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SUCCESSIVE PHASE TRANSITIONS IN THE MeLiBO_4 TYPE CRYSTALS

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Abstract The properties of pseudo-proper ferroelectrics of the CsLiMoO_4 group are reviewed. The structures of distorted phases and calorimetry of the crystals are discussed. The model of the order-disorder type transitions is proposed and solved in a cluster approximation. Comparison with experimental data is made.

1. INTRODUCTION

Ferroelectric properties of the double alkaline molybdates and tungstates: CsLiMoO_4 (CLM), CsLiWO_4 (CLW) and RbLiMoO_4 (RLM) were found and studied recently in this laboratory ¹⁻³. CLM and CLW crystals at room temperature belong to the cubic acentric space group $G_0 = T_d^2 = F\bar{4}3m$ and show a remarkable piezoelectric effect and second optic harmonic generation. Their structure is based on a frame of corner-linked MoO_4 and LiO_4 tetrahedra, and topologically related to the well-known structure of the high cristobalite form of SiO_2 . Large alkaline cations occupy one half of the 12-coordinated Laves polyhedra of the frame. In the course

of the G_o -structure determination ⁴ it has been noticed that Cs-O distances in this polyhedron for CLM substantially exceed the sum of their ionic radii and the thermal parameters of oxygens are abnormally large if these atoms are located on the 3-fold axes of the structure (16-fold positions). These thermal parameters and R-factors were remarkably lowered when the statistical disordering of oxygens on six general positions around 3-fold axis was included in the model of structure (96-fold positions, Δr_o 0,26 Å). The analogous conclusion was independently made in the course of the G_o -structure study for CLW ⁵.

The existence of statistical disorder in G_o -phases initiates both our study of the probable structural phase transitions (PT's) in CLM and CLW below room temperature and efforts to synthesize the Rb- and K-isomorphs of the crystals. Cristobalite-like phase was found ⁷ in RLM above 400 K. Potassium-lithium molybdate and tungstate transform to the same structure above 630 K but the cubic phase is unstable and the crystals have the tridimite-like structure at room temperature ⁶.

In this paper the previous results on the study of PT's, ferroelectric and elastic properties of the CLW, CLM and RLM crystals are shortly reviewed and then the new data on structures of the low temperature phases and the adiabatic calorimetry of the crystals are discussed in the connection with the statistical theory of PT's which was shortly presented in ⁷. The results of the theory in the cluster approximation may be now compared with the experimental data.

2. PHASE TRANSITIONS

Single crystals of CLM, CLW and RLM were grown by Bridgman method in the sealed platinum ampoules from the melt of corresponding stoichiometric substances which were prepared beforehand by means of the solid-phase synthesis from the anhydrous salts, e.g. Cs_2MoO_4 and Li_2MoO_4 for CLM⁴. Experimental samples were cut out from annealed boules (diameter ~ 10 mm, ~ 30 mm in length) which were optically clean and lightly coloured. X-ray method was used for the orientation of the samples. The dielectric, ferroelectric, elastic properties and the optical twinning below PT's were studied earlier¹⁻³, Raman-spectrum and NMR data were presented in⁹, some calorimetric data in^{7,10}.

The properties of the CLM and CLW crystals are closely related. Both crystals undergo the sequence of the two first order PT's $G_0 \rightarrow G_1 \rightarrow G_2$ at temperatures $T_{c1}=220$ K, $T_{c2}=185$ K for CLW and 209 K and 171 K for CLM. These PT's proceed without multiplication of the formula unit number in the (primitive) unit cells and the following symmetry changes at PT's were determined^{1,3,7}:

$$T_d^2 (Z=1) \rightarrow C_{3v}^5 (Z=1) \rightarrow C_s^1 (Z=1) \quad (1)$$

Unit cell parameters are presented in Table 1, where F-centered unit cell ($Z=4$) is used for G_0 -phases.

