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Monte Carlo investigation of the phase transition in CsLiSO₄ and CsLiCrO₄ crystals

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Abstract. We have studied a model of the order–disorder phase transitions in CsLiSO₄ and CsLiCrO₄. In this model a BX₄ tetrahedron has four equilibrium orientations in a disordered hexagonal phase. The constants of the interaction between ordered BX₄ groups are calculated in the framework of the electrostatic model. It is shown that these constants have a competitive nature. The Monte Carlo method is applied to study the phase diagrams and thermodynamic properties of the phase transitions. The results obtained are in good agreement with experimental data.

1. Introduction

The isomorphous crystals CsLiSO₄ and CsLiCrO₄ belong to a large class of compounds with the general chemical formula ACBX₄, where A and C are alkali metals and BX₄ is the tetrahedral group: SO₄, SeO₄, CrO₄, ZnCl₄, etc. This family of the crystals has recently been the subject of extensive experimental investigations and several hundreds of papers on this topic have been published to date. This interest is caused by the great variety of structural phase transitions in these compounds including the transitions into incommensurate phases. Information concerning the crystal structures, phase diagrams and behaviour of the physical properties near the phase transition in these compounds can be found in the review papers by Eysel (1975) and Muller and Roy (1974) and in the book by Aleksandrov and Beznosikov (1993).

It is important to emphasize here that all the known crystal structures of these compounds have a common feature, namely they can be considered as slight distortions of the prototype α -K₂SO₄ structure of D_{6h}⁴ (*P6₃/mmc*) symmetry. The difference between the structures of the different compounds are caused by the orientations of BX₄ tetrahedra relative to each other as well as to the crystallographic axes. In the hexagonal phase D_{6h}⁴ (figure 1) it is obligatory that the tetrahedral groups BX₄ have several equivalent orientations and the observed variety of structural phase transitions occurs because of the different schemes of ordering of the BX₄ groups accompanied by the slight ionic displacements.

Despite the huge experimental literature, only a few papers on the microscopic theory of the topic considered are available (Yamada and Hamaya 1983, Zinenko and Blat 1978, Lu and Hardy 1990, Edwardson *et al* 1987, Zamkova and Zinenko 1992). Zamkova and Zinenko (1992) have calculated the effective constants of the interaction between BX₄ tetrahedra in the framework of an electrostatic model and have shown that these constants are of a competitive nature. This competition of the interactions leads to a large variety of phase diagrams and behaviours of the physical properties near the phase transitions in the ACBX₄ compounds.

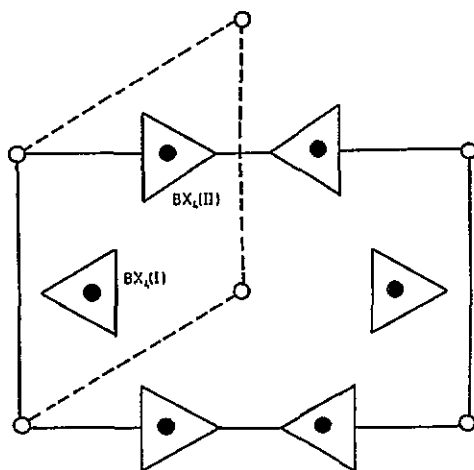


Figure 1. The crystal structure of the high-temperature phase of $ACBX_4$ viewed down $[001]$. The triangles represent the BX_4 molecular ions. The A and C metals are shown as open and full circles, respectively.

In the present paper we apply the Monte Carlo (MC) method to investigate the phase transitions in the crystals $CsLiSO_4$ and $CsLiCrO_4$. The model of the phase transitions in the $ACBX_4$ compounds, the method and results of the calculations of the interaction constants are presented in section 2. The thermodynamic characteristics of the phase transitions calculated by the MC method are presented in section 3. The results are compared with the experimental data and discussed in section 4.

2. The model and calculation of the interaction constants

$CsLiSO_4$ and $CsLiCrO_4$ have orthorhombic symmetry with the space group D_{2h}^{16} and with four molecules in the unit cell at high temperatures, $CsLiSO_4$ at $T_c = 202$ K (Aleksandrov *et al* 1980) and $CsLiCrO_4$ at $T_c = 427$ K (Aleksandrov *et al* 1988) undergo a ferroelastic phase transition into a monoclinic phase with the space group C_{2h}^2 ($Z = 4$). In these compounds the hexagonal phase is not experimentally observed as the temperature is increased up to the decomposition value (about 600 K for $CsLiSO_4$ and about 1000 K for $CsLiCrO_4$). The unit-cell parameters of both crystals are rather similar ($a = 5.456$ Å, $b = 9.456$ Å and $c = 8.820$ Å for $CsLiSO_4$; $a = 5.684$ Å, $b = 9.860$ Å and $c = 8.904$ Å for $CsLiCrO_4$). This difference is neglected in our calculation.

