ІНСТИТУТ
ФІЗИКИ
КОНДЕНСОВАНИХ
СИСТЕМ

ICMP–99–19E

I.V.Stasyuk, O.V.Velychko

MICROSCOPIC MODEL OF PHASE TRANSITIONS IN
DMAGaS AND DMAAlS CRYSTALS

**Мікроскопічна модель фазових переходів в кристалах DMA-GaS і DMAAlS**

I.В.Стасюк, О.В.Величко

**Анотація.** Запропоновано чотирьохстанову модель для опису послідовності фазових переходів у сегнетоелектричних кристалах типу DMAGaS і DMAAlS. Процеси впорядкування в підсистемі груп DMA розглядаються як головна причина таких перетворень. Взаємодію між групами в їх різних орієнтаційних станах враховано у диполь-дипольному наближенні. Отримано термодинамічні характеристики моделі (спонтанна поляризація, заселеність орієнтаційних станів, фазова діаграма), що якісно узгоджуються з даними експерименту. Припустивши, що основний вплив гідростатичного тиску на кристал зводиться до зміни різниці енергій орієнтаційних станів груп DMA, пояснено експериментальний факт зникнення сегнетофази зі збільшенням тиску.

**Microscopic model of phase transitions in DMAGaS and DMAAlS crystals**

I.V.Stasyuk, O.V.Velychko

**Abstract.** The four-state model is proposed for description of the sequence of phase transitions in ferroelectric crystals of DMAGaS and DMAAlS type. The ordering processes in the subsystems of DMA groups are considered as a main reason of such transformations. The interaction between groups in their various orientational states is taken into account in the dipole-dipole approximation. Obtained thermodynamical characteristics of the model (spontaneous polarization, occupancy of orientational states, phase diagram) are in good agreement with experimental data. The experimental fact of suppression of ferroelectric phase at increase of hydrostatic pressure is explained under assumption that the main role of the pressure is the change of the difference between energies of various orientational states of DMA groups.

## 1. Introduction

The family of isomorphous crystals with ferroelectric properties to which e.g. $(CH_3)_2NH_2Al(SO_4)_2 \cdot 6H_2O$ (DMAAlS) and $(CH_3)_2NH_2Ga(SO_4)_2 \cdot 6H_2O$ (DMAGaS) belong to is experimentally studied during the last ten years. A peculiar feature of the family is the possibility of existence of crystal in three different phases at change of temperature: at room temperature crystal is paraelectric, at lowering of temperature it sequentially becomes ferroelectric and antiferroelectric [1–4]. For example, it has been measured $T_{c1} = 136$ K and $T_{c2} = 113$ K [4] (or 122 K and 114 K correspondingly [3]) for DMAGaS crystal, but it has been only found $T_{c1} = 150$ K [1–3] for DMAAlS. The phase transition between the ferroelectric and antiferroelectric phases is of the first order [3,4]. There are evidences, supplied by optical, ultrasonic, pyroelectric, dilatometric and dielectric measurements, that 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).

A lot of ferroelectric compounds have some structural elements which reorientation leads to polarisation of crystal. Changes in the rest of the crystal are insignificant and can be neglected in description of the phenomenon. Crystals DMAAlS and DMAGaS belong to this type of ferroelectrics. In this case the element, which can be reoriented, is the dimethylammonium cation (more strictly $NH_2$ group) [3,5–7]. This element can occupy four equilibrium positions which are related in pairs by inversion centre forming a slightly deformated cross (Figs. 1 and 2). It is very likely that this asymmetry (and corresponding differences of pair interaction constants) is responsible for so complicated behaviour of the crystal. In the paraelectric phase site in one pair ($(k,1)$ and $(k,2)$; $k = 1, 2$) is occupied with probability 40% and in another ($(k,3)$ and $(k,4)$) with probability 10% at 300 K.

According to the experimental data in the ferroelectric and antiferroelectric phases only positions in the first pair are occupied with appropriate ordering.

