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Comment on "The Role of Hydrogen Bonds in Antiferroelectricity of $\text{NH}_4\text{H}_2\text{PO}_4$ "

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Matsushita and Matsubara¹⁾ (herein abbreviated MM) in their analysis of the role of hydrogen bonds in antiferroelectricity of $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) misinterpreted our related work,²⁾ probably because its limited length in the Proceedings of the Sixth International Meeting on Ferroelectricity did not allow sufficient explanation. Accordingly we provide such explanation and discuss the relation of our model to that of MM.

Our model introduces only one (not two as stated by MM) additional short-range interaction ε_a besides the Slater interaction ε_o . This "cross-cation" ε_a interaction contributes an amount

$$U_a = (\sigma_1\sigma_3 + \sigma_2\sigma_4)\varepsilon_a/2, \quad (1)$$

per ammonium ion to the internal energy U .

Here $\sigma_i = 1(-1)$ for an O-H...O proton far from (close to) an N-H...O oxygen, following the notation of MM. Protons 1 and 3 are on opposite sides of the ammonium ion, as are 2 and 4 and these four protons form a flattened tetrahedron around the ammonium ion, as shown in Fig. 2 of MM.

The average U_a in eq. (1) is given by

$$\langle U_a \rangle = -\frac{\varepsilon_a}{2} \sum_{i,j=\pm 1} (-1)^{(i+j)/2} (w_{1i}w_{3j} + w_{2i}w_{4j}), \quad (2)$$

where the probabilities w_{mn} that proton m has pseudospin $n = \pm 1$ are given by

$$\begin{aligned} w_{1,1} &= n_u + n_r + n_b, & w_{1,-1} &= n_d + n_g + n_f, \\ w_{3,1} &= n_u + n_g + n_f, & w_{3,-1} &= n_d + n_r + n_b, \\ w_{2,1} &= n_d + n_g + n_b, & w_{2,-1} &= n_u + n_r + n_f, \\ w_{4,1} &= n_d + n_r + n_f, & w_{4,-1} &= n_u + n_g + n_b. \end{aligned}$$

Here n_k is the fractional population of the k th H_2PO_4 configuration, where $k=u$ (d) for H_2PO_4 of type found in up (down) ferroelectric (FE) domain,

$k=r$ (g) for right (gauche) antiferroelectric (AFE) domain,

$k=f$ (b) for front (back) AFE domain.

Note that $n_r, n_g, n_f, n_b, (n_{\pm a}$ and $n_{\pm b}$ in eq. (5.1) of MM) do not correspond to number fractions of transverse dipoles as stated by MM, but are number fractions of H_2PO_4 groups corresponding to dipoleless AFE domains.

Evaluation of eq. (2) gives

$$\langle U_a \rangle \varepsilon_a [(n_d - n_u)^2 - (n_r - n_g)^2 - (n_f - n_b)^2], \quad (3)$$

corresponding to the ε_a term in eq. (1) of our previous work,²⁾ except that N is omitted because this is an energy per molecular unit and 2 is omitted because in ref. 2 $\varepsilon_a/2$ should be replaced by ε_a everywhere except in the definition of ε_a . (This factor of 2 error does not affect the fit of the phase diagram in Fig. 2 of ref. 2, but merely changes the numerical value of ε_a giving best fit. Also, in eq. (9) of ref. 2, the factor $2f^{-f}$ should be $(2f)^{-f}$. The correct form of eq. (9) was used to find f_g and other subsequent results.)

We see that eq. (3) follows directly from eq. (1) which in turn is based on a short-range interaction of the same form as that in one term of eq. (3.9) of MM. The statement by MM that it corresponds to a long-range interaction is incorrect.

Our interaction in eq. (1) does not lift the degeneracy of configurations (a), (b), and (c) of Fig. 1 of MM, contrary to the discussion by MM of eq. (5.1) which corresponds to our eq. (3). The H_2PO_4 groups are classified in eq. (3) in terms of FE domains and of AFE domains of type (a) which are observed in nature, so the possibility of (b) or (c) type ordering does not arise in our mean-field calculation. But in Monte Carlo simulations we must introduce the parallel-bond interaction³⁾ which favours (a) over (b) or (c) ordering.

In comparing our eq. (3) with eq. (3.9) of MM, which is

$$\begin{aligned} -\varepsilon U &= C(\sigma_1\sigma_3 + \sigma_2\sigma_4) + D(\sigma_1 + \sigma_3)(\sigma_2 + \sigma_4) \\ &\quad + F\sigma_1\sigma_2\sigma_3\sigma_4, \end{aligned}$$

we see that eq. (3) has the same form as the $C(\sigma_1\sigma_3 + \sigma_2\sigma_4)$ term of eq. (3.9) of MM. In our model, $D=F=0$. The F term, like the parallel-bond interaction,³⁾ affects the temperature at

which ordering occurs but does not affect the type of ordering, because $\sigma_1\sigma_2\sigma_3\sigma_4=1$ for FE or AFE ordering, while the average $\langle\sigma_1\sigma_2\sigma_3\sigma_4\rangle$ is zero in the paraelectric (PE) state. The D term inhibits the FE phase for which $(\sigma_1+\sigma_3)(\sigma_2+\sigma_4)=1$ because $D<0$ according to MM. It has no effect on the PE-AFE transition because that product is zero in the AFE phase and has average value zero in the PE phase.

Our model is able to fit the observed FE and AFE phase boundaries in the mixed crystal system $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ quite well over the whole x - T phase diagram, if ε_a is assumed proportional to x (we chose $\varepsilon_a=x\varepsilon_0$) to reflect the fact that the number of cross-ammonium interactions is proportional to x . So far, MM have not attempted a similar fit with their new model.

To summarize this comparison, our renormalization of the ammonium proton interactions with each other and with acid protons

results in one of the three terms in the MM renormalization. Their model portrays the ADP crystal somewhat more accurately than ours, at the cost of introducing three short-range energy parameters (η, J, ζ which they transform into C, D, F) instead of one (our ε_a which is related to their C). In both models the renormalization results in effective interactions between acid protons. Such renormalization simplifies analytic models^{1,2)} and facilitates Monte Carlo calculations. We thank Professor R. Blinc for bringing ref. 1 to our attention.

References

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