Microscopic model of phase transition in the crystals of DMAAlS and DMAGaS type

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The four-state model is proposed for description of phase transition in ferroelectric crystals of DMAGaS and DMAAlS type. Thermodynamical functions of the model are obtained in the mean field approximation. The phase transition between paraelectric and ferroelectric phases is investigated. It is established that order of the phase transitions depends on relations between model parameters.

**Keywords:** DMAAlS, DMAGaS, ferroelectrics, phase transitions, quantum statistical model

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1 Introduction

A peculiar feature of isomorphous crystals with ferroelectric properties (CH$_3)_2$NH$_2$Al(SO$_4$)$_2$·6H$_2$O (DMAAlS) and (CH$_3)_2$NH$_2$Ga(SO$_4$)$_2$·6H$_2$O (DMAGaS) is the possibility of existence in three different phases at change of temperature: at room temperature crystal is paraelectric, at lowering of temperature it sequentially becomes ferroelectric and antiferroelectric state [1, 2, 3, 4].

It has been measured $T_{c1} = 136$ K and $T_{c2} = 113$ K [4] (or 122 K and 114 K respectively [3]) for DMAGaS crystal, but it has been only found $T_{c1} = 150$ K [1, 2, 3] for DMAAlS. The phase transition between the ferroelectric and antiferroelectric phases is of the first order [3, 4]. The phase transition paraelectric – ferroelectric is of the first order close to the second one in DMAGaS and of the second order in DMAAlS. Crystallographic analysis shows that in all three phases crystal belongs to monoclinic space groups: high-temperature paraelectric phase has P2$_1$/n space group [1, 2], ferroelectric and antiferroelectric ones have Pn [2, 3] and P2$_1$ [3] groups respectively. It should be mentioned that low-symmetry space groups are subgroups of the high-symmetry group obtained by the loss of rotation axis and mirror plane, respectively (point symmetry group 2/m changes to m or 2).

Data of investigation of various physical properties of the crystals were presented in a range of publications. First of all it should be mentioned dielectric, pyroelectric and dilatometric measurements [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15], ultrasonic and NMR investigations [13, 14, 15], studies of relaxational dynamics and lattice dynamics [16, 17] by
Figure 1: Projection of N and C atoms in the dimethylammonium groups of DMAGaS crystal at ambient temperature onto the XZ plane (position indices are indicated in parenthesis). The Y coordinates of atoms are as follows: $Y_{N(1,1)}=-0.1469\ \text{Å}, Y_{N(1,2)}=0.1469\ \text{Å}, Y_{N(1,3)}=-0.6736\ \text{Å}, Y_{N(1,4)}=0.6736\ \text{Å}, Y_{N(2,1)}=5.5099\ \text{Å}, Y_{N(2,2)}=5.2161\ \text{Å}, Y_{N(2,3)}=4.6894\ \text{Å}, Y_{N(2,4)}=6.0366\ \text{Å}, Y_{C(1,1)}=-0.2606\ \text{Å}, Y_{C(1,2)}=0.2606\ \text{Å}, Y_{C(2,1)}=5.6236\ \text{Å}, Y_{C(2,2)}=5.1024\ \text{Å}$.

Figure 2: Projection of N atoms onto the plane perpendicular to the C–C$'$ axis of the dimethylammonium group.
means of radiospectroscopy and Raman spectroscopy methods. Such issues as dielectric anomalies in the vicinity of phase transition points (mainly near $T_{c1}$), clarification of the order of phase transition, dynamics of ionic groups and protons on hydrogen bonds in the wide range of temperatures [16, 17], influence of external hydrostatic pressure [13, 19, 21] were considered. Temperatures of phase transitions were justified; according to the latest data $T_{c1} = 136$ K, $T_{c2} = 117$ K (DMAGaS) and $T_{c1} = 155$ K (DMAAlS).

Crystals DMAAlS and DMAGaS belong to the type of ferroelectrics which have some structural elements which reorientation leads to polarisation of crystal. In this case the element, which can be reoriented, is the dimethylammonium cation (more strictly NH$_2$ group). Crystals contain two symmetrically nonequivalent DMA groups per unit cell (Fig. 1).

