INFLUENCE OF VIOLATION OF ELECTRONEUTRALITY ON A PHASE TRANSITION IN A FERROELECTRIC WITH HYDROGEN BONDING

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The two-dimensional model of a ferroelectric, considered by Wu in [6], and the more general model with partial violation of the electroneutrality condition, are calculated with the aid of the technique developed for the Ising model. It is shown that arbitrarily small violations of the electroneutrality condition alter the values of the critical indices (the singularity of the thermodynamic quantities near the phase-transition point). The same example is used to discuss the contradiction between the Wu model (and the Slater model) and certain principles of statistical physics. A formulation that eliminates this contradiction is proposed.

THE electroneutrality condition or the "ice rule," namely that the total charge of a lattice site is equal to zero (see below for details) is usually satisfied in models of ferroelectrics with hydrogen bonding. It is assumed[1] that the energy of a charged site is lower by one order of magnitude than the energy of a neutral site.

Takagi has observed,[2] however (within the framework of the self-consistent field method), that in the Slater model[3] (see below) allowance for the violation of electroneutrality transforms a first order transition (which is the usual one for the Slater model) into a second-order transition. Using exact methods developed for two-dimensional Ising lattices, Wu[4] has shown that even small violations of electroneutrality change the character of the transition in the F-model considered by Rys.[5] We shall show below, by means of an exact calculation, that the same situation obtains in the model proposed by Wu.[6] Since the Wu model is a modification of the Slater model, and since the problems discussed below are common to both models, it is meaningful to start with the description of the Slater model. Figure 1 shows a two-dimensional variant of the Slater model[3] of the ferroelectric KH_2PO_4 (KDP). The lattice sites are PO_4 tetrahedra, and the lines joining them are the hydrogen bonds. The protons H^+, one per bond, are near one of the ends of the bond. For each site there are 16 possible configurations, 8 of which are shown in Fig. 2a. Each configuration n is ascribed an energy ϵ_n. The problem consists of calculating the partition function

$$Z=\prod_{\{n\}}\exp\left\{-\frac{\sum\varepsilon_n}{kT}\right\}. \qquad (1)$$

The energy levels of the neutral configurations (1–6 in Fig. 2) are much lower, according to Slater, than the energy levels of the charged configurations (7–8 in Fig. 2). The electroneutrality conditions makes it possible to confine oneself in the partition function (1) to summation over the six neutral configurations 1–6 of Fig. 2. In the ferroelectric KH_2PO_4 the PO_4 tetrahedra are not equilateral, viz., if the energies of configurations 1–2 are taken as the origin, then the remaining four configurations 3–6 must be assigned an energy ϵ. The statistical weights of the sites in the Slater model are shown in Fig. 2c [$x = \exp -\epsilon/kT$)]. In the three-dimensional variant, this model has been constructed on the basis of x-ray structure data and adopted by most investigators. It has, however, a strange property, in that it has no partition function. To establish this circumstance, let us set in correspondence, following Wu,[4] each bond with an arrow going from the end of the bond occupied by the proton to the end free of the proton. We then assign to each upward arrow a line joining the sites, and do not show the downward arrows. We obtain the configurations shown in Fig. 2b.

For sites 1–6 (Slater model), the paths go in a vertical direction without breaks and without turning back. This means that the number of paths in any arbitrary horizontal cross section is constant and the proton configurations on the boundaries, in the first place, cannot be chosen arbitrarily, and in the second, they determine the number of paths in any cross section of the crystal. In this case the partition function depends on the boundary conditions and does not exist in the usual sense.

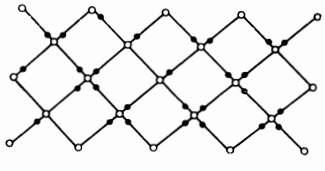


FIG. 1. Two-dimensional KH_2PO_4 crystal with hydrogen bonding: O–PO_4, ●–H^+ (the potassium ions are not shown).

