PHASE TRANSITIONS IN THE SLATER MODEL WITH IMPURITIES

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Submitted March 3, 1971

Zh. Eksp. Teor. Fiz. 61, 801–815 (August, 1971)

We obtain an exact solution of the Slater model with impurities; we consider two ways of introducing the impurities: substitution of sites or substitution of ions on the bonds. It turned out that the first-order phase transition in the model without impurities is split into two phase transitions between which the spontaneous polarization smoothly changes from its maximum value to zero. The specific heat has a discontinuity at the lower critical point and its first derivative at the upper critical point. In a weak external field Δp is between the critical points proportional to $\sqrt{E}$ while close to and below the upper critical point the susceptibility diverges as τ^{-2}. We obtained for comparison an approximate solution which is independent of the dimensionality. We considered also the analogous antiferroelectric model.

1. INTRODUCTION

THE model proposed in 1940 by Slater[1] is the model used to describe the phase transition in ferroelectrics of the KH_2PO_4 type. According to x-ray and neutron diffraction studies the crystalline structure of ferroelectrics (and antiferroelectrics) of this type reduces to the following.

Each phosphate group $(PO_4)^{--}$ is surrounded by four other such groups situated at the tetrahedron corners so that something similar to the diamond lattice is formed. The hydrogen ions are situated on the bonds linking pairs of neighboring phosphate groups. Slater assumed that: 1) there can be only one hydrogen ion on each bond; 2) this ion can take up one of two positions which are symmetrically displaced with respect to the center of the bond; 3) there can be only two hydrogen ions near each phosphate group. These conditions are sometimes called the "ice conditions" since similar assumptions were made by Pauling[2] to explain the residual entropy of ice, the crystalline structure of which is similar to the above-described one, except that then the oxygen ions play the role of the phosphate groups.

If we take the phosphate groups as the lattice sites and indicate by an arrow the position of the hydrogen atom along the bond, then all allowable configurations can be drawn in the form shown in the Table.

Thanks to the anisotropy of the KH_2PO_4 lattice, caused by the presence of the potassium ions, the energy of two of the allowable configurations differs from that of the other four. (The problem of the residual entropy of ice corresponds to the fact that the energies of all six configurations are the same). In the second column of the table we show the distribution of the energy over the configurations in Slater's original model; other distributions are also possible corresponding either to placing the Slater model in an external electric field or to an antiferroelectric variant of the model (third column of the table). Rys introduced[3] a generalized model with an arbitrary distribution of the energy over the configurations and called it the F-model but this name was subsequently given to the antiferroelectric model.[4,5]

Distribution of energy over the configurations

Configuration	Slater model	F-model
1 	0	ε
2 	0	ε
3 	ε	ε
4 	ε	ε
5 	ε	0
6 	ε	0

Slater himself[1] obtained an approximate solution of his model and quite recently Lieb[6] found exact solutions of the two-dimensional variants of both the original Slater model and the F-model of an antiferroelectric;[5] This result was later generalized in[4]. The main features of the exact and approximate solutions (the latter is independent of the dimensionality of the model) are very similar: 1) at the critical temperature $T_c = \epsilon/\ln 2$ a first-order phase transition takes place from a completely ordered state with a saturated polarization $(p = 1)$ to a disordered state without spontaneous polarization; 2) the entropy of the transition is $\frac{1}{2}\ln 2$ per site; 3) above T_c the susceptibility is described by a Curie-Weiss law. Only the specific heat behavior near and above T_c turns out to be different: In the approximate solution it remains finite but in the exact one it diverges as $(\Delta T/T_c)^{-1/2}$. More detailed results necessary for what follows are given in Appendix A.

The exact solution of the two-dimensional model found by Lieb allows us, using a method proposed by one of the authors,[7] to obtain an exact solution of the corresponding model with impurities. It is interesting to compare such a solution with the approximate solution of the same problem which allows us to estimate the validity of the approximate method, since the latter—as in the case of the model without impurities—leads to results which are independent of the dimensionality of the model.

2. PARTITION FUNCTION OF THE SLATER MODEL WITH IMPURITIES

We assume that M of the total number of N lattice sites are replaced by another kind of sites so that the energy of the configurations 1 and 2 (see the table) near those sites is equal to ϵ_0 while the energy of the configurations 3 to 6 is ϵ'; the energies of the corresponding configurations near sites with atoms of the first kind are, respectively, equal to 0 and ϵ. For a real ferroelectric such a substitution of the sites corresponds, apparently, in the replacement of phosphor atoms in the phosphate groups by arsenic atoms. Our next problem is to express the partition function of such a model "with impurities" in terms of the partition function of the model without impurities.

We ascribe to each bond a variable $\sigma = \pm 1$ depending on the direction of the arrow corresponding to that bond. In a given state of the lattice there corresponds thus to each site a set of four values of the variables σ referring to the four bonds starting from that site. We can then write the partition function of the model without impurities in the form

$$Z = \sum_{\{\sigma\}} \prod_{i=1}^{N} [a_i(\sigma) + z b_i(\sigma)],$$

where the summation is over all allowable configurations $\{\sigma\}$, while the product is over all lattice sites and where we have introduced the notation $z = e^{-\epsilon/T}$; moreover, $a_i(\sigma) = 1$, $b_i(\sigma) = 0$ for configurations 1 and 2 (see the table), and $a_i(\sigma) = 0$, $b_i(\sigma) = 1$ for the configurations 3 to 6 near the i-th site.

