

New type of transitions in the Ising model with nonequivalent sublattices

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(Submitted January 23, 1980)

Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 7, 385–388 (5 April 1980)

It is shown that in the model of interacting linear Ising spin chains in an asymmetrical potential, the short-range correlations can lead to a splitting of the continuous transition into two transitions, one of which is a first-order transition.

PACS numbers: 5.50. + q

It is known that crystals, in which the ordered “dipoles” in a highly symmetrical phase have two nonequivalent (asymmetrical) equilibrium positions, exhibit various and often unique physical properties. The most successful microscopic model, which reflects the influence of the asymmetry parameter on the phase transition, was proposed by Mitsui for Rochelle-salt crystal (see, for example, Ref. 1). However, an investigation of the properties of different substances on the basis of this model was conducted primarily in the molecular-field (MF) approximation, which is often inadequate even for a qualitative description of experimental data in crystals of the Rochelle-salt group.² This important fact indicates that substances with an asymmetrical arrangement of the ordered ions are a rare and curious example of a system for which MF theory does not correctly describe the general thermodynamic mechanisms. Therefore, attempts to find more precise methods of studying the phase transitions in these systems are desirable. It will be shown in this paper that a simple consideration of short-range forces in the Mitsui model can lead to a new, qualitative effect—a splitting of the continuous phase transition into two transitions, close in temperature, that are not realized within the framework of the MF approximation.

Let us examine a model consisting of two linear Ising spin chains in an asymmetrical potential. We shall describe the interactions between the chains and the not nearest neighbors in the MF approximation. However, we shall determine exactly the interaction of nearest neighbors in the chains. We write the Hamiltonian of the problem in the form

$$H = -V \sum_i (s_i s_{i+1} + \sigma_i \sigma_{i+1}) - H_1 \sum_i s_i - H_2 \sum_i \sigma_i + \frac{J}{2} (\langle s \rangle^2 + \langle \sigma \rangle^2) + K \langle s \rangle \langle \sigma \rangle, \quad (1)$$

where $s_i, \sigma_i = \pm 1$ refer to the first and second chains (sublattices) and V is the interaction potential in the sublattices. The longitudinal “fields” $H_{1,2}$ are defined as follows:

$$H_1 = J \langle s \rangle + K \langle \sigma \rangle + \Delta ; \quad H_2 = J \langle \sigma \rangle + K \langle s \rangle - \Delta . \quad (2)$$

In Eqs. (1) and (2) K and J are the interaction constants between the chains and the not nearest neighbors, respectively, $\langle s \rangle$ and $\langle \sigma \rangle$ are the average polarization values in dipole-moment units, and Δ is the asymmetry parameter. If we introduce the following dimensionless values

$$a = (K - J) R , \quad \gamma = \Delta R , \quad t = TR , \quad v = VR , \quad R = (K + J)^{-1} ,$$

$$L = \exp(-4v/t), \quad \xi = \frac{\langle s \rangle + \langle \sigma \rangle}{2}, \quad \eta = \frac{\langle s \rangle - \langle \sigma \rangle}{2},$$

$$\frac{\xi}{t} = x , \quad z = \frac{\gamma - a\eta}{t},$$

which are convenient for further discussion, then the expression for the free energy assumes the form

$$F = \xi^2 - a\eta^2 - t \{ \ln [\cosh(z+x) + (\sinh^2(z+x) + L)^{1/2}] + \ln [\cosh(z-x) + (\sinh^2(z-x) + L)^{1/2}] \}. \quad (3)$$

The equilibrium values of the polarization ξ and antipolarization η can be determined from the minimum conditions

$$\left(\frac{\partial F}{\partial \xi} \right)_{\eta} = \left(\frac{\partial F}{\partial \eta} \right)_{\xi} = 0. \quad (4)$$

The results of a study of Eq. (4) and free energy (3) as a function of the energy parameters a and γ are shown in Fig. 1 [curve AC corresponds to $v = 2.5$; AD corresponds to the MF approximation¹ with $V = 0$ in (1)]. In regions I, II, and III the ferroelectric phase ($\xi \neq 0$) is preserved to absolute zero temperatures; in region III the transitions to the polar state are first-order transitions and in regions I and II they are second-order transitions; in region IV the ferroelectric phase exists at intermediate temperatures; in region V the state with $\xi \neq 0$ does not appear. Compared with the MF results, allowance for the short-range correlations, first, "deforms" the phase diagram, expands region III, and narrows region IV (the boundary AP evidently remains the same as before); secondly, it leads to the appearance of the new region VI, in which three transitions successively occur with decreasing temperature: to the polar phase with a bell-shaped polarization behavior, to a state with no polarization and to a phase in which the ferroelectric properties are retained to $T = 0$. The function $\xi(T)$ in region

