

## Transverse susceptibility in $\text{KH}_2\text{PO}_4$ -type crystals

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A well-known model of ferroelectricity in potassium dihydrogen phosphate type crystals is extended to provide a description of observed transverse susceptibility in  $\text{KH}_2\text{PO}_4$  and  $\text{KH}_2\text{AsPO}_4$ , the temperature dependence of which exhibits the expected antiferroelectric characteristics. Experimental data can be used in principle to determine the bond-bond interaction parameter  $J$  and the tunneling integral  $\Gamma$ . Available data provide satisfactory order-of-magnitude results, and are in qualitative agreement with determinations based on other experiments with regard to the relative values of  $\Gamma$  in two isomorphs. It is shown that more refined experimental data would contribute to a further understanding of this example of simultaneous ferroelectricity and antiferroelectricity in a single medium.

### I. INTRODUCTION

It is well known that potassium dihydrogen phosphate (KDP)-type crystals possess ferroelectric properties along the  $c$  axis and that the longitudinal susceptibility exhibits Curie-Weiss behavior in the neighborhood of the transition temperature.<sup>1-4</sup> The experimental facts are well described in terms of the known crystal structure using either the Slater-Takagi procedure for decomposition of the crystal into elementary constituents<sup>5-7</sup> or the Blinc-de Gennes procedure based on a pseudospin formalism.<sup>8,9</sup>

Up to now, however, the subject of transverse susceptibility in these crystals has been largely ignored. This is due in part to the fact that the available data<sup>1,10</sup> are meager and in part to the assumed irrelevance of such information to an understanding of the nature of the phase transition. However, we now find that these data, and with them also any new data along similar lines that may be forthcoming in the future, are of considerable interest for two reasons: (a) evidence of the phase transition is as clearly seen in the transverse as in the longitudinal susceptibility but, of course, not in the Curie-Weiss sense; and (b) an interpretation of the data using a theory of the transverse susceptibility based on the Blinc-de Gennes model provides a numerical value of the tunneling integral, which is one of the important phase-transition parameters. The latter is of considerable interest, for example, in the attempt to understand large differences which seem to exist between such isomorphs as  $\text{KH}_2\text{PO}_4$  and  $\text{KH}_2\text{AsO}_4$ , which are otherwise similar.

### II. THEORY

Though the crystal structure of KDP-type crystals is well known and fully described in the literature already cited, certain features need to be emphasized in the present context. The relevant

structural unit is the hydrogen bond. These bonds lie very nearly along the  $a$  and  $b$  axes of the crystal of which the  $c$  axis is the direction of spontaneous polarization in the ferroelectric state. The fact that the hydrogen bonds connect linear arrays of alternating  $\text{PO}_4$  groups and K ions stretching along the  $c$  axis will not play a direct role in the present discussion. Our attention will be directed solely to the hydrogen bonds which will be assumed to lie precisely along the  $x$  and  $y$  axes of a rectangular coordinate system. The hydrogen ion of these bonds is known to occupy one or the other of two equilibrium positions in the bond symmetrically placed with respect to the bond center. At sufficiently high temperatures in the paraelectric state there is complete disorder in the distribution of hydrogen ions over their two positions. As the temperature is lowered and the ferroelectric state is approached, a certain order in the distribution sets in, and at zero temperature the distribution is a completely ordered one. A remarkable feature of the ordered state is that as one moves along the crystalline  $a$  or  $b$  axis following a chain of hydrogen bonds and their intervening  $\text{PO}_4$  groups the hydrogen ion is found alternately on the left and on the right side of their bonds. Hence, if an electric field is directed, for example, along the  $x$  axis, half of the hydrogen ions in  $x$ -directed bonds are on the high-field side of their bonds and half on the low-field side. We distinguish these two kinds of bonds as plus and minus bonds. Figure 1 illustrates how a typical bond, say a plus- $x$  bond, is located with respect to two minus- $x$  bonds and four  $y$  bonds for the case of an applied field along the  $x$  axis. These six bonds are also the nearest-neighbor bonds to the specified bond.