The deformed hysteresis loops were observed in G_1 and G_2 phases. The values of the spontaneous polarization (P_s) were measured by the pyroelectric charge method¹ only for G_1 -phases. Just above T_{c2} the values are equal $\sim 0,4$ and $0,07$ (in $10^{-2} \text{ C}\cdot\text{m}^{-2}$) for CLM and CLW respectively. In G_2 -phases this method gives the lowered values of P_s due to the complex twinning

of the samples. Single domain samples were obtained only in the G_1 -phases by applying dc electric field or mechanical stresses. The main peculiarities of the physical properties in both crystals are the absence of dielectric anomaly and the strong decrease of shear elastic stiffness c_{44} in G_0 above T_{c1} . Due to their G_0 structure both crystals in trigonal phases belong to the class of ferroelectrics where $P_S \parallel [111]_C$ can not be reversed under biasing electric field but changes its direction to other 111 -type directions.

These data allow to conclude that both CLM and CLW are the pseudoproper ferroelectrics and ferroelastics. Thermodynamical theory of $G_0 \rightarrow G_1 \rightarrow G_2$ transitions was published earlier ¹. The potential of the acentric G_0 phase contains both even and odd order terms of three-component order parameter η_i ($i=1,2,3$), which transforms as the irreducible representation F_2 . The bilinear coupling of η with elastic subsystem is much stronger than its interaction with the electric one. The properties of CLM were analysed in neighbourhood of $G_0 \rightarrow G_1$ transition.

Rubidium lithium molybdate (RLM) undergoes three successive PT's at $T_{c1}=390$ K, $T_{c2}=380$ K, $T_{c3}=375$ K. Above T_{c1} it is isomorphous with CLM and CLW. The twinning structure, dielectric properties and X-ray powder data show that the G_1 , G_2 and G_3 -phases belong to trigonal, orthorhombic and monoclinic systems respectively (see Table 1 and Section 3). The crystal is also ferroelectric below T_{c1} . The primitive unit cell of the room temperature G_3 -phase contains two formula units ($Z=2$). The thermodynamical potential ¹ can not be used for the description of PT with multiplication of the unit cell. Another order parameter should be

included for RLM crystal. In Section 5 the statistical model is presented which can explain the main features of physical properties and the sequence of PT's in the whole group of crystals.

3. STRUCTURES OF DISTORTED PHASES

In addition to X-ray powder analysis of distorted phases (Table 1) the atomic structures of the G_1 -phase s CLW and G_3 -phase RLM were determined. Automatic X-ray diffractometer Syntex P1 (MoK α -line, $2\theta, \theta$ method with the variable scanning rate). Cylindrical sample of CLW in a capillary was stressed mechanically and cooled by the nitrogen vapour stream below T_{c1} . Single domain state was optically controlled. 230 independent F_{hkl} at $T=203.2$ K were collected. Computing program Roentgen-80 was used for the solving of the structure.

It is worthwhile to compare the atomic coordinates of basic atoms for G_0 ⁵ and G_1 -phases of CLW in the same presentation (R3m, hexagonal unit cell: $a_h = 5,904$, $c_h = 14,462$ Å for G_0 and $a_h = 5,836$, $c_h = 14,322$ for G_1), Table 2. The comparison shows that all cations have nearly unchanged atomic coordinates in G_1 in respect to G_0 ones. The main changes take place in WO_4 tetrahedron. The W-O distance along 3-fold axis increases on 0,05 Å and three other bonds slightly decrease. It is also seen that both in G_0 and in G_1 (models I in Table 2) the isotropic thermal parameters of oxygens are abnormally large. Anisotropic thermal ellipsoids of O-atoms have a tablet-like form, their short axes are parallel to W-O-Li bonds. R-factor is 0,083 for the "ordered" model I of G_1 -phase. Model II for both phases corresponds to disordered oxygens, they were shifted from their mean positions of Model

TABLE 1 The main crystallographic data

	CsLiMoO_4	CsLiWO_4	RbLiMoO_4
G_0	T_d^2 , $a_0=8,318(4)$ $Z=4$	T_d^2 , $a_0=8,250(4)$ $Z=4$	$T_d(?)$, $a_0=8,115(6)$ $Z=4$
G_1	C_{3v} , $a=b=5,812(5)$ $c=14,298(8)$ $Z=3$	C_{3v}^5 , $a=b=5,836(3)$ $c=14,322(8)$ $Z=3$	C_{3v}^5 , $a=b=5,740(3)$ $c=14,112(8)$ $Z=3$
G_2	I_m $a = 5,84(3)$ $b = 5,86(2)$ $c = 8,34(5)$ $= 90^\circ 40'(8)$ $Z=2$	I_m $a = 5,85(3)$ $b = 5,86(2)$ $c = 8,34(5)$ $= 90^\circ 48'(8)$ $Z=2$	C_{2v} , $a=5,739(3)$ $b=5,751(3)$ $c=8,110(6)$ $Z=2$
G_3			$I111/b$ $a = 10,018(2)$ $b = 11,272(2)$ $c = 5,702(1)$ $= 125,48'(2)$ $Z=4$

I in m -planes. In this case each oxygen is statistically distributed on three positions. Disordered models II lead to the definite reduction of R-factors ($R=0,062$ for G_1) and to the "normal" isotropic thermal parameters of atoms (Table 2).