Following the method of[7] we can write down an expression for the partition function Z^*_{NM} with a random distribution of sites of the second kind in terms of the partition function Z_N of the model without impurities:

$$Z_{NM}{}^* = e^{-M\varepsilon_0/T} \frac{(N-M)!}{N!} \prod_{n=N-M+1}^{N} \left[n + (z_2 - z_1) \frac{\partial}{\partial z_1} \right] Z_N(z_1), \quad (2.1)$$

where

$$z_1 = e^{-\varepsilon_1/T}, \quad z_2 = e^{-\varepsilon_2/T}; \qquad \varepsilon_1 = \varepsilon, \quad \varepsilon_2 = \varepsilon' - \varepsilon_0.$$

Each of the operators under the product sign describes mathematically the replacement of one of the sites of the lattice (it eliminates the term corresponding to a site of the first kind and introduces a term describing a site of the second kind).

Writing now $Z_N(z_1)$ as a contour integral ($Z_N(z_1)$ is for finite N a polynomial in z_1) and substituting this contour integral into (2.1) we find by the method of steepest descent the asymptotic behavior of Z^*_{NM} as $N, M \to \infty$, $M/N = c_2$, $(N - M)/N = c_1$. (In what follows we drop the unimportant factor $e^{-M\epsilon_0/T}$). Let

$$Z^* = e^{Nf^*};$$

we then get

$$f^*(T) = f(z) + c_1 \ln c_1 \frac{z_2 - z_1}{z_2 - z} + c_2 \ln c_2 \frac{z_2 - z_1}{z - z_1} \equiv f(z) + G(z, T), \quad (2.2)$$

where

$$f(z) = \lim_{N\to\infty} \left(\frac{1}{N} \ln Z_N(z) \right),$$

while z is the saddle point determined from the condition

$$\frac{df(z)}{dz} = \frac{c_1}{z - z_2(T)} + \frac{c_2}{z - z_1(T)} \equiv g(z, T) = -\frac{\partial G}{\partial z}. \quad (2.3)$$

The function $f^*(T)$ and the functions $G(z, T)$ and $g(z, T)$ which have been defined to ease the notation depend on the parameters ϵ_1, ϵ_2, and c_1 of the problem.

We note that all results of this section are independent of the dimensionality of the model and refer therefore completely also to the three-dimensional case.

3. TEMPERATURE OF THE PHASE TRANSITIONS

We apply the results obtained in the preceding section to the two-dimensional Slater model. First of all we consider Eq. (2.3) for the saddle point. We have shown schematically the graphical solution of this equation in Fig. 1, where the solid curve represents the function $f'(z)$ (see Appendix A; the construction was done using the results of the computer calculation), which shows a discontinuity at $Z = 1/2$, and the dotted lines show $g(z, T)$ for different values of T. We show only one, inner, branch of the function $g(z, T)$, since the other two branches of this function do not intersect the curve of $f'(z)$. When the temperature is increased the curve of $g(z, T)$ shifts to the right which leads to an increase in the value of the root $z(T)$. It is at once clear from the figure that there are three regions of analyticity and two singular points corresponding to two phase transitions which are determined by the equations

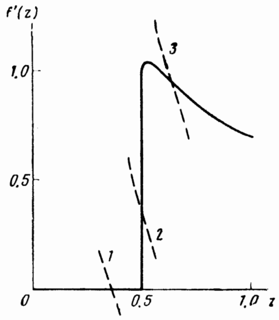

FIG. 1. Graphical solution of the equation for the saddle point. Full-drawn curve: f'(z). Dotted curves: g(z, T) for different values of T: 1:1: $T < T_1$; 2: $T_1 < T_2$; 3: $T_2 < T$.

$$g\left(\frac{1}{2}, T_1\right) \equiv \frac{c_1}{1/2 - z_2(T_1)} + \frac{c_2}{1/2 - z_1(T_1)} = 0, \quad (3.1)$$

$$g\left(\frac{1}{2}, T_2\right) \equiv \frac{c_1}{1/2 - z_2(T_2)} + \frac{c_2}{1/2 - z_1(T_2)} = 1. \quad (3.2)$$

The temperature range $T < T_1$ corresponds to a state with a saturation value of the spontaneous polarization ($p = 1$); the region $T > T_2$ to a disordered state without spontaneous polarization; in the region $T_1 < T < T_2$ the spontaneous polarization changes smoothly from 1 to 0, as we shall see.

4. THERMODYNAMICS OF THE MODEL

The free energy of the Slater model with impurities is equal to

$$-F/NT \equiv f^*(T) = f(z) + G(z, T). \quad (4.1)$$

Its behavior is essentially different in the three regions of analyticity.

1. In the region below the first critical point ($T < T_1$) it follows from Eq. (2.3) and Fig. 1 that

$$f(z) = 0, \quad G(z, T) = 0, \quad -F/NT \equiv f^*(T) = 0.$$

The free and the internal energy and also the specific heat are thus equal to zero: the system is in a completely ordered state.

2. Between the first and the second critical points ($T_1 < T < T_2$) we have

$$z = {}^1/_2, \quad f(z) = 0,$$

and hence

$$-\frac{F}{NT} \equiv f^*(T) = G\left(\frac{1}{2}, T\right) = c_1 \ln c_1 \frac{z_2 - z_1}{z_2 - {}^1/_2} + c_2 \ln c_2 \frac{z_2 - z_1}{{}^1/_2 - z_1}. \tag{4.2}$$

We consider in more detail how this function behaves near the singular points T_1 and T_2. Near T_1

$$f^* = \frac{C_1}{2T_1^2}(T - T_1)^2 + \ldots, \tag{4.3}$$

where the coefficient C_1 is determined by the parameters of the problem:

$$C_1 = \frac{1}{c_1 c_2 T_1^2}\left(\frac{c_1 \varepsilon_1 z_1(T_1) + c_2 \varepsilon_2 z_2(T_1)}{z_2(T_1) - z_1(T_1)}\right)^2 \tag{4.4}$$

and is equal to the specific heat per site for $T = T_1 + 0$. Hence it follows that the internal energy is $\mathcal{E} = C_1(T - T_1)$. The energy is thus continuous at the lower critical point while the specific heat shows a discontinuity: we have a second-order phase transition.

