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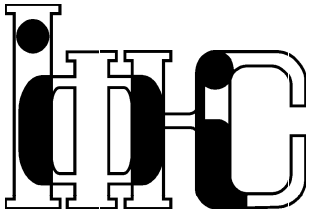

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THERMODYNAMICS AND DIELECTRIC ANOMALIES OF DMAAS AND DMAGaS CRYSTALS IN THE PHASE TRANSITIONS REGION (LANDAU THEORY APPROACH)

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Термодинаміка та діелектричні аномалії в області фазових переходів у кристалах DMAAS та DMAGaS (наближення теорії Ландау)

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Анотація. Запропоновано простий опис термодинаміки сегнетоелектричних кристалів типу DMAAS і DMAGaS за допомогою розкладу Ландау. Встановлено умови реалізації фазових переходів і отримано їх температури. Описано зміни температур фазових переходів під впливом зовнішнього всестороннього тиску. Досліджено температурну поведінку компонент діелектричної сприйнятливості та їх аномалії в околі точок фазових переходів. Отримані результати порівнюються з експериментальними даними.

Thermodynamics and dielectric anomalies of DMAAS and DMAGaS crystals in the phase transitions region (Landau theory approach)

I.V.Stasyuk, O.V.Velychko, Z.Czapla, R.Czukwinski

Abstract. A simple description of thermodynamics of DMAAS and DMAGaS ferroelectric crystals by means of Landau expansion is proposed. Conditions of occurrence of phase transitions are established and their temperatures are obtained. The influence of external hydrostatic pressure on phase transitions is described. The temperature behaviour of dielectric susceptibility components and their anomalies in the vicinity of phase transition points are investigated. Obtained results are compared with experimental data.

1. Introduction

Ferroelectric crystals $(CH_3)_2NH_2Al(SO_4)_2 \cdot 6H_2O$ (DMAAS) and $(CH_3)_2NH_2Ga(SO_4)_2 \cdot 6H_2O$ (DMAGaS) are intensively studied in recent years. Their interesting feature is possible existence of crystal in ferroelectric or antiferroelectric state depending on external conditions (e.g. temperature, hydrostatic pressure). There is a significant difference in thermodynamical behaviour of crystals despite on isomorphism of their structure. At ambient pressure DMAGaS crystal has three phases: paraelectric ($T > T_c$), ferroelectric ($T_1 < T < T_c$) and antiferroelectric ($T < T_1$) with temperatures of phase transitions $T_c = 136$ K (first order transition close to the tricritical point) and $T_1 = 117$ K (first order transition). There is only two phases in DMAAS crystal at ambient pressure: paraelectric ($T > T_c$) and ferroelectric ($T < T_c$) with $T_c = 155$ K.

A set of structural [1–3], dilatometric, dielectric, pyroelectric and ultrasonic [4–12] measurements is made for considered systems, what allows to establish their main dielectric, mechanical and dynamical characteristics (see below). At the same time these investigations are incomplete and of preliminary stage in many directions.

The nature of phase transitions in DMAAS and DMAGaS crystals was unclear up to recent time. During the last years conviction on important role of dimethyl ammonium (DMA) groups in phase transitions due to their orientational ordering-disordering is established (see, for example, [3,6,13,14]). In [15] the microscopic approach based on the order-disorder model with account of different orientational states of DMA groups was proposed. In the framework of the model the phase transition to ferroelectric state has been described and conditions of realization of this transition as of the first or of the second order have been established. Order parameters of the system have been constructed. They are connected with differences of occupancies of four possible positions of nitrogen ions corresponding to different orientations of groups. As a result of symmetry analysis it has been established that components of the order parameters belonging to irreducible representation B_u of point symmetry group $2/m$ of the high-temperature (paraelectric) phase describe ferroelectric ordering of DMA group along the ferroelectric axis OX (in crystallographic plane (ac)) and their antiferroelectric ordering along the OY axis (crystallographic axis b). The inverse ordering (antiferroelectric along OX and ferroelectric one along OY) corresponds to order parameter components belonging to irreducible representation A_u. Appearance of nonzero order parameters of B_u type turns the system into ferroelectric state (point group m) while nonzero order parameters

of A_u type cause antiferroelectric state (point group 2).

