Study of Condensed Matter by Neutron Scattering and Complementary Methods

Nonclassical Critical Behaviour and Low Temperature Anomalies in Ferroelectric DMACA as Described by Many-Sublattice Model

M. Gałązka^{a,*} and P. Zieliński^{a,b}

^aThe H. Niewodniczański Institute of Nuclear Physics, PAS, E. Radzikowskiego 152, 31-342 Kraków, Poland ^bCracow University of Technology, Institute of Physics, Podchorążych 1, 30-084 Kraków, Poland

A model based on the crystallographic data on dimethylammonium nonachlorodiantimonate (DMACA) is constructed. Gradual orientational ordering of three inequivalent sublattices of the dimethylammonium cations is shown to be at the origin of the anomalous behaviour of the spontaneous polarisation in this material. A quantitative comparison with the experimental data reveals a temperature dependence of a coupling between two sublattices and a strong deformability of the underlying structure.

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1. Introduction

The phenomenon of ferroelectricity may essentially involve two mechanisms. In simple ionic crystals, for example BaTiO₃, SrTiO₃, KTaO₃ [1–8], the spontaneous polarisation results from mutual displacements of the positive and negative charges of atomic ions. Then the phase transition is accompanied with a soft phonon mode involving displacements of atoms and one speaks of displacive phase transition. The saturation of the order parameter in displacive phase transitions has some quantum grounds, such as a freezing of fluctuation degrees of freedom [1-7], or it can be a result of an anharmonicity of local potentials and, usually, it takes place in very low temperatures, lower than 50 K that is far away from the critical temperatures [1-7]. In more complex molecular crystals (for example Rochelle salt, MAPCB, MAPBB, DMACA, DMABA, TMACA, etc. [8–34]) phase transitions arise from orientational ordering of permanent dipolar moments of molecules having a rotational freedom in high temperatures. The orientational disorder is usually a result of jumps among few discrete minima of energy, which minima become inequivalent in the ordered phase. In such cases one deals with an order-disorder phase transition. Then the saturation of the order parameter corresponds to all the permanent dipoles oriented parallel [8, 12, 16].

The rate at which the spontaneous polarisation attains its saturation varies from material to material. The first reason for that comes from the number of accessible equilibrium states of the ions (see the Potts model [8, 12, 35]). Another reason for that lies in a coupling with additional degrees of freedom forming what is known as secondary order parameters and it takes place in temperatures a few dozens below the critical temperatures that is a few times higher than for displacive phase transitions. In fact any realistic example is a mixture of both mechanisms, because even the positions of single atomic ions may show a number of discrete minima of energy and an orientational ordering is often coupled with translational displacements of the mass centres of the molecular ions [4, 6, 13, 36, 37].

The equations of state based on the scaling hypothesis [8, 12, 35], and references cited therein, reproduce adequately the power law behaviour of the order parameter, of the susceptibility as well as of the specific heat and entropy in the vicinity of the critical point (for example see Refs. [8, 12, 35]) with the effective critical exponents usually different from what is known as classical and universal critical exponents [13]. The difference originates from experimental conditions such as the size of the sample, impurities and defects, amplitude and frequency of a measuring field, a too fast variation rate of external parameters in comparison with internal relaxation times. Therefore, to reproduce the results of real experiments in the vicinity of the critical point one should take into account the effective exponents reflecting the properties of the sample itself together with the experimental conditions. These numbers are, in fact, no longer critical exponents, but still effective ones (for example see Refs. [13–16]). However, the scaling equations of state cannot be used far below the phase transition where effects due to the order parameter saturation become dominating.