In the upper critical point the internal energy and the specific heat (per site) are, respectively, equal to

$$\mathcal{E}_2 = T_2^2 \frac{\partial G({}^1/_2, T)}{\partial T}\bigg|_{T=T_2}, \quad C_2 = T_2^2 \frac{\partial^2 G({}^1/_2, T)}{\partial T^2}\bigg|_{T=T_2} + 2\frac{\mathcal{E}_2}{T_2}. \tag{4.5}$$

From this we easily get, using the definition (4.2) of the function $G({}^1/_2, T)$, very complicated expressions for the energy and the specific heat.

3. Above the second critical point the general expression (4.1) for the free energy simplifies when $\tau = (T - T_2)/T_2 \ll 1$. Using the expansion (A.9) of $f(z)$ in $\zeta = z - {}^1/_2$ and using Eq. (2.3) we find

$$-\frac{F}{NT} = f^*(T) = G\left(\frac{1}{2}, T\right) - \frac{2}{3\pi}\zeta^{3/2} + O(\zeta^2). \tag{4.6}$$

Solving now the equation (2.3) for the saddle point up to terms of first order in $\sqrt{\zeta}$ we find that $\sqrt{\zeta} = \pi\beta_2\tau/2$, where

$$\beta_2 = T_2 \frac{\partial g({}^1/_2, T)}{\partial T}\bigg|_{T=T_2} = \frac{c_2\varepsilon_2 z_2({}^1/_2 + z_1)^2 + c_1\varepsilon_1 z_1({}^1/_2 + z_2)^2}{c_1 c_2 T_2 (z_2 - z_1)^2}. \tag{4.7}$$

The free energy close to and above T_2 is thus equal to

$$-\frac{F}{NT} = f^*(T) = G\left(\frac{1}{2}, T\right) - \frac{\pi^2}{12}\beta_2^3\tau^3. \tag{4.8}$$

Comparison with (4.2) shows that in the upper critical point T_2 the free energy, the internal energy, and the specific heat are continuous. The temperature derivative of the specific heat has a discontinuity:

$$\frac{dC}{dT}\bigg|_{T_2+0} - \frac{dC}{dT}\bigg|_{T_2-0} = -\frac{\pi^2\beta_2^3}{2T_2}, \tag{4.9}$$

i.e., there is in the point T_2 a third-order phase transition according to Ehrenfest's classification.

In all expressions obtained in this section one can easily take the limit to the model without impurities. This can be done in two ways: either we let one of the concentrations tend to zero (for instance, $c_1 \to 0$, $c_2 \to 1$), or we put $|\epsilon_1 - \epsilon_2| \to 0$. In both cases $T_2 \to T_1 \to \epsilon/\ln 2$, and the specific heat tends to infinity in such a way that

$$\int_{T_1}^{T_2} C\, dT \to \frac{\varepsilon}{2},$$

giving thereby the latent heat of the transition in the model without impurities, while

$$C_{T>T_2} \to \frac{(\ln 2)^{3/2}}{2\pi\sqrt{2}}\left(\frac{T - T_c}{T_c}\right)^{-1/2},$$

which is the same as the result for the model without impurities (in the expression for the specific heat obtained by Lieb[6] there was an error in the coefficient, see (A.11)).

5. SPONTANEOUS POLARIZATION

We noted above that in the low temperature region ($T < T_1$) $p = 1$, and in the high temperature region ($T > T_2$) $p = 0$. We now study the region between the critical points where, according to Fig. 1, the curve $g(z, T)$ intersects the vertical section of the straight line. We must bear in mind that the whole region $z > {}^1/_2$ is completely filled by the family of curves $f'(z, p)$ (we denote by a prime differentiation with respect to z) which lie between the curve $f'(z, 0)$ shown in Fig. 1 and the abscissa axis, corresponding to the curve $f'(z, 1)$, and the curve $g(z, T)$ intersects both of them. The minimum of the free energy can easily be seen to correspond in that case to the point $z = {}^1/_2$, i.e., we get for the spontaneous polarization the equation

$$g\left(\frac{1}{2}, T\right) \equiv \frac{c_1}{{}^1/_2 - z_2(T)} + \frac{c_2}{{}^1/_2 - z_1(T)} = \frac{\partial f}{\partial z}\left(\frac{1}{2}, p\right) \equiv 1 - p_0^2. \tag{5.1}$$

We used here the result (B.4) from Appendix B and assumed for the sake of simplicity that the polarization is independent of the kind of site. Solving (5.1) for p_0, we get

$$p_0 = \left[\frac{1 + 2(c_1 - c_2)(z_1 - z_2) - 4z_1 z_2}{(2z_2 - 1)(1 - 2z_1)}\right]^{1/2}. \tag{5.2}$$

Near the critical points we obtain the following expansions:

$$p_0(T) \cong 1 - \beta_1\left(\frac{T - T_1}{T_1}\right) + \ldots, \quad 0 < \frac{T - T_1}{T_1} \ll 1, \tag{5.3}$$

$$p_0(T) \cong \left[\frac{\beta_2(T_2 - T)}{T_2}\right]^{1/2} + \ldots, \quad 0 < \frac{T_2 - T}{T} \ll 1, \tag{5.4}$$

where

$$\beta_1 = \frac{c_1\varepsilon_1 z_1(T_1) + c_2\varepsilon_2 z_2(T_1)}{c_1 c_2 T_1 [z_2(T_1) - z_1(T_1)]^2}, \tag{5.5}$$

while β_2 is defined by Eq. (4.7).