Notwithstanding further perspectives of microscopic approach by means of the four-state order-disorder model, the more simple but more general thermodynamical description based on Landau expansion is of interest. One can construct corresponding Landau free energy and in standard way investigate possible phase transitions and obtain criteria of their realization with the use of data of the mentioned above symmetry analysis. This is a main goal of the present work. Results obtained in the framework of Landau expansion will be used for interpretation of the induced by the external pressure changes in the picture of phase transitions and for description of dielectric anomalies in the phase transition points of the investigated crystals.

2. Thermodynamics of phase transitions (Landau theory approach)

Let us make thermodynamical description of phase transition in DMAAS and DMAGaS crystals with the use of Landau expansion. We consider a simplified version when only one linear combination of the initial order parameters type is included for each of B_u and A_u irreducible representations. The combinations included are true order parameters: coefficients at their squared values tend to zero in the points of corresponding second order transitions.

Order parameters, which transform according to irreducible representations B_u and A_u of point symmetry group $2/m$ of high-symmetry phase, are denoted as η_b and η_a correspondingly. The first parameter η_b describes polarization of ferroelectric type along the OX axis with simultaneous antiferroelectric type ordering along the OY axis; the second one corresponds to inverse orientation where antipolarization along OX is accompanied by polarization along OY.

We restrict ourself to the case of second order phase transition from the nonpolar high-temperature phase to ordered one. In this case Landau expansion of free energy can be limited by terms of the fourth order:

$$F = F_0 + \frac{1}{2}a\eta_a^2 + \frac{1}{2}b\eta_b^2 + \frac{1}{4}c\eta_a^4 + \frac{1}{4}d\eta_b^4 + \frac{1}{2}f\eta_a^2\eta_b^2 - E_x\eta_b - E_y\eta_a\,. \quad (1)$$

A linear dependence of coefficients a and b on temperature is assumed

$$a = a'(T - T_c'), \qquad b = b'(T - T_c), \quad (2)$$

where condition $T_c > T_c'$ is satisfied for normal state of the crystal what corresponds to the transition from the paraelectric phase (phase P) to

the ferroelectric phase (phase F) as to the first one at lowering of the temperature.

Conditions of thermodynamical equilibrium correspond to the minimum of free energy and look like

$$\begin{aligned} \frac{\partial F}{\partial \eta_a} &= \eta_a(a + c\eta_a^2 + f\eta_b^2) - E_y = 0, \\ \frac{\partial F}{\partial \eta_b} &= \eta_b(b + c\eta_b^2 + f\eta_a^2) - E_x = 0. \end{aligned} \tag{3}$$

At zero external fields there are following solutions

$$\eta_a = \eta_b = 0 \tag{4}$$

– paraphase (P-phase);

$$\begin{aligned} &\eta_a = 0, \quad \eta_b \neq 0, \\ &\eta_{b0} = \sqrt{-b/d} = \sqrt{(b'/d)(T_c - T)} \end{aligned} \tag{5}$$

– ferroelectric phase (F-phase);

$$\begin{aligned} &\eta_a \neq 0; \quad \eta_b = 0 \\ &\eta_{a0} = \sqrt{-a/c} = \sqrt{a'/c(T_c' - T)} \end{aligned} \tag{6}$$

– antiferroelectric phase (AF-phase). [1]

Corresponding expressions for free energy in these phases are as follows

$$\begin{aligned} F_{(P)} &= F_0\,, \\ F_{(F)} &= F_0 - \frac{1}{4d} b'^2 (T - T_c)^2, \\ F_{(AF)} &= F_0 - \frac{1}{4c} a'^2 (T - T_c')^2. \end{aligned} \tag{7}$$

The phase transition P→F which is of the second order in the used approximation takes place at temperature T_c. The phase transition F→AF which can take place at lower temperatures occurs at

$$F_{(F)} = F_{(AF)}. \tag{8}$$

The condition above determines the temperature of this first order phase transition:

$$T_1 = \frac{\varkappa T_c' - T_c}{\varkappa - 1}, \tag{9}$$

[1] We follow here to the terminology widely used in literature on the subject.