In the ferroelectric phase positions (1,2) and (2,2) (or (1,1) and (2,1))
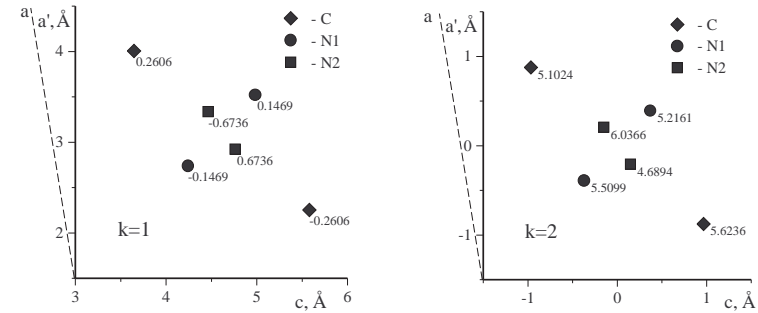


Figure 1. Projection of N and C atoms in the dimethylammonium groups of DMAGaS crystal at ambient temperature [1] onto the XZ plane (the Y coordinate is indicated in parenthesis).
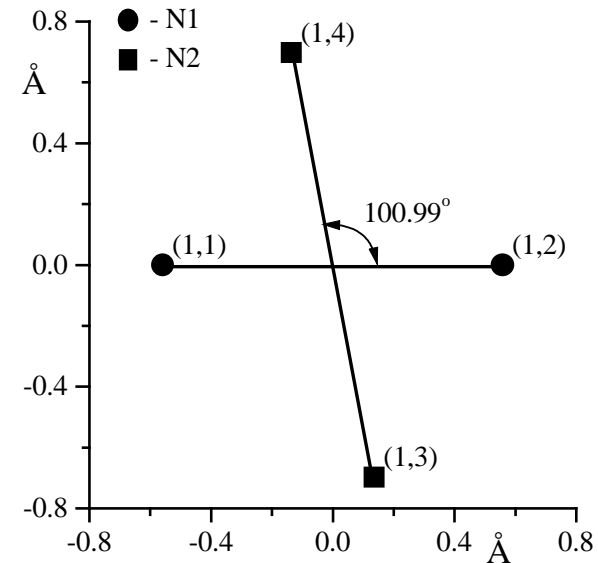


Figure 2. Projection of N atoms onto the plane perpendicular to the C–C′ axis of the dimethylammonium group for the same crystal as in Fig. 1.

| | | (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 | 1/2 | 0 | 0 |
| | $z_+$ | 0 | 0 | 1/2 | 1/2 | 0 | 0 | 1/2 | 1/2 |
| $B_g$ | $x_-$ | 1/2 | 1/2 | 0 | 0 | -1/2 | -1/2 | 0 | 0 |
| | $z_-$ | 0 | 0 | 1/2 | 1/2 | 0 | 0 | -1/2 | -1/2 |
| $B_u$ | $y_+$ | 1/2 | -1/2 | 0 | 0 | 1/2 | -1/2 | 0 | 0 |
| | $u_-$ | 0 | 0 | 1/2 | -1/2 | 0 | 0 | -1/2 | 1/2 |
| $A_u$ | $y_-$ | 1/2 | -1/2 | 0 | 0 | -1/2 | 1/2 | 0 | 0 |
| | $u_+$ | 0 | 0 | 1/2 | -1/2 | 0 | 0 | 1/2 | -1/2 |

Table 1. Coefficients of symmetrized occupancies of orientational states which correspond to irreducible representations of the point symmetry group 2/m.

are mainly occupied while in the antiferroelectric state occupancies of position (1,2) and (2,1) (or (1,1) and (2,2) respectively) prevail [1]. In [8] we have performed the symmetry analysis of functions being linear combinations of occupancies of positions of $NH_2$ groups in elementary cell. Symmetrized linear combinations, which transform according to irreducible representations of point symmetry group 2/m of the high-temperature phase, are presented in Tab. 1. Combinations $y_+$, $u_-$ ($y_-$, $u_+$) belonging to representation $B_u$ ($A_u$) correspond to orderings appearing in ferroelectric (antiferroelectric) phase, and form order parameters for these phases. Existing orderings are of the mixed nature: ferroelectric ordering in positions $(k,1)$, $(k,2)$ (along the OX axis) is accompanied by antiferroelectric one in $(k,3)$, $(k,4)$ (along the OY axis) and vice versa.

Proceeding from these facts we have proposed microscopic four-state model [8] for description of thermodynamics of order-disorder phase transitions in the subsystem of reorientationable DMA groups. The phase transition between paraelectric and ferroelectric phases in the considered crystals was described and criteria of order of this transition were established in the approach with the allowance for the direct interaction between variously oriented groups (site-site approach). This approach however can not be extended on a wide temperature range including e.g. the region of the low-temperature phase transition in DMAGaS because total occupancies of "longitudinal" positions $n_k = \langle X_k^{11} + X_k^{22} \rangle$ (and "transverse" positions $n_b = \langle X_k^{33} + X_k^{44} \rangle$ respectively) have been assumed as temperature independent parameters of theory.

