PHYSICAL REVIEW B VOLUME 39, NUMBER 16 1 JUNE 1989

Quantum effects and competing interactions in crystals of the mixed rubidium and ammonium dihydrogen phosphate system

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(Received 3 October 1988)

Quantum corrections are introduced in a simple two-sublattice model, which describes well both para-ferro (T_C) and para-antiferroelectric (T_N) phase transitions in mixed crystals of the potassium dihydrogen phosphate family, leading to a determination of the phase diagram in satisfactory agreement with that observed in rubidium and ammonium dihydrogen phosphate mixed crystals.

Considerable attention has been devoted in recent years to the investigation of phase transitions in mixed crystals with competing interactions, and, in particular, to the mixed ferro-antiferroelectric system[1] $(\mathrm{RDP})_{1-x}(\mathrm{ADP})_x$ made up of rubidium and ammonium dihydrogen phosphate. The phase diagram of this system is shown in Fig. 1. In this article we will investigate first a simple two-sublattice classical model for ferro and antiferroelectricity, which will be shown to describe consistently the transitions for pure RDP and pure ADP. Next, we will consider the behavior to be expected for the phase transition classically, i.e., in the absence of quantum fluctuations of the elementary dipole moments. Finally, we will introduce the appropriate quantum corrections in the expressions for T_C and T_N, and we will show that satisfactory agreement with the observed phase diagram is obtained.

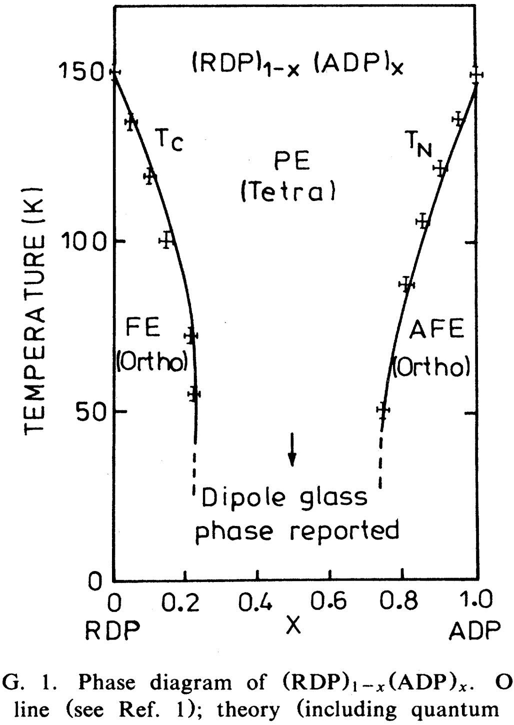

FIG. 1. Phase diagram of $(\mathrm{RDP})_{1-x}(\mathrm{ADP})_x$. Observed, solid line (see Ref. 1); theory (including quantum effects), crosses [Eqs. (22) and (23) with $x_C=0.22$ and $y_N=0.26$, respectively; see text].

It is well known that crystals isomorphous with potassium dihydrogen phosphate (KDP) often show ferroelectric or antiferroelectric phases at low temperatures. The fact that an antiferroelectric arrangement of dipoles is sometimes realized suggests that a simple two-sublattice model, similar to the one for antiferromagnets,[2] may be useful to describe the phase transition in the KDP family. Since there are four chemical units ($Z=4$) per (conventional) tetragonal unit cell in KDP crystals, the system may be thought of as a superposition of two interpenetrating bcc sublattices, each containing two chemical units. Let us call these two sublattices A and B, and take into account that we must consider intralattice (AA,BB) and interlattice (AB,BA) interactions. In the mean-field approximation, the local effective field acting on unit dipoles at points in lattice A and B, respectively, will be

$$(E_{\mathrm{eff}})_a=E+\alpha P_a+\beta P_b\ , \tag{1}$$

$$(E_{\mathrm{eff}})_b=E+\beta P_a+\alpha P_b\ , \tag{2}$$

where E is the external field, $\alpha(AA)=\alpha(BB)$ and $\beta(AB)=\beta(BA)$ are mean-field coefficients, and P_a and P_b are the pertinent sublattice polarizations per unit volume.