DMA can occupy four equilibrium positions which are related in pairs by inversion centre forming a slightly deformed cross (Fig. 2). It is very likely that this asymmetry (and corresponding difference of energies of interaction between groups in various positions) is responsible for so complicated behaviour of the crystal. In the paraelectric phase the site in one pair is occupied with probability 40% and in another with probability 10% at 300 K.

Possible role of reorientations of DMA groups in phase transitions of the considered family of crystals was pointed out in a range of articles [3, 6, 14, 21]. This assumption is directly confirmed by the data of structural investigations [14, 21]. Performed recently NMR measurements [14] have proved that reorientations and orderings of DMA groups can be considered as an origin of ferroelectrics (F) and antiferroelectrics (AF) phase transitions while other changes in a lattice structure (rotations of SO$_4$ groups, freezing of protons in certain positions on hydrogen bonds) are just accompanying phenomena.

So for theoretical description of phase transitions to ferro- and antiferroelectric states in DMAAlS and DMAGaS crystals and development of appropriate microscopic model one should take into account reorientation of DMA groups on and their influence on the state of crystal. Such an approach is a main goal of the present paper. Our task is to formulate this type model, to introduce order parameters responsible for appearance of low-symmetry phases, to calculate thermodynamical potential proceeding from the model and to investigate thermodynamically stable states. The transition from paraelectric to ferroelectric state and the dependence of the order of this transition on the system parameter values will be studied in more detail.

2 Hamiltonian of the model

In both high- and low-temperature phases ionic groups belong to two different sublattices (an elementary cell consist of two translationally nonequivalent groups). We shall characterize orientations of the groups by the spatial localization of nitrogen atoms belonging to the groups. Four possible positions of N atom are described by the Hubbard projection operators $X_{nk}^{pp}$, where $n$ is the number of a lattice site (an elementary cell), $\alpha = 1, 2$ is the sublattice index, $p = 1, \ldots, 4$ is the position number ($X_{n\alpha}^{pp} = 0$ or 1; $\sum_p X_{n\alpha}^{pp} = 1$). Energies of different positions are pairwise equivalent: $\varepsilon_1 = \varepsilon_2$, $\varepsilon_3 = \varepsilon_4$ (see notations in Figs. 1 and 2).
The model Hamiltonian can be written down as follows:

\[ H = \sum_{n\alpha p} \varepsilon_p X_{n\alpha}^{pp} - \frac{1}{2} \sum_{nn'} \sum_{\alpha \alpha'} J_{\alpha \alpha'}^{pp'} (nn') X_{n\alpha}^{pp} X_{n'\alpha'}^{pp'} , \tag{1} \]

where the first and the second terms describe energy of separate complexes and pair interaction \( J_{\alpha \alpha'}^{pp'} (nn') \) depending on their orientational states, respectively.

Further consideration will be performed in the mean field approximation. By substitution \( XX \rightarrow 2 \langle X \rangle X - \langle X \rangle \langle X \rangle \) in (1) one can obtain

\[ H_{MF} = NH_c + \sum_{n\alpha p} [\varepsilon_p - f_{\alpha p}] X_{n\alpha}^{pp} , \tag{2} \]

where the mean field is introduced

\[ f_{\alpha p} = \sum_{n'\alpha' p'} J_{\alpha \alpha'}^{pp'} (nn') \langle X_{n'\alpha'}^{pp'} \rangle \langle X_{n\alpha}^{pp} \rangle - \langle X_{n\alpha}^{pp} \rangle \langle X_{n'\alpha'}^{pp'} \rangle \] \tag{3}

and

\[ H_c = \frac{1}{2} \sum_{n'\alpha' p'} \sum_{\alpha \alpha'} J_{\alpha \alpha'}^{pp'} (nn') \langle X_{n\alpha}^{pp} \rangle \langle X_{n'\alpha'}^{pp'} \rangle \] \tag{4}