Here a continuation of this work is presented where an approach

of dipole-dipole interaction between ionic groups is used; temperature change of total occupancies $n_a$ and $n_b$ is taken into account as well as the effect of reorientational hopping of groups between positions $(k, p)$. Ordering of ionic groups corresponding to order parameters of both $B_u$ and $A_u$ symmetry is described in the mean field approximation. Equilibrium states are investigated, temperature dependences of order parameters (spontaneous polarization) and occupancies of positions of $NH_2$ groups are studied. Both phase transitions (at temperatures $T_{c1}$ and $T_{c2}$) are described; the regions of existence of para-, ferro- and antiferroelectric phases depending on temperature and model parameters are established. Observed by experiment changes of picture of phase transitions in DMA-GaS crystal under the influence of hydrostatic pressure are interpreted in the framework of microscopic description.

## 2. The model Hamiltonian

Let us formulate Hamiltonian of the subsystem of DMA groups on the basis of four orientational states with an account of differences of nonequivalent configuration energies, possibility of orientational hopping and interaction between groups in dipole approximation.

$$H = \sum_{nk} \sum_{ss'} \lambda_k^{ss'} X_{nk}^{ss'} - \frac{1}{2} \sum_{nn'} \sum_{kk'} \sum_{\alpha\beta} \Psi_{\alpha\beta}^{kk'}(nn') D_{nk}^{\alpha} D_{n'k'}^{\alpha'} , \qquad (1)$$

where

$$\hat{\lambda}_1 = \begin{pmatrix} \varepsilon_1 & 0 & \Omega_1 & \Omega_2 \\ 0 & \varepsilon_1 & \Omega_2 & \Omega_1 \\ \Omega_1 & \Omega_2 & \varepsilon_2 & 0 \\ \Omega_2 & \Omega_1 & 0 & \varepsilon_2 \end{pmatrix}, \quad \hat{\lambda}_2 = \begin{pmatrix} \varepsilon_1 & 0 & \Omega_2 & \Omega_1 \\ 0 & \varepsilon_1 & \Omega_1 & \Omega_2 \\ \Omega_2 & \Omega_1 & \varepsilon_2 & 0 \\ \Omega_1 & \Omega_2 & 0 & \varepsilon_2 \end{pmatrix}, \quad (2)$$

$$D_{nk}^x = d_x(X_{nk}^{22} - X_{nk}^{11}), \quad D_{nk}^y = d_y(X_{nk}^{44} - X_{nk}^{33}), \quad D_{nk}^z = 0, \qquad (3)$$

$X_{nk}^{ss'}$ is the Hubbard transfer operator from the state $s'$ on the state $s$ of the DMA complex in the lattice site $n$ and the sublattice $k$, $D_{nk}^{\alpha}$ is the $\alpha$-component of the dipole moment of complex, $\Psi_{\alpha\beta}^{kk'}(nn')$ is the energy of the dipole interaction, $\varepsilon_1$ and $\varepsilon_2$ are energies of DMA groups in positions $(k, 1)$, $(k, 2)$ and $(k, 3)$, $(k, 4)$ respectively, $\Omega_1$ and $\Omega_2$ are parameters of the reorientational hopping.

Here the coordinate system with the X axis along the axis of spontaneous polarization of the crystal and the Y axis perpendicular to the DMA plane (parallel to the crystallographic $b$ axis) is used.

It should be mentioned that the Hamiltonian (1) simplifies the real structure of DMA complexes in DMAGaS crystals, which are oriented not exactly along the chosen axes (as assumed in definitions of $D^x_{nk}$ (3)). Next, the dipole-dipole interaction is only the first nonzero term of the multipole expansion. Nevertheless, as will be shown below, the model described by the Hamiltonian (1) can give a satisfactory explanation of the behaviour of DMAGaS and DMAAlS-type crystals despite of simplifications made.