Using these effective fields in the standard[3] mean-field expression for the polarization as a function of temperature we get

$$\frac{P_a}{N\mu_a}=\tanh\left[\frac{(E_{\mathrm{eff}})_a\mu_a}{kT}\right], \tag{3}$$

$$\frac{P_b}{N\mu_b}=\tanh\left[\frac{(E_{\mathrm{eff}})_b\mu_b}{kT}\right], \tag{4}$$

where N is the total number of sublattice sites (or unit cells) per unit volume, and μ_a, μ_b are the respective sublattice unit dipoles, which, in the ordered phase can be pointing parallel (ferroelectric case: $\mu_a=\mu_b$) or antiparallel (antiferroelectric case: $\mu_a=-\mu_b$) to each other, depending on the geometry of the lattice. Since the two sublattices are chemically identical, we take $|\mu_a|=|\mu_b|=\frac{1}{2}|\mu|$. From Eqs. (1)-(4) we get

$$E=\frac{kT}{\mu_a}\tanh^{-1}\frac{P_a}{N\mu_a}-\alpha P_a-\beta P_b\ , \tag{5}$$

$$E=\frac{kT}{\mu_b}\tanh^{-1}\frac{P_b}{N\mu_b}-\beta P_a-\alpha P_b\ , \tag{6}$$

which, together, define an equation of state for E, $P \equiv P_a + P_b$ and T.

Let us consider first the *ferroelectric case,* in which at $T < T_C$ we have a nonzero spontaneous polarization $P_s = P_{sa} + P_{sb} \neq 0$ for $E = 0$. Adding Eqs. (5) and (6), and taking into account that

$$\tanh^{-1} Z_1 \pm \tanh^{-1} Z_2 = \tanh^{-1} (Z_1 \pm Z_2)/(1 \pm Z_1 Z_2)$$

and that $\mu_a = \mu_b = \mu/2$, we get

$$2E = 2\frac{kT}{\mu}\tanh^{-1} 2\frac{(P_a+P_b)/N\mu}{1+4(P_a/N\mu)(P_b/N\mu)} - (\alpha+\beta)(P_a+P_b)\,. \tag{7}$$

It is easy to get from here the spontaneous polarization below the transition temperature, but not very far from it, as

$$P_s/N_\mu \simeq \sqrt{3}(T_C/T - 1)^{1/2}, \quad T_C = \frac{\alpha+\beta}{4}\frac{N\mu^2}{k}\,. \tag{8}$$

The low-amplitude ($\delta E \rightarrow \delta P \ll N\mu$) inverse dielectric constant $\epsilon^{-1} \equiv dE/4\pi dP$ can be obtained from Eq. (7) with the following results:

$$\epsilon^{-1} = (T - \Theta_C)/C_+ \quad \text{at } T \gtrsim \Theta_C (P_s = 0), \qquad C_+ = 2\pi N\mu^2/k, \quad \Theta_C = T_C\,, \tag{9}$$

and

$$\epsilon^{-1} = (\Theta_C - T)/C_- \quad \text{at } T \lesssim \Theta_C (P_s \neq 0), \quad C_- = \pi N\mu^2/k\,. \tag{10}$$

Next, we consider the *antiferroelectric case.* At $E = 0$ we have now $P_s = P_{sa} + P_{sb} = 0$, being $P_{sa} = -P_{sb} = P_{ss}$ the sublattice spontaneous polarization, obtained solving

$$\frac{4(P_{ss}/N\mu)}{\tanh^{-1}\{4(P_{ss}/N\mu)/[1+4(P_{ss}/N_\mu)^2]\}} = \frac{T}{T_N}\,, \qquad T_N = \frac{\alpha-\beta}{4}\frac{N\mu^2}{k}\,, \tag{11}$$

which has a nonvanishing solution for P_{ss} at $T < T_N$, the antiferroelectric transition temperature. Below T_N, and not very far from it, we can get from Eq. (11)

$$P_{ss}/N\mu \simeq (\sqrt{3}/2)(1 - T/T_N)^{1/2}\,. \tag{12}$$

The low-amplitude expression for ϵ^{-1} can be obtained from the sum of Eqs. (5) and (6) for $\delta E \rightarrow \delta P \ll N\mu$, resulting in

$$\epsilon^{-1} = (T - \Theta_N)/C_+ \quad \text{at } T > T_N (P_{ss} = 0), \qquad C_+ = 2\pi N\mu^2/k\,, \qquad \Theta_N = \frac{\alpha+\beta}{4}\frac{N\mu^2}{k}\,, \tag{13}$$

and in another, more complicated expression, at $T < T_N$, which leads to

$$\epsilon^{-1}(T_N^-) = \epsilon^{-1}(T_N^+) = -\beta/8\pi\,, \qquad \epsilon^{-1}(0) = \infty \tag{14}$$

[i.e., $\epsilon(0) = 0$].

