

CRITICAL BEHAVIOR OF HYDROGEN-BONDED FERROELECTRICS*

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(Received 3 April 1970)

The Slater KDP (potassium dihydrogen phosphate) model of hydrogen-bonded ferroelectrics is generalized by relaxing the ice condition. For a class of realistic choices of energy parameters, it is shown that this model is equivalent to an Ising model and consequently exhibits an Ising-type transition. Our result suggests that the singularity in the specific heat of an Ising model can be asymmetric if crossing interactions are included. It also suggests that experiments on the hydrogen-bonded ferroelectrics may yield information on the critical behavior of the three-dimensional Ising model.

In the past three years, a number of two-dimensional models which exhibit ferroelectric or antiferroelectric phase transitions have received considerable attention. The descriptions of these models are very similar to that of the Ising model, but the critical behaviors turn out to be completely different. It is known from Onsager's solution that the two-dimensional Ising model exhibits a logarithmic second-order phase transition.¹ However, for the ferroelectric and antiferroelectric models, one finds that the Slater potassium dihydrogen phosphate (KDP) (ferroelectric) model possesses a first-order transition with a latent heat,² whereas the Rys F (antiferroelectric) model has a peculiar type of infinite-order transition.³ It was then suggested that the "unusual" behaviors of the ferroelectric and antiferroelectric models may have something to do with the imposition of the "ice rule."⁴ Since the ice rule constitutes only a first approximation to the realistic situations, it would be of interest to investigate the effect of relaxing this rigid condition. Many years ago, Takagi⁵ made a mean-field calculation on the ferroelectric KDP model and showed that the relaxation of the ice rule does lead to a modification of the critical behavior. Because of the nature of the approximate treatment, however, his result cannot be considered as conclusive. Recently, exact results of this type have been established for the antiferroelectric F model.^{4,6} It was shown rigorously that the infinite-order transition peculiar to the F model disappears and changes over to the more familiar logarithmic second-order transition, when the ice rule is relaxed in certain directions in the parameter space. This result is of interest because it shows that the Ising-type transition appears as a general rule for the model problems of phase transitions. This belief is further supported by the result to be reported in this Letter. In the following, we shall extend the discussion of Ref. 6 to include the

ferroelectric models. That is, we shall show that the first-order transition of the KDP model also changes over to an Ising-type transition when the ice rule is relaxed in the same way as in Ref. 6.

Our result brings out two interesting points. Firstly, it shows that, contrary to the usual belief, the singularity in the specific heat of an Ising model, even in the two-dimensional case, is not necessarily symmetric. That is to say, it is possible to have $A_+ \neq A_-$ in the critical behavior near the transition temperature T_c :

$$c \sim A_{\pm} \ln|T - T_c|, \quad T = T_c^{\pm}. \quad (1)$$

This observation makes the Ising model more flexible in reconciling with experiments. Secondly, our discussion holds also for the three-dimensional models. Therefore, we may be able to use the experimentally observed critical behaviors of hydrogen-bonded ferroelectrics to learn something about the three-dimensional Ising model.

Our discussion is similar to that of Ref. 6. For clarity of presentation, we shall in the following consider a square lattice. The extension to the three-dimensional case is straightforward. The model is specified by attaching arrows to the lattice edges with energies associated with the vertices. In the most general case without the constraint of the ice rule, there are 16 different kinds of vertex configurations. These are shown in Fig. 1. The vertex energies of a ferroelectric model are

$$\begin{aligned} e_1 = e_2 &= 0, \\ e_3 = e_4 = e_5 = e_6 &= \epsilon > 0, \\ e_7 = e_8 &= b\epsilon > 0, \\ e_9 = e_{10} = \dots = e_{16} &= a\epsilon > 0, \end{aligned} \quad (2)$$

where e_i is the energy of the i th kind of vertex. The Slater KDP model is recovered by taking

