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EXACTLY SOLUBLE MODEL OF THE FERROELECTRIC PHASE TRANSITION IN TWO DIMENSIONS

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(Received 17 March 1967)

The Slater model of the two-dimensional potassium dihydrogen phosphate crystal is solved exactly under the additional assumption that the dipoles are excluded from pointing along one direction of the crystal axis. The Curie temperature T_c is not affected by this additional assumption but the phase change becomes a second-order transition. Complete polarization occurs below T_c with specific heat $\sim (T - T_c)^{-1/2}$ near and above the Curie point.

This Letter reports a model of the ferroelectric phase transition which is exactly soluble in the two-dimensional case. We fix our attention on the potassium dihydrogen phosphate (KDP) crystal, KH_2PO_4 , which undergoes a second-order phase transition at 123°K. Slater¹ was the first to point out the important role played by the hydrogen atoms in the mechanism of this phase transition. The detailed structure of the KDP crystal proposed by him allows six possible configurations for the four hydrogen atoms attached to each PO_4 group. This simplified picture permits one to construct a well-defined mathematical model for the KDP crystal by associating arrows to the lattice bonds and energies to the lattice sites.² However, in spite of the simplicity of the statement of this problem, rigorous approaches to the solution have been lacking. Most of the previous

treatments based on the Slater model and its modifications have been essentially mean-field methods yielding a first-order phase transition,²⁻⁵ while the experimentally observed transition is a second-order one. The best statistical mechanical treatment to date has been given by Nagle,⁵ who obtained both the high and low temperature expansions of the partition function and located the Curie point. These expansions, however, yield no information about the behavior of the specific heat, which is of considerable theoretical interest. It therefore seems desirable to have an exactly soluble model which can exhibit the character of the discontinuity, while serving as a model for testing the validity of other approximation procedures.

We first describe the Slater KDP model.^{1,2} Consider a diamond-type lattice (four nearest

neighbors to each site) with directed arrows attached to all the lattice bonds. The rule is that there are always two arrows pointing toward and two arrows pointing away from a given lattice site. Then there are altogether six possible arrow configurations that can be associated to a site. A zero site energy is associated with two of the six configurations and an energy $\epsilon > 0$ with the remaining four (see Fig. 1). Each distinct way of associating arrows to the lattice as a whole will be called a state of the lattice. The energy of a given state is simply $n(\epsilon)\epsilon$, where $n(\epsilon)$ is the number of sites with energy ϵ . The partition function is now given by

$$Z = \sum_{\text{all states}} e^{-n(\epsilon)\epsilon/kT} \tag{1}$$

The model we propose is the same as above

except that we impose the further restriction that only one of the zero-energy configurations is allowed. Physically this corresponds to the assumption that the dipoles are excluded from pointing along one direction of the crystal axis.¹ Nevertheless, this provides us with a model which can now be treated with mathematical rigor.⁶

In this note we shall only write down the final results and give a brief description of the intermediate steps, while reserving the details, together with some interesting observations on the dimer method, for another communication. The partition function of our model is still given by (1), although the summation is now taken over a more restricted set of states. For an infinite rectangular lattice wrapped around a torus, the logarithm of the partition function, the energy, and the specific heat are given, respectively, by (N = number of lattice sites)

$$\ln Z = \frac{N}{8\pi^2} \int_0^{2\pi} d\theta \int_0^{2\pi} d\varphi \ln [1 + 2e^{-2\epsilon/kT} + 2e^{-2\epsilon/kT} \cos(\theta - \varphi) - 2e^{-\epsilon/kT} (\cos\theta + \cos\varphi)]; \tag{2}$$

$$\begin{aligned} E = 0, & \quad T < T_c = \epsilon/k \ln 2; \\ & = N(2\epsilon/\pi) \cos^{-1}(\frac{1}{2}e^{\epsilon/kT}), \quad T > T_c; \\ C = 0, & \quad T < T_c; \\ & = (N\epsilon^2/\pi kT^2)(e^{-2\epsilon/kT} - \frac{1}{4})^{-1/2}, \quad T > T_c. \end{aligned}$$

Clearly a phase change occurs at $T_c = \epsilon/k \ln 2$ with $c \sim (T - T_c)^{-1/2}$ near and above the Curie point. The location of the Curie temperature T_c is in agreement with previous results on the Slater KDP model.¹⁻⁵ There is also total polarization below T_c : All sites take the zero-energy configuration to form an ordered state in which all dipoles point in the same direction. It is interesting to note that E is continuous at $T = T_c$ as is the case for the three-dimensional KDP crystal (previous theoretical dis-

cussions have always led to a first-order phase transition).

