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Published online: 07 Feb 2011.

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# ORDER–DISORDER TYPE PHASE TRANSITIONS WITH TWO-ORDER PARAMETERS

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The model of phase transitions with two-order parameters is considered. Every order parameter is related to the ordering of radicals in a crystal. The radicals move in symmetric (asymmetric) double-well type potential above $T_c$. The thermodynamics of the model is discussed in a mean-field approximation.

The unusual dependence of order parameters, such as spontaneous polarization, has been observed in experimental study of the structural phase transitions in some crystals. The ferroelectric and structural phase transitions in such crystals as $(NH_4)_2SO_4$ (AS), $NH_4HSO_4$ (AHS), $(NH_4)_2BeF_4$ (AFB), $Ca_2Sr(C_2H_5COO_6)$ (DSP) can be taken as examples.

It has been shown that the unusual behaviour of spontaneous polarization in AS and DSP crystals can be related to the presence of two coupling order parameters.[1-3] On the basis of experimental data the conclusion has been made about tetrahedral ordering groups $NH_4$ in AS[4] and $SO_4$ in AHS.[5] These groups move in the double-well potentials in the paraelectric phase. It has been found recently that the same crystals are twinned in the paraelectric phase.[6,7] The paraelectric phase was assumed to be a slightly distorted form of a higher symmetrical structure and the distortions are caused by the partial ordering of structural elements.

The purpose of this paper is to discuss the phase transitions in a model with two-order parameters related to the ordering of structural elements in a crystal. Below we shall refer to the ordering groups of one sort as "spins" of the lattice $\Sigma$, and to another one as "spins" of the lattice $S$.

The Hamiltonian of the model is written as[8]

$$H = -\tfrac{1}{2} \sum_{ij} J_{ij}(\sigma_i^{zI} \sigma_j^{zI} + \sigma_i^{zII} \sigma_j^{zII})$$

$$-\tfrac{1}{2} \sum_{ij} I_{ij}(S_i^{zI} S_j^{zI} + S_i^{zII} S_j^{zII}) - \sum_{ij} K_{ij} \sigma_i^{zI} \sigma_j^{zII}$$

$$- \sum_{ij} L_{ij} S_i^{zI} S_j^{zII} - \sum_{ij} M_{ij}(\sigma_i^{zI} S_j^{zI} + \sigma_i^{zII} S_j^{zII})$$

$$- \Delta_1 \sum_i (\sigma_i^{zI} - \sigma_i^{zII}) - \Delta_2 \sum_i (S_i^{zI} - S_i^{zII})$$

$$- E \sum_i [(p_1(\sigma_i^{zI} + \sigma_i^{zII}) + p_2(S_i^{zI} + S_i^{zII})], \tag{1}$$

where $\sigma^z, S^z$ are the Pauli matrices describing the movement of the spins of $\Sigma$ and $S$ types in double-well potentials. I and II are the indices of sublattices in $\Sigma$ and $S$ with deep minima on the left and right, respectively. $\Delta_1$ and $\Delta_2$ are the asymmetry values of the $\Sigma$ and $S$ lattices potential, respectively. $E$ is the external electric field, $p_1$ and $p_2$ are the effective dipole moments per one "spin" in $\Sigma$ and $S$ lattices.

The qualitative results of the model solved for some cases in mean-field approximation were discussed in Ref. 9.

Here we will discuss the case when the spins of the lattices $\Sigma$ and $S$ move in the asymmetric and symmetric potential, respectively, i.e. in (1) $\Delta_1 \neq 0$, $\Delta_2 = 0$ and will suppose that "antiferromagnetic" interaction between the "spins" in lattice $S$ takes place. Hamiltonian in mean-field approximation is written as:

$$H_{M.n.} = \tfrac{1}{2}J(\langle \sigma^{zI} \rangle^2 + \langle \sigma^{zII} \rangle^2) + K\langle \sigma^{zI} \rangle \langle \sigma^{zII} \rangle$$

$$+ I\langle S_a^z \rangle \langle S_b^z \rangle + M(\langle \sigma^{zI} \rangle \langle S_a^z \rangle + \langle \sigma^{zII} \rangle \langle S_b^z \rangle)$$

$$- (J\langle \sigma^{zI} \rangle + K\langle \sigma^{zII} \rangle + \Delta_1 + M\langle S_a^z \rangle) \sigma^{zI} - (J\langle \sigma^{zII} \rangle$$

$$+ K\langle \sigma^{zI} \rangle - \Delta_1 + M\langle S_b^z \rangle) \sigma^{zII} - (I\langle S_b^z \rangle$$

$$+ M\langle \sigma^{zI} \rangle)S_a^z - (I\langle S_a^z \rangle + M\langle \sigma^{zII} \rangle)S_b^z, \tag{2}$$

where $J = \sum_{ij} I_{ij}$, $I = \sum_{ij} I_{ij}$, $K = \sum_{ij} K_{ij}$, $M = \sum_{ij} M_{ij}$

are the mean constants of interaction. The free energy is given by:

$$f = \xi^2 - a\eta^2 + b(\sigma^2 - \phi^2) + 2c(\xi\sigma + \eta\phi)$$

$$- t[\ln 2 \, ch\beta(\gamma - a\eta + \xi + c\sigma + c\phi) + \ln 2ch\beta(\gamma$$