So we can conclude that a disorder of oxygens taking place in G_0 remains in G_1 -phase and the trigonal symmetry of the structure is preserved due to dynamical disordering of the WO_4 -tetrahedra around 3-fold axis. It can be supposed that the main increment to P_g in G_1 is determined by the small dipole moments of slightly distorted WO_4 -groups; according to NMR-data⁹ the distortions of Li-environment in G_1 are extremely small.

The froasing of tetrahedra in the shifted positions "in phase" leads to the monoclinic structure of G_2 -phase. The straight determination of the G_2 -structure is a difficult problem due to superposition of several systems of twins in a sample. The efforts to detwin the G_2 -phase were unsuccessful yet.

The structure of RLM (G_3 -phase) was published earlier^{7,8}. After three phase transformations the structure maintains the cristobalite-like tetrahedral frame. The displacements of Rb ($0,13 \text{ \AA}$) and Li ($0,06 \text{ \AA}$) in respect to their G_0 -positions take place. Slightly distorted tetrahedral MoO_4 -groups as a whole turn on angles 20° around c and b axes of monoclinic unit cell (directions $[011]$ and $[01\bar{1}]$ in G_0). The tilts of tetrahedra around c are "in phase". Their antiphase tilts around b lead to doubling of the unit cell. The thermal parameters of all atoms have the normal values and we can conclude that tetrahedral groups are completely ordered in the G_3 -phase of RLM.

TABLE 2 Atomic coordinates and isotropic thermal parameters of CsLiMoO_4 in the T_d^2 and C_{3v}^5 phases

The changes in the structure at $G_0 \rightarrow G_1$ can be seen by comparison of the G_0 -coordinates (~ 300 K) taken from 5 (upper lines) to the G_1 -coordinates at 200 K (lower lines). The data for the ordered (I) and disordered (II) models with the corresponding B_j values are presented. Both sets of the data are shown in the hexagonal unit cells ($Z=3$), Table 1.

I. Ordered models				
	x	y	z	B_j
Cs	0	0	0	
	0	0	0	1,7(1)
W	0	0	0,5	
	0	0	0,5021(1)	0,8(1)
O_1	0	0	0,3790	
	0	0	0,3789(5)	7,2(1,7)
O_2	-0,1613	0,1613	0,5403	
	-0,1772(8)	0,1772(8)	0,5279(3)	6,3(1,5)
Li	0	0	0,250	
	0	0	0,251(2)	1,9(7)
II. Disordered models				
Cs	0	0	0	
	0	0	0	1,8(1)
W	0	0	0,5	
	0	0	0,5013(1)	1,0(1)
O_1	-0,0247	0,0247	0,3777	
	-0,0254(7)	0,0254(7)	0,3809(3)	2,8(6)
O_2	-0,1713	0,1713	0,5243	
	-0,1450(7)	0,1450(7)	0,5579(4)	2,2(5)
O_3	-0,1220	-0,3179	0,5490	
	-0,1492(5)	-0,3165(6)	0,5335(6)	2,2(5)
Li	0	0	0,250	
	0	0	0,251(2)	1,9(7)

Thus according to X-ray data it can be supposed that PT's in the group of crystals under consideration (or some of them) are the order-disorder type transi-

tions. The spectroscopic data ⁹ have given the indirect confirmation of the supposition. For a definite choice of the PT's model the calorimetric study of the group of ferroelectrics was made.

4. CALORIMETRIC DATA

Specific heat C_p study of CLW ¹⁰ and CLM was carried out with the adiabatic calorimeter in temperature range 90-320 K. Discontinuous heating and cooling method was used. In order to determine the equilibrium temperature of transitions T_{c1} , the thermal hysteresis values δT_i and the entropy changes δS_i at T_{ci} the continuous heating and cooling experiments with the rate as low as $dT/dt \sim 10^{-4}$ Ksec⁻¹ were made.