6. MODEL WITH IMPURITIES IN AN EXTERNAL FIELD

To find the free energy of the system in an external electrical field we must minimize the expression

$$F(T, E; p)/N = -Tf^*(T, p) - pE, \tag{6.1}$$

with respect to p; here $f^*(T, p)$ is defined by Eq. (2.2) and the equation (2.3) for the saddle point except that we must now substitute instead of f(z) the function f(z, p). When $T < T_1$ the result is trivial as for any $p^2 \leq 1$ and $z < 1/2$, the function f(z, p) = 0. Hence

$$f^*(T, p) = 0, \quad T < T_1, \quad p^2 \leqslant 1. \tag{6.2}$$

To temperatures $T > T_1$ there corresponds $z \geq 1/2$, where f(z, p) is a very complicated function (see Appendix A) so that we shall only consider in detail the case when the polarization differs little from the spontaneous polarization $p_0(T)$. Under that condition we find, using the result (B.5) obtained in Appendix B.

$$f^*(T, p) = G(1/2, T) = f^*(T, p_0), \quad T_1 < T < T_2, \tag{6.3}$$
$$p^2 < p_0{}^2 = 1 - g(1/2, T);$$

$$f^*(T, p) = G\left(\frac{1}{2}, T\right) - \frac{\pi^2}{12}\left[\frac{g(1/2, T)}{1 - p^2} - 1\right]^3, \quad 0 < \frac{g(1/2, T)}{1 - p^2} - 1 \ll 1. \tag{6.4}$$

We can rewrite the last formula for $T_1 < T < T_2$ and sufficiently small positive $p^2 - p_0^2$ in the form

$$f^*(T, p) = f^*(T, p_0) - \frac{\pi^2}{12}\left(\frac{p^2 - p_0{}^2}{1 - p^2}\right)^2. \tag{6.5}$$

Minimizing (6.1) with the expression which is here written down, for $f^*(T, p)$ we find in a weak external field

$$\Delta p = |p| - p_0 = \frac{1}{\sqrt{2}\pi}\left(\frac{1 - p_0{}^2}{p_0}\right)^{3/2}\sqrt{\frac{E}{T}}. \tag{6.6}$$

This expression is valid of $\Delta p \ll \min(p_0, 1 - p_0)$. Using (5.3) and (5.4) we get near the critical points

$$\Delta p = \frac{2\beta_1^{3/2}}{\pi}\left(\frac{T - T_1}{T_1}\right)^{3/2}\sqrt{\frac{E}{T_1}}, \tag{6.7}$$

$$\Delta p = \frac{1}{\pi\sqrt{2}}\left(\beta_2\frac{T_2 - T}{T_2}\right)^{-3/4}\sqrt{\frac{E}{T_2}}. \tag{6.8}$$

We consider now temperatures in the vicinity of the second critical point T_2 ($(T - T_2)/T_2 = \tau$). From (6.4) we find

$$f^*(p, T) = G\left(T, \frac{1}{2}\right) - \frac{\pi^2}{12}(p^2 + \beta_2\tau)^3, \quad 0 < p^2 + \beta_2\tau \ll 1. \tag{6.9}$$

Using this formula and minimizing (6.1) we are led to an equation determining all electrical properties near T_2 in a weak external field:

$$E = 1/2\pi^2 T_2 p(p^2 + \beta_2\tau)^2. \tag{6.10}$$

When $\tau < 0$ we get from this (6.8), when $\tau = 0$

$$p = (2E/\pi^2 T_2)^{1/5}, \tag{6.11}$$

while for $\tau > 0$, the susceptibility is

$$\chi = \frac{\partial p}{\partial E}\bigg|_{E=0} = \frac{2}{\pi^2\beta_2{}^2 T_2}\tau^{-2}. \tag{6.12}$$

We must draw attention to the unusual behavior ($\Delta p \sim \sqrt{E}$) of the polarization for $T_1 < T < T_2$ and the peculiar divergence of the susceptibility close to and above T_2: $\chi \sim \tau^{-2}$.

7. APPROXIMATE SOLUTION

As already mentioned above, the approximate solution is independent of the dimensionality of the model. To find it we use a method which is similar to the one applied by Slater[1] for the model without impurities, namely, we add to the lattice one more site, assuming that the configurations in the two sites which are situated above the new site and are its neighbors are uncorrelated. The entropy per site is then equal to

$$S = \frac{1}{2}(c_1 + x - \nu_1)\ln\left\{\frac{(1 + x + y)^2 c_1}{2(c_1 + x - \nu_1)}\right\} + \frac{1}{2}(c_1 - x - \nu_1)$$
$$\times \ln\left\{\frac{(1 - x - y)^2 c_1}{2(c_1 - x - \nu_1)}\right\} + \nu_1\ln\left\{\frac{(1 - x - y)(1 + x + y)c_1}{\nu_1}\right\}$$
$$+ \frac{1}{2}(c_2 + y - \nu_2)\ln\left\{\frac{(1 + x + y)^2 c_2}{2(c_2 + y - \nu_2)}\right\} + \frac{1}{2}(c_2 - y - \nu_2)\cdot$$
$$\times \ln\left\{\frac{(1 - x - y)^2 c_2}{2(c_2 - y - \nu_2)}\right\} + \nu_2\ln\left\{\frac{(1 - x - y)(1 + x + y)c_2}{\nu_2}\right\}, \tag{7.1}$$

where x and y are the differences in the numbers of configurations 1 and 2 respectively, for sites of the first and the second kind, ν_1 and ν_2 the corresponding average numbers of configurations 3 to 6, and c_1 and c_2 as before the concentrations of sites of the first and second kind.