On the other hand, mean field approximations provide a description down to helium temperatures but they invariably imply classical critical exponents in the vicinity of the critical temperature [3, 5, 10, 12]. Therefore, one should look for the equations of state that are valid in both regions and capable of reproducing the real experimental data. This means that the equation of state should give power laws in the very vicinity of the critical

^{*}corresponding author; e-mail: Miroslaw.Galazka@ifj.edu.pl

temperature and describe saturation of the order parameters, at the adequate temperatures. A method of construction of the equation of state with the use of microscopic models based on the crystallographic structure will be presented in Sect. 3. This method will be exemplified on the ferroelectric $[NH_2(CH_3)_2]_3Sb_2Cl_9$ — dimethylammonium nonachlorodiantimonate, abbreviated DMACA [17-20], undergoing continuous phase transition at 242 K. Another smooth anomaly of the spontaneous polarisation has been observed in the low temperature region about 215 K. The anomaly is attributed to subsequent orientational ordering of a sublattice of polar molecular ions. A scheme of the construction of Hamiltonians involving multiple deformable sublattices (many-sublattice pseudospin Ising model, MS-PIM) will be presented.

2. Experimental details and properties of ferroelectric DMACA

2.1. Experimental details

Single crystals of $[NH_2(CH_3)_2]Sb_2Cl_9$ were grown by slow evaporation from aqueous solution containing 3:2 mole fraction of $[NH_2(CH_3)_2]Cl$ and Sb_2O_3 with an excess of HCl. The synthesis of the crystal DMACA is given in detail elsewhere, for example see Refs. [17, 18]. Thin slices of DMACA were cut from single crystals normal to the *c* and *b* crystallographic axes of the room temperature structure.

The polarisation along the *a* and *c* crystallographic axes have been measured by two different methods, and they are presented elsewhere: pyroelectric method [21] and Chynoweth technique [17] with the temperature rate of 1 K/min and of 3.8 K/min, respectively. The temperature dependence of the spontaneous polarization, by the pyroelectric technique, was measured continuously by a charge-integration technique using a digital electrometer Keithley 617. The samples were of dimensions of about $5 \times 5 \times 1 \text{ mm}^3$. The errors of the measured polarisations are not higher than 1%.

The other physical quantities as lattice cell parameters, a, b, and c [18, 21], the specific heat [22], the susceptibility in zero and non-zero biasing fields [23–25], the linear birefringence [26], the Brillouin scattering [27] and the structure [28] have also been measured.

2.2. Phase sequence in DMACA

The ferroelectric DMACA undergoes a continuous phase transition at $T_{\rm C} = 242$ K [17–28]. The symmetry relation is $Pc \rightarrow P2_1/c$ [28]. The crystal structure of DMACA at low temperature phase is built of anionic sublattice in the form of two-dimensional layers, lying in the *bc* plane, formed by a distorted hexachloroantimonate octahedra joint by corners, and six dimethylammonium cations (DMA) in the cell [28]. The DMA cations can be divided into three classes in the low temperatures phase and into two classes in the high temperature phase. One of the DMA cation class (abbreviated as DMA1 in both phases) is located between the layers and the remaining two cation classes (abbreviated as DMA2, DMA3^{*} in the ferroelectric phase and DMA2^{*} in the paraelectric phase) — inside the layers.

The mechanism of the phase transition at 242 K involves ordering of four of the six DMA cations [18, 21, 23–25, 28] in the unit cell. The cations of the class DMA1 are disordered so that they occupy two orientations with an occupancy factor of 0.5 in the paraelectric phase [28]. This class of cations becomes ordered in the ferroelectric phase. The reorientational motions of these cations freeze at $T_{\rm C}$. Every cation of the class DMA2^{*}, shows three non-equivalent orientations DMA21, DMA22 and DMA23 in the paraelectric phase with the occupancy factors: 0.48, 0.37 and 0.15, respectively [28]. Below $T_{\rm C}$ two of the four cations, abbreviated as DMA21 in paraelectric phase, become ordered (in ferroelectric phase they are abbreviated as DMA2) and two other cations remain still disordered, but with two non-equivalent positions DMA31 and DMA32 with the occupancy factors 0.73 and 0.27, respectively [28], and this cations class is abbreviated as DMA3^{*}.