Averages \( \langle X_{n\alpha}^{pp} \rangle \) do not depend on cell number \( (\langle X_{n\alpha}^{pp} \rangle \equiv \langle X_{\alpha}^{pp} \rangle) \) due to translational symmetry which does not change at the transition to low-symmetry phases (e.g. lattice period is not doubled in antiferroelectric phase). The averages have meaning of occupation numbers of corresponding orientational states and can be grouped in linear combinations

\[ \xi_\mu = \sum_{\alpha p} U_{\mu, \alpha p} \langle X_{\alpha}^{pp} \rangle , \tag{5} \]

which transform according to irreducible representations of point symmetry group \( 2/m \) of high-temperature phase. Coefficients of transformation (5) are presented in Tab. 1. As one can see all possible irreducible representations \( (A_g, B_g, B_u, A_u) \) are realized, two linear combinations of a type of (5) belong to each of them.

Combinations \( \xi_\mu \), which are transformed according to \( B_u \) and \( A_u \) representations, are connected with differences of occupations of \( (\alpha, 1), (\alpha, 2) \) and \( (\alpha, 3), (\alpha, 4) \) positions and can play a role of order parameters for phase transitions to ferroelectric \( (B_u) \) and antiferroelectric \( (A_u) \) phases.

As one can see in Tab. 1 the first of parameters belonging to the \( B_u \) representation \( (y_+ \) describes ferroelectric ordering along the ferroelectric axis (the \( OX' \) axis in the crystallographic plane \( (ac) \)) while the second one \( (u_-) \) corresponds to antiferroelectric ordering along \( OY \) (the crystallographic axis \( b \)). For the \( A_u \) representation the ordering is inverse: the parameter \( y_- \) describes antiferroelectric ordering along \( OX' \) and the parameter \( u_+ \) defines ferroelectric ordering along \( OY \). Thus, the states of ferro- and antiferrophase observed in DMAAlS and DMAGaS crystals in reality are mixed.

Using (3) and (5) one can write down

\[ f_{\alpha p} = \sum_{\mu \mu'} (U^{-1})_{\alpha p, \mu} \tilde{j}_{\mu \mu'} \xi_{\mu'} , \tag{6} \]
where

\[ \tilde{j}_{\mu\mu'} = \sum_{\alpha p} \sum_{\alpha' p'} U_{\mu,\alpha p} j_{\alpha' \alpha'}^{pp'} (U^{-1})_{\alpha' \mu, \mu'}, \]

\[ j_{\alpha\alpha'}^{pp'} = \sum_{n'} J_{\alpha\alpha'}^{pp'} (nn'); \]

and

\[ H_c = \frac{1}{2} \sum_{\mu\mu'} \tilde{j}_{\mu\mu'} \xi_{\mu} \xi_{\mu'}. \] (8)

### 3 Free energy and equations for order parameters

Proceeding from expressions (2), (6) and (8) one can easily derive main thermodynamical functions of the model in the mean field approximation and construct a set of equations for selfconsistency parameters \( \xi_{\mu} \).

Corresponding partition function is

\[ Z = e^{-\beta NH_c} \left[ \sum_{p=1}^{4} e^{-\beta (\varepsilon_p - f_{1p})} \right]^N \left[ \sum_{p=1}^{4} e^{-\beta (\varepsilon_p - f_{2p})} \right]^N \] (9)

or

\[ Z = e^{-\beta NH_c} [2Z_1]^N [2Z_2]^N, \] (10)

where

\[ Z_1 = Q_x^+ \cosh \beta (k_{y+} + k_{y-}) + Q_z^+ \cosh \beta (k_{u+} - k_{u-}), \]

\[ Z_2 = Q_x^- \cosh \beta (k_{y+} - k_{y-}) + Q_z^- \cosh \beta (k_{u+} - k_{u-}), \] (11)

and

\[ Q_x^\pm = e^{-\beta \varepsilon_1} \exp[-\beta (k_{x+} \pm k_{x-})], \quad Q_z^\pm = e^{-\beta \varepsilon_3} \exp[-\beta (k_{z+} \pm k_{z-})], \] (12)

\[ k_{x+} = (A_1 x_+ + C_1 z_+) / 2, \quad k_{x-} = (A_2 x_- + C_2 z_-) / 2, \]

\[ k_{z+} = (C_1 x_+ + B_1 z_+) / 2, \quad k_{z-} = (C_2 x_- + B_2 z_-) / 2, \]

\[ k_{y+} = (A_3 y_+ + C_3 u_+) / 2, \quad k_{y-} = (A_4 y_- + C_4 u_-) / 2, \]

\[ k_{u+} = (C_3 y_+ + B_3 u_-) / 2, \quad k_{u-} = (C_4 y_- + B_4 u_-) / 2. \] (13)