The two-position feature of hydrogen ions in symmetric bonds permits the use of a pseudospin formalism<sup>9,11</sup> to describe the order-disorder state in terms of tunneling, nearest-neighbor interac-

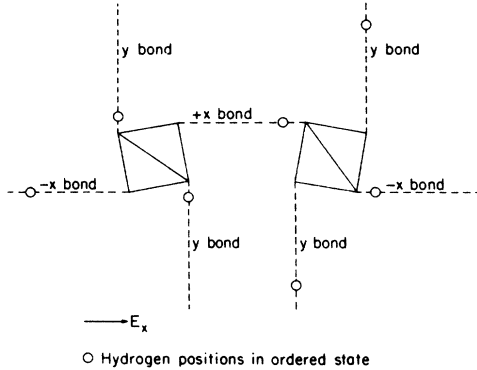


FIG. 1.  $c$  ( $z$ )-axis projection showing the six nearest neighbors of a plus- $x$  bond.

tions among bonds, and the presence of an externally applied electric field. In this formalism the Ising spin operator  $S^z$  is the important dynamical variable, and from its expectation value other physical quantities can be calculated. This is one of the two procedures mentioned in the Introduction which have been used to calculate the longitudinal susceptibility.

The theory of transverse susceptibility requires no additions to this model beyond the recognition of one simple fact. When the field is transverse (say, along the  $a$  or  $b$  axis in the simplest case) plus- and minus- $x$  bonds must be distinguished from each other and from the  $y$  bonds, and different order parameters must be used to describe their different physical states. This is in contrast to the longitudinal case when all bonds are similarly placed with respect to the electric field and a single ordering parameter, to which the  $c$ -axis polarization is directly proportional, adequately describes the physical state. In the transverse case it is precisely the difference between the ordering parameters in two kinds of bonds which provides the major contribution to transverse polarization and susceptibility.

It should be noted that this explanation of transverse electric susceptibility in KDP-type crystals is entirely different from that of transverse magnetic susceptibility in ferromagnetic or antiferromagnetic crystals, though both, in accordance with the interpretation we are now using in the ferroelectric case, are based on an Ising model. If in both cases the interaction term in the Hamiltonian is  $\sum_{ij} J_{ij} S_i^z S_j^z$ , then transverse susceptibility in the magnetic case comes from the term proportional to  $S^x = \sum_i S_i^x$  or  $S^y = \sum_i S_i^y$ , whereas in the ferroelectric case it comes from the term proportional to  $S^z = \sum_i S_i^z$ .<sup>12</sup>

The longitudinal polarization in KDP-type crystals is due to heavy-ion displacements along the crystalline  $c$  axis which are strongly coupled to

the hydrogen-ion distribution and hence to the state of order-disorder in the hydrogen bonds. If the expectation value of  $\sum_i S_i^z$  is  $\langle S^z \rangle$ , then the  $c$ -axis polarization is

$$P_c = 2N\mu_1 \langle S^z \rangle, \quad (1)$$

where  $N$  is the number of  $\text{PO}_4$  groups which are connected to each other by  $2N$  hydrogen bonds and  $\mu_1$  is the effective value of the  $z$ -axis dipole moment per bond associated with heavy-ion displacements. Thus the *magnitude* of hydrogen-ion displacements plays no role in the determination of longitudinal susceptibility.

On the other hand, the transverse polarization is directly related to hydrogen-ion displacements, and, while other heavy-ion displacements in the transverse plane may also contribute, it may be assumed provisionally that the polarization is directly calculable from the hydrogen-ion motions. Distinguishing between plus and minus bonds as described above, the polarization along the crystalline  $a$  axis for a field in the  $x$  direction is given by

$$P_a = \frac{1}{2} N \mu_2 (\langle S_+^x \rangle - \langle S_-^x \rangle), \quad (2)$$

where  $\mu_2$  is the  $x$ -axis dipole moment which is directly associated with off-center positions of hydrogen ions in their bonds and  $\frac{1}{2}N$  represents the number of each kind of bond, plus or minus, parallel to the crystalline  $a$  axis. The  $N$  bonds parallel to the crystalline  $b$  axis make no contribution to the  $a$ -axis polarization.

