CRITICAL BEHAVIOR OF TWO-DIMENSIONAL HYDROGEN-BONDED ANTIFERROELECTRICS*

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The Rys F model of hydrogen-bonded antiferroelectrics is generalized to include all ionized vertices. For a class of realistic choices of energy parameters, it is shown that this model is equivalent to a two-dimensional Ising model and consequently exhibits a logarithmically second-order phase transition.

Recently, the statistical problem of two-dimensional hydrogen-bonded crystals has been the center of considerable interest.[1-3] The model one usually considers is a square lattice of N vertices with one hydrogen atom per lattice edge. Since the hydrogen atoms assume off-center positions on the edges, one usually assumes that each lattice site has precisely two near and two distant hydrogen atoms (the ice rule). Obviously, this is only a crude approximation and, for a better description of real physical situations, the other (ionized) types of vertices must be included. Unfortunately, the previous methods of exact solution are incapable of straightforward extension to the realistic models and the precise nature of the phase transition, when the rigid ice rule is broken, has not been clearly understood.[4]

In this Letter we report some results related to this problem. We consider the Rys F model[5] of an antiferroelectric and modify it by including all ionized vertices. For a large class of realistic energy parameters we are able to show that the modified model exhibits a logarithmically second-order phase transition. This is in contradistinction to the peculiar infinite-order phase transition of the F model.[2] Since our model includes the F model as a special case, it is then possible to see that the infinite-order transition of the F model arises as a limiting situation of the more familiar lambda-type transitions.

Following the usual convention,[1-3] we specify the positions of the hydrogen atoms by drawing arrows on the lattice edges. Then, as shown in Fig. 1, there are 16 different kinds of vertex configurations. The vertex energies for an antiferroelectric model are

$$e_1 = e_2 = e_3 = e_4 = \epsilon > 0,$$
$$e_5 = e_6 = 0,$$
$$e_7 = e_8 = b\epsilon > 0,$$
$$e_9 = e_{10} = \cdots = e_{16} = a\epsilon > 0. \tag{1}$$

where e_i is the energy of the ith kind of vertices.

If only the vertices (1) through (6) are allowed ($a = b = \infty$), we have the Rys F model. The vertices (7) and (8), each with four arrows in or four arrows out, are the doubly ionized vertices. The vertices (9) through (16) are the singly ionized ones. In the following we shall consider the case

$$b = 4a - 2, \tag{2}$$

with the parameter a otherwise arbitrary. For a suitable choice of a, e.g., $a = 10$, this model should provide a reasonable description of the real physical situations.

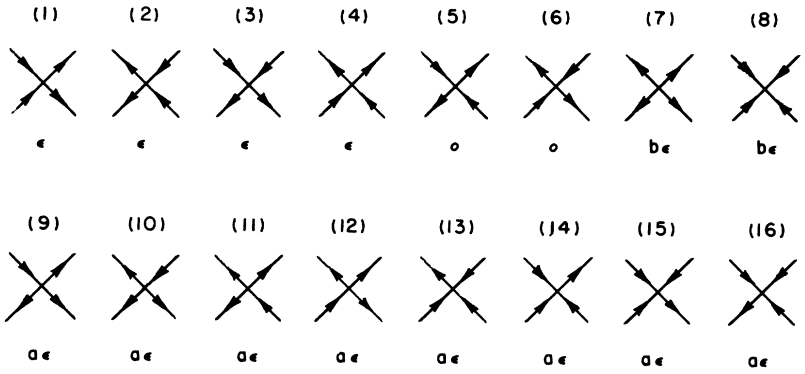

FIG. 1. The 16 kinds of vertex configurations and the vertex energies.