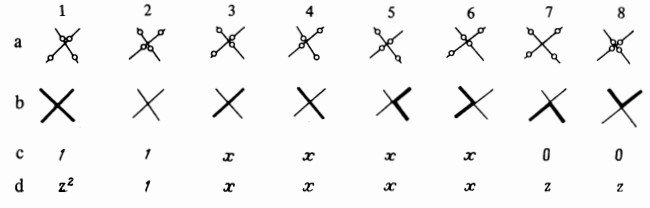


FIG. 2. Statistical weights of the configurations: a–possible proton configurations; b–corresponding path configurations; c–statistical weights in the Slater model; d–statistical weights in the model with symmetric violations of electroneutrality.

The same property is possessed by the Wu model,[6] which differs from the Slater model in that the configuration 1 is forbidden (see Fig. 2). The Wu model is even more artificial (there are no physical reasons why configuration 1 should be forbidden), but it is more interesting than the Slater model, since it contains a second-roder transition,[6] whereas exact calculation of the two-dimensional Slater model (Sutherland[7] and Lieb[8]) revealed a first-order transition, although with complicated singularities of the thermodynamic quantities.

The transition in the Wu model turned out to be unusual. The critical indices (exponents) defining the singularity of the thermodynamic quantities are different above and below the transition point. This contradicts the similarity hypothesis[9] assumed in the theory of second-order phase transitions) and the general transition picture described, for example, in [10].

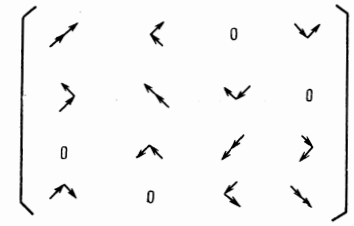
The purpose of the present investigation is to explain these contradictions and to determine the partition function for the aforementioned models. This will be done with the Wu model as an example, for it will be shown below that not only the Wu model, but also the more general model with violation of electroneutrality admit of an exact solution within the framework of the devices employed to calculate the Ising model. It will be shown that the Wu model cannot determine the character of the singularities near the transition point, for the form of the singularity is altered by an arbitrarily small admixture of sites violating the electroneutrality condition. In a sufficiently small vicinity of the transition point the critical indices are the same, in full agreement with the requirements of similarity theory.

Let us proceed to the calculation. Violations of electroneutrality can be of two types, symmetrical (configurations 7 and 8 in Fig. 2) and asymmetrical (the remaining 8 configurations, which are not shown in Fig. 2). Let us consider first the case of symmetrical violations, assigning to each symmetrical violation a weight z ($z = \exp(-\epsilon'/kT)$, where ϵ' is the energy of the site), and to each asymmetrical violation a weight 0. In order not to go outside the framework of the solved model, we assign the configuration 1 a weight z^2. In Slater's model this configuration enters the weight 1, and in Wu's model, without any reason, it is forbidden with weight 0. The weights of the remaining configurations are indicated in Fig. 2d.

All these configurations (1–8) have one common property on going over to summations over the paths (Fig. 2b), viz., not one of the paths is broken. As a result we obtain the sum over paths customarily obtained in the Ising model.[11] To be sure, unlike in the Ising model, the statistical weights are assigned not to the bonds but to the transitions, but in Vdovichenko's method,[11] which will be used below, the problem of calculating the partition function of the Ising model reduces to the random-walk problem, and the statistical weights are assigned during the course of the solution indeed to the transitions. In [11] these weights are chosen such as to obtain just Ising's model, whereas in our paper the weights are specified by the model itself.

To exclude paths passing twice through the same bond, an additional factor was assigned in [11] to each transition, namely $\exp i\varphi/2$, where φ is the angle of rotation of the tangential vector after passage through the given path. For a closed loop these multipliers result in an additional factor (-1), which is cancelled in the sum over the paths by the special multiplier $(-1)^n$, where n is the number of loops. The weight of the configuration 1 ("cross") is uniquely given in this case, and is equal to the product of the weights of configurations 5 and 6 (x^2) plus the product of the weights of configurations 7 and 8 (z^2) minus the product of the weights of the configurations 3 and 4 (x^2). The minus in the latter case is connected with the change of the number of loops (two loops in the first two cases, and one figure-8 loop in the second), and was chosen to compensate for the aforementioned factor $(-1)^n$ in the sum over the paths. The weight of configuration 1 was therefore chosen to be z^2.