In the calculations of the BX_4 - BX_4 interaction constants and in investigations of the phase transitions the model proposed by Zinenko and Blat (1978) is used. In this model a BX_4 tetrahedron has four equilibrium orientations (figure 2). The BX_4 - BX_4 interaction constants $V_{ij}(R)$ were calculated from the electrostatic model (Zamkova and Zinenko 1992).

The Hamiltonian of the model is

$$H = -\frac{1}{2} \sum_{\substack{i,j \\ r,r'}} \mathbf{V}_{oo}^{I,I}(r-r') C_i^I(r) C_j^I(r') - \frac{1}{2} \sum_{\substack{i,j \\ r,r'}} \mathbf{V}_{oo}^{II,II}(r-r') C_i^{II}(r) C_j^{II}(r') \\ - \sum_{\substack{i,j \\ r,r'}} \mathbf{V}_{oo}^{I,II}(r-r') C_i^I(r) C_j^{II}(r') + \sum_{i,r,r'} \mathbf{F}_{od}^{IA}(r-r') C_i^I(r) d_A(r')$$

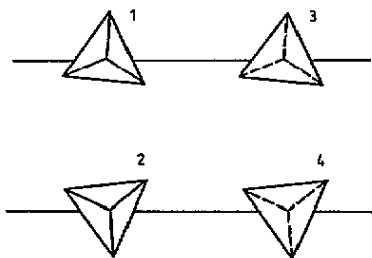


Figure 2. Four positions of BX₄ tetrahedra in the hexagonal phase.

$$\begin{aligned}
 & + \sum_{i,r,r'} \mathbf{F}_{\text{od}}^{\text{IC}}(r-r') C_i^{\text{I}}(r) d_{\text{C}}(r') + \sum_{i,r,r'} \mathbf{F}_{\text{od}}^{\text{IIA}}(r-r') C_i^{\text{II}}(r) d_{\text{A}}(r') \\
 & + \sum_{i,r,r'} \mathbf{F}_{\text{od}}^{\text{IIC}}(r-r') C_i^{\text{II}}(r) d_{\text{C}}(r') + \frac{1}{2\alpha_{\text{A}}} \sum_r d_{\text{A}}^2(r) + \frac{1}{2\alpha_{\text{C}}} \sum_r d_{\text{C}}^2(r) \\
 & + \frac{1}{2} \sum_{\alpha,\beta,r,r'} D_{\alpha\beta}^{\text{A}}(r-r') d_{\alpha}^{\text{A}}(r) d_{\beta}^{\text{A}}(r') + \frac{1}{2} \sum_{\alpha,\beta,r,r'} D_{\alpha\beta}^{\text{C}}(r-r') d_{\alpha}^{\text{C}}(r) d_{\beta}^{\text{C}}(r') \\
 & + \sum_{\alpha,\beta,r,r'} D_{\alpha\beta}^{\text{AC}}(r-r') d_{\alpha}^{\text{A}}(r) d_{\beta}^{\text{C}}(r') \tag{1}
 \end{aligned}$$

where

$$C_i^{\text{I,II}} = \begin{cases} 1 & \text{if BX}_4 \text{ group occupies the position } i \\ 0 & \text{in the opposite case} \end{cases}$$

and the fact that the unit cell of the hexagonal phase has two non-equivalent molecules is taken into account (I and II relate to the sublattices indicated in figure 1). $\mathbf{V}_{\text{oo}}^{kl}(r-r')$ is the octupole–octupole interaction matrix; d_{A} and d_{C} are the dipole moments of metals A and C which have polarizabilities α_{A} and α_{C} , respectively. It should be noted that, in the present calculations, α_{A} and α_{C} are parameters of the theory because they have both electronic and ionic contributions. $\mathbf{D}_{\alpha\beta}$ and \mathbf{F}_{od} are dipole–dipole and dipole–octupole interaction matrices, respectively. So, the effective BX₄–BX₄ interaction is a sum of the direct octupole–octupole interaction and indirect interaction through polarizable metal ions:

$$\begin{aligned}
 \mathbf{H}_{\text{eff}} = & -\frac{1}{2} \sum \mathbf{V}_{ij}^{\text{I}}(r-r') C_i^{\text{I}}(r) C_j^{\text{I}}(r') - \frac{1}{2} \sum \mathbf{V}_{ij}^{\text{II}}(r-r') C_i^{\text{II}}(r) C_j^{\text{II}}(r') \\
 & - \sum \mathbf{V}_{ij}^{\text{I,II}}(r-r') C_i^{\text{I}}(r) C_j^{\text{II}}(r') \tag{2}
 \end{aligned}$$