Temperature dependences of C_p for CLM and CLW are shown on Fig.1. The two C_p -anomalies correspond to $G_0 \rightarrow G_1 \rightarrow G_2$ PT's. Both curves are similar, the C_p value at 300 K for CLW is 1,6 per cent greater than the corresponding one for CLM. For the determination of the excess part of heat capacity ΔC_p associated with the first order transitions the graphic interpolation of the lattice heat capacity was used (dashed lines on Fig.1). The total entropy changes were estimated as $\Delta S_i = \int \Delta C \cdot T^{-1} dT + \delta S_i$. δS -values were calculated from the enthalpy changes δH_i at $T=T_{ci}$ as $\delta S_i = \delta H_i / T_i$ (Table 3).

Calorimetric data show that in cubic phases of both crystals the excess part of heat capacity exists in a broad region above T_{c1} ($\sim T_{c1} + 60$ K), Fig.1. The increments to the entropy change $\int \Delta C T^{-1} dT$ ($T > T_{c1}$) are equal to $\sim 0,05R$ (CLW) and $0,03R$ (CLM). These increments were not included to the ΔS_1 data of Table 3. The behaviour of the enthalpy at $T=T_{c1}$ gives no indi-

cation to the "smearing" of PT's. It points out both at rather high quality of the crystals used in calorimetric experiments and at the fact that the ΔC_p above T_{c1} is not connected with imperfections of the crystal.

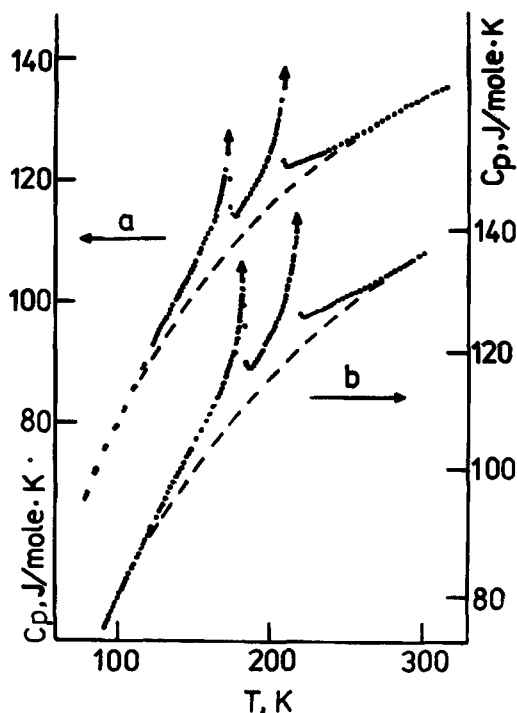


FIGURE 1 Temperature dependences of specific heat $C_p(T)$ for the CLM (a) and CLW (b) crystals.

that the error in δS_1 for RLM does not exceed 10 per cent.

5. MODEL THEORY

Both structural and calorimetric data have given some indications to the transitions of order-disorder type which connected with the ordering of the tetrahedral

RLM single crystal ($\sim 0,09$ g) was studied by DTA method. The sensitive copper-constantan thermocouple was used. The change of S at $G_0 \rightarrow G_1$ PT is equal to $\delta S_1 = 0,22R$. It was impossible to subdivide δS_2 and δS_3 for the close located PT's $G_1 \rightarrow G_2$ and $G_2 \rightarrow G_3$. The sum of the values ($\approx 0,64R$) is shown in Table 3. In order to check the reliability of the δS_1 data for RLM the same values were estimated by DTA for the CLW crystal. The comparison with the data δS_1 and δS_2 (Table 3) allows to conclude

TABLE 3 Thermodynamical characteristics of phase transitions

The comparison between the experimental (E) and theoretical data is made. Two sets of the theoretical values correspond to molecular field (MF) and cluster approximation (CA) of the theory. R is the gas constant.