For RDP (ferroelectric, second-order transition) we can get the sum of the sublattice mean-field coefficients from Eqs. (8) and (9), and the observed values for $\Theta_C = 147$ K and $C_+ = 4.14 \times 10^3$ K, as

$$\alpha + \beta = 8\pi\Theta_C/C_+ = 8\pi T_c/C_+ = 0.89 > 0\,. \tag{15}$$

For ADP (antiferroelectric, first-order transition) we get the sum and difference of α and β from Eqs. (13) and (11), along[4] with $\Theta_N = -14$ K, $T_N = 148$ K, and $C_+ = 2.67 \times 10^3$ K, as

$$\alpha + \beta = 8\pi\Theta_N/C_+ = -0.13 < 0\,, \tag{16}$$

$$\alpha - \beta = 8\pi T_N/C_+ = 1.39 > 0\,, \tag{17}$$

and, therefore, $\alpha = 0.63$, $\beta = -0.76$.

That the two-sublattice mean-field relations obtained for KDP-type crystals show a fair degree of internal consistency can be checked in several ways. For instance, for RDP we get $\mu = (kC_+/2\pi N)^{1/2} \simeq 6.2 \times 10^{-18}$ esu from Eq. (9) and $\mu = P_{\text{sat}}/N \simeq 7.0 \times 10^{-18}$ esu from the low-temperature (saturation) value of the spontaneous polarization $P_{\text{sat}} \simeq 5.6$ $\mu C/\text{cm}^2 = 5.6 \times 3000$ esu; $N = (ca^2)^{-1} = 2.36 \times 10^{21}$ unit cells/cm^3. For ADP we can use Eq. (14) to get an independent estimate of $\beta = -\epsilon(T_N)/8\pi$. Using[4] $\epsilon(T_N^-) \simeq 14$ and $\epsilon(T_N^+) \simeq 30$, one gets, respectively, $\beta_- = -0.55$ and $\beta_+ = -1.19$. These values average out very close to the one previously obtained from Eqs. (16) and (17). It is of interest to point out that, since α and β depend on the tetragonality $(c/a - 1)$ of the lattice (they should be zero for a cubic lattice if they are originated by electric dipole-dipole interactions) we are entitled to assume $\alpha = \tilde{\alpha}(c/a - 1)$ and $\beta = \tilde{\beta}(c/a - 1)$, and we can use the calculated values for ADP, namely $\alpha_A = 0.63$ and $\beta_A = -0.76$, together[1] with $(c/a - 1)_A = 0.0067$, to estimate $\tilde{\alpha} \simeq 0.94 \times 10^2$ and $\tilde{\beta} = -1.14 \times 10^2$. For RDP, on the other hand, $(c/a - 1)_R = -0.041$, from which value we obtain estimates for $\alpha_R = \tilde{\alpha}(-0.41) = -3.90$ and $\beta_R = \tilde{\beta}(-0.41) = 4.72$, which imply $(\alpha + \beta)_R = 0.81$, in fair agreement with the value previously obtained from Eqs. (8) and (9).

Having set the grounds for calculating (classically) T_C and T_N for the pure ferroelectric case (RDP) and the pure antiferroelectric case (ADP), we examine now the mixed-crystal case. The simplest mixed case is that of a ferroelectric (or antiferroelectric) and a nonferroelectric isomorph, for instance,[5] that of $\text{K}_x\text{Nb}_{1-x}\text{TaO}_3$ or[6] $(\text{TSCC})_{1-x}(\text{TSCB})_x$ (where TSCC is tris-sarcosine calcium chloride and TSCB is tris-sarcosine calcium bronide). Looking at the phase diagram (T_C versus composition x) in these systems, one sees, not unexpectedly, a linear decrease of T_C with increasing x, which extrapolates approximately to $T_C = 0$ at $x = 1$. Quantum fluctuations, however, tend to depress T_C already at a certain $x < 1$, suppressing the transition sometimes close to, sometimes considerably below $x = 1$.