where

$$\mathbf{V}_{ij}^{kl}(r) = \mathbf{V}_{\text{oo}}^{kl}(r) + \xi_{\text{A}} \xi_{\text{C}} \mathbf{W}(r) \quad \xi_{\text{A,C}} = \frac{\alpha_{\text{A,C}}}{a_0^3}$$

$$\mathbf{W}(r) = \frac{1}{v_0} \int \int \int \mathbf{W}(\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3\mathbf{q}$$

$$\begin{aligned}
 \mathbf{W}(\mathbf{q}) = & \sum \{ J_{\alpha\beta}^{\text{A}}(\mathbf{q}) J_{\alpha\beta}^{\text{C}}(\mathbf{q}) - [D_{\alpha\beta}^{\text{AC}}(\mathbf{q})]^2 \xi_{\text{A}} \xi_{\text{C}} \}^{-1} \\
 & \times \left(\sum [F_{\alpha n}^{\text{A}}(\omega_1, \mathbf{q}) F_{\beta m}^{\text{C}}(\omega_2, \mathbf{q}) + F_{\beta m}^{\text{A}}(\omega_2, \mathbf{q}) F_{\alpha n}^{\text{C}}(\omega_1, \mathbf{q})] D_{\alpha\beta}^{\text{AC}}(\mathbf{q}) \right. \\
 & \left. - F_{\alpha n}^{\text{A}}(\omega_1, \mathbf{q}) F_{\beta m}^{\text{A}}(\omega_2, \mathbf{q}) J_{\alpha\beta}^{\text{C}}(\mathbf{q}) / \xi_{\text{C}} - F_{\alpha n}^{\text{C}}(\omega_1, \mathbf{q}) F_{\beta m}^{\text{C}}(\omega_2, \mathbf{q}) J_{\alpha\beta}^{\text{A}}(\mathbf{q}) / \xi_{\text{A}} \right) \tag{3}
 \end{aligned}$$

$J_{\alpha\beta}^{A,C}(\mathbf{q}) = E_{\alpha\beta} + \xi_{A,C} D_{\alpha\beta}^{A,C}(\mathbf{q})$, $E_{\alpha\beta}$ is the unit matrix and ω_i are the Euler angles. The interaction matrices $\mathbf{V}^{I,I}$, $\mathbf{V}^{I,II}$ and $\mathbf{V}^{II,II}$ have four independent terms owing to the symmetry of the hexagonal phase and the equilibrium orientations (see figures 1 and 2):

$$\mathbf{V} = \begin{pmatrix} V_{11} & V_{12} & V_{13} & V_{14} \\ V_{12} & V_{11} & V_{14} & V_{13} \\ V_{13} & V_{14} & V_{11} & V_{12} \\ V_{14} & V_{13} & V_{12} & V_{11} \end{pmatrix}. \quad (4)$$

The interaction tetrahedron BX_4 with five nearest metals of C type and six nearest metals of A type is taken into account in the calculations of matrices \mathbf{F}_{od} in (3). The matrices \mathbf{D} in (3) are calculated by the Ewald method. Integration in \mathbf{q} -space was performed by the Gauss method. The values of polarizabilities were taken as $\alpha_{\text{Cs}} = 0.392 \text{ \AA}^3$ and $\alpha_{\text{Li}} = 0.058 \text{ \AA}^3$. The octupole moment value I_3 of the SO_4 group, was fitted using the experimental value of the phase transition temperature ($\text{D}_{2\text{h}}^{16} \rightarrow \text{C}_{2\text{h}}^5$) for CsLiSO_4 , $T_c = 202 \text{ K}$:

$$I_3(\text{SO}_4) = 35.49 \times 10^{-34} \text{ esu cm}^3.$$

The octupole moment I_3 of CrO_4 in comparison with $I_3(\text{SO}_4)$ was changed in proportion to the cube ratio of length Cr–O to the length S–O:

$$I_3(\text{CrO}_4) = 54.62 \times 10^{-34} \text{ esu cm}^3.$$

The effective interaction constants $V_{ij}^{I,I}(R) = V_{ij}^{II,II}(R)$ and $V_{ij}^{I,II}(R)$ were calculated within six coordination spheres up to $R = \sqrt{3}\alpha_0$ and their values are presented in table 1. As seen from this table the dependence of interaction constants on R is of a competitive character.

Table 1. The effective interaction constants.