$$- a\eta - \xi - c\sigma + c\phi) + \ln 2ch\beta(b\sigma - b\phi + c\xi$$

$$+ c\eta) \ln 2ch\beta(b\sigma + b\phi + c\xi - c\eta)], \qquad (3)$$

where

$$f = F/(K + I), \qquad a = \frac{K - I}{K + I}, \qquad \gamma = \frac{\Delta_1}{K + I},$$

$$b = \frac{I}{K + I}, \qquad c = \frac{M}{K + I}, \qquad t = T/(K + I),$$

$$\beta = 1/t, \qquad \xi = \tfrac{1}{2}(\langle\sigma^{zI}\rangle + \langle\sigma^{zII}\rangle),$$

$$\eta = \tfrac{1}{2}(\langle\sigma^{zI}\rangle - \langle\sigma^{zII}\rangle), \qquad \sigma = \tfrac{1}{2}(\langle S_a^z\rangle + \langle S_b^z\rangle),$$

$$\varphi = \tfrac{1}{2}(\langle S_a^z\rangle - \langle S_b^z\rangle)$$

Values $\xi, \eta, \sigma, \phi$ can be found from

$$\xi = \tfrac{1}{2}(th1 - th2)$$
$$\eta = \tfrac{1}{2}(th1 + th2)$$
$$\sigma = \tfrac{1}{2}(th3 + th4)$$
$$\phi = \tfrac{1}{2}(th3 - th4)$$

$$(4)$$

$$th1 \equiv th\beta(\gamma - a\eta + \xi + c\sigma + c\phi)$$
$$th2 \equiv th\beta(\gamma - a\eta - \xi - c\sigma + c\phi)$$
$$th3 \equiv th\beta(b\sigma - b\phi + c\xi + c\eta)$$
$$th4 \equiv th\beta(b\sigma + b\phi + c\xi - c\eta)$$

Thermodynamics of the model can be obtained from the analysis of Eqs. (3) and (4). To study temperature dependencies of order parameters at different values of constants $a$, $b$, $c$, $\gamma$, these equations were investigated with the help of a computer. The analysis shows that different solutions can be obtained for different values of the parameters. As an example, the temperature dependencies of the order parameters for definite sets of $a$, $\gamma$, $b$, $c$ are shown in Figure 1.

The case which is shown in Figure 1c will be discussed below. In this case the temperature behaviour of the spontaneous polarization corresponds to the experimental results for the $NH_4HSO_4$ crystal.

The model of the ferroelectric phase transitions in the AHS was solved by Blat and Zinenko.[10]

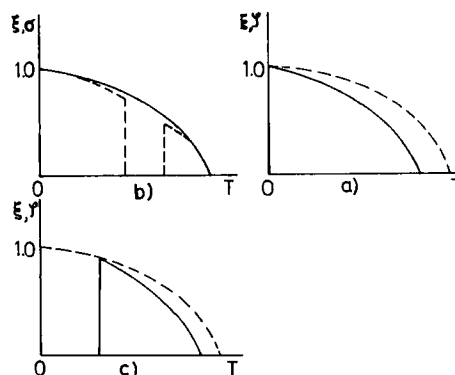In the model it was supposed that the phase transitions in AHS are due to the ordering of $SO_4$



FIGURE 1 Qualitative temperature dependence of order parameters: (a), (c) ("antiferromagnetic" interaction in the lattice $S$). Solid line—polarization of $\Sigma$; dotted line—antipolarization of $S$. (b) ("ferromagnetic" interaction) the solid and dotted lines—polarizations of $\Sigma$ and $S$, respectively.

groups. The result of the paper[6] where it has been shown that AHS is twinned in the paraelectric phase was not taken into consideration in the theory.[10]

If we suppose that besides the $SO_4$ groups there are some other ordering structural elements in AHS, the experimentally observed phase transitions in AHS corresponds to the case shown in Figure 1c.

For the values of parameters $I = 140°$, $K = 160°$, $\Delta_1 = 90°$, $I = 190°$ and $M = 90°$ the transition temperatures are $T_{O_2} = 270°K$ and $T_{O_1} = 160°K$. The upper transition temperature is then $T_{O_1} = 550°K$. Below $T_{O_1}$ one of the sublattices of the AHS crystal is ordered (see Figure 1c). The twinning in the paraelectric phase is the result of the ordering. The value $T_{O_1}$ is considerably higher than the melting point. The temperature dependence of AHS polarization below $T_{O_2}$ at the parameter values listed above is shown in Figure 2. More detailed results of the model theory will be published elsewhere.
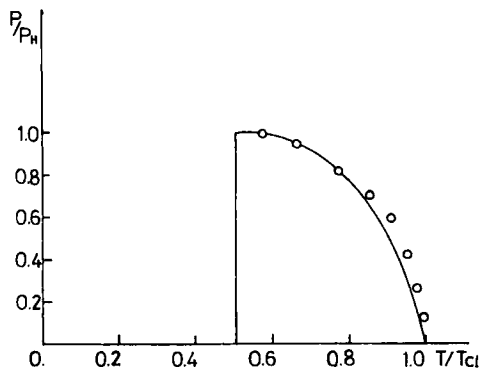


FIGURE 2 The temperature dependence of the spontaneous polarization of the crystal $NH_4HSO_4$ (solid line—theory, points—experiment).

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