In the mixed ferroelectric-antiferroelectric system, one expects an approximately linear decrease in T_C at $x \gtrsim 0$ and also a linear increase in T_N at $x < 1$. Since $T_C(\text{RDP}) = 147$ K, $T_N(\text{ADP}) = 148$ K, and $N(\text{RDP}) = 2.36 \times 10^{21}$, $N(\text{ADP}) = 2.37 \times 10^{21}$ are very close to each other, one may expect a similar linear trend of transition temperature with composition from both sides towards zero.

Then, classically, from Eqs. (8) and (11), we have

$$kT_C^*(0)\equiv\frac{\alpha+\beta}{4}N\mu^2,\quad kT_C^*(x)=\frac{\alpha+\beta}{4}N(1-x)\mu^2=kT_C^*(0)(1-x)\,, \tag{18}$$

$$kT_N^*(0)\equiv\frac{\alpha-\beta}{4}N\mu^2,\quad kT_N^*(x)=\frac{\alpha-\beta}{4}N(1-y)\mu^2=kT_N^*(0)(1-y)\,, \tag{19}$$

where $y\equiv 1-x$, and $T_C^*(0)$, $T_N^*(0)$ are the classical transition temperatures for the pure ferroelectric and antiferroelectric systems.

Quantum mechanically, on the other hand, we have

$$h\omega_{0C}(\tfrac{1}{2}+\langle n\rangle_{T_C})=\frac{\alpha+\beta}{4}N\mu^2 \quad \text{for } x=0\,,$$

$$h\omega_{0N}(\tfrac{1}{2}+\langle n\rangle_{T_N})=\frac{\alpha=\beta}{4}N\mu^2 \quad \text{for } y=0\,,$$

where $\frac{1}{2}h\omega_{0C}$ and $\frac{1}{2}h\omega_{0N}$ are the zero point energies and $\langle n\rangle$ is the average number of energy quanta excited above the ground state at temperature T, given by Planck's relationship. Therefore,

$$h\omega_{0C}/2\tanh[h\omega_{0C}/2kT_C(0)]=\frac{\alpha+\beta}{4}N\mu^2=kT_C^*(0)\,,$$

$$h\omega_{0N}/2\tanh[h\omega_{0N}/2kT_N(0)]=\frac{\alpha-\beta}{4}N\mu^2=kT_N^*(0)\,,$$

where $T_C(0)$ and $T_N(0)$ are the quantum-mechanical transition temperatures, which reduce to $T_C^*(0)$ and $T_N^*(0)$, respectively, for $h\omega_{0C}/2kT_C(0)\ll 1$ and $h\omega_{0N}/2kT_N(0)\ll 1$. The last two equations yield

$$T_C(0)=(h\omega_{0C}/2k)/\tanh^{-1}(Z_C)\,, \qquad Z_C\equiv h\omega_{0C}/2kT_C^*(0)\,, \tag{20}$$

$$T_N(0)=(h\omega_{0N}/2k)/\tanh^{-1}(Z_N)\,, \qquad Z_N\equiv h\omega_{0N}/2kT_N^*(0)\,, \tag{21}$$

and, therefore, we finally get

$$T_C(x)=T_C(0)\tanh^{-1}(Z_C)/\tanh^{-1}[Z_C/(1-x)]\,, \tag{22}$$

$$T_N(y)=T_N(0)\tanh^{-1}(Z_N)/\tanh^{-1}[Z_N/(1-y)]\,. \tag{23}$$

Since $T_C(x_C)=0$ for $Z_C=1-x_C$ and $T_N(y_N)=0$ for $Z_N=1-y_N$, it is sufficient to know the experimental value for x_C and for y_N to completely specify the phase diagram. For the $(\mathrm{RDP})_x(\mathrm{ADP})_{1-x}$ system, $x_C\simeq 0.22$, $y_N\simeq 0.26$ (see Fig. 1). The agreement between theory and experiment for this mixed system is excellent, as seen in Fig. 1.

I thank Professor W. Windsch and Professor H. Braeter (University of Leipzig) for helpful discussions. The support of la Comisión de Investigación Científica y Técnica Grant No. PB86-0562, NATO Research Collaborative Grant No. 808/86, and U.S.-Spain Grant No. 8604/012 is acknowledged.

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