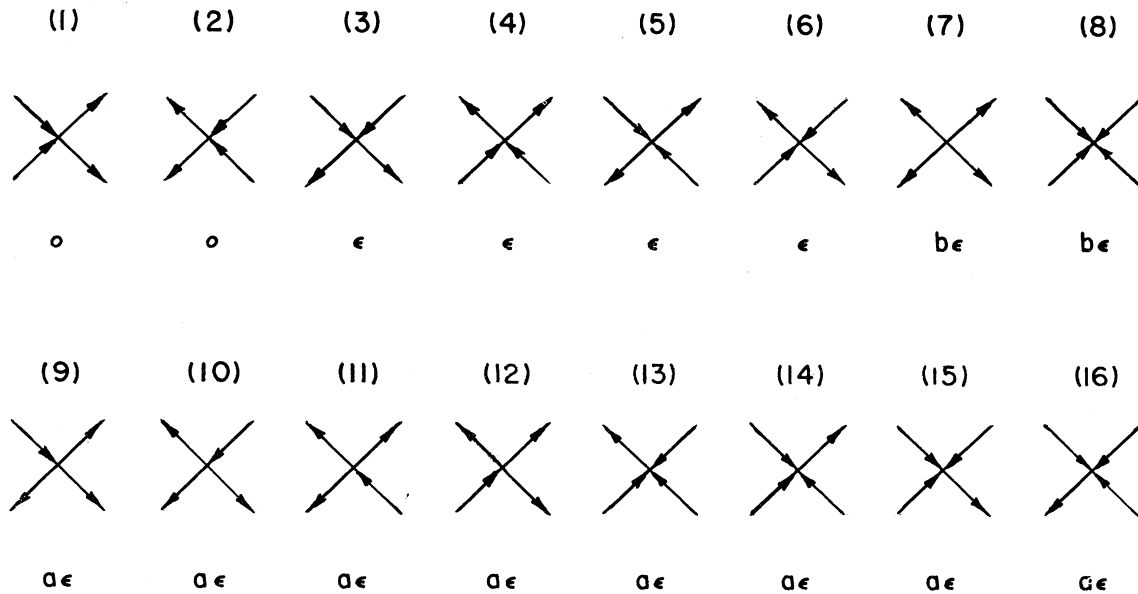


FIG. 1. The 16 kinds of vertex configurations and the vertex energies for a ferroelectric model.

$a = b = \infty$. A realistic model is characterized by the condition $b \gg a \gg 1$. As in Ref. 6, we shall restrict our considerations to the case

$$b = 4a - 2 \tag{3}$$

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

Our main result is that the ferroelectric model specified by (2) and (3) is equivalent to an Ising model. The Ising lattice L_I , shown in Fig. 2, is the same as that of Ref. 6. The new feature is that now we have three interaction parameters J_1 , J_2 , and J' ($J_1 = J_2$ in Ref. 6) and this allows us to extend the discussion to the ferroelectric case. As in Ref. 6, we superimpose the KDP lattice L upon L_I such that each lattice edge of L covers precisely one spin of L_I . The following simple⁷ rule of correspondence then maps a spin configuration of L_I into an arrow configuration of L and conversely: spin +1 (-1) on $L_I \leftrightarrow$ upward (downward) arrow on L . We now take

$$J_1 = -J' = -\frac{1}{4}(2a-1)\epsilon, \tag{4}$$

$$J_2 = \frac{1}{2}(a-1)\epsilon.$$

If the Ising energies of a unit cell consisting of two $-J_1$, two $-J_2$, and two $-J'$ interactions are

taken to be the corresponding vertex energies for L , it is then a simple matter to confirm that, upon using (3) and (4), these vertex energies are precisely

$$e_i' = e_i - a\epsilon, \quad i = 1, 2, \dots, 16, \tag{5}$$

where the e_i 's are given by (2). Thus, the ferroelectric and the Ising models are completely equivalent and, consequently, we have the rela-