As the internal energy of the system is $N\mathscr{E} = N(\epsilon_1\nu_1 + \epsilon_2\nu_2)$ we can find the free energy of the system which is expressed in the parameters used above:

$$F/N = \mathscr{E} - TS.$$

To find the free energy as function of the temperature we must find the absolute minimum of this expression with respect to all parameters occuring in it. The solution obtained after differentiating the set of equations and taking into account the boundary conditions $x^2 = c_1^2$, $y^2 = c_2^2$, $\nu_1 = 0$, $\nu_2 = 0$, which also can lead to an absolute minimum of the free energy, gives the following results.

1. The system possesses two phase transition points by the equations

$$2c_1\exp\left(-\frac{\varepsilon_1}{T_1}\right) + 2c_1\exp\left(-\frac{\varepsilon_2}{T_1}\right) = 1,$$
$$4\exp\left[-\frac{\varepsilon_1 + \varepsilon_2}{T}\right] + 2(c_1 - c_2)\left[\exp\left(-\frac{\varepsilon_1}{T_2}\right) - \exp\left(-\frac{\varepsilon_2}{T_2}\right)\right] = 1. \tag{7.2}$$

2. In the temperature range $T < T_1$ we have

$$F = 0, \quad \mathscr{E} = 0, \quad C = 0.$$

3. In the intermediate temperature range ($T_1 < T < T_2$)

$$\nu_1 = \frac{z_1(2c_1z_1 + 2c_2z_2 - 1)}{(z_2 - z_1)(1 - 2z_1)}, \quad \nu_2 = \frac{z_2(2c_1z_1 + 2c_2z_2 - 1)}{(z_2 - z_1)(2z_2 - 1)},$$
$$x^2 = \frac{(2z_2 - 1)[1 + 2(c_1 - c_2)(z_1 - z_2) - 4z_1z_2]}{4(1 - 2z_1)(z_1 - z_2)^2}, \quad \frac{x}{y} = \frac{2z_2 - 1}{1 - 2z_1}. \tag{7.3}$$

The free energy, internal energy, and specific heat are given by the same expressions as in the exact solution for the temperature range considered.

4. Above the second critical point

$$x = 0, \quad y = 0, \quad \nu_1 = \frac{2c_1z_1}{1 + 2z_1}, \quad \nu_2 = \frac{2c_2z_2}{1 + 2z_2}, \tag{7.4}$$

$$\frac{F}{NT} = -\left(c_1\ln\frac{1 + 2z_1}{2} + c_2\ln\frac{1 + 2z_2}{2}\right). \tag{7.5}$$

5. For $T = T_2 + 0$ the specific heat is given by the formula

$$C = \frac{1}{T_2^2}\left[\frac{2\varepsilon_1^2 c_1 z_1}{(1+2z_1)^2} + \frac{2\varepsilon_2^2 c_2 z_2}{(1+2z_2)^2}\right]\Bigg|_{T=T_2}, \tag{7.6}$$

while for $T = T_2 - 0$ it is, as in the exact solution, determined by Eq. (4.5). In the upper phase transition point the specific heat thus undergoes a negative jump, i.e., in contrast to the exact solution, the approximate one leads to a second-order phase transition also at $T = T_2$ (see Fig. 2).

Using (7.3) we can find the polarization in the intermediate region $T_1 \leq T \leq T_2$: $p = x + y$ which is the same as Eq. (5.2) found in the exact solution.

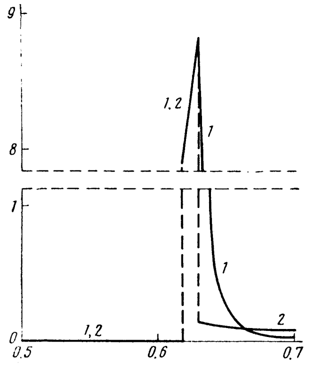

FIG. 2. Specific heat (per site) of the Slater model with impurities as function of $\exp(-\epsilon_2/T)$ for $\epsilon_1 = 2\epsilon_2$ and $c_1 = c_2 = ½$. Curve 1: exact solution; 2: approximate solution. The model without impurities shows a first-order phase transition when the argument is equal to ½ when $c_2 = 1$ or $1/\sqrt{2}$ when $c_1 = 1$.

To find the susceptibility near the upper critical point we use an expansion of the function $F(T, x, y)$ in terms of the parameters x and y in the presence of an external electrical field:

$$\begin{aligned}\frac{F}{NT} &= -c_1\ln\frac{1+2z_1}{2} - c_2\ln\frac{1+2z_2}{2} - \frac{E}{T}(x+y) - 2xy\\ &+\frac{(2z_1+1-2c_1)x^2}{2c_1} + \frac{(2z_2+1-2c_2)y^2}{2c_2} + \frac{(1+2z_1)(1+z_1-2z_1^2)x^4}{12c_1^3}\\ &+\frac{(1+2z_2)(1+z_2-2z_2^2)y^4}{12c_2^3} - \frac{(x+y)^4}{6} + \ldots\end{aligned} \tag{7.7}$$

Minimizing this expression we find

$$\chi|_{T\to T_2+0} \cong A_1/\tau, \quad \chi|_{T\to T_2-0} \cong A_2/|\tau|, \tag{7.8}$$

where

$$\begin{aligned}A_1 &= \frac{1+2c_1z_2+2c_2z_1}{\varepsilon_1+\varepsilon_2+2(c_1-c_2)(z_2\varepsilon_2-z_1\varepsilon_1)}\Bigg|_{T=T_2},\\ A_2 &= \frac{4c_1c_2(c_1z_1+c_2z_2+2z_1z_2)}{\varepsilon_1+\varepsilon_2+2(c_1-c_2)(z_2\varepsilon_2-z_1\varepsilon_1)}\Bigg|_{T=T_2}\end{aligned} \tag{7.9}$$

In Fig. 3 we have sketched the dependence of the function $F(p, T)$ on the spontaneous polarization for different values of the temperatures. We saw that the spontaneous polarization is continuous in both critical points. The position of the minima in the region $T_1 < T < T_2$ is determined by Eqs. (7.3); the value of F for $p = 0$ is given by Eq. (7.5).