Here such notations are introduced

\[ A_1 = a + b + g + h, \quad B_1 = e + f + l + m, \quad C_1 = c + d + j + k, \]

\[ A_2 = a + b - g - h, \quad B_2 = e + f - l - m, \quad C_2 = c + d - j - k, \]

\[ A_3 = a - b + g - h, \quad B_3 = e - f + l + m, \quad C_3 = c - d + j + k, \]

\[ A_4 = a - b - g + h, \quad B_4 = e - f - l - m, \quad C_4 = c - d - j - k, \]

\[ a = j_{11}(0), \quad b = j_{12}(0), \quad c = j_{13}(0), \quad d = j_{14}(0), \]

\[ e = j_{21}(0), \quad f = j_{31}(0), \quad g = j_{12}(0), \quad h = j_{22}(0), \]

\[ j = j_{13}(0), \quad k = j_{14}(0), \quad l = j_{33}(0), \quad m = j_{34}(0). \] (15)
Table 1: Coefficients of symmetrized occupancies of orientational states which correspond to irreducible representations of the point symmetry group 2/m.

|       | (1,1) | (1,2) | (1,3) | (1,4) | (2,1) | (2,2) | (2,3) | (2,4) |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $A_g$ | $x_+$ | 1/2   | 1/2   | 0     | 0     | 1/2   | 0     | 0     |
|       | $z_+$ | 0     | 0     | 1/2   | 1/2   | 0     | 1/2   | 1/2   |
| $B_g$ | $x_-$ | 1/2   | 1/2   | 0     | 0     | -1/2  | 0     | 0     |
|       | $z_-$ | 0     | 0     | 1/2   | 1/2   | 0     | 1/2   | 1/2   |
| $B_u$ | $y_+$ | 1/2   | -1/2  | 0     | 0     | 1/2   | -1/2  | 0     |
|       | $u_-$ | 0     | 0     | 1/2   | -1/2  | 0     | 1/2   | 1/2   |
| $A_u$ | $y_-$ | 1/2   | -1/2  | 0     | 0     | -1/2  | 1/2   | 0     |
|       | $u_+$ | 0     | 0     | 1/2   | -1/2  | 0     | 1/2   | -1/2  |

Free energy per site $F$ is

$$F = H_c - \Theta \ln(2Z_1) - \Theta \ln(2Z_2).$$  \hspace{0.5cm} (16)

By direct averaging or with the use of free energy (16) one can obtain the set of equations for the parameters $\hat{\xi}_\mu$:

$$x_{\pm} = \frac{[Z_1^{-1}Q_x^+ \cosh \beta(k_{y+} + k_{y-}) \pm Z_2^{-1}Q_x^- \cosh \beta(k_{y+} - k_{y-})]}{2},$$

$$z_{\pm} = \frac{[Z_1^{-1}Q_z^+ \cosh \beta(k_{u+} + k_{u-}) \pm Z_2^{-1}Q_z^- \cosh \beta(k_{u+} - k_{u-})]}{2},$$

$$y_{\pm} = \frac{[Z_1^{-1}Q_x^+ \sinh \beta(k_{y+} + k_{y-}) \pm Z_2^{-1}Q_x^- \sinh \beta(k_{y+} - k_{y-})]}{2},$$

$$u_{\pm} = \frac{[Z_1^{-1}Q_z^+ \sinh \beta(k_{u+} + k_{u-}) \pm Z_2^{-1}Q_z^- \sinh \beta(k_{u+} - k_{u-})]}{2}.$$