The Hamiltonian (1) can be rewritten to separate the mean field part

$$H = NH_C + H_{MF} + H',\tag{4}$$

$$H_C = \frac{1}{2}\sum_{kk'}\sum_{\alpha\beta}\psi^{kk'}_{\alpha\beta}\langle D^\alpha_k\rangle\langle D^\beta_{k'}\rangle,\tag{5}$$

$$H_{MF} = \sum_{nk'}\sum_{ss'}\lambda^{ss'}_k X^{ss'}_{nk} - \sum_n\sum_{kk'}\sum_{\alpha\beta}\psi^{kk'}_{\alpha\beta}\langle D^\beta_{k'}\rangle D^\alpha_{nk}$$

$$= \sum_{nk}\sum_{ss'}\lambda^{ss'}_k X^{ss'}_{nk} - \sum_{nk}\sum_\alpha F^k_\alpha D^\alpha_{nk},\tag{6}$$

$$H'_n = -\frac{1}{2}\sum_{nn'}\sum_{kk'}\sum_{\alpha\beta}\Psi^{kk'}_{\alpha\beta}(nn')\Big(\langle D^\alpha_k\rangle - D^\alpha_{nk}\Big)\Big(\langle D^\beta_{k'}\rangle - D^\beta_{n'k'}\Big),\tag{7}$$

where

$$F^k_\alpha = \sum_{k'}\sum_\beta\psi^{kk'}_{\alpha\beta}\langle D^\beta_{k'}\rangle,\quad \psi^{kk'}_{\alpha\beta} = \sum_{n'}\Psi^{kk'}_{\alpha\beta}(nn');$$

$N$ is the total number of sites. Further considerations will be restricted to the mean field approximation (MFA) and the fluctuative term $H'$ will be neglected.

It is convenient to make a unitary transformation to linear combinations of dipole moments

$$\langle D_\eta\rangle = \sum_{k\alpha}U_{\eta,k\alpha}\langle D^\alpha_k\rangle\tag{8}$$

transforming according to the irreducible representations of the high-temperature symmetry group of the crystal. After that the MFA Hamiltonian looks like

$$H_{MFA} = NH_C + H_{MF},\tag{9}$$

$$H_C = \frac{1}{2}\sum_{\eta\eta'}\langle\tilde D_\eta\rangle\psi_{\eta\eta'}\langle\tilde D_{\eta'}\rangle,\tag{10}$$

$$H_{MF} = \sum_{nk}\sum_{ss'}B^{ss'}_k X^{ss'}_{nk},\tag{11}$$

$$B^{ss'}_k = \lambda^{ss'}_k - \delta_{ss'}\sum_\eta\left(\sum_\alpha U_{\eta,k\alpha}d^{ss}_{k\alpha}\right)\tilde F_\eta,\tag{12}$$

where

$$\tilde F_\eta = \sum_{\eta'}\psi_{\eta\eta'}\langle\tilde D_{\eta'}\rangle,\quad \psi_{\eta\eta'} = \sum_{kk'}\sum_{\alpha\alpha'}U_{\eta,k\alpha}\psi^{\alpha\alpha'}_{kk'}U_{\eta',k'\alpha'}.\tag{13}$$

Symmetrized averages of dipole moments form two pairs, which belong to different irreducible representations:

$$A_u : \langle\tilde D_1\rangle = (\langle D^x_1\rangle - \langle D^x_2\rangle)/\sqrt2,\ \langle\tilde D_2\rangle = (\langle D^y_1\rangle + \langle D^y_2\rangle)/\sqrt2;\tag{14}$$

$$B_u : \langle\tilde D_4\rangle = (\langle D^x_1\rangle + \langle D^x_2\rangle)/\sqrt2,\ \langle\tilde D_5\rangle = (\langle D^y_1\rangle - \langle D^y_2\rangle)/\sqrt2.\tag{15}$$

Matrix $\psi_{\eta\eta'}$ has a block-diagonal structure with nonzero blocks belonging to the given representation (see Appendix A).

As follows from the expressions (14)–(15) the antiferroelectric ordering along the X axis is accompanied by the ferroelectric one along the Y axis and vice versa.

In general case $\Omega_i \neq 0$ the diagonalization procedure should be applied to the matrix $\hat{\tilde B}_k$ in expression (11):

$$H_{MF} = \sum_r\tilde\lambda^r_k\tilde X^{rr}_{nk},\tag{16}$$

where

$$\tilde\lambda^r_k = \sum_{ss'}V^k_{sr}B^{ss'}_k V^k_{s'r},\quad \tilde X^{rr'}_{nk} = \sum_{ss'}V^k_{sr}X^{ss'}_{nk}V^k_{s'r'}\tag{17}$$

and

$$\langle D^\alpha_k\rangle = \sum_{rr'}\tilde d^{rr'}_{k\alpha}\langle\tilde X^{rr'}_k\rangle,\quad \tilde d^{rr'}_{k\alpha} = \sum_{ss'}V^k_{sr}d^{ss'}_\alpha V^k_{s'r'}.\tag{18}$$

Now all necessary thermodynamical functions could be derived from the Hamiltonian (9) with corresponding terms expressed by (10) and (16).