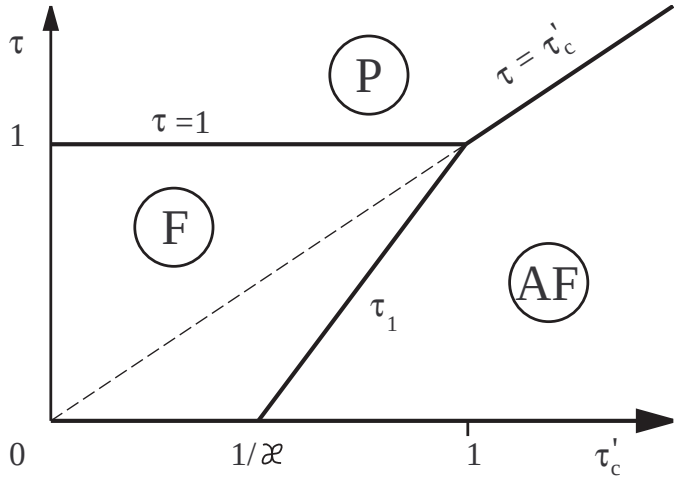

Figure 1. Dependence of phase number of the system and phase transition temperatures on values of system parameters

where

$$\varkappa = \frac{a'\sqrt{d}}{b'\sqrt{c}}, \qquad \varkappa > 1. \tag{10}$$

Nonequalities

$$0 < T_1 < T_c \tag{11}$$

define the region of temperature T_c' values where the F-phase exists as an intermediate one:

$$\frac{1}{\varkappa} < \frac{T_c'}{T_c} < 1. \tag{12}$$

These conditions are illustrated by the phase diagram in Fig. 1. In the case $T_c' > T_c$ a direct phase transition P→AF from the paraelectric phase to antiferroelectric one can take place.

Observed by experiment changes of temperatures of P→F and F→AF phase transitions and consecutive disappearance of the F-phase as the result of increasing of external hydrostatic pressure can be easily explained with the use of the obtained diagram. Under assumption that the influence of pressure leads mainly to shifts of temperatures T_c and T_c'

$$\begin{aligned} T_c &= T_{c0} + xp, \\ T_c' &= T_{c0}' + x'p, \end{aligned} \tag{13}$$

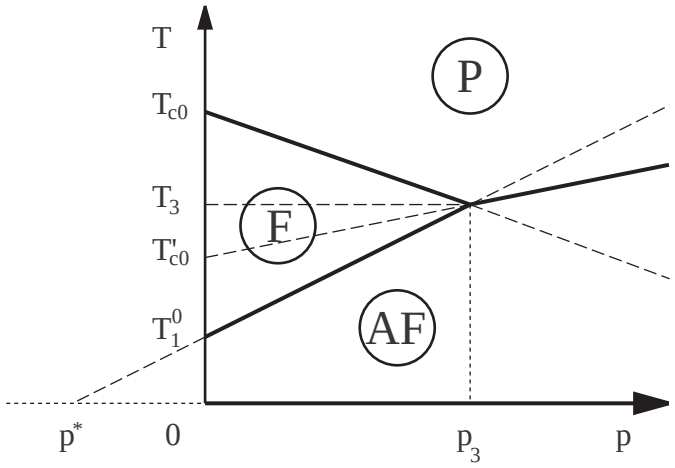

Figure 2. Dependence of the phase transition temperatures on the external hydrostatic pressure

and the changes of other Landau expansion parameters are negligible, the following relation is obtained

$$T_1 = T_1^0 + \frac{\varkappa x' - \varkappa}{\varkappa - 1} p, \tag{14}$$

where

$$T_1^0 = \frac{\varkappa T'_{c0} - T_{c0}}{\varkappa - 1}. \tag{15}$$

According to the data published in [16], $dT_c/dp \equiv x = -0.277$ K/MPa; $\partial T_1/\partial p = 1.95$ K/MPa and if one applies a linear approximation to the dependence of T'_c on p then $dT'_c/dp \equiv x' = 0.86$ K/MPa.