### 4 Phase transition between paraelectric and ferroelectric phases

Let us consider phase transition (PT) from paraelectric phase to the ferroelectric one which corresponds to irreducible representation $B_u$ with the two-component order parameter (OP). In this case averages $x_-, z_-, y_-$ and $u_+$ are equal to zero, averages $y_+$ and $u_-$ are the components of OP and $Z_1 = Z_2$. Then the expression for free energy (16) simplifies

$$F = H_c - 2\Theta \ln(2Z_1),$$  \hspace{0.5cm} (18)

$$H_c = \frac{1}{2} (A_1N_1^2 + 2C_1N_1N_2 + B_1N_2^2 + A_3\xi^2 + 2C_3\xi\eta + B_3\eta^2),$$

$$Z_1 = e^{-\beta\xi_1} \exp \left[ -\frac{1}{2} \beta(A_1N_1 + C_1N_2) \right] \cosh \left[ \frac{1}{2} \beta(A_3\xi + C_3\eta) \right]$$

$$+ e^{-\beta\xi_1} \exp \left[ -\frac{1}{2} \beta(C_1N_1 + B_1N_2) \right] \cosh \left[ \frac{1}{2} \beta(C_3\xi + B_3\eta) \right].$$

Here

$$N_1 = x_+, N_2 = z_+, \xi = y_+, \eta = u_-.$$  \hspace{0.5cm} (19)
It is convenient to separate the term in the expression for the free energy which depends on $\xi$ and $\eta$

$$F = F_0 + F_1(\xi, \eta),$$  \hspace{1cm} (20)

$$F_0 = \frac{1}{2} (A_1 N_1^2 + 2C_1 N_1 N_2 + B_1 N_2^2) - 2\Theta \ln 2 - 2\Theta \ln (a + b),$$

$$F_1(\xi, \eta) = (A_3 \xi^2 + 2C_3 \xi \eta + B_3 \eta^2) - 2\Theta \ln \left\{ n_1 \cosh \left[ \frac{1}{2} \beta (A_3 \xi + C_3 \eta) \right] + n_2 \cosh \left[ \frac{1}{2} \beta (C_3 \xi + B_3 \eta) \right] \right\},$$  \hspace{1cm} (21)

where the following symbols are introduced

$$a = e^{-\beta \varepsilon_1} \exp \left[ -\frac{1}{2} \beta (A_1 N_1 + C_1 N_2) \right] , \quad b = e^{-\beta \varepsilon_3} \exp \left[ -\frac{1}{2} \beta (C_1 N_1 + B_1 N_2) \right] ,$$

$$n_1 = a/(a + b), \quad n_2 = b/(a + b), \quad n_1 = 1 - n_2. \hspace{1cm} (22)$$

Expressions $n_1$ and $n_2$ describe an effective occupancy of equilibrium positions 1,2 and 3,4, respectively, in disordered state. One can assume they have a weak dependence on temperature in the region of the paraelectric-ferroelectric phase transition. In the framework of this approach $n_1$ and $n_2$ could be considered as model parameters. The main contribution to the change of free energy is given by the term $F_1(\xi, \eta)$. Then the averages $\xi$ and $\eta$ are given by a set of equations

$$\xi = \frac{(1 - n) \sinh[\tilde{\beta}(\xi + C\eta)]}{(1 - n) \cosh[\tilde{\beta}(\xi + C\eta)] + n \cosh[\beta(C\xi + Bn)]},$$

$$\eta = \frac{n \sinh[\tilde{\beta}(C\xi + Bn)]}{(1 - n) \cosh[\tilde{\beta}(\xi + C\eta)] + n \cosh[\beta(C\xi + Bn)]}, \hspace{1cm} (23)$$

where following symbols are used for normalized parameters

$$B = B_3/A_3, \quad C = C_3/A_3, \quad \tilde{\beta} = \beta A_3/2, \quad n = n_2.$$  

The set of equations (23) is invariant with respect to the inversion operation $\xi, \eta \rightarrow -\xi, -\eta$ and has, as usually, a trivial paraelectric solution $\xi = \eta = 0$. It can be established that at $\Theta = 0$ two another solutions ($\xi = 0, \eta = 1$ at $C < B$ and $\xi = 1, \eta = 0$ at $C < 1$) exist.