2.3. Spontaneous polarisation along a and c crystallographic axes

Figure 1a and b shows the spontaneous polarisation along a and c crystallographic axes measured by pyroelectric method, respectively. One sees that spontaneous polarisations are increasing functions of temperature up to about 215 K and then they change the behaviour and become decreasing functions of temperature. The dipole moment of the DMA1 cations, in the low temperature phase, has non-vanishing component along a and c crys-



Fig. 1. Spontaneous polarisations measured by pyroelectric method along (a) a axis, (b) c axis.



Fig. 2. Spontaneous polarisations measured by Chynoweth technique along (a) a axis, (b) c axis. Spontaneous polarisations are given in the arbitrary units.

tallographic axes, the component along the a axis being few times higher than the one along the c axis. The dipole moments of the DMA2 cations have components along c axis a few times higher than along a axis. The aand c components of the dipoles of the DMA3^{*} cations are almost equal but the component along the a axis is opposite to the corresponding component of the DMA1 dipoles.

The cations class DMA2^{*} starts ordering in temperatures lower than $T_{\rm C}$ and therefore their contribution to the total spontaneous polarisation is visible along *a* axis as a decreasing function of lowering temperature. The phase transition temperatures are about 241.88 K and 241.12 K for *a* and *c* axes, respectively. Figure 2a and b shows the spontaneous polarisations along *a* and *c* crystallographic axes measured by the Chynoweth technique. In this technique the phase transition temperatures are estimated as the inflection points and they are about 241.88 K and 241.78 K for *a* and *c* axes, respectively. Huge values of the spontaneous polarisation tails above these temperatures, together with the high rate of the temperature variations, makes these data rather indicative than quantitative.

3. Many-sublattice pseudospin Ising model

To give the equation of state for the ferroelectric material DMACA one needs to write the Hamiltonian containing interaction terms between dipole moments of: (i) DMA1 cations $\sigma_i - \sigma_j$; (ii) DMA2 cations $\mu_i - \mu_j$; (iii) DMA3^{*} cations $\eta_i - \eta_j$; (iv) DMA1-DMA2 and DMA1–DMA3^{*} cations $\sigma_i - \mu_j$ and $\sigma_i - \eta_j$; (v) DMA2– DMA3^{*} cations $\mu_i - \eta_j$. The interaction strengths must reflect that the DMA2 and DMA3^{*} cations start to order in temperatures lower than $T_{\rm C}$. They will then order in the effective field of the ordered DMA1 cations. Introducing

$$s_i \equiv \mu_i + \eta_i \quad \text{and} \quad r_i \equiv \mu_i - \eta_i$$
 (1)

one can write that the n-th element of the mean field many-sublattice pseudospin Ising model Hamiltonian is

$$H_n^{(\mathrm{MS-PIM})} \equiv -\frac{1}{2} \left(k_s \langle s \rangle^2 + k_r \langle r \rangle^2 + j \langle \sigma \rangle^2 + 2g \langle r \rangle \langle \sigma \rangle \right) - \left(h_0 + k_s \langle s \rangle \right) s_n + \left(k_r \langle r \rangle + g \langle \sigma \rangle \right) r_n + \left(g \langle r \rangle + j \langle \sigma \rangle \right) \sigma_n,$$
(2)

where j is a coupling coefficient between $\sigma_i - \sigma_j$, k_s is the coupling coefficient between $s_i - s_j$, k_r is the coupling coefficient between $r_i - r_j$, g is the coupling coefficient between $\sigma_i - r_j$; $\langle \sigma \rangle$, $\langle s \rangle$, $\langle r \rangle$ are average values of dipole moment in the mean field of the other dipoles and h_0 is the effective field of the ordered DMA1 acting on the DMA2 and DMA3* cations. The σ_n can take two positions, let us say, up and down and μ_n and η_n — three positions, let us say, A, B, and C with adequate occupancy factors. Therefore, the Hamiltonian is a sum over n = 1-18, for all of the possible combinations of σ_n , μ_n , and η_n positions. The partition function Z and the free energy density function F are given by following relations:

$$Z = \sum_{n=1}^{18} \exp\left(-\frac{H_n^{(\rm MS-PIM)}}{k_{\rm B}T}\right),\tag{3a}$$

$$F = -k_{\rm B}T\ln Z,\tag{3b}$$

where $k_{\rm B}$ is the Boltzmann constant.