## 3. Thermodynamics of the model

The partition function of the model in general form is presented as

$$Z = Z^N_1 Z^N_2\exp(-\beta NH_C),\tag{19}$$

where

$$Z_k \quad = \quad \sum_s \exp(-\beta\tilde{\lambda}_k^s), \quad k = 1, 2; \tag{20}$$

$$H_{\mathrm{C}} \quad = \quad \frac{1}{2}\Big(a_1\langle\tilde{D}_1\rangle^2 + d_1\langle\tilde{D}_2\rangle^2 + 2b_1\langle\tilde{D}_1\rangle\langle\tilde{D}_2\rangle$$
$$+ a_2\langle\tilde{D}_4\rangle^2 + d_2\langle\tilde{D}_5\rangle^2 + 2b_2\langle\tilde{D}_4\rangle\langle\tilde{D}_5\rangle\Big). \tag{21}$$

As a result free energy per particle looks like

$$F = -\frac{1}{\beta N}\ln Z = H_{\mathrm{C}} - \frac{1}{\beta}\ln Z_1 - \frac{1}{\beta}\ln Z_2. \tag{22}$$

Now one can calculate averages

$$\langle X_k^{rr}\rangle = \exp(-\beta\tilde{\lambda}_k^r)\Big/ \sum_s \exp(-\beta\tilde{\lambda}_k^s) \tag{23}$$

and after substitution into formulae (14), (15) and (18) selfconsistency equations for $\langle\tilde{D}_n\rangle$ can be obtained.

In the case $\Omega_1 = \Omega_2 = 0$ the matrix $\hat{B}_k$ is diagonal and expressions for thermodynamical functions are more simple. For example, the set of selfconsistency equations looks like

$$\langle\tilde{D}_{1,4}\rangle \quad = \quad \frac{d_x}{\sqrt{2}}\exp(\beta\Delta)\Big[\mathcal{Z}_1^{-1}\sinh(\beta\varkappa_1^x) \mp \mathcal{Z}_2^{-1}\sinh(\beta\varkappa_2^x)\Big],$$

$$\langle\tilde{D}_{2,5}\rangle \quad = \quad \frac{d_y}{\sqrt{2}}\exp(-\beta\Delta)\Big[\mathcal{Z}_1^{-1}\sinh(\beta\varkappa_1^y) \pm \mathcal{Z}_2^{-1}\sinh(\beta\varkappa_2^y)\Big], \tag{24}$$

where

$$\mathcal{Z}_k \quad = \quad \exp(\beta\Delta)\cosh(\beta\varkappa_k^x) + \exp(-\beta\Delta)\cosh(\beta\varkappa_k^y), \quad k = 1, 2,$$

$$\varkappa_k^x \quad = \quad \frac{d_x}{\sqrt{2}}\Big[(-1)^{\delta_{k,2}}(a_1\langle\tilde{D}_1\rangle + b_1\langle\tilde{D}_2\rangle) + a_2\langle\tilde{D}_4\rangle + b_2\langle\tilde{D}_5\rangle\Big],$$

$$\varkappa_k^y \quad = \quad \frac{d_y}{\sqrt{2}}\Big[b_1\langle\tilde{D}_1\rangle + d_1\langle\tilde{D}_2\rangle + (-1)^{\delta_{k,2}}(b_2\langle\tilde{D}_4\rangle + d_2\langle\tilde{D}_5\rangle)\Big], \tag{25}$$

$$\varepsilon = (\varepsilon_2 + \varepsilon_1)/2, \quad \Delta = (\varepsilon_2 - \varepsilon_1)/2.$$