Landau expansion of the free energy is a convenient tool for investigation of PTs of the second order (PT2) and of the first order (PT1) which are close to second order. But in this case the use of Landau expansion meets with problems due to a negative sign of the coefficient at the sixth order of OP for the some range of parameter values. For this reason Landau expansion plays an auxiliary role in our investigations. Besides that we perform all calculations of $\xi$ and $\eta$ averages, free energy and the temperature of PT numerically using the expression (20) and the set (23).

Landau expansion up to fourth order was used for calculation of temperature of possible PT2 and boundaries of the regions where PT1 can occur. In this case OP is two-component, hence for diagonalization of the quadratic form, which looks like

$$F_1(\xi, \eta) = U\xi^2 + V\eta^2 + 2S\xi\eta, \hspace{1cm} (24)$$
\[
U = \frac{1}{2} \left[ 1 - (1 + (C^2 - 1)n) \frac{\beta}{2} \right], \quad V = \frac{1}{2} \left[ B - (C^2 + (B^2 - C^2)n) \frac{\beta}{2} \right], \quad (25)
\]
\[
S = \frac{C}{2} \left[ 1 - (1 + (B - 1)n) \frac{\beta}{2} \right],
\]

one should make the following transformation

\[
\begin{pmatrix}
  r_1 \\
  r_2
\end{pmatrix} = \hat{T} \begin{pmatrix}
  \xi \\
  \eta
\end{pmatrix}, \quad \hat{T} = \begin{pmatrix}
  \cos \varphi & -\sin \varphi \\
  \sin \varphi & \cos \varphi
\end{pmatrix}, \quad (26)
\]
\[
\cos 2\varphi = \frac{V - U}{\sqrt{(V - U)^2 + 4S^2}}, \quad \sin 2\varphi = \frac{2S}{\sqrt{(V - U)^2 + 4S^2}}. \quad (27)
\]

Now the expression \( (24) \) is as follows

\[
F_2(r_1, r_2) = \Lambda_1 r_1^2 + \Lambda_2 r_2^2, \quad (28)
\]
\[
\Lambda_1 = \frac{1}{2} \left[ (V + U) - \sqrt{(V - U)^2 + 4S^2} \right], \quad \Lambda_2 = \frac{1}{2} \left[ (V + U) + \sqrt{(V - U)^2 + 4S^2} \right].
\]

Coefficients \( \Lambda_1 \) and \( \Lambda_2 \) are equal to zero at temperatures

\[
\tilde{\Theta}_{1,2} = \left[ (B - C^2)(1 - n)n \right] \sqrt{(1 - (1 - B)n)^2 + 4C^2(1 - n)n}. \quad (29)
\]

One can obtain conditions on parameters \( A_3, B_3 \) and \( C_3 \)

\[
A_3 > 0, \quad B_3 > 0, \quad A_3B_3 > C_3; \quad B > 0, \quad B > C^2, \quad (30)
\]

taking into account that at \( \Theta = \infty \) \( (\beta = 0) \) the system is paraelectric (coefficients \( \Lambda_1 \) and \( \Lambda_2 \) are positive). If the conditions \( (31) \) are satisfied, the temperature \( \tilde{\Theta}_1 \) is always higher than the temperature \( \tilde{\Theta}_2 \). Hence it determines the temperature of possible PT2 and variable \( r_1 \) in the expression \( (28) \) becomes the OP.

The region of parameter values, where PT1 takes place, can be established by the criterion of a negative fourth order term proportional to \( r_1^4 \) of Landau expansion. This term can be obtained from the expression

\[
F_1^{(4)}(\xi, \eta) = -\frac{\beta}{32} \left\{ \left( 2k_1 + 2k_2 C^4 - (1 - n)nC^2 \right) \xi^4 + \left( k_1 C^4 + 2k_2 B^4 - (1 - n)nB^2 C^2 \right) \eta^4 + 2C \left( 4k_1 + 4k_2 BC^2 - (1 - n)n(B + C^2) \right) \xi^3 \eta + 2C \left( 4k_1 C^2 + 4k_2 B^3 - (1 - n)nB(B + C^2) \right) \xi^2 \eta^3 + (12(k_1 + k_2 B^2)C^2 - (1 - n)nC^2(B^2 + 4BC^2 + C^4)) \xi^2 \eta^2 \right\},
\]
\[
k_1 = (1 - n)/12 - (1 - n)^2/4, \quad k_2 = n/12 - n^2/4,
\]

using the transformation \( (29) \).