Just as in [11] we calculate the partition function by setting up the transition matrix



and calculate the matrix Λ produced when each transition shown above is replaced by the number resulting from multiplying the statistical weight of the transition (according to Fig. 2d), the angle factor $\exp i\varphi/2$, and the Fourier-transformation multiplier $\exp\{2\pi i L^{-1} \times (p\Delta x + q\Delta y)\}$, where Δx is the displacement along the x axis, Δy the displacement along the y axis, L the lattice dimension, and p and q the numbers of the Fourier components.

Introducing the notation $\alpha = \exp i\pi/4$ and $\epsilon = \exp 2\pi i/L$, we obtain

$$\Lambda = \begin{bmatrix} \varepsilon^{p+q_x} & \alpha\varepsilon^{p_x} & 0 & \alpha^{-1}\varepsilon^{q_z} \\ \alpha^{-1}\varepsilon^{p_x} & \varepsilon^{p-q_x} & \alpha\varepsilon^{-q_z} & 0 \\ 0 & \alpha^{-1}\varepsilon^{-q_z} & \varepsilon^{-p-q_x} & \alpha\varepsilon^{-p_x} \\ \alpha\varepsilon^{q_z} & 0 & \alpha^{-1}\varepsilon^{-p_x} & \varepsilon^{q-p_x} \end{bmatrix}.$$

The partition function[11] is

$$Z = \det(I - \Lambda), \tag{2}$$

where I is a unit matrix. By calculating this determinant we obtain for the free energy F per site (for an infinite lattice):

$$\frac{F}{kT} = -\frac{1}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{2\pi} d\beta \ln\{1 + 2(2x^2\cos^2\beta - z^2\cos 2\beta) + z^4 - 4x(1 - z^2)\cos\alpha\cos\beta\}. \tag{3}$$

In differentiating the free energy, the curly bracket is under the integration sign in the denominator, and therefore the transition point is determined by the condition that this bracket vanish:

$$1 - 2x - z^2 = 0. \tag{4}$$

This equation determines the temperature of the transition.

Let us determine the behavior of the thermodynamic quantities near the transition point at small values of z. In place of z we introduce the variable $\tau = 1 - 2x - z^2$, which vanishes at the transition point. It is more con-

venient to calculate the entropy S, and therefore we differentiate (3) with respect to the temperature and obtain under the integral sign a fraction with the curly bracket of (3) in the denominator. After integrating with respect to α we obtain under the integral sign a fraction with a denominator

$$[(1-2x\cos\beta-z^2)^2+2z^2(1-\cos 2\beta)]^{1/2}\approx[(\tau-\beta^2)^2+4z^2\beta^2]^{1/2}, \quad (5)$$

and the entire entropy takes the form ($x = \exp -\epsilon/kT$)

$$S=\frac{\varepsilon}{\pi T_c}\int_0^\infty\left(1+\frac{\tau-\beta^2}{\sqrt{(\tau-\beta^2)^2+4z^2\beta^2}}\right)d\beta. \quad (6)$$

The specific heat near the transition point ($|\tau| \ll 1$) is

$$C=\frac{\varepsilon^2}{\pi kT_c^2}\begin{cases}1/\sqrt{\tau} & \text{if } \tau\gg 4z^2,\\ (2z)^{-1}\ln(4z^2/|\tau|) & \text{if } |\tau|\ll 4z^2,\\ 0 & \text{if } \tau\ll -4z^2.\end{cases} \quad (7)$$

When $|\tau| \gg 4z^2$ the specific heat behaves just as in the Wu model, and when $|\tau| \ll 4z^2$ it behaves just as in the Ising model, although in both cases we have $|\tau| \ll 1$, i.e., the system is in the vicinity of the transition point. The requirements of the similarity theory are always satisfied in a sufficiently narrow region near T_c, but when $z \to 0$ this region, as can be seen from (7), tends to zero.

The determination of the Wu-model partition function (the choice of the conditions on the boundary) is now clear, viz., it is necessary to determine the partition function of the model described above, find the limiting value of the specific free energy as $N \to \infty$, and then put $z = 0$.

If we assume asymmetrical violations of the electroneutrality (such sites are not shown in Fig. 2) with identical weight y for each site, then the resultant partition function reduces, as can be easily shown, to the partition function of the Ising model in an external field $\mu H/kT = \tanh^{-1} y$. In this case the phase transition vanishes.

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