Some details of the calculation of the transverse polarization based on this model will be clarified if we first review the calculation of the longitudinal polarization using the same model. For a field in the  $z$  direction the Hamiltonian including tunneling energy is<sup>9,11</sup>

$$\begin{aligned} H &= -\Gamma \sum_i S_i^z - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z - \mu_1 E_z \sum_i S_i^z \\ &= -\sum_i \vec{H}_i \cdot \vec{S}_i, \end{aligned} \quad (3)$$

where

$$\vec{H}_i = \Gamma \vec{X}_1 + \left( \sum_j J_{ij} S_j^z + \mu_1 E_z \right) \vec{Z}_1$$

and  $\vec{X}_1$  and  $\vec{Z}_1$  are unit vectors. In the mean-field approximation we make use of the expectation value of  $\vec{H}_i$ :

$$\langle \vec{H}_i \rangle = \Gamma \vec{X}_1 + (J(0) \langle S^z \rangle + \mu_1 E_z) \vec{Z}_1,$$

where

$$J(0) = \sum_i J_{ij},$$

and then from Eq. (3) one obtains<sup>11</sup>

$$\langle S^z \rangle = (1/W) [J(0) \langle S^z \rangle + \mu_1 E_z] \tanh \beta W, \quad (4)$$

where

$$W = [\Gamma^2 + (J(0)\langle S^z \rangle + \mu_1 E_x)^2]^{1/2},$$

$$\beta = 1/kT.$$

Then, from Eq. (1),

$$P_c = \frac{2N\mu_1}{W} \left( \frac{J(0)P_c}{2N\mu_1} + \mu_1 E_x \right) \tanh \beta W, \quad (5)$$

where

$$W = \left[ \Gamma^2 + \left( \frac{J(0)P_c}{2N\mu_1} + \mu_1 E_x \right)^2 \right]^{1/2}.$$

Immediate consequences of Eq. (5) are the following:

(a) the existence of a spontaneous polarization ( $P_c \neq 0$  when  $E_x = 0$ ) for  $T < T_c$ , provided that  $\Gamma < J(0)$ .  $T_c$  is given by  $\tanh(\Gamma/kT_c) = \Gamma/J(0)$ ; (b) a Curie-Weiss law for the susceptibility. For  $T > T_c$ ,

$$\chi_c = \frac{\partial P_c}{\partial E_x} = \frac{2N\mu_1^2 k T_c}{J(0)^2 - \Gamma^2} \frac{T_c}{T - T_c}.$$

For a field in the  $x$  direction we replace the field term in Eq. (3) by

$$- \mu_2 E_x \left( \sum_i^+ S_i^z - \sum_i^- S_i^z \right),$$

where  $\sum_i^\pm$  means that the sum is to be taken over plus- and minus- $x$  bonds and that the  $y$  bonds are to be excluded. In the mean-field approximation there is a solution analogous to Eq. (4) for  $\langle S_x^z \rangle$ ,  $\langle S_y^z \rangle$ , and for the  $\langle S^z \rangle$  of  $y$  bonds. We are interested only in the first two. They differ from Eq. (4) in two respects.

(a) In the expression for  $\langle S_x^z \rangle$  the term  $\mu_2 E_x$  should appear with a positive sign, and for  $\langle S_y^z \rangle$  it should appear with a negative sign, since in the first case, the field tends to enhance the order and in the second case it tends to decrease the order.

(b) The term  $J(0)\langle S^z \rangle$  must be expressed so as to provide an accurate representation of the interaction of a given bond with all others. There are several ways of doing this. The one which appears to be most satisfactory is based on the assumption that each of the six nearest-neighbor bonds contribute equally to the mean-field energy of the central bond. Of these six bonds only the two  $x$  bonds, plus and minus, have order parameters which, in the lowest order of approximation, differ from the mean value for all bonds in the crystal. Hence the mean-field energies of plus and minus bonds may be expressed as

$$J(0) \left( \frac{2}{3} \frac{P_c}{2N\mu_1} + \frac{1}{3} \langle S_x^z \rangle \right),$$

where the order parameter of the four  $y$  bonds,  $\langle S^z \rangle$ , has been replaced by its equivalent according to Eq. (1).

