Ferroelectrics

ISSN: 0015-0193 (Print) 1563-5112 (Online) Journal homepage: https://www.tandfonline.com/loi/gfer20

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To cite this article: V. I. Zinenko , D. H. Blat & K. S. Aleksandrov (1980) The theory of the phase transitions in the crystals MeIMeIIBX4, Ferroelectrics, 29:1, 201-204, DOI: 10.1080/00150198008008480

To link to this article: https://doi.org/10.1080/00150198008008480

Published online: 16 Mar 2011.

Ferroelectrics, 1980, Vol. 29, pp. 201–204
0015-0193/80/2903-0201$06.50/0

THE THEORY OF THE PHASE TRANSITIONS IN THE CRYSTALS $Me^{I}Me^{II}BX_4$†

V. I. ZINENKO, D. H. BLAT, and K. S. ALEKSANDROV

L. V. Kirensky Institute of Physics, USSR Academy of Sciences, 660036 Krasnoyarsk, U.S.S.R.

(*Received September 3, 1979*)

The model of the order-disorder phase transitions in crystals $Me^{I}Me^{II}BX_4$ is investigated in a mean field approximation. It is supposed in the model that group BX_4 in the α-phase (D^4_{6h}) moves in four-well potential.

In recent years much attention has been paid to a large family of crystals with general formula $Me^{I}Me^{II}BX_4$.[1,2] It was shown experimentally that the majority of the crystals has the order-disorder phase transitions which are due to the ordering of the tetrahedral groups. The tetrahedral groups have two or more equivalent equilibrium orientations in the paraelectric phase. It has been shown recently that some crystals ($(NH_4)_2SO_4$ for example)[3] have a domain structure in the paraelectric phase. Thus this phase is a distorted form of the higher symmetry phase with space group D^4_{6h} ($Z = 2$).

In this paper the basic results of the statistical model of the phase transitions in crystals $Me^{I}Me^{II}$-BX_4 and the thermodynamical properties of the model will be discussed. More detailed analysis of the model is given in the paper.[4]

Let us suppose the initial phase for all crystals of the family to be hexagonal α-phase with the space group D^4_{6h} ($Z = 2$). The projection of the structure of $Me^{I}Me^{II}BX_4$ in α-phase is shown in Figure 1. It is considered in the model that BX_4 groups in α-phase move among four potential wells. Four possible equilibrium orientations of BX_4 group are shown in Figure 1. These positions are described by the operator $C_i(R)$ which is equal to 1, when a molecule in R unit cell has the orientation i. The mean value of the operator $C_i(R)$ describes the probability of the state. It was found experimentally that the crystals $Me^{I}Me^{II}BX_4$ in the paraelectric β-phase belong to the space group D^{16}_{2h} ($Z = 4$) and the ordered phase of the crystals is one of the four phases: γ-phase (C^9_{2v} ($Z = 4$)), δ-phase (C^5_{2h}($Z = 4$)), φ-phase (C^5_{2h}($Z = 8$)), ε-phase (C^9_{2v} ($Z = 8$)). Therefore the phase transition $\alpha \rightarrow \beta$ is followed by the doubling of the α-phase unit cell volume, the phase transitions from β-phase into one of the ordered phases take place either without changing or with the doubling of the β-phase unit cell volume. For the explanation of such change of the unit cell volume the matrices of

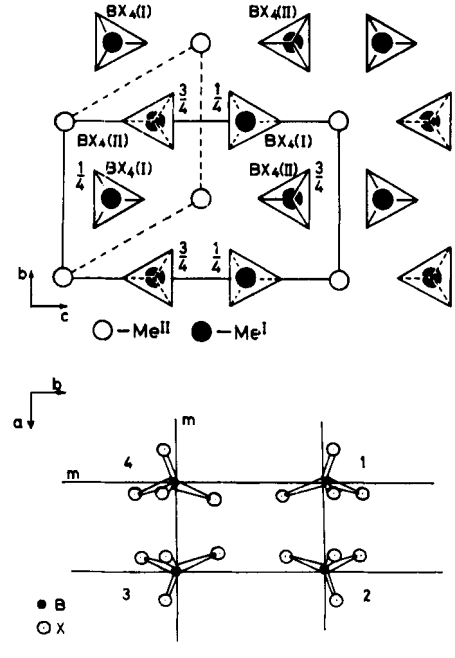

FIGURE 1a The projection of the crystal on the *ab* plane. b) Four equivalent equilibrium orientations of the group BX_4 in α-phase.

† Paper presented by I. Aleksandrova at 4th European Meeting on Ferroelectricity, Portoroz, Yugoslavia, September 1979).

interaction corresponding to vectors $k_0 = 0$, $k_1 = \frac{1}{2}b_1$, $k_2 = \frac{1}{2}b_2$, $k_3 = \frac{1}{2}(b_1 + b_2)$ in Brillouin zone of α-phase were taken into account in calculating the free energy. Each matrix has four eigenvalues which are parameters of the theory. Depending on the relations between these constants the second-order phase transitions into one of the ordered phases through the partly ordered intermediate β-phase are possible in the model. In β-phase the groups BX_4 occupy preferably and with the equal probability two of the four orientations.