The obtained relations are illustrated by the diagram shown in Fig. 2. This diagram qualitatively matches the experimental (T,p) diagram for DMAGaS crystal (at $T_{c0} = 136$ K, $T_{10} = 116$ K) [16]. Obtained coordinates of triple point

$$T_3 = \frac{x' T_{c0} - x T'_{c0}}{x' - x}, \qquad P_s = \frac{T_{c0} - T'_{c0}}{x' - x}, \tag{16}$$

where lines of phase transitions P→F, F→AF and P→AF come together are in good agreement with experimental ones ($T_3^{exp} = -140.3$ °C; $P_3^{exp} = 8.75$ MPa). At $p \gg p_3$ there take place a deviation of the theoretical prediction of temperature of the P→AF phase transition from

experimental data. Unlike to relationship (13) experimental dependence is nonlinear at large pressures.

The pressure value

$$p^* = \frac{\varkappa T'_{c0} - T_{c0}}{x - \varkappa x'} \tag{17}$$

(see Fig. 2) is an important characteristic of the model. At $p^* < 0$, what is realized at $T'_{c0}/T_{c0} > 1/\varkappa$, AF-phase exists in the region of low temperatures at ambient pressure (this situation takes place for DMAGaS). At $p^* > 0$ (i.e. $T'_{c0}/T_{c0} < 1/\varkappa$) and ambient pressure only P- and F-phases occur; this case can correspond to DMAAS crystal.

3. Dielectric susceptibility

The approach used in the previous section allows to derive expressions for components of dielectric susceptibility tensor in the vicinity of phase transition points and to describe their temperature dependencies in general. In the used approximation the components P_x and P_y of polarization vector are defined by parameters η_b and η_a correspondingly. Hence

$$\chi_{xx} = \frac{\partial \eta_b}{\partial E_x}, \qquad \chi_{yy} = \frac{\partial \eta_a}{\partial E_y} \tag{18}$$

and proceeding from equations (3) one can obtain

$$\begin{aligned} \chi_{xx} &= \frac{1}{D}(a + 3c\eta_a^2 + f\eta_b^2), \\ \chi_{yy} &= \frac{1}{D}(b + 3d\eta_b^2 + f\eta_a^2), \end{aligned} \tag{19}$$

where

$$D = (a + 3c\eta_a^2 + f\eta_b^2)(b + 3d\eta_b^2 + f\eta_a^2) - 4f^2\eta_a^2\eta_b^2 \,. \tag{20}$$

The following particular cases follow from expression (19):

1. Paraphase (P):

$$\chi_{xx} = \frac{1}{b} = \frac{1}{b'(T - T_c)}, \quad \chi_{yy} = \frac{1}{a} = \frac{1}{a'(T - T'_c)}. \tag{21}$$

2. Ferroelectric phase (F):

$$\chi_{xx} = -\frac{1}{2b} = \frac{1}{2b'(T_c - T)}, \quad \chi_{yy} = \frac{1}{(\xi - 1)a'(T^* - T)}, \tag{22}$$

here the notations are used:

$$T^* = T_c + \frac{T_c - T_c'}{\xi - 1}, \quad \xi = \frac{fb'}{da'} \quad (\xi > 1). \tag{23}$$

In this case susceptibility χ_{yy} can be also expressed in the form

$$\chi_{yy} = [a + f\eta_{b0}^2]^{-1}, \tag{24}$$

where η_{b0} is a spontaneous value of order parameter (polarization P_s) in the ferroelectric phase.

3. Antiferroelectric phase (AF):

$$\chi_{xx} = \frac{1}{(\varkappa^2\xi - 1)b'(T^{**} - T)}, \quad \chi_{yy} = -\frac{1}{2a} = \frac{1}{2a'(T_c' - T)}, \tag{25}$$

where the temperature

$$T^{**} = T_c + \frac{T_c - T_c'}{1 - 1/\varkappa^2\xi}, \tag{26}$$

is introduced such that $T^{**} > T^* > T_c$. A similar to the previous one expression

$$\chi_{xx} = [b + f\eta_{a0}^2]^{-1}, \tag{27}$$

relating the temperature dependence of longitudinal susceptibility in AF phase with the equilibrium value of the order parameter (polarization in one of sublattices) takes place.

The temperature behaviour of dielectric susceptibility components and their anomalies in the phase transition points are illustrated in Fig. 3 and 4 as temperature dependencies of inverse susceptibilities $\chi_{\alpha\alpha}^{-1}$.