It is convenient to make a qualitative analysis of PT2 region in the case \( C = 0 \), when the free energy \( (24) \) has a diagonal form and OP is equal to \( \xi \) or \( \eta \). The equation \( B = 1/n - 1 \) describes the curve, which separates regions with different OP on the \( B - n \) diagram. This equation can be obtained by setting equal the temperatures at
Figure 3: Diagram of order of the paraelectric-ferroelectric phase transition at \( C = 0 \). Filled regions correspond to PT1, blank regions – PT2.

Figure 4: Boundaries of PT1 region (inside the curves) at \( B = 5 \). Solid line corresponds to numerical calculations, dashed one – the result of Landau expansion analysis.

which coefficients at \( \xi \) and \( \eta \) in the quadratic form (24) are equal to zero. It is found that the sign of the coefficient at the fourth order of OP depends on \( n \) only. Obtained diagram of a PT order is depicted in Fig. 3.

Increase of \( C \) leads to the narrowing of the region of \( n \) where PT1 is possible (Fig. 4). One can see that the region, determined by the \( F^{(4)} \) sign change, is smaller than obtained by direct numerical calculation. This difference can be explained on the example of the case \( C = 0 \). The point \( n' \) is situated on the OP \( \xi \rightarrow \eta \) change curve of the diagram in Fig. 3. On the left from the \( n' \) point the OP is \( \xi \), hence PT2 on \( \xi \) should takes place before PT2 in \( \eta \). But actually PT1 in \( \eta \) takes place before them. It is illustrated in Fig. 5 where dependences of free energy and parameters \( \xi, \eta \) on temperature are depicted. It is also possible to find PT2 in \( \xi \) firstly and PT1 with jump of \( \eta \) at lower temperature. One should note that at \( C \neq 0 \) the OP \( r_1 \) is a mixture of \( \xi \) and \( \eta \). But at considered here values of parameters the main contribution to the jump is given by \( \eta \). The diagram in Fig. 3 shows that PT1 with prevailing jump of \( \xi \) is typical for the region of small values of \( B \) and large \( n \); with prevailing jump of \( \eta \) – for large \( B \) and small \( n \). Increase of \( C \) cause a stronger “mixing” of \( \xi \) and \( \eta \), but there is the limit \( C^2 < B \) (30) of \( C \) value. Thus it seems difficult to find in this approach PT1 with the prevailing jump of \( \xi \) (i.e. with the prevailing occupancies of positions 1 and 2) at small values of \( n \) what is characteristic of DMAGaS crystals at PT from paraelectric into ferroelectric phase. At small values of \( n \) the model exhibits PT2 (close to PT1) with prevailing change of \( \xi \) parameter (Fig. 6). So, we see that despite the simplicity of the model its thermodynamics is very complicated. As an example an exotic case with sophisticated dependencies of \( \xi \) and \( \eta \) on temperature is shown in Fig. 7.
Figure 5: Dependences of free energy and order parameters on temperature at values of system parameters as $B = 5$, $C = 0.1$, $n = 0.12$.

Figure 6: *Ibid.* $B = 0.5$, $C = 0.7$, $n = 0.05$.

Figure 7: *Ibid.* $B = 5$, $C = 2$, $n = 0.05$
5 Conclusions

A microscopic approach based on the allowance for different orientational states of DMA ionic groups in crystal lattice is proposed in the present work for description of phase transition in DMAAlS and DMAGaS crystals. In the framework of a simple four-state model order parameters are introduced and calculations of thermodynamical characteristics are made. The phase transition from paraelectric to ferroelectric state is studied at different relations between parameters describing interactions of orientational states of different ionic groups.

An interesting feature which follows from the symmetry analysis is the strict correlation between the ordering along the 1–2 position axis (ferroelectric one) and the 3–4 position axis. Namely, as follows from table [1], ferroelectric ordering along the 1–2 axis is accompanied by the antiferroelectric one along the 3–4 axis and vice versa.