The equations of state correspond to the requirement of a minimum of the free energy density F

$$\frac{\partial F}{\partial \langle \sigma \rangle} = 0, \quad \frac{\partial F}{\partial \langle s \rangle} = 0, \quad \frac{\partial F}{\partial \langle r \rangle} = 0.$$
 (4a, 4b, 4c)

Equations (4a)–(4c) give temperature dependence of the order parameters $\langle \sigma \rangle$, $\langle s \rangle$, $\langle r \rangle$. Six general cases are possible with the corresponding values of the coefficients j, g, k_s , and k_r in Eq. (2).

Case 1. The coefficient j is the only non-zero one, $j \neq 0$, whereas $g = k_s = k_r = 0$. Figure 3a shows the dependence of the order parameter $\langle \sigma \rangle$ on temperature, with the coefficient $j = 240k_{\rm B}$. In this case one deals with one-lattice phase transition only. The critical temperature is equal to 240 K and, generally, is defined as $T_{\rm C} = j/k_{\rm B}$. This dependence can be compared with pseudospin Ising model for uniaxial material (for example see Refs. [15, 16]).

Case 2. The coefficients k_s and k_r are different from zero, $k_s \neq 0$ and $k_r \neq 0$, and the remaining vanish, g = j = 0. Figure 3b shows the dependence of the order parameter $\langle r \rangle$ on temperature, with the coefficients $k_s = 273k_{\rm B}$ and $k_r = 310k_{\rm B}$. In this case one deals with two-lattices phase transitions (DMA2 and DMA3^{*}). The phase transition is discontinuous one at temperature about $T_{\rm C} \approx (k_r/k_{\rm B})f_1 \approx 13.4$ K.



Fig. 3. Temperature dependences of the order parameters: (a) $\langle \sigma \rangle$ for the only non-zero coefficient $j, j \neq 0$ (cases 1 and 3), (b) $\langle r \rangle$ for coefficients k_s and k_r different from zero, $k_s \neq 0$ and $k_r \neq 0$, and the remaining vanishing, g = j = 0 (cases 2 and 3).

Case 3. The coefficient g is equal to zero, g = 0, and the other are non-zero, $j \neq 0$, $k_s \neq 0$ and $k_r \neq 0$. Figure 3a and b presents the temperature dependences of the order parameters $\langle \sigma \rangle$ and $\langle r \rangle$, respectively, with the coefficients from cases 1 and 2. One sees that in this case one deals with two separate, non-coupled phase transitions. One of them is continuous and the other discontinuous.

Case 4. The coefficients j and g are non-zero ones, $j \neq 0$ and $g \neq 0$, and the other vanish, $k_s = k_r = 0$. This means that one deals with the interactions between order parameters $\sigma_i - \sigma_j$ and $\sigma_i - r_j$ and, moreover, the order parameter $\langle r \rangle$ is in the effective field of the order parameter $\langle \sigma \rangle$.

Figure 4a and b shows the temperature dependences of the order parameters $\langle \sigma \rangle$ and $\langle r \rangle$, respectively, with the coefficients $j = 240k_{\rm B}$ and $g = 30k_{\rm B}$. The critical temperatures for both transitions are about $T_{\rm C} \approx j/k_{\rm B} + g^2 j^{-1} k_{\rm B}^{-1} f_1$ and equal to 240.7 K. Both transitions are continuous.