A comparison of the results of this section with the formulae obtained in the exact solution of the two-dimensional model with impurities allows us to conclude that the approximate solution leads to good expressions for the thermodynamic functions and the spontaneous polarization even in the two-dimensional case (in the three-dimensional case the accuracy of the approximate solution must be even better). The only exception is the behavior of the specific heat for $T \cong T_2$ and the shape of the susceptibility curve.

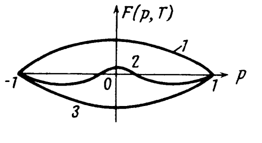

FIG. 3. Sketch of the function F(p, T) 1: $T < T_1$; 2: $T_1 < T < T_2$; 3: $T_2 < T$.

We note that although above we constructed directly the approximate solution of the Slater model with impurities one can also obtain it using the method described in sections 2 to 4 by merely replacing f(z) by Slater's function (A.1). Comparison shows that all results are then the same.

8. SECOND METHOD FOR INTRODUCING IMPURITIES

Let M of the total number of 2N hydrogen ions be replaced by another kind of ions (for instance, deuterium ions) in such a way that they are randomly distributed over all 2N bonds. We assume that for such a substitution only the energy of those sites in the immediate vicinity of which the new ions are situated will be changed, in such a way that if the originally given site had an energy ϵ_1 after the substitution its energy became ϵ_1', and if it were zero, it became ϵ_0'; when both ions close to the site are replaced, the energies will be, respectively, ϵ_1'' and ϵ_0''. To simplify the calculations we put

$$\varepsilon_1' = {}^1/_2(\varepsilon_1+\varepsilon_1''), \quad \varepsilon_0' = {}^1/_2(\varepsilon_0''+0). \tag{8.1}$$

To find the free energy we use the method of Sec. 2. Calculations lead to the following result:

$$f^* = f(z^2) + 2c_1\ln c_1\frac{z_2-z_1}{z_2-z} + 2c_2\ln c_2\frac{z_2-z_1}{z-z_1} \equiv f(z^2) + 2G(z, T), \tag{8.2}$$

where the saddle point $z = z(T)$ is found from the condition $\partial f^*/\partial z = 0$, i.e., from the equation

$$zf'(z^2) = \frac{c_1}{z-z_2} + \frac{c_2}{z-z_1} \equiv g(z, T). \tag{8.3}$$

We have here introduced a notation which differs slightly from the one used before

$$\begin{gathered}z_1^2 = e^{-\varepsilon_1/T}, \quad z_2^2 = e^{-(\varepsilon_1''-\varepsilon_0'')/T},\\ c_1 = (2N-M)/2N, \quad c_2 = M/2N.\end{gathered} \tag{8.4}$$

The behavior of the system turns out to be analogous to the case considered above where the sites were replaced; we shall therefore only give the final results.

As before the system shows two phase transitions. Their temperatures are now determined by the equations

$$g(1/\sqrt{2}, T_1) = 0; \quad g(1/\sqrt{2}, T_2) = 0. \tag{8.5}$$

When $T < T_1$ the system is completely ordered and the free energy vanishes. In the first critical point the specific heat shows a jump which is now equal to

$$C_1 = \frac{1}{2c_1c_2T_1^2}\left(\frac{c_1\varepsilon_1z_1 + c_2\varepsilon_2z_2}{z_2(T_1) - z_1(T_1)}\right)^2. \tag{8.6}$$

When $T_1 < T < T_2$ the free energy is equal to (compare (4.2))

$$-F/NT = f^*(T) = 2G(1/\sqrt{2}, T), \tag{8.7}$$

and the spontaneous polarization is determined by an equation similar to (5.1):

$$g(1/\sqrt{2}, T) = 1 - p_0^2. \tag{8.8}$$

Near T_2 the spontaneous polarization behaves according to Eq. (5.3) if we now put β_1 equal to

$$\beta_1 = \frac{c_1\varepsilon_1 z_1(T_1) + c_2\varepsilon_2 z_2(T_2)}{2\sqrt{2}c_1c_2T_1[z_2(T_1) - z_1(T_1)]^2}. \tag{8.9}$$

The jump in the derivative of the specific heat in the second critical point is determined by the earlier Eq. (4.9), if we put

$$\beta_2 = \sqrt{2}T_2\frac{\partial g(1/\sqrt{2}, T)}{\partial T}\Bigg|_{T=T_2} = \frac{c_2\varepsilon_2 z_2(T_2)}{\sqrt{2}T_2(1/\sqrt{2} - z_2)} + \frac{c_2\varepsilon_1 z_1(T_2)}{\sqrt{2}T_2(1/\sqrt{2} - z_1)}. \tag{8.10}$$

All equations of Sec. 6 remain valid, which describe the behavior of the system in an external field, if we substitute for $G(1/2, T)$ and $g(1/2, T)$, respectively, $2G(1/\sqrt{2}, T)$ and $g(1/\sqrt{2}, T)$, determined in this section, as well as making the above-mentioned change in β_2.