	CsLiMoO_4			CsLiWO_4			RbLiMoO_4	
	E	MF	CA	E	MF	CA	E	MF
T_{c1}, K	220	220	220	209	209	209	390	390
$\Delta S_1/R$	0,3	0,71	0,4	0,34	0,71	0,4	-	0,71
$\delta S_1/R$	0,17	0,55	0,32	0,18	0,55	0,32	0,22	0,55
T_{c2}, K	185	185	185	171	171	171	380	380
$\Delta S_2/R$	0,33	1,77	1,2	0,28	1,77	1,2	-	1,74
$\delta S_2/R$	0,12	0,77	0,3	0,16	0,77	0,3		0,74
T_{c3}, K	-	-	-	-	-	-	375	
$\delta S_3/R$							0,64	0,03

group orientations in the structure with the temperature lowering. The following points were taken into consideration for the choice of the PT's model. In trigonal G_1 -phases the WO_4 (MoO_4) tetrahedra are disordered on three states around the 3-fold axis. In the monoclinic G_2 -phases one of these three states is realized. In accordance to the symmetry we can conclude that in the cubic phase each tetrahedron has twelve equivalent states. Then the Hamiltonian of the model is

$$H = -\frac{1}{2} \sum V_{ij}(R-R') c_i(R) \cdot c_j(R) \quad (2)$$

where

$$c_i(R) = \begin{cases} 1 & \text{if a tetrahedron occupies the state } i \\ 0 & \text{in opposite cases} \end{cases}$$

12x12 Matrix of the nearest neighbours interaction V_{ij} in (2) has six independent constants. Some eigenvalues of the matrix can be found from the solution of the second-order equation. Even in mean field (MF) approximation the calculation of the free energy is difficult. The problem was simplified when it was supposed that some of V_{ij} are equal each other. The V_{ij} matrix in this case (4 independent values) has the block-diagonal form

$$V_{ij} = \begin{matrix} & A & C & C \\ C & A & C & \\ C & C & A & \end{matrix} \quad \text{with } A = \begin{matrix} a & b & b & b \\ b & a & b & b \\ b & b & a & b \\ b & b & b & a \end{matrix}, \quad C = \begin{matrix} c & d & d & d \\ d & c & d & d \\ d & d & c & d \\ d & d & d & c \end{matrix} \quad (3)$$

Free energy (F) of the simplified model can be found in the analytical form which was written in ⁷. It contains three order parameters η_i which were found from the conditions $\partial F / \partial \eta_i = 0$.

The free energy describing the PT's sequence in RLM crystal

$$T_d^2 (Z=1) \rightarrow C_{3v}^5 (Z=1) \rightarrow C_{2v}^2 (Z=2) \rightarrow C_s^4 (Z=2) \quad (4)$$

is much more complicated and is not presented here.

The calculated MF temperature dependences of for CLM crystal are shown in Fig.2 in the comparison with some experimental data (see Figure Caption). MF-values of ΔS_i and δS_i for the three crystals are

presented in Table 3. It is seen that the entropy changes are in poor agreement with the experimental data.