Our method of attacking the problem consists of first converting the problem of counting the arrow configurations into a problem of drawing restricted closed polygons on the crystal lattice. The latter is equivalent to a dimer problem⁷ and hence the evaluation of a Pfaffian.⁸

Let us take any state of the crystal lattice L as a standard state. Then, as compared with this standard one, an arbitrary state of L has either 0, 2, or 4 arrows reversed at each site. If we denote each of these reversed arrows by a bond connecting the two corresponding sites, then an arbitrary state of L is now transformed into a bond diagram made of closed polygons. The original restrictions on the ar-

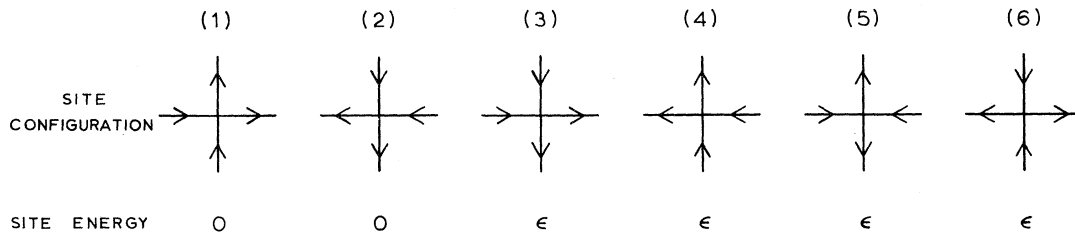


FIG. 1. Site energies of the six allowed site configurations for the Slater KDP model in two dimensions.

row configurations at each site now impose the restriction that there are only five possible bond configurations at each site.

Next we expand the lattice L into a terminal (dimer) lattice L^Δ by replacing each site of L by a "city" of internally connected points.⁹ The one-to-one correspondence between the configurations of closed polygons on L and the dimer configurations on L^Δ (provided that each city contains an even number of points) is well known.^{7,10} We need only to choose the cities and the weights associated with their internal bonds properly, to take care of the restrictions on the bond configurations.

It is found that this trick can be accomplished by the dimer city shown in Fig. 2, where the standard state has been taken to have the configuration (1) of Fig. 1 at all sites.

Once the dimer cities are properly drawn

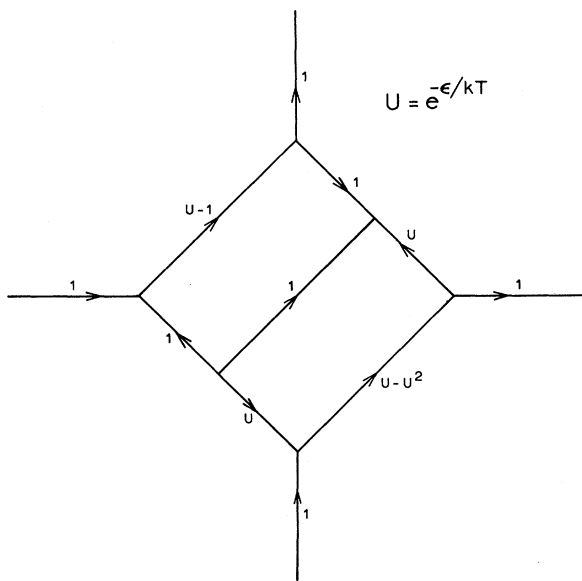


FIG. 2. The cities of the terminal (dimer) lattice L^Δ .

and the arrows on the terminal lattice L^Δ properly attached,^{10,11} the evaluation of the partition function (1) is straightforward⁷ and yields

$$\lim_{N \rightarrow \infty} \ln Z = \frac{N}{8\pi^2} \int_0^{2\pi} d\theta \int_0^{2\pi} d\varphi \ln D,$$

where D is the determinant given by

$$D = \begin{vmatrix} 0 & 0 & 0 & U-1 & -e^{-i\theta} & -1 \\ 0 & 0 & 0 & -1 & -U & -1 \\ 0 & 0 & 0 & -e^{-i\varphi} & U-U^2 & -U \\ 1-U & 1 & e^{i\varphi} & 0 & 0 & 0 \\ e^{i\theta} & U & U^2-U & 0 & 0 & 0 \\ 1 & 1 & U & 0 & 0 & 0 \end{vmatrix}$$

with $U = e^{-\epsilon/kT}$. Substitution now leads to Eq. (2).

The author is indebted to Professor Elliott Lieb for a valuable conversation.

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