9. THE F-MODEL OF AN ANTIFERROELECTRIC WITH IMPURITIES

Applying the method described above to an antiferroelectric model, the necessary information about which is given in Appendix A, we obtain an expression for the free energy of the model with two kinds of sites. This expression is the same as (2.2), (2.3) if we take for $f(z)$ the corresponding function (A.12) of the antiferroelectric model without impurities. As in contrast to the ferroelectric model $f'(z)$ is here continuous and has only one singular point, the system with impurities has a single phase transition point determined by the intersection of the central branch of the function $g(z, T)$ with the curve of $f(z)$ for the value $z = 1/2$. As $f'(1/2) = 2/3$, the equation for the critical point has the form

$$g(1/2, T_c) = 2/3. \tag{9.1}$$

The expansion of the internal energy in terms of $(T - T_c)/T_c$ near the critical point has the form

$$\mathscr{E} = \mathscr{E}_0 + C_0(T - T_c) + \ldots, \tag{9.2}$$

where

$$\mathscr{E}_0 = \frac{(\varepsilon_2 z_2 - \varepsilon_1 z_1) - 2z_1z_2(\varepsilon_2 - \varepsilon_1)}{3(z_2 - z_1)}; \tag{9.3}$$

the quantity C_0 is also determined by the parameters of the problem, but the expression for it is very complicated although it can be obtained by the method described above.

The expansion (9.2) is valid both above and below the phase transition point, i.e., as in the model without impurities this is a phase transition of "infinite order." Below the critical point an ordered (but not completely ordered as in the ferroelectric Slater model) state occurs with an enhancement of the configurations of type 5 and 6 (see the table).

Unfortunately it is not possible to compare our results with the results of the approximate solution for the three-dimensional model as the latter has so far not been found; in any case there is no satisfactory description of the region $T < T_c$ in the model without impurities.

APPENDIX A

1. Some results of Slater's approximate solution.[1] The phase transition point is determined by the condition

$$T_c = \varepsilon / \ln 2.$$

The free energy below the critical point vanishes and above it is determined by the equation

$$-\frac{F}{NT} = f(z) = \ln\frac{1+2z}{2}; \quad z = e^{-\varepsilon/T}. \tag{A.1}$$

The internal energy per site can be written in the form $(T > T_c)$

$$\mathscr{E} = 2\varepsilon z / (1 + 2z). \tag{A.2}$$

The specific heat in this region is

$$C = 2\varepsilon^2 z / T^2(1 + 2z)^2. \tag{A.3}$$

2. The exact solution of the two-dimensional Slater model leads to the following results.[6] The free energy is given by the equations

$$-\frac{F(z,p)}{NT} \equiv f(z,p)$$
$$= \begin{cases} 0, & z \leqslant 1/2 \\ \dfrac{Ep}{T} - \dfrac{1}{4\pi}\displaystyle\int_{-b}^{b} R(\alpha)\ln\left[\frac{\operatorname{ch}\alpha - \cos 3\mu}{\operatorname{ch}\alpha - \cos\mu}\right]d\alpha, & z \geqslant 1/2 \end{cases} \tag{A.4}$$

where we have used the notation

$$\cos\mu = -1/2z, \quad 2\pi/3 < \mu \leqslant \pi,$$

E is the external electrical field, and the distribution $R(\alpha)$ is the solution of the integral equation

$$R(\alpha) = \varphi(\alpha) - \int_{-b}^{b} K(\alpha - \beta)R(\beta)\,d\beta, \tag{A.5}$$

where b as function of p is given by the condition

$$\pi(1 - p) = \int_{-b}^{b} R(\alpha)\,d\alpha. \tag{A.6}$$

We have here written

$$\varphi(\alpha) = \frac{\sin\mu}{\operatorname{ch}\alpha - \cos\mu}, \quad K(\alpha) = \frac{1}{2\pi}\frac{\sin 2\mu}{\operatorname{ch}\alpha - \cos 2\mu}. \tag{A.7}$$

When there is no external field $\min_p F(z, p)$ is reached for $b = \infty$, $p = 0$. This makes it possible to solve the integral equation and to obtain an explicit expression for the free energy:

$$f(z) \equiv f(z, 0)$$
$$= \begin{cases} 0, & z \leqslant 1/2 \\ -\dfrac{1}{4}\displaystyle\int_{-\infty}^{\infty}\frac{d\alpha}{\operatorname{ch}\pi\alpha}\ln\left[\frac{\operatorname{ch}2\mu\alpha - \cos 3\mu}{\operatorname{ch}\mu\alpha - \cos\mu}\right], & z \geqslant 1/2. \end{cases} \tag{A.8}$$

The expansion of the function $f(z)$ near the singularity $z = 1/2 + 0$ has the form

$$f(z) = \zeta + \frac{4}{3\pi}\zeta^{3/2}, \tag{A.9}$$

where $\zeta = z - 1/2$; hence

$$\frac{df}{dz}(z) = \begin{cases} 0, & z < 1/2 \\ 1 + \dfrac{2}{\pi}\zeta^{1/2}, & z > 1/2 \end{cases}. \tag{A.10}$$

We obtain for the specific heat of the system as $T \to T_c + 0$

$$C \approx \frac{\varepsilon^{3/2}}{2\sqrt{2}\pi T_c}\frac{1}{(T-T_c)^{1/2}} \tag{A.11}$$

3. Results of the exact solution of the two-dimensional F-model of antiferroelectricity.[5] When there is no electrical field we can write the free energy of the system as follows:

$$-\frac{F}{NT} \equiv f$$

$$= \begin{cases} -\dfrac{\varepsilon}{T}+\dfrac{\lambda}{2}+\displaystyle\sum_{n=1}^{\infty}\frac{\operatorname{th} n\lambda}{ne^{n\lambda}}, & z<\dfrac{1}{2},\quad T<T_c \\ -\dfrac{\varepsilon}{T}+\dfrac{1}{4\pi}\displaystyle\int_{-\infty}^{\infty}\ln\left\{\frac{\operatorname{ch}\alpha-\cos 2\mu}{\operatorname{ch}\alpha-1}\right\}\frac{\pi}{2\mu}\frac{d\alpha}{\operatorname{ch}(\pi\alpha/2\mu)}, & z>\dfrac{1}{2},\quad T>T_c. \end{cases} \tag{A.12}$$