Case 5. The coefficient j is equal to zero, j = 0, and the remaining are non-zero, $g \neq 0$, $k_s \neq 0$ and $k_r \neq 0$. This means that one deals with the interactions between order parameters $r_i - r_j$, $s_i - s_j$, and $\sigma_i - r_j$ and, moreover, the order parameter $\langle \sigma \rangle$ is in the effective field of the order parameter $\langle r \rangle$.

Figure 5a and b shows the temperature dependences of the order parameters $\langle \sigma \rangle$ and $\langle r \rangle$, respectively, with the coefficients $k_s = 210k_{\rm B}$, $k_r = 310k_{\rm B}$ and $g = 30k_{\rm B}$. Both transitions are continuous and take place at about $T_{\rm C} \approx (k_r/k_{\rm B})f_1 + g^2k_r^{-1}k_{\rm B}^{-1}f_2/f_1 \approx 18.1$ K.

Case 6. Il of the coefficients differ from zero, $j \neq 0$, $g \neq 0$, $k_s \neq 0$ and $k_r \neq 0$. Figure 6a and b presents



Fig. 4. Temperature dependences of the order parameters: (a) $\langle \sigma \rangle$, (b) $\langle r \rangle$ for coefficients j and g being non--zero ones, $j \neq 0$ and $g \neq 0$, and the other vanishing, $k_s = k_r = 0$ (case 4).



Fig. 5. Temperature dependences of the order parameters: (a) $\langle \sigma \rangle$, (b) $\langle r \rangle$ for coefficient *j* being equal to zero, j = 0, and the remaining ones are non-zero, $g \neq 0$, $k_s \neq 0$, $k_r \neq 0$ (case 5).

the temperature dependences of the order parameters $\langle \sigma \rangle$ and $\langle r \rangle$, respectively, with the coefficients $j = 240k_{\rm B}$, $k_s = 180k_{\rm B}$, $k_r = 210k_{\rm B}$ and $g = 50k_{\rm B}$. The both transitions are continuous ones and take place at about $T_{\rm C} \approx j/k_{\rm B} + g^2 k_r^{-1} k_{\rm B}^{-1} f_1 \approx 243.8$ K. Even for the very weak coupling coefficient g one deals with continuous phase transitions.



Fig. 6. Temperature dependences of the order parameters: (a) $\langle \sigma \rangle$, (b) $\langle r \rangle$ for all of the coefficients differing from zero, $j \neq 0, g \neq 0, k_s \neq 0, k_r \neq 0$ (case 6).

The functions f_i , i = 1, 2, in cases 1–6 are some combinations of the model coefficients and of the material constants. They are given in ppendix A.

4. Discussion

Comparing the experimental curves of the spontaneous polarisations along a and c axes in Figs. 1a–2b, with the theoretical ones, shown in Figs. 3a-6b, one sees that in order to obtain the best fit all the coefficients of the model should be non-zero. In particular, in the case of a non-zero coefficient g all of sublattices are coupled to each other. Moreover, in cases 4–6, the presence of the non-zero coefficient q in Eq. (2) results in equating of the critical temperatures for the order parameters $\langle \sigma \rangle$ and $\langle r \rangle$. Additionally, comparing Figs. 3b and 5b one sees that in the presence of the coupling term between cations classes DMA1 and DMA2 or DMA3^{*} the phase transition changes from discontinuous to continuous. This means that the effective field due to the ordered cations DMA1 changes the kind of the phase transition of cations classes DMA2 and DMA3^{*}. This is very similar to the ordering of the systems showing the first order phase transitions in the very strong fields that causes changes in the character of the phase transitions [8, 12, 38].