Our approach is based on the observation that the antiferroelectric model specified by expressions (1) and (2) is equivalent to an Ising model. The Ising lattice, which is shown in Fig. 2, consists of $2N$ spins and has the following energy parameters:

$$J=\tfrac{1}{4}(2a-1)\epsilon,$$
$$J'=-\tfrac{1}{2}(a-1)\epsilon. \quad (3)$$

To see this equivalence, let us superimpose L, the square lattice with $2N$ edges, along the diagonals of the Ising lattice L_{I} with $2N$ spins. This superposition is carried out in such a way that each edge of L covers precisely one spin of L_{I}. Now each spin in L_{I} can assume two values ± 1 and similarly each edge in L can be directed in two different directions. Thus there clearly exists a one-to-one correspondence between the 2^{2N} spin configurations of L_{I} and the 2^{2N} arrow configurations of L. More specifically, we shall adopt the following rule of correspondence: spin $+1$ in an even column and spin -1 in an odd column $\rightarrow$ arrow in the upward directions, spin $+1$ in an odd column and spin -1 in an even column $\rightarrow$ arrow in the downward directions. Here, the columns of the Ising spins are numbered alternately even and odd. The Ising energies of a unit cell consisting of four $-J$ and two $-J'$ interactions are taken to be the corresponding vertex energies for the antiferroelectric lattice L. It is then easy to derive the 16 vertex energies from the energies of the spin configurations. We find

$$e_1=e_2=e_3=e_4=2J'=(1-a)\epsilon,$$
$$e_5=e_6=-4J-2J'=-a\epsilon,$$
$$e_7=e_8=4J-2J'=(3a-2)\epsilon,$$
$$e_9=e_{10}=\cdots=e_{16}=0. \quad (4)$$

When we add a constant energy $a\epsilon$ to (4), the resulting vertex energies are identical to those specified by (1), and this completes our proof. More precisely, we have established the following relationship:

$$f=a\epsilon+2f_{\mathrm{I}}. \quad (5)$$

Here, f is the free energy per vertex of the antiferroelectric model specified by (1) and f_{I} is the free energy per spin of the Ising model defined by (3).

The critical behavior of the antiferroelectric model is now obtained from the properties of the Ising model. The associated Ising problem cannot be solved exactly because of the presence of the "crossed" interactions. However, the problem is now much more tractable and various techniques useful in treating the Ising problems can be employed. In particular, it is generally believed, and strongly supported by the results of numerical studies,[6] that for two-dimensional Ising models with finite-range interactions the critical indices are likely to be the same. Consequently, we conclude that the modified F model possesses a lambda-type transition and that the specific heat is likely to have a logarithmic singularity.

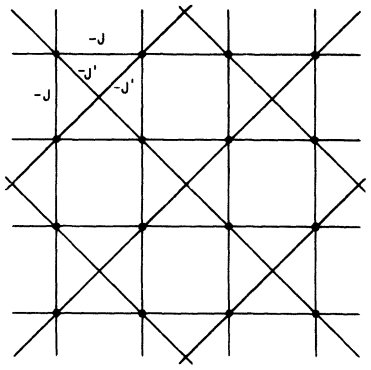

FIG. 2. The equivalent Ising lattice. The black dots denote the spins, and the lines denote the interactions. The interactions J and J' are given by Eq. (3).

Our model is exactly soluble in the following special cases: (i) For $a=\frac{1}{2}$, $b=0$, or $J=0$, $J'=\frac{1}{4}\epsilon$, the model reduces to a one-dimensional Ising problem and consequently exhibits no phase transition. (ii) For $a=1$, $b=2$, or $J=\frac{1}{2}\epsilon$, $J'=0$, the associated Ising problem is soluble, and the specific heat is known to possess a logarithmic singularity. (iii) For $a=\infty$ and $b=2$, the model is again soluble by an independent approach[7] with critical behavior identical to that of (ii). (iv) For $a=\infty$ and $b=\infty$, the latter is the F model solved by Lieb,[2] who showed that all derivatives of the free energy are continuous at the singular point (an infinite-order phase transition). The critical temperatures in these soluble cases are as follows:

$$a=\tfrac{1}{2} \text{ and } b=0, \quad T_c=0; \quad \text{(i)}$$
$$a=1 \text{ and } b=2, \quad kT_c/\epsilon=\tfrac{1}{2}\ln(\sqrt{2}+1)=0.567\,296; \quad \text{(ii)}$$
$$a=\infty \text{ and } b=2, \quad kT_c/\epsilon=1/\ln(\sqrt{2}+1)=1.134\,59; \quad \text{(iii)}$$