We have written here $z = e^{-\epsilon/T}$,

$$\operatorname{ch}\lambda = (1-2z^2)/2z^2, \quad \text{when } z<1/2; \quad z=1/2 \leftrightarrow \lambda=0,$$
$$\cos\mu = (1-2z^2)/2z^2, \quad \text{when } z>1/2: \quad z=1/2 \leftrightarrow \mu=0. \tag{A.13}$$

The value $z = 1/2$ corresponds to the phase transition point near which, both above and below, we have the same asymptotic expansions with zero radius of convergence:

$$f = 2\ln\left(\frac{\Gamma(1/4)}{2\Gamma(3/4)}\right)-\frac{\varepsilon}{T}+\frac{1}{2}\sum_{n=1}^{\infty}\frac{B_{2n}\mu^{2n}}{n(2n)!}[(-1)^n-|E_{2n}|], \tag{A.14}$$

where B_{2n} and E_{2n} are the alternating Bernoulli and Euler numbers, respectively.

The fact that the asymptotic expansions are the same indicates that all thermodynamic functions and their derivatives of any order are continuous in the phase transition point, i.e., the system has an "infinite-order" phase transition. However, in the temperature range $T < T_C$ there exists some ordered state.

The expansion of the function f in powers of $\zeta = z - 1/2$ has the form

$$f = f_0 + {}^2/_3\zeta + {}^{106}/_{45}\zeta^2 + \dots \tag{A.15}$$

The internal energy and the specific heat at $T = T_C$ are, respectively, equal to

$$\mathscr{E} = \varepsilon/3, \quad C = {}^{68}/_{45}\,(\ln 2)^2. \tag{A.16}$$

APPENDIX B

To evaluate the spontaneous polarization and the susceptibility of the model with impurities it is necessary for us to study the equation (A.5) of the model without impurities for $\zeta \ll 1$, i.e., for $(\pi - \mu) \ll \pi$. It turns out that under those conditions Eq. (A.5) can be solved for any value of b, i.e., for any value of the polarization p (in ref. 8, the results of which were used by Lieb,[6] this equation was solved only for $b \gg 1$, i.e., $p \ll 1$ and for $b \ll (\pi - \mu)$, i.e., for $\sqrt{(1 - p)} \gg \pi - \mu$). As the inhomogeneous term tends to zero as $(\pi - \mu) \to 0$, we transform Eq. (A.5) using (A.7) and integrating both sides over α:

$$2\operatorname{arctg}\left[\operatorname{th}\frac{\alpha}{2}\operatorname{tg}\frac{\pi-\mu}{2}\right] = \frac{1}{\pi}\int_{-b}^{b}\operatorname{arctg}\left[\frac{\operatorname{tg}(\pi-\mu)}{\operatorname{th}(\alpha-\beta)/2}\right]R(\beta)\,d\beta. \tag{B.1}$$

We have taken here on the right-hand side the normal branch of the arctan which has a discontinuity of π at the point $\alpha = \beta$ so that for $\tanh\frac{1}{2}(\alpha - \beta) \gg \tan(\pi - \mu)$ we have

$$\operatorname{arctg}\left[\frac{\operatorname{tg}(\pi-\mu)}{\operatorname{th}(\alpha-\beta)/2}\right] \sim \frac{\operatorname{tg}(\pi-\mu)}{\operatorname{th}(\alpha-\beta)/2}.$$

If $(\pi - \mu) \ll \pi$ and $(\pi - \mu) \ll b$, we can write Eq. (B.1) in the form

$$\operatorname{th}\frac{\alpha}{2} = \frac{1}{\pi}\int_{-b}^{b}\frac{R(\beta)\,d\beta}{\operatorname{th}(\alpha-\beta)/2} - 2(\pi-\mu)\frac{dR(\alpha)}{d\alpha}. \tag{B.2}$$

Strictly speaking this equation is, because of the last term, valid everywhere except in a small neighborhood, of the oder of $(\pi - \mu)$, of the ends. However, the contribution of this neighborhood to the final result is unimportant. Expressing the tanh in the denominator of the integral in terms of the tanhs of $\alpha/2$ and $\beta/2$, using the fact that $R(\beta)$ is an even function, and changing variables,

$$\operatorname{th}\frac{\alpha}{2} = \operatorname{th}\frac{b}{2}\cos\varphi,$$

we get the equation

$$\operatorname{th}\frac{b}{2}\cos\varphi = \frac{1}{\pi}\int_{0}^{\pi}\frac{R(\varphi')\sin\varphi'\,d\varphi'}{\cos\varphi-\cos\varphi'} + (\pi-\mu)\frac{1-\operatorname{th}^2(b/2)\cos^2\varphi}{\operatorname{th}(b/2)\sin\varphi}\frac{dR(\varphi)}{d\varphi} \tag{B.3}$$

which can be solved, using the well-known expansion

$$\frac{\sin\varphi'}{\cos\varphi-\cos\varphi'} = 2\sum_{n=1}^{\infty}\cos n\varphi\sin n\varphi'.$$

In zeroth approximation, neglecting the last term in (B.3) we find

$$R(\varphi) = \operatorname{th}\frac{b}{2}\sin\varphi$$

and, substituting this result into (A.6) and (A.8) we get

$$f(z) = \zeta(1-p^2), \quad \zeta = z - 1/2 \ll 1. \tag{B.4}$$

To find the solution of Eq. (B.3) in first order in $(\pi - \mu)$ we substitute into the differential term of this equation the zeroth order solution which we found. Finally, we get

$$f(z,p) = \zeta(1-p^2)+\frac{4}{3\pi}\zeta^{3/2}(1-p^2)^{3/2}, \quad \zeta = z-\frac{1}{2} \ll 1-p^2. \tag{B.5}$$

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Translated by D. ter Haar
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