In order to obtain the different phase transition temperatures for the order parameters $\langle \sigma \rangle$ and $\langle r \rangle$ one needs



Fig. 7. Temperature dependences of the order parameters for different cases: (a) and (c) the order parameter $\langle \sigma \rangle$, (b) and (d) the order parameter $\langle r \rangle$ for coefficients given in Table. Solid curves are dependences in noncompressible model (all of coefficients do not depend on strain); dashed curves (compressible "1") — only coefficient *j* depends on strain up to the linear term; shortdashed curves (compressible "2") — coefficient *j* depends on strain up to the square term; dotted curves (compressible "3") — coefficients k_s and k_r — up to the linear terms; and dash-dotted curves (compressible "4") — coefficients *j*, k_s and k_r — up to the square terms.

to put a temperature dependence to the coefficient g. In the case 3 the temperatures of the phase transitions become different. part from that the phase transitions become of different kinds and the temperature of the phase transition for the order parameter $\langle r \rangle$ becomes rather low.

To obtain a saturation of the spontaneous polarisations in temperatures similar as in the real materials one has to replace the constant coefficients j, k_s and k_r with functions depending on the secondary order parameter, as in the case of uniaxial ferroelectric materials MAPCB and MAPBB [14, 16, 29, 39]. Then one deals with polarisation-strain coupling.

Figure 7a and b shows the temperature dependences of the order parameters $\langle \sigma \rangle$ and $\langle r \rangle$, respectively, for the case 6 with coefficients: solid curves — all of the coefficients are temperature independent, dashed curves — the coefficient j does depend on the strain up to the linear term, short-dashed curves — the coefficient j depends on the strain up to the square term.

Figure 7c and d presents the temperature dependences of the order parameters $\langle \sigma \rangle$ and $\langle r \rangle$, respectively, for the case 6 with coefficients: solid curves — all of the coefficients are temperature independent, short-dashed curves — the coefficient j depends on the strain up to the square term, dotted curves — the coefficient j depends on the strain up to the square term and the coefficients k_s and k_r — up to the linear terms, dash-dotted curves — the coefficients j, k_s and k_r do depend on the strain up to the square terms. The coefficients j, k_s and k_r are given, generally, by

$$j = j_0 + j_1 \varepsilon + j_2 \varepsilon^2, \tag{5a}$$

$$k_s = k_{s_0} + k_{s_1}\varepsilon + k_{s_2}\varepsilon^2, \tag{5b}$$

$$k_r = k_{r_0} + k_{r_1}\varepsilon + k_{r_2}\varepsilon^2.$$
(5c)

The values of the coefficients in Eqs. (5a), (5b) and (5c)are given in Table. Il of the values of the coefficients in the cases 1-6 and presented in Table are chosen to be close to the real ones [14, 16, 29, 39]. One sees that for the case of compressible model the saturation of the order parameter is much faster. Additionally, the temperatures of the phase transitions are very weakly dependent functions of the coefficients j_1 and j_2 , see Figs. 7a and b the critical temperatures changes between incompressible and compressible models are smaller than 0.01 K. But the temperatures of the phase transitions do stronger depend on the coefficients k_{s_i} and k_{r_i} , for i = 1, 2. The critical temperature for only coefficient j given by Eq. (5a) and with the remaining coefficients independent of the strain is about 241.7 K. When the coefficients k_s and k_r do depend on the strain, Eqs. (5b) and (5c), then the critical temperatures are about 245.5 K, for the linear dependences on the strain, and about 245.9 K, for the square dependences on the strain.

TABLE

Values of coupling coefficients between primary order parameters, polarisations along a and c crystallographic axes, and secondary order parameter, strain, used in Eqs. (2), (5a), (5b) and (5c) to obtain Fig. 7a–d. Il values of coefficients are multiplications of the Boltzmann constant $k_{\rm B}$.