## 4. Numerical results

The model under consideration demonstrate a complicated thermodynamical behaviour and a some numbers of qualitatively different phase
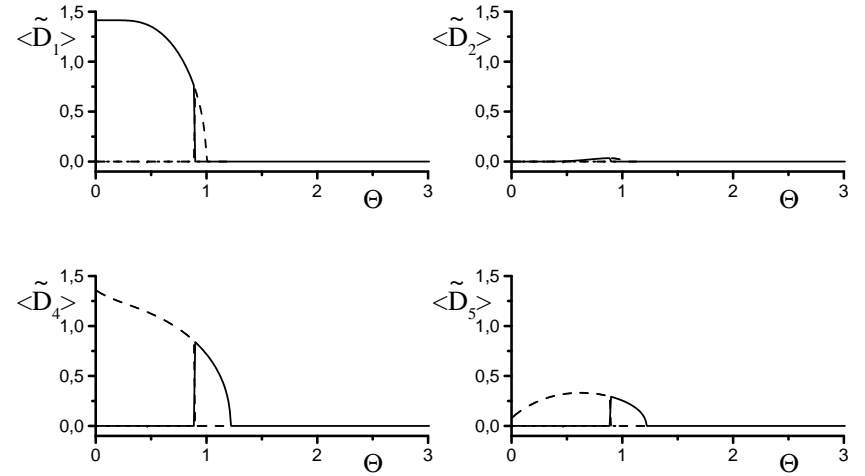


Figure 3. Dependences of $\langle\tilde{D}\rangle$ on temperature at specified below values of parameters: $b_1/a_1$=0.7, $d_1/a_1$=0.5, $a_2/a_1$=0.4, $b_2/a_1$=2.6, $d_2/a_1$=0.8, $\Delta/a_1 d_x^2$=1.52, $\Omega_1=\Omega_1=0$, $d_y/d_x = 1.4$; $\Delta$ and $\Theta$ are given in $a_1 d_x^2$ units.
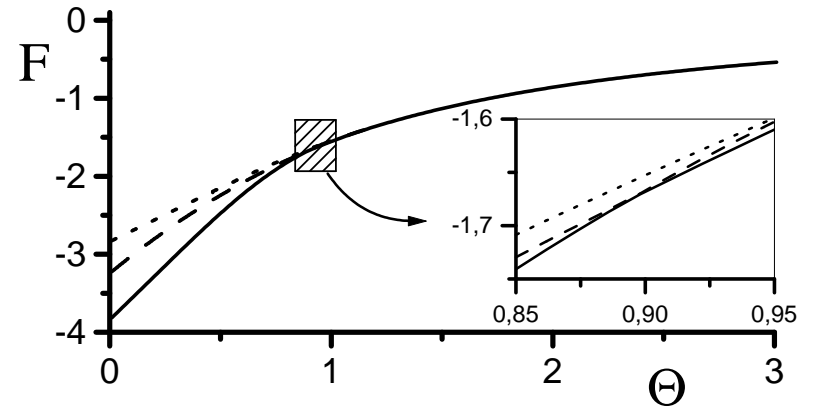


Figure 4. Dependences of free energy $F$ on temperature at the same values of parameters as in Fig. 3
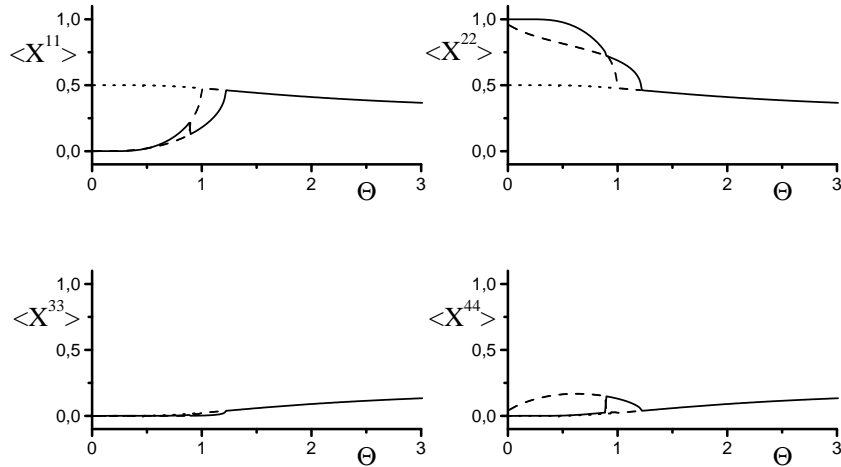.