The first-order phase transitions between the ordered phases are possible in the model too. Such possibility appears according to the following reason. Let us consider for example the first-order phase transition between γ and φ-phases. At $T = 0$ the free energies of the phases are

$$F_\gamma = -(a + b + c), \qquad F_\varphi = -(a + p + q), \quad (1)$$

where a, b, c, p, q are the parameters of the model, which are linear combinations of the interaction matrices eigenvalues. It is seen from (1) that the phase with the larger sum of the interaction constants will correspond to the ground state of the crystal. The temperature of the phase transition from the β-phase into γ and φ-phases is given by

$$t_0^\gamma = b + c - \frac{bc}{b + c}\Delta$$

$$t_0^\varphi = p + q - \frac{pq}{p + q}\Delta, \qquad \Delta = th\beta a\eta_{11} \quad (2)$$

where η_{11} is the order parameter of the phase transition $\alpha \to \beta$. It is seen from (1), (2) that, for example $(b + c) < (p + q)$ and $t_0^\gamma > t_0^\varphi$ the succession of the phase transitions $\alpha \to \beta \to \gamma \to \varphi$ takes place. The temperature t_c of the first-order phase transition can be obtained from the equation $F_\gamma(t_c) = F_\varphi(t_c)$.

Some crystals of the family $Me^{I}Me^{II}BX_4$ in which the successions of phase transitions are experimentally observed (excluding the phase transition $\alpha \to \beta$) are given in Table I. The temperature dependencies of the order parameters

TABLE I

Successions of phase transitions	Crystals
$(\alpha) \to \beta \to \gamma$	$(NH_4)_2SeO_4$
$(\alpha) \to \beta \to \varepsilon' \to \varepsilon$	$(NH_4)_2BeF_4$
$(\alpha) \to \beta \to \gamma \to \phi$	$(NH_4)LiSO_4$

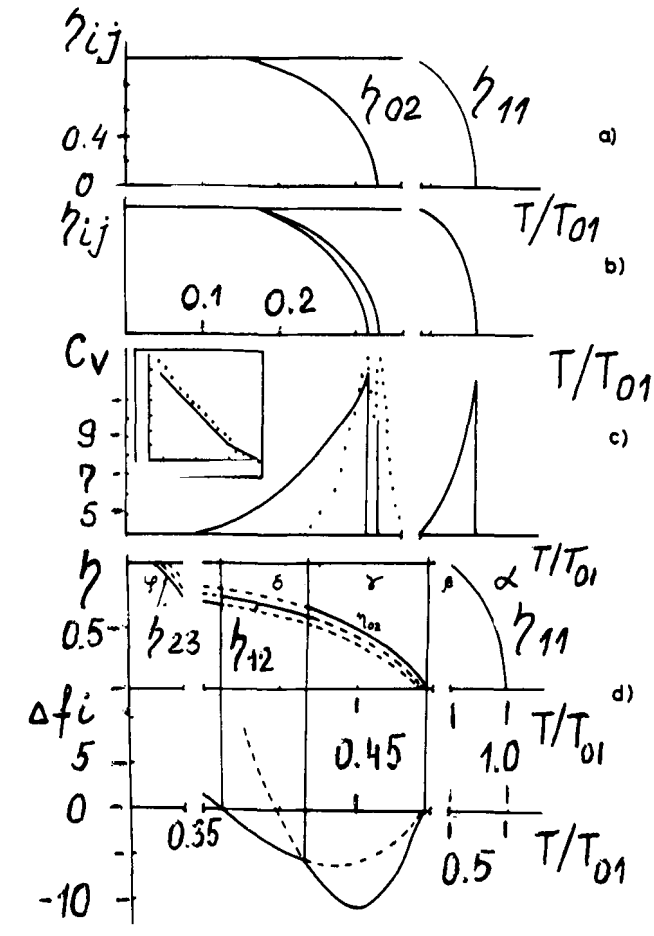

FIGURE 2 The temperature dependences: a) of the order parameters for the succession of phase transitions $\alpha \to \beta \to \gamma$ b), c) of the order parameters, specific heat and birefringence for the succession of phase transitions $\alpha \to \beta \to \varepsilon' \to \varepsilon$. The experimental temperature dependence of the specific heat[5] and birefringence[6] are shown by dots. d) of the order parameters and the free energies differences for the succession of phase transitions $\alpha \to \beta \to \gamma \to \delta \to \phi$.

TABLE II

	$(NH_4)_2SO_4$		$(NH_4)_2BeF_4$	
	Theory	Experiment	Theory	Experiment
T_{c1}	670.3	–	550	–
T_{c2}	223	223	183	183
T_{c3}	–	–	177	177.2
$\Delta S_1/R$	1.35	–	1.35	–
$\Delta S_2/R$	1.32	1.85	0.06	–
$\Delta S_3/R$	–	–	1.36	–
C	2	10	–	–

and the free energies differences are shown in Figure 2. The theoretical and experimental thermodynamical characteristics of the phase transitions in the crystals $(NH_4)_2SO_4$ and $(NH_4)_2BeF_4$ are given in Table II.

The model can basically describe the phase transitions in the crystals of the family $Me^{I}Me^{II}BX_4$ and be a ground for more detailed investigations. It should be noted that in some crystals of the family so-called incommensurate phases have been observed. The model[4] does not explain the phase transition into these phases.

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