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Fig. No.	j_0	j_1	j_2	g	k_{s_0}	k_{s_1}	k_{s_2}	k_{r_0}	k_{r_1}	k_{r_2}
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	7a	240	1.6×10^4	5.5×10^5	30	220	-	_	310	-	-
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$7\mathrm{b}$	240	1.6×10^4	5.5×10^5	30	220	-	_	310	-	-
$7d \qquad 240 \qquad 1.6 \times 10^4 \qquad 5.5 \times 10^5 \qquad 30 \qquad 220 \qquad 500 \qquad 1.3 \times 10^5 \qquad 310 \qquad 500 \qquad 1.5 \times 10^5$	7c	240	1.6×10^4	5.5×10^5	30	220	500	1.3×10^{5}	310	500	1.5×10^{5}
	7d	240	1.6×10^4	5.5×10^5	30	220	500	1.3×10^5	310	500	1.5×10^5

5. Conclusions

The above general model of three sublattices of interacting dipolar cations show that the model coefficients should depend on strain. Moreover, the coupling coefficient of the sublattices ought to be function of temperature for DMACA. A discontinuous phase transition in two of the sublattices is smeared out over a range 10 K because of this coupling giving rise to a broad thermal anomaly. The sublattices DMA2 and DMA3* show the strongest coupling with the strain than DMA1 that is essential in the fast saturation of the order parameter below the critical temperature.

Appendix

The temperatures of the phase transitions $T_{\rm C}$ in the cases 1–6 are estimated from the self-consistent equations given above, in the cases 1–6, with

$$f_1 = \left[(+B)^2 \exp\left((-B)\gamma_{hs} \right) + (+C)^2 \right]$$

$$\begin{aligned} & \times \exp\left((-C)\gamma_{hs}\right) + (B+C)^{2} \exp\left((B-C)\gamma_{hs}\right) \right] \\ & / \Big\{ \Big[\exp\left(2h_{0}/k_{\rm B}T_{\rm C}\right) + \exp\left(2Bh_{0}/k_{\rm B}T_{\rm C}\right) \\ & + \exp\left(2Ch_{0}/k_{\rm B}T_{\rm C}\right) \Big] / 2 + \Big[\exp\left((-B)\gamma_{hs}\right) \\ & + \exp\left((-C)\gamma_{hs}\right) + \exp\left((B-C)\gamma_{hs}\right) \Big] \Big\}, \\ f_{2} &= \Big[(+B) \exp\left((-B)\gamma_{hs}\right) + (+C) \\ & \times \exp\left((-C)\gamma_{hs}\right) + (B+C) \exp\left((B-C)\gamma_{hs}\right) \Big] \\ & / \Big\{ \Big[\exp\left(2h_{0}/k_{\rm B}T_{\rm C}\right) + \exp\left(2Bh_{0}/k_{\rm B}T_{\rm C}\right) \\ & + \exp\left(2Ch_{0}/k_{\rm B}T_{\rm C}\right) \Big] / 2 + \Big[\exp\left((-B)\gamma_{hs}\right) \\ & + \exp\left((-C)\gamma_{hs}\right) + \exp\left((B-C)\gamma_{hs}\right) \Big] \Big\}, \end{aligned}$$

where $\gamma_{hs} = \frac{h_0 + k_s \langle s \rangle_{T_C}}{k_B T_C}$ and $\langle s \rangle_{T_C}$ is the value of the order parameter $\langle s \rangle$ exactly at T_C .

In the case 4 one got to put into the function f_1 the value $k_s = 0$.

The order parameters $\langle \sigma \rangle$ and $\langle r \rangle$ are equal to zero in the high temperature phase, but the parameter $\langle s \rangle$, not breaking the symmetry operation, is different from zero value. Therefore, knowing the occupancy factors for the states denoted as A, B, and C, at the temperature 298 K,one can obtain equations relating these quantities and h_0 from the partition function. Generally, the effective field h_0 does a dependence on the average value of the dipole moment DMA1 in the low temperature phase and takes a constant value in the high temperature phase. In the first approximation we have taken constant value of the effective field h_0 , similarly as for ferroelectric MAPCB [10, 40], calculated in the paraelectric phase. To obtain values for B and h_0 we assumed that A and C are equal to 1 and 0, respectively. Then B equals to 0.776 and h_0 equals to $346.62k_{\rm B}$. To obtain dependence of the effective field h_0 on temperature more sophisticated method should be applied (e.g. *ab initio*, etc.).

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