Figure 5. Dependences of occupancies of states on temperature at the same values of parameters as in Fig. 3.
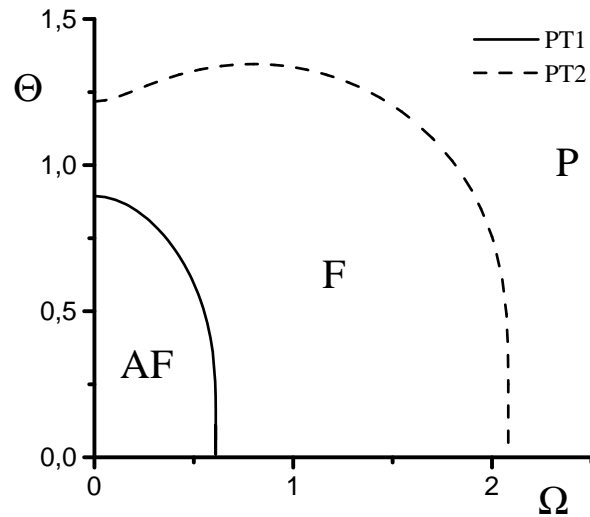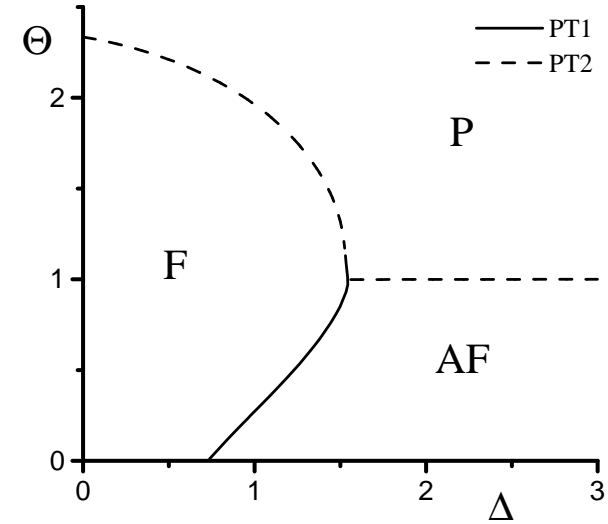


Figure 7. Phase diagram $\Theta - \Delta$ at the same values of parameters as in Fig. 3.

diagrams dependently on parameter values. Further study will be restricted to the case of sequence of phase transition which is characteristic of the DMAGaS crystal (antiferroelectric → ferroelectric → paraelectric phases with temperature increase).

Such a sequence of phase transition is achieved at next relationships between parameters

$$0 < b_1, d_1, a_1 < b_2, d_2;$$
$$a_1 > a_2 > 0. \tag{26}$$

If the above nonequalities are fulfilled antiparallel orientation of $D_x$- and $D_y$-dipoles of neighbour DMA groups is energetically favourable. At low temperatures (when occupancies of positions $(k,3)$ and $(k,4)$ tend to zero) the antiferroelectric phase related with antiparallel dipoles $D_x$ is realized. In the result of increased probability of appearance of groups in the mentioned position at temperature growing the interaction with participation of $D_y$ dipoles becomes significant. The phase transition to phase with their antiferroelectric orientation occurs when respective interaction constants become prevailing. This phase is simultaneously ferroelectric along the OX axis.

Results of numerical calculations of temperature dependences of sym-



Figure 6. Phase diagram $\Theta - \Omega$ at the same values of parameters as in Fig. 3.

metrized dipole moments (14), (15) (obtained as solutions of equation set (24)) having meaning of order parameters are depicted in Fig. 3. The corresponding temperature dependence of free energy calculated with use of expression (22) one can see in Fig. 4. Here the case of the second order high-temperature phase transition is illustrated.

As one can see in Fig. 3 and expressions (14), (15) antiferroelectric orientation along the X axis is accompanied by ferroelectric one along the Y axis and vice versa. Polarization along the X axis is larger than along the Y one due to larger occupancies of positions 1 and 2 comparatively to positions 3 and 4 (Fig. 5).

The influence of the orientational hopping on the phase transition in the system resemble one for Ising model (Fig. 6 – for simplicity is assumed $\Omega_1 = \Omega_2 = \Omega$). Namely the increase of $\Omega$ value leads as a whole to the decrease of temperatures of PT1 and PT2. Antiferroelectric phase is suppressed at relatively low values of $\Omega$ when the temperature of PT2 is still changed insignificantly.

According to the experimental data on pressure effects in DMAGaS [9] the increase of hydrostatic pressure leads to the narrowing of the temperature region of the existence of ferroelectric phase. At certain pressure ferroelectric phase is completely suppressed. Thermodynamical description in the framework of Landau theory allows to reproduce observed phase diagram by setting coefficients at the second order terms in the Landau expansion of free energy to be temperature dependent [10]. Microscopic description of influence of hydrostatic pressure is rather complicated question. One can assume, that due to limited compressibility of the crystal interaction constants change insignificantly and the main effect is due to the increase of the difference of site energies $\Delta$. In this case the obtained phase diagram remarkably good coincide with the qualitative form of the experimental one (Fig. 7). This confirms the above assumption of the prevailing influence of pressure on site energies. Nevertheless, it seems that a more complete reproducing of the observed dependences (in particular, the increase of temperature of phase transition into the antiferroelectric phase at the pressure values above the triple point) can be achieved when additional factors (such as a change of interaction constants or the parameter $\Omega$) will be taken into account.

