table I that the transverse long-range interaction λ is of the same order as the short-range energy ϵ_0 , indicating that both play an important role in the antiferroelectric ordering. This is in contrast to the ferroelectric ordering in the iso-

TABLE I. Values of ϵ_0 , λ , μ_1 , and μ_2 as obtained by fitting the theoretical expression for χ_a and χ_c , Eqs. (9) and (10), to the experimental data, Ref. 7.

Crystal	T_c (°K)	ϵ_0/k_B (°K)	λ/k_B (°K)	$10^{18}\mu_1$ (cgs)	$10^{18}\mu_2$ (cgs)
NH ₄ H ₂ PO ₄ (ADP)	148	-42	49.0	1.86	3.2
ND ₄ D ₂ PO ₄ (dADP)	242	-85	73.0	2.99	3.83
NH ₄ H ₂ AsO ₄ (ADA)	216	+37	100.6	1.1	5.88

morph KDP where the longitudinal long-range ordering interaction is small compared to the short-range energy.¹³ As mentioned above, examination of Eqs. (6) and (7) shows that the antiferroelectric transition is permissible for both positive or negative values for ϵ_0 . It is interesting to note that for ADA, the best fit to the data occurs for positive ϵ_0 , which is consistent with what was recently indicated by ESR experiment.¹⁷

The increase of ϵ_0 with deuteration is nearly the same as that of μ_1^2 . This behavior is also found in KDP-type crystals.¹⁶ It should be noted that the values of the transverse dipole moment μ_2 which are given in Table I are higher than the expected contribution of the proton displacements along the hydrogen bonds. This result, which is similar to that found for the μ_2 of KDP-type crystals,⁴ indicates that lattice transverse displacements coupled to the proton displacement also contribute to the transverse dipole moment μ_2 . As for the long-range-interaction parameter along the c direction γ , it has been found that excellent fit can be achieved with $\gamma=0$ for all the above-mentioned ADP-type crystals. We therefore conclude that this parameter plays a negligible role in the antiferroelectric transition.

The good agreement between Eqs. (9) and (10) and the experimental data provide further support to the above assumption that the three-proton configuration energy ϵ_1 is very large, which means that these configurations may be discarded. Neglecting the three-proton configurations is consistent with our neglecting the proton-tunneling term $-\Gamma\sum X_i$ in the Hamiltonian, Eq. (1). This is due to the fact that all the matrix elements of the spin operators X_i in the subspace of *two* proton configurations vanish. Therefore, the addition of a tunneling term to the four-cluster Hamiltonian, Eq. (2), would not contribute to the free energy and hence would not affect our above results.

IV. COMPARISON WITH IOT THEORY

It is useful at this point to elaborate on the differences between our model and that of IOT. In our approach the polarization along the a direction of the H_2PO_4 groups is directly related to dipole moment induced by the individual hydrogen ion displacement in that same direction.^{3,4} The same applies to the b direction, see Fig. 3(a). By contrast, in the IOT model the dipoles associated with the displacement of the individual protons are not taken into account and the polarization of the PO_4 groups in the a direction is determined by the four-proton configuration around the groups in the same way as for the c direction, see Fig. 3(b).

Therefore, according to the present approach, all the H_2PO_4 groups which are transversely polarized contribute simultaneously to the polarization along both the a and b directions, unlike the IOT model in which each H_2PO_4 group is polarized only in one direction.

Finally, it should be noted that only because we associate the transverse dipole moments of the crystal with the proton displacements along their bonds are we able to consider the total transverse polarization as composed of contributions from individual protons. This, in turn, made it possible for us to extend the convenient pseudospin formalism so as to include also the transverse dielectric properties, for KDP- and ADP-type crystals.

V. CONCLUSION

We have shown that the transverse pseudospin model whose ferroelectric version has been successfully applied to explain the transverse dielectric properties of KDP^{3,4} explains in its antiferroelectric version also the available dielectric data of ADP-type crystals.

The present simplified theoretical treatment can be improved by taking into account all the Slater configurations and the protonic tunneling energy. However, these subtle corrections to the present treatment could be checked only if additional and more accurate dielectric measurements in ADP-type crystals were carried out. While the present

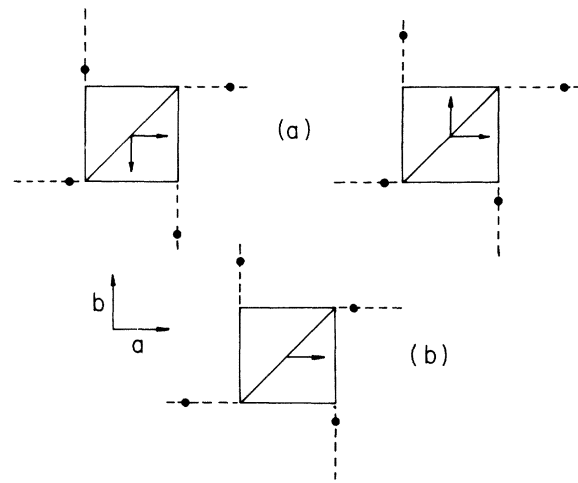


FIG. 3. Configurations of the H_2PO_4 groups which contribute positively to the polarization along the a direction according to the present model (a) and that of IOT (Ref. 11) (b). The arrows represent the components of the polarization in the a and b directions.

work deals only with the static properties of ADP we believe that the present model serves as a proper basis for the investigation of the dynamic properties as well. The description of these

properties of ADP, which can be established in a fashion similar to that suggested by the authors for the dynamics of KDP¹⁸ will be discussed elsewhere.

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