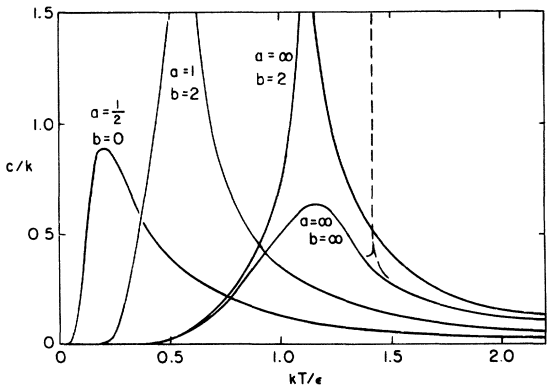

FIG. 3. The specific heat per vertex for various energy parameters a and b. The dashed curve illustrates the residual "spike" expected for some large a and b.

$$a=\infty \text{ and } b=\infty, \quad kT_c/\epsilon = 1/\ln 2 = 1.442\,69. \quad \text{(iv)}$$

The specific heats for these cases are plotted in Fig. 3.[8,9]

It is of interest to investigate the behavior of our model as the parameters a and b vary. As a or b increases, the disordered states will carry smaller statistical weights. One then expects that the long-range order would increase and, as a consequence, the transition temperature cannot decrease.[10] This resembles very much the situation of the Ising ferromagnet for which the Curie point cannot be lowered by an increase of the ferromagnetic interactions.[11] For our model, as a varies from $\frac{1}{2}$ to ∞,[12] the transition temperature increases from the absolute zero to the value[2] $\epsilon/k \ln 2$. Since it is known that for $a=\infty$ all derivatives of the free energy are continuous,[2] it appears that, as $a\to\infty$, the "spike" in the specific heat eventually disappears with zero width and, as a result, the phase transition goes over to an infinite-order one. The dashed curve in Fig. 3 illustrates one such residual "spike" expected for some large a and b.

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[1]F. Y. Wu, Phys. Rev. Letters 18, 605 (1967), and Phys. Rev. 168, 539 (1968).

[2]E. H. Lieb, Phys. Rev. Letters 18, 1046 (1967), and 19, 108 (1967).

[3]B. Sutherland, Phys. Rev. Letters 19, 103 (1967); C. P. Yang, Phys. Rev. Letters 19, 586 (1967); B. Sutherland, C. N. Yang, and C. P. Yang, Phys. Rev. Letters 19, 588 (1967).

[4]Early investigation in this direction includes the mean-field approximation of Y. Takagi, J. Phys. Soc. Japan 3, 273 (1948). Takagi relaxed the ice rule for the ferroelectric KDP model and found a second-order transition, whereas with the ice rule the transition is of first order (Ref. 2). His method is too crude for determination of the critical indices.

[5]F. Rys, Helv. Phys. Acta 36, 537 (1963).

[6]See, for example, C. Domb and N. W. Dalton, Proc. Phys. Soc. (London) 89, 859 (1966), and N. W. Dalton and D. W. Wood, to be published.

[7]In this special case, the model is again reducible to a nearest-neighbor Ising problem. [F. Y. Wu, Phys. Rev. (to be published)].

[8]The specific heat for case (iii) is taken from Ref. 7 and is related to that of case (ii) by a change of scales in c and T by factors 2 and $\frac{1}{2}$, respectively.

[9]The specific heat for the Rys F model is taken from E. H. Lieb and F. Y. Wu, to be published.

[10]We conjecture in general that the transition temperature of a model of hydrogen-bonded crystals is a nondecreasing function in all the vertex energies measured from the lowest ones. This conjecture holds for the known results of all soluble models but appears to be rather difficult to prove in the general case.

[11]R. B. Griffiths, J. Math. Phys. 8, 478 (1967).

[12]It can be shown by a symmetry argument that the models with $a<\frac{1}{2}$ are included in our considerations for $a>\frac{1}{2}$.