Ferroelectric state in these crystals is simultaneously improper antiferroelectric one along an other axis and antiferroelectric state is accompanied by ferroelectric ordering along the mentioned axis. Factors affecting order of the phase transition at $T_{c1}$ are studied in more details on the base of the model. At small values of $n$ this phase transition is established to be of the second order close to the first order one (close to the tricritical point) under approximation that total occupancies of positions (1,2) and (3,4) are assumed to be the same as in disordered phase and temperature independent. This behaviour coincides with the known result for DMAAlS crystal but does not match with data observed in DMAGaS crystals. For the last case it should be necessary abandon the approximation made and explicitly take into account temperature dependences of $n_1$ and $n_2$ values with the use of expressions (22). Such an approach should also be adopted for description of the low-temperature transition (at $T_{c2}$) to antiferroelectric phase and investigation of conditions of its realization. This can be the closest perspective of development of the model.

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References

[1] Pietraszko A., Łukaszewicz K., Kirpichnikova L.F. // Polish J. Chem., 1993, vol. 67, p. 1877–1884.

[2] Pietraszko A., Łukaszewicz K. // Polish J. Chem., 1994, vol. 68, p. 1239–1243.

[3] Pietraszko A., Łukaszewicz K., Kirpichnikova L.F. // Polish J. Chem., 1995, vol. 69, p. 922–930.

[4] Tchukvinskyi R., Cach R., Czapła Z. // Z. Naturforsch., 1998, vol. 53a, p. 105–111.
[5] Andreev E.F., Varikash V.M., Shuvalov L.A. // Izv. AN SSSR, ser. fiz., 1999, vol. 53, p. 572–574 (in Russian).

[6] Sobiestinskas P., Grigas Y., Andreev E.F., Varikash E.M. // Phase Transitions, 1992, vol. 40, p. 85.

[7] Kapustianik V., Bublyk M., Polovinko I., Sveleba S., Trybula Z., Andreev E. // Phase Transitions, 1994, vol. 49, p. 231–235.

[8] Dacko S., Czapla Z. // Ferroelectrics, 1996, vol. 185, p. 143–146.

[9] Pykacz H., Czapla Z. // Ferroelectrics Letters, 1997, vol. 22, p. 107–112.

[10] Tchukvinskyj R., Cach R., Czapla Z. // Z. Naturforsch., 1998, vol. 53a, p. 105–111.

[11] Czapla Z., Tchukvinskyj R. // Acta Phys. Polonica A, 1998, vol. 93, p. 527–530.

[12] Podsiadla D., Czapla Z., Andrievsky B., Myshchysyn O. // Acta Phys. Polonica A, 1999, vol. 96, p. 409–416.

[13] Furtak J., Czapla Z. // Ferroelectrics Letters, 1997, vol. 23, p. 63–67.

[14] Dolinšek J., Klanjšek M., Arčon D., Hae Jin Kim, Selinger J., Žagar V. // Phys. Rev. B, 1999, vol. 59, p. 3460–3467.

[15] Alsabbagh N., Michel D., Furtak J., Czapla Z. // Phys. stat sol. (a), 1998, vol. 167, p. 77–87.

[16] Bednarski W., Waplak S., Kirpichnikova L.F., Shuvalov L.A. // Phys. stat sol. (a), 1997, vol. 160, p. R1–R2.

[17] Torgashev V.I., Yuzyuk Yu.I., Kirpichnikova L.F., Shuvalov L.A., Andreev E.F. // Kristallografiya, 1991, vol. 36, p. 677–685 (in Russian).

[18] Yasuda N., Kaneda A., Czapla Z. // Ferroelectrics, 1999, vol. 223, p. 71.

[19] Yasuda N., Tajima H., Czapla Z. // Physics Letters A, 1994, vol. 192, p. 137–140.

[20] Yasuda N., Tajima H., Czapla Z. // J. Korean Phys. Soc., 1998, vol. 32, p. S283–S285.

[21] Kazimirov V.Yu., Rieder E.E., Sarin V.A., Belushkin A.V., Shuvalov L.A., Fykin L.E., Ritter C. // J. Korean Phys. Soc., 1998, vol. 32, p. S91–S93.