The inverse susceptibility χ_{xx}^{-1} is equal to zero at the temperature T_c. Its linear dependence on temperature in the vicinity of this point has an inclination b' at $T > T_c$ and $2b'$ in the ferroelectric phase (Fig. 3). This typical behaviour for second order phase transition changes if the phase transition P→F is of the first order. Such a situation takes place in the DMAGaS crystal where the first order phase transition close to the tricritical point is observed. Then the susceptibility χ_{xx}^{-1} remains nonzero at T_c and has a small jump (according to data [11], $T_c - T_0 \simeq 1.2$ K, where T_0 is the temperature at which $\chi_{xx}^{-1} \to 0$; $\chi_{xx}^{-1}(T = T_c) \simeq 6 \cdot 10^{-4}$). Mentioned changes are relevant only to a small vicinity of T_c; in a large temperature scale dependence $\chi_{xx}^{-1}(T)$ in para- and ferroelectric phase is almost the same as for the second order transition. The phase transition

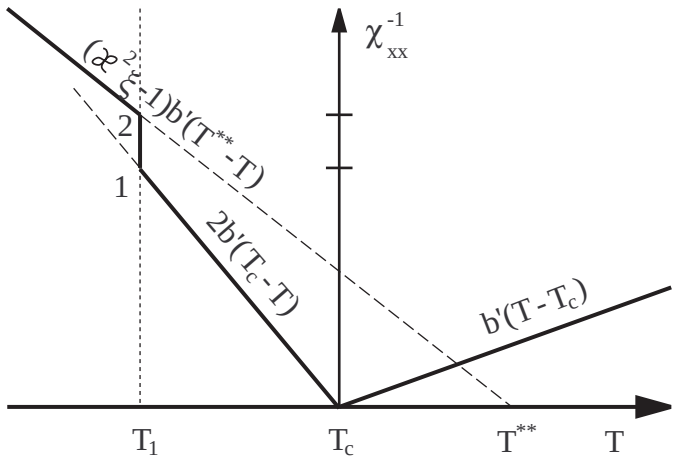

Figure 3. Temperature dependences of χ_{xx}^{-1} component of inverse susceptibility.

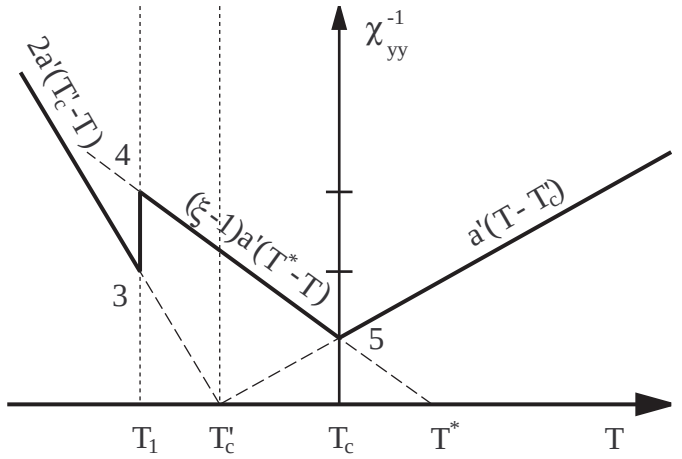

Figure 4. Temperature dependences of χ_{yy}^{-1} component of inverse susceptibility.

F→AF is a well pronounced first order phase transition accompanied by jump of the χ_{xx}^{-1} function. The continuation of the straight line describing the temperature dependence of χ_{xx}^{-1} in the AF phase passes the point T^{**} (see Fig. 3). χ_{xx}^{-1} has the following values at the ends of its jump

$$\begin{aligned} \chi_{xx}^{-1}\big|_1 &= 2b'\frac{\varkappa}{\varkappa-1}(T_c-T_c'), \\ \chi_{xx}^{-1}\big|_2 &= \left[\frac{\varkappa}{\varkappa-1}(\varkappa^2\xi-1)+\varkappa^2\xi\right]b'(T_c-T_c'). \end{aligned} \tag{28}$$

Value of susceptibility jump $\Delta\chi_{xx}^{-1} = \chi_{xx}^{-1}\big|_2 - \chi_{xx}^{-1}\big|_1$ can be positive or negative depending on values of theory parameters.