Incorporating these two modifications into the analog of Eq. (4) valid for field in the  $x$  direction one obtains

$$\langle S_x^z \rangle = \frac{1}{W_+} \left[ \frac{1}{3} J(0) \left( \frac{P_c}{N\mu_1} + \langle S_x^z \rangle \right) + \mu_2 E_x \right] \tanh \beta W_+, \quad (6)$$

$$\langle S_y^z \rangle = \frac{1}{W_-} \left[ \frac{1}{3} J(0) \left( \frac{P_c}{N\mu_1} + \langle S_x^z \rangle \right) - \mu_2 E_x \right] \tanh \beta W_-,$$

where

$$W_\pm = \left\{ \Gamma^2 + \left[ \frac{1}{3} J(0) \left( \frac{P_c}{N\mu_1} + \langle S_x^z \rangle \right) \pm \mu_2 E_x \right]^2 \right\}^{1/2}.$$

The transverse susceptibility is obtained by using Eq. (2) and taking the derivative with respect to  $E_x$ . One obtains after some algebra, and in the limit of  $E_x = 0$ ,

$$\chi_a = \frac{N\mu_2^2}{W^3} \frac{\Gamma^2 \tanh \beta W + \beta W (W^2 - \Gamma^2) (1 - \tanh^2 \beta W)}{1 + [J(0)/3W^3] [\Gamma^2 \tanh \beta W + \beta W (W^2 - \Gamma^2) (1 - \tanh^2 \beta W)]}, \quad (7)$$

where

$$W = \left[ \Gamma^2 + \left( \frac{J(0)P_c}{2N\mu_1} \right)^2 \right]^{1/2}.$$

The generalization of this result to a field at an arbitrary angle  $\theta$  in the  $xy$  plane is obtained simply by multiplying by the factor  $\cos \theta + \sin \theta$ .

### III. COMPARISON WITH EXPERIMENT

We wish to relate these results to the available experimental data.<sup>1,10</sup> This will be accomplished by comparing the shape of experimental and theoretical curves as a function of temperature using a single choice of numerical values of the parameters  $\Gamma$ ,  $J(0)$ , and  $\mu_2$ . From the approximate nature of the theory however, it is appropriate to distinguish between  $T > T_c$  and  $T < T_c$ . For  $T > T_c$ ,  $P_c = 0$  and the mean-field approximation is expected

to be good. For  $T < T_c$  the mean-field approximation is known to fail, but the approximate validity of the derived expression for the susceptibility is expected to be improved if the experimental value of  $P_c$  is used in that expression instead of the theoretical value. The only other parameters are  $N = 10^{22}/\text{cm}^3$  for both isomorphs to be considered here and  $\mu_1 = P_c(0)/2N$  where  $P_c(0)$  is the spontaneous polarization at 0 °K.

Then for  $T > T_c$ ,  $P_c = 0$ , and  $W = \Gamma$ , Eq. (7) becomes

$$\chi_a = \frac{N\mu_2^2}{\Gamma} \frac{\tanh \beta \Gamma}{1 + [J(0)/3\Gamma] \tanh \beta \Gamma}. \quad (8)$$

It is of interest to put this expression in another form by expanding it around  $T = T_c$  for  $T > T_c$  using the known relation connecting  $\Gamma$ ,  $J(0)$ , and  $T_c$  which has been discussed above in connection with

Eq. (5). One obtains

$$\chi_a^{-1} = \frac{4}{3} \frac{J(0)}{N\mu_2^2} \left( \frac{T + \Theta}{T_c + \Theta} \right), \quad (9)$$

where

$$\Theta = T_c \left[ \frac{4}{3} \frac{J(0)kT_c}{J^2(0) - \Gamma^2} - 1 \right]$$

is a positive number which has the minimum value  $\frac{1}{3}T_c$  when  $\Gamma = 0$ . Thus the transverse susceptibility is antiferroelectric in character, as is expected from the known crystal structure, and as indicated already by the experimental curves. Some features in the determination of parameters from the experimental data are now clear

(a)  $\mu_2$  is obtained from the slope of the curve

$$\chi_a^{-1} = kT/N\mu_2^2 \text{ for } T \gg T_c,$$

(b)  $J(0)/N\mu_2^2$  is obtained from the value of

$$\chi_a^{-1} = \frac{4}{3} J(0)/N\mu_2^2 \text{ at } T = T_c,$$

(c)  $\Theta$  is obtained from the intercept of the straight line represented by Eq. (9).

The effect of  $\Gamma$  on the shape of the curve is most clearly indicated by noting that the value of  $\Theta$  increases monotonically with  $\Gamma$  from  $\Theta = \frac{1}{3}T_c$  for  $\Gamma = 0$ , and that the transition temperature  $T_c$  decreases monotonically with increasing  $\Gamma$  from the value  $J(0)/k$  which it has for  $\Gamma = 0$ .