As one can mention there are both triple and tricritical points on the diagram. A narrow region of $\Delta$ values near the triple point exists where both phase transition are of the first order as in the case of DMAGaS crystals.

## 5. Conclusions

A simple dipole approximation for the four state model proposed for description of thermodynamics of DMAGaS-DMAAlS family of crystals is developed. The model exhibits complicated thermodynamical behaviour depending on values of system parameters. At certain values of parameters the model gives the same sequence phase transitions as is found experimentally in DMAGaS.

Numerical exploration of the model shows that the increase of the orientational hopping between sites leads to the suppression of ordered phases in the Ising model like way.

Attemption to give theoretical explanation of the experiment on the influence of hydrostatic pressure on phase diagram of DMAGaS crystal results in good qualitative agreement. It is assumed that the main effect of pressure is the change of the difference of site energies.

## 6. Acknowledgements

## 7. Appendix A. Transformation of the matrix of dipole-dipole interactions to irreducible representations of the high-temperature symmetry group

$$\hat{\psi} = \begin{pmatrix} a' & b' & c' & d' & e' & f' \\ b' & g' & h' & -e' & k' & l' \\ c' & h' & m' & f' & -l' & n' \\ d' & -e' & f' & a' & -b' & c' \\ e' & k' & -l' & -b' & g' & -h' \\ f' & l' & n' & c' & -h' & m' \end{pmatrix}. \qquad (27)$$

Here axis indices are changed first (e.g. $\{k\alpha\} = \{1x, 1y, 1z, 2x, 2y, 2z\}$).

Matrix of unitary transformation is as follows:

$$\hat{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & -1 \\ 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 \end{pmatrix}. \tag{28}$$

After the transformation the matrix of interactions

$$\begin{aligned} \hat{\tilde{\psi}} &= \frac{1}{2} \begin{pmatrix} a'-d' & b'+e' & c'-f' & 0 & 0 & 0 \\ b'+e' & g'+k' & h'-l' & 0 & 0 & 0 \\ c'-f' & h'-l' & m'-n' & 0 & 0 & 0 \\ 0 & 0 & 0 & a'+d' & b'-e' & c'+f' \\ 0 & 0 & 0 & b'-e' & g'-k' & h'+l' \\ 0 & 0 & 0 & c'+f' & h'+l' & n'+m' \end{pmatrix} \\[2mm] &= \begin{pmatrix} a_1 & b_1 & c_1 & 0 & 0 & 0 \\ b_1 & d_1 & e_1 & 0 & 0 & 0 \\ c_1 & e_1 & f_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & a_2 & b_2 & c_2 \\ 0 & 0 & 0 & b_2 & d_2 & e_2 \\ 0 & 0 & 0 & c_2 & e_2 & f_2 \end{pmatrix} \end{aligned} \tag{29}$$

becomes block-diagonal, where the upper left block corresponds to the $A_u$ representation and the bottom right one to the $B_u$.

# 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., Czapla Z. // Z. Naturforsch., 1998, vol. 53a, p. 105–111.
5. Sobiestinskas P., Grigas Y., Andreev E.F., Varikash E.M. // Phase Transitions, 1992, vol. 40, p. 85.
6. Dolinšek J., Klanjšek M., Arčon D., Hae Jin Kim, Selinger J., Žagar V. // Phys. Rev. B, 1999, vol. 59, p. 3460–3467.
7. 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.
8. Stasyuk I.V., Velychko O.V. // Journ. Phys. Studies (in print).
9. Yasuda N., Kaneda A., Czapla Z. // Ferroelectrics, 1999, vol. 223, p. 71.
10. I.V.Stasyuk, O.V.Velychko, Z.Czapla, R.Czukwinski Thermodynamics and dielectric anomalies of DMAAS and DMAGaS crystals in the phase transitions region (Landau theory approach). Preprint of the Institute for Condensed Matter Physics, ICMP–99–23E, Lviv, 1999, 11 p.

Ігор Васильович Стасюк
Олег Володимирович Величко

Мікроскопічна модель фазових переходів в кристалах
DMAGaS і DMAAlS