Temperature behaviour of the inverse susceptibility χ_{yy}^{-1} is essentially different. In the point of the second order phase transition P→F it remains nonzero with value

$$\chi_{yy}^{-1}(T_c) = a'(T_c-T_c') \tag{29}$$

Its continuation to lower temperatures goes to zero at $T \to T_c'$. The continuation of the line of the inverse susceptibility in the antiferroelectric phase $\chi_{yy}^{-1}(T) = 2a'(T_c'-T)$ also goes across this point. In the ferroelectric phase region the function $\chi_{yy}^{-1}(T)$ is linear with the continuation passing the point T^{**}. At the F→AF phase transition this function has a jump between points

$$\begin{aligned} \chi_{yy}^{-1}\big|_3 &= \frac{2a'}{\varkappa-1}(T_c-T_c'), \\ \chi_{yy}^{-1}\big|_4 &= \frac{\varkappa\xi-1}{\varkappa-1}a'(T_c-T_c'). \end{aligned} \tag{30}$$

Similarly to the case of the function χ_{xx}^{-1} the jump can have positive or negative value.

4. Discussion

Proceeding from obtained in the previous section formulae one can try to interpret available data on the temperature dependence of dielectric susceptibility components of DMAAS and DMAGaS crystals. The majority of performed measurements is devoted to the longitudinal dielectric permittivity ε_x (or its real part ε_x' for low frequency alternating current measurements) mainly in the region of the high-temperature phase transition for DMAGaS and the corresponding phase transition in DMAAS. Such data are reported in works [5,8,9,11] (DMAGaS) and [4,7,8] (DMAAS);

only in paper [7] the temperature behaviour of all permittivity components (ε_a', ε_b', ε_c') for DMAAS crystal in the wide range of temperatures (from ≃90 K to ≃280 K) was measured. In some papers dependence of spontaneous polarization on temperature in the ferroelectric phase was investigated and coercivity fields were measured [8,9] (the value of P_s in the state close to saturation is about 1.4–1.9 C/m^2 for DMAAS and 0.9–2.0 C/m^2 for DMAGaS). Particular investigation of the T_c point vicinity in DMAGaS devoted to influence of the external electric field on the first order phase transition point and the difference $T_c - T_0$ is made in [11]. On the basis of available experimental data Curie-Weiss constant (from the paraphase side) is estimated as 2700–3060 K for DMAGaS crystal and 2700–3000 K for DMAAS crystal. The phase transition to the ferroelectric phase in DMAGaS crystal is of the first order and close to the tricritical point; this fact however does not affect the behaviour of χ_{xx} and χ_{yy} far from the T_c point.

The mentioned experimental data are incomplete, hence only partial comparison with results of thermodynamical description is possible. For example one can obtain values of the temperature T_c', parameters b' and $\varkappa$ for the DMAGaS crystal $T_c' = 125$ K, $\varkappa = 2.22$, $b' = 0.33 \cdot 10^{-3}$ K^{-1} with use of above mentioned data on the influence of external hydrostatic pressure on phase transitions in DMAGaS crystal [16] and results of measurements of dielectric characteristics.

More comprehensive and selfconsistent evaluation of temperatures T_c', T^* and T^{**} as well as Landau expansion parameters (or parameters a', b', $\varkappa$, ξ and f) by means of presented in this section relationships become possible after goal-oriented investigations of temperature dependencies of χ_{xx}^{-1} and χ_{yy}^{-1} in a wide temperature interval including regions of existence of all phases for DMAGaS and DMAAS. Proceeding from obtained results will be possible to ascertain suitability of the simple thermodynamical description where Landau expansion is limited to only one order parameter for each of B_u and A_u representations. Such a description is obviously much simplified comparatively to results of the microscopic approach based on the four-state model of order-disorder type [15]. Investigation of DMA group ordering in the configurational space of four orientational states needs two-component order parameters η_b^α (B_u) and η_a^α (A_u), $\alpha = 1, 2$. This fact could complicate temperature dependencies of dielectric characteristics of the model even for thermodynamical description in the framework of Landau expansion.

Furthermore, considered here expression for Landau expansion of free energy (1) includes terms up to the fourth order. A consistent description of the first order phase transition P→F and related dielectric anomalies

demands the inclusion of the sixth order terms into expansion. Such a generalization is necessary for comprehensive description of experimental data and can be performed relatively easy.

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Термодинаміка та діелектричні аномалії в області фазових переходів у кристалах DMAAS та DMAGaS

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