A comparison of the results of a theoretical calculation with the data of Busch<sup>1</sup> is shown in Fig. 2. This comparison is based on the choice of parameters which is given in Table I. In view of the approximate nature of the theory the fit may be regarded as good and perhaps better than should be expected. The results in any case can be regarded only as suggestive of a need for further study.

It is of particular interest to note that  $\Gamma$  is much smaller in  $\text{KH}_2\text{AsO}_4$  than in  $\text{KH}_2\text{PO}_4$ . This result has already been obtained in two other kinds of experiments,<sup>13,14</sup> though there is considerable uncertainty with respect to the magnitude of the difference. That uncertainty still remains. In the present experiment it is due possibly to an inadequacy in the theoretical approximation and to the lack of sufficiently accurate experimental data. Also, the results obtained are extremely sensitive to specific details in the model. This may be illustrated by using other assumptions regarding the mean-field energy than that leading to Eq. (6). Two extreme assumptions are (a) the mean-field energy in plus and minus bonds depends only on the order parameters in minus and plus bonds respectively; and (b) the mean-field energy depends only on the average order parameter for all bonds in the crystal. In the first case one would find  $\Gamma \sim 0$  for  $\text{KH}_2\text{AsO}_4$ , and in the second one would find  $\Gamma$  in  $\text{KH}_2\text{AsO}_4$  approximately equal to  $\Gamma$  in

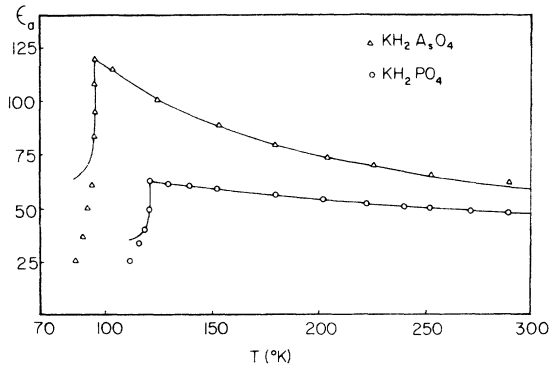


FIG. 2. Comparison of calculated and experimental transverse dielectric constants  $\epsilon_a = 4\pi\chi_a + 1$  for  $\text{KH}_2\text{PO}_4$  and  $\text{KH}_2\text{AsO}_4$ . Experimental points from the data of Busch (Ref. 1).

$\text{KH}_2\text{PO}_4$ . The fact that the curves based on these extreme assumptions fit the experimental data somewhat less well than those shown in Fig. 2 lends some additional support, beyond that of appropriateness in terms of the actual crystal structure, to the assumption used here.

The derived value of  $\mu_2$  is probably not of great interest. It may be compared, however, with the value  $\mu_2 = e\Delta x = 1.2 \times 10^{-18}$  cgs where  $e$  is the electronic charge and  $2\Delta x$  is the distance of separation of equilibrium positions in the hydrogen bond. The relatively large experimental values of  $\mu_2$  suggests that other transverse-ion displacements accompany the displacement in hydrogen bonds.

A background susceptibility of  $\chi_a = 10/4\pi$ , which is clearly indicated in the data of Barkla and Finlayson<sup>10</sup> and is assumed to be present also in the data of Busch,<sup>1</sup> was subtracted before making the above evaluations. A discrepancy in the slopes of the curves at  $T_c$  between the two sets of data in the case of  $\text{KH}_2\text{PO}_4$  was ignored. More accurate data especially in the neighborhood of  $T_c$  and leading to a more precise determination of the slope of the experimental curve at this point is necessary before more definitive conclusions along the lines suggested here can be obtained.

#### ACKNOWLEDGMENTS

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TABLE I. Parameters for  $\text{KH}_2\text{PO}_4$  and  $\text{KH}_2\text{AsO}_4$  used to obtain the theoretical curves shown in Fig. 2.

	$J(0)/k$ (°K)	$\Gamma/k$ (°K)	$10^{18}\mu_2$ (cgs units)
$\text{KH}_2\text{AsO}_4$	101	40	4.05
$\text{KH}_2\text{PO}_4$	204	185	3.90

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