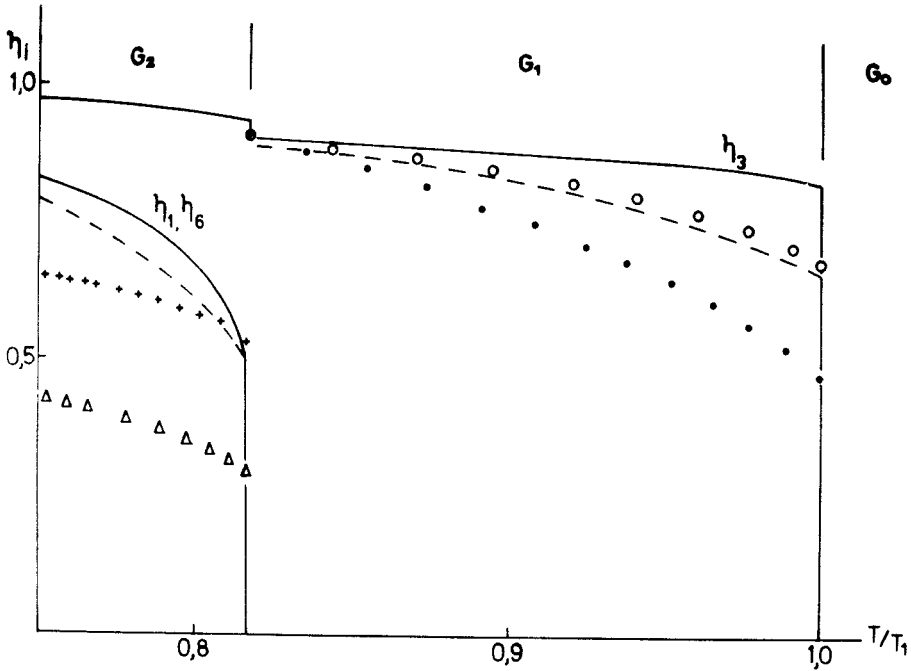


FIGURE 2 Order parameters behaviour versus relative temperature around T_{c1} and T_{c2} for the CLM crystal. The comparison of the experimental and theoretical data of mean field (dashed lines) and cluster approximations (full lines) is made. Full and empty circles correspond to the $P_S(T)$ data ¹ and to the square root of the quadrupole splitting ($\Delta\nu$) of the ^{131}Cs NMR lines ⁹, respectively. Both sets of the data were tied to the theoretical curve at T_{c2} . In G_2 -phase the comparison with the ^7Li NMR data ⁹ is made: triangles and crosses correspond to $\Delta\nu(T)$ and $[\Delta\nu(T)]^{1/2}$, respectively.

The existence of ΔC_p on a broad region above T_{c1} and the rather small experimental values of the transition entropies (see Fig.1,3 and Table 3) were supposed to be indications to the presence of strong corre-

lations in the ordering system. Such correlations may be connected with the energetically unfavourable orientations of the neighbouring BO_4 -tetrahedra. Each MoO_4 (WO_4) tetrahedron in the G_o -structure is surrounded by four LiO_4 tetrahedra and vice versa. The structural data have shown that in most cases the PT's in crystals with tetrahedral groups are connected with the tilts of tetrahedra without essential distortions¹¹. It indicates on the high energy of such configurations of the BO_4 -groups which lead to distortions of LiO_4 -tetrahedron in cubic phase.

This correlations were taken into consideration in the cluster approximation (CA) of the model theory. Group of four BO_4 tetrahedra was chosen as a cluster. Energies of configurations which distort the LiO_4 tetrahedron have been equated to infinity. Then from $12^4 = 20736$ configurations only 8746 ones give contributions to the free energy. The analytical form of F is very complicated and will not be written here. The calculated values of $\eta_i(T)$ and $\Delta C_p(T)$ for the CLM crystal are shown on Fig.2 and 3. The CA-values of ΔS_i and δS_i are included in Table 3.

It is clearly seen that in the cluster approximation the agreement of theoretical results with the ex-

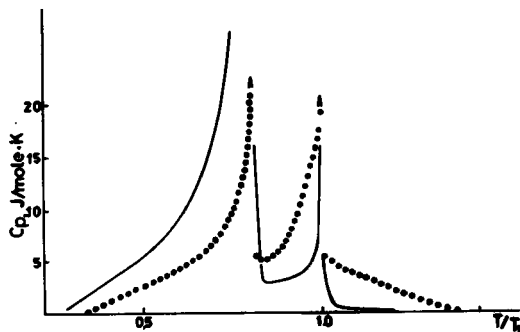


FIGURE 3 Excess part of specific heat ΔC_p versus relative temperature for CLM. Full lines - cluster approximation of the theory, dotted lines - experimental data extracted from the $C_p(T)$ dependence shown on Fig.1.

perimental values is more satisfactory than that of the MF-data. But there exist some definite differences in $\Delta C_p(T)$ above T_{c1} and ΔS_i , δS_i values.

6. SUMMARY

In this paper the results of theoretical and experimental study of PT's in ferroelectrics of CsLiMoO_4 type were presented. The following conclusions could be made on the basis of the study.

(i) PT's in the family of ferroelectrics belong to the order-disorder type, and the ordering process of tetrahedral groups determines the mechanism of PT's.

(ii) Statistical model of PT's was treated and analyzed in the MF- and CA approximations. The last approximation, where some correlations of the tetrahedral tilts in the G_0 -phase were taken into account, the correspondence between the experimental and theoretical data was considerably improved.

(iii) The model gives the correct qualitative description of the symmetry changes and the thermodynamical behaviour of the crystals in a broad temperature range around the PT's. But the full quantitative description has not been obtained yet. Some new experimental study on the properties of the G_0 -phase should be made in order to select more satisfactory model of the correlations.

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