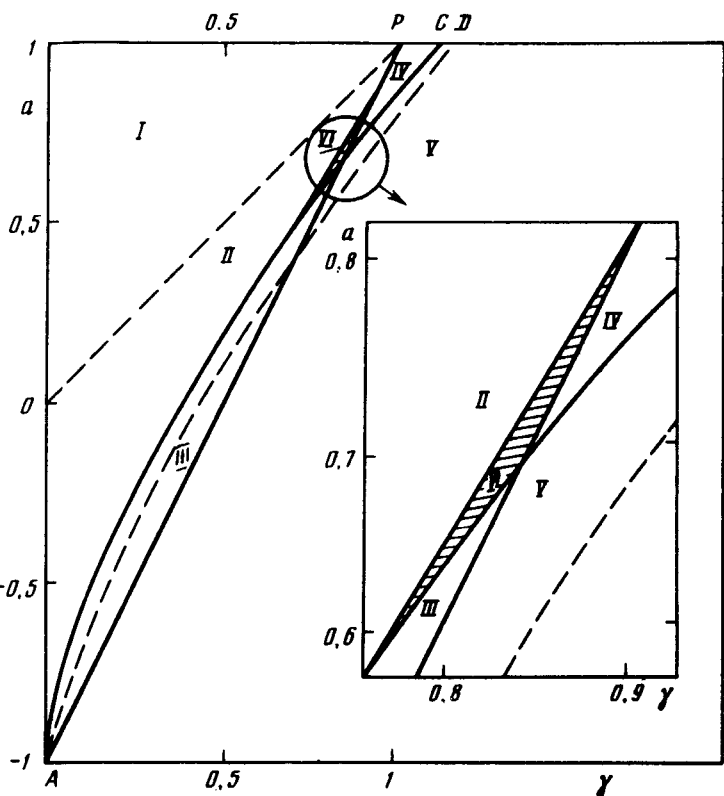


FIG. 1. Phase diagram for the model (1) in the a - γ coordinates.

VI is shown in Fig. 2. As an analysis shows, our results are almost independent of v , starting with $2v/T_{c1} \gtrsim 1$. An important fact here is that region VI is retained when the approximation is refined, for example, by adding the term $u \sum_i s_i \sigma_i$ to Eq. (1), where u corresponds to interaction between the chains and K describes the interaction between

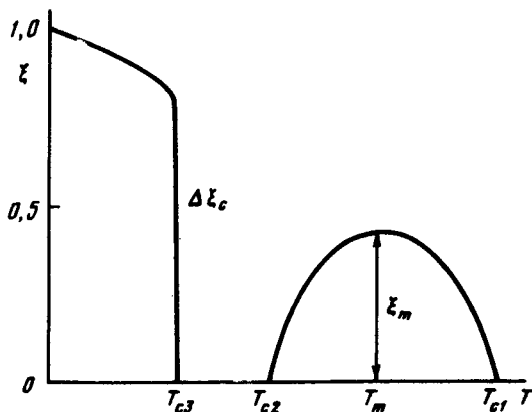


FIG. 2. Schematic representation of the temperature dependence $\xi(T)$ in region VI ($T_{c1} > T_{c2} > T_{c3}$). For $a = 0.7$, $\gamma = 0.841$, and $v = 2.5$ the ratios are $T_{c3}/T_{c1} = 0.66$, $T_{c2}/T_{c1} = 0.76$, $\tau = 0.07$, $\Delta\xi_c = 0.87$, and $\xi_m = 0.3$.

the chains that are not the nearest. The appearance of the unusual behavior of $\xi(T)$ in region VI is apparently due to the following causes. As is known,¹ in the MF approximation for $a < \gamma$ there are two points T_{01} and T_{02} at which the derivative $(\partial^2 F / \partial \xi^2)_{\xi=0}$ becomes zero. In region II, however, the polarization does not disappear at $T = T_{02}$ in the MF approximation because at these T values a deeper minimum exists in the free energy $F(\xi \neq 0)$ than for $T(\xi = 0)$ and it is not advantageous for the system to be in the state with $\xi = 0$. The short-range correlations, as can easily be proved, lead to the fact that the quantity $F(\xi = 0, T_{02})$ is smaller than $F(\xi \neq 0, T_{02})$ in a narrow interval of the parameters a and γ , and spontaneous polarization vanishes at $T_{02} = T_{c2}$. At low T the stable state is the phase with $\xi \rightarrow 1, \eta \rightarrow 0$, and then a first order phase transition occurs with decreasing $T < T_{c2}$ at the point T_{c3} . Thus, short-range action leads to the fact that the phase transition to the ferroelectric phase ($\xi = 1$) occurs via an intermediate state that is not energetically advantageous from the viewpoint of MF theory, and the "splitting temperature interval" $\tau = (T_{c2} - T_{c3}) / (T_{c2} + T_{c3}) \ll 1$ for any v . The described model apparently describes quite completely the quasi-one-dimensional structures in which the transverse interactions are small compared with the longitudinal interactions. However, we can assume that it will also be useful for a qualitative study of thermodynamic features in the three-dimensional case. Thus, in the $(\text{ND}_4)_3 \text{D}(\text{SO}_4)_2$ crystal belonging to the Rochelle salt group, the temperature dependence of the spontaneous polarization corresponding to region VI was observed in Ref. 3: $\xi_m / \xi_s \approx 0.42, \Delta \xi_c / \xi_s \approx 0.8, \tau \approx 0.06$, where ξ_s is the experimental value of saturation polarization. When D is completely replaced by $H, \tau = 0$ and the behavior of $\xi(T)$ is characteristic of region II.³

The authors wish to thank V. G. Vaks and A. P. Levanyuk for valuable advice and discussion of this work.

¹V. G. Vaks, *Vvedenie v mikroskopicheskuyu teoriyu segnetoelektrikov* (Introduction to the Microscopic Theory of Ferroelectrics), Moscow, 1973, p. 23.

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