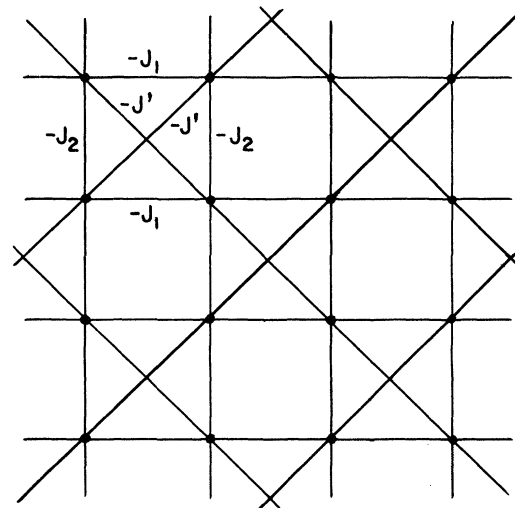


FIG. 2. The equivalent Ising lattice. The black dots denote the spins, and the lines denote the interactions.

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$$2f_1 = f - a\epsilon. \quad (6)$$

Here f is the free energy per vertex of the ferroelectric model and f_1 is the free energy per spin of the Ising lattice.

For two-dimensional models, the Ising model with a short-range interaction is believed to have the same critical behavior as the Onsager solution.⁸ Consequently, the model under consideration possesses a λ -type transition and the specific heat exhibits a logarithmic singularity. However, it is known² that in the limit of $a \rightarrow \infty$, $b \rightarrow \infty$ (KDP model), the specific heat vanishes identically below T_c and has a $(T - T_c)^{-1/2}$ singularity above T_c ; i.e., the singularity is highly asymmetric about T_c . Therefore, at least for some large values of a , the singularity of the Ising model is also asymmetric. As we have mentioned earlier, one possible implication of this asymmetry is that the coefficients A_+ and A_- in (1) are unequal. This is in contrast to the result of Onsager's solution for regular planar Ising lattices which always leads to a symmetric singularity. It appears that this asymmetry is due to the presence of the crossing interactions.

Finally, we remark that our discussion is not restricted to the two-dimensional case. In a three-dimensional ferroelectric crystal, each lattice vertex is hydrogen-bonded to four nearest neighbors. We can again imagine an Ising lattice superimposed on the ferroelectric crystal such that each spin sits on a hydrogen bond. The one-to-one correspondence between the hydrogen and spin configurations again holds. The Ising interactions can then be introduced and the isomorphism of the two models follows as before. Now no exact result is known for the three-dimensional Ising model.⁹ However, for the limiting case of $a \rightarrow \infty$, $b \rightarrow \infty$, it has been established rigorously that a first-order transition exists and that the specific heat vanishes below T_c .¹⁰ Therefore, our result also suggests some sort of asymmet-

ric singularity in the specific heat of the corresponding three-dimensional Ising model. Furthermore, if one believes that our model adequately describes the hydrogen-bonded ferroelectrics, then the experimentally observed critical behavior of the latter can be used to deduce some useful information on the critical behavior of the three-dimensional Ising model. Thus, the logarithmic divergence observed¹¹ in the heat capacity of KH_2PO_4 (KDP) for $T = T_c^-$ may be taken to indicate that the specific heat of the three-dimensional Ising model also possesses a logarithmic singularity ($\alpha' = 0$). This is certainly not far from the value $\alpha' = \frac{1}{16}$ determined through numerical analyses.¹² Unfortunately, other experimental situations do not seem to be as clear-cut to draw useful conclusions.

I am indebted to Dr. W. Reese for an informative correspondence.

*Work supported in part by National Science Foundation Grant No. GP-9041.

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⁷A somewhat involved rule of correspondence was used in Ref. 6 because of the restriction $J_1 = J_2$. Allowing $J_1 \neq J_2$, the model considered in Ref. 6 can also be included under the present rule of correspondence by taking $J_1 = -J_2 = \frac{1}{4}(2a-1)\epsilon$, $J' = \frac{1}{2}(a-1)\epsilon$.

⁸See, for example, N. W. Dalton and D. W. Wood, J. Math. Phys. **10**, 1271 (1969).

⁹The elegant proof of R. B. Griffiths [J. Math. Phys. **8**, 478 (1967)] that a transition exists for a three-dimensional ferromagnetic Ising model does not apply here because of the presence of the antiferromagnetic interactions.

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