R	$V_{ij}^{I,II}(R)$, CsLiSO ₄ (K)				$V_{ij}^{I,II}(R)$, CsLiCrO ₄ (K)			
	V_{11}	V_{12}	V_{13}	V_{14}	V_{11}	V_{12}	V_{13}	V_{14}
$(a^2/3 + c^2/4)^{1/2}$	175.5	251.66	-544.15	-467.89	240.16	344.39	-744.63	-640.28
$(4a^2/3 + c^2/4)^{1/2}$	101.37	65.32	86.4	50.28	138.72	89.39	118.24	68.79
R	$V_{ij}^{I,I}(R) = V_{ij}^{II,II}(R)$, CsLiSO ₄ (K)				$V_{ij}^{I,I}(R) = V_{ij}^{II,II}(R)$, CsLiCrO ₄ (K)			
	V_{11}	V_{12}	V_{13}	V_{14}	V_{11}	V_{12}	V_{13}	V_{14}
a	500.5	325.14	-325.93	-501.29	684.91	444.94	-446.02	-685.99
c	-42.72	-41.14	43.83	45.4	-58.45	-56.3	59.98	62.13
$(a^2 + c^2)^{1/2}$	-3.38	-2.78	6.12	6.72	-4.63	-3.8	8.37	9.19
$a\sqrt{3}$	13.9	14.59	-14.92	-14.22	19.02	19.97	-20.41	-19.46

3. Calculation of the thermodynamic properties

The MC technique, which is applicable to Ising-like lattice models (Landau 1976, Binder 1979) is used in the present study. The only change relates to the presence of four equilibrium positions of BX_4 groups (instead of two positions in Ising-like models).

The process of determining the thermodynamic values begins with the choice of an initial 'spin' configuration for a system as a whole. Two initial 'spin' configurations (ordered and disordered) are used for the initial MC procedure at a low temperature and the procedure starts with the last 'spin' configuration generated in the preceding calculation at increasing temperature. The program then proceeds through the lattice, considering each 'spin' (in order) as the reference 'spin' for trial turning. One of three positions for turning is chosen randomly. The relative probability of the two states is considered (Binder 1979):

$$\rho_{\mu\nu} = \rho_{\mu}/\rho_{\nu} = \exp[-(E_{\mu} - E_{\nu})/k_B T]. \quad (5)$$

Equation (5) describes the probability of producing the ν th state from the μ th state. If $\rho_{\mu\nu} > 1$, the reference 'spin' is turned; otherwise a random number r is chosen from a set of random numbers generated uniformly in the interval from 0 to 1 and compared with $\rho_{\mu\nu}$. If $r < \rho_{\mu\nu}$, the reference 'spin' is turned. E_{μ} and E_{ν} in (5) are the energies of the states μ and ν . In the present work, only periodic boundary conditions were considered. The calculations were carried out on the $N \times N \times N_1$ hexagonal three-dimensional lattice. Three sizes of the lattice ($N = 16$; $N_1 = 6, 12, 24$) are treated here. As seen from figure 3, the results of MC calculations are close to each other for different lattices, and below we shall discuss the results of calculations only for the lattice with $N = 16$ and $N_1 = 12$.

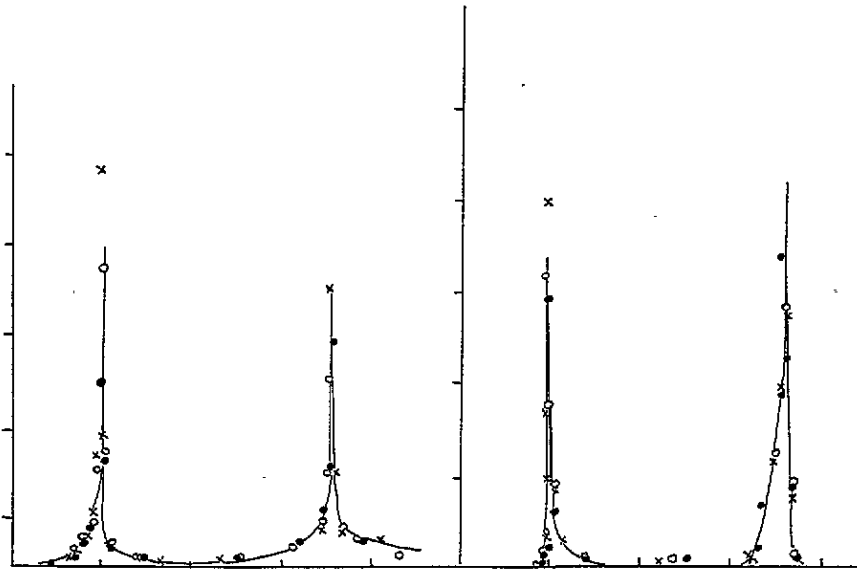


Figure 3. The temperature dependences of specific heat and susceptibility (arbitrary units) for lattices of different sizes with periodic boundary condition: \times , $N = 16$, $N_1 = 6$; \circ , $N = 16$, $N_1 = 12$; \bullet , $N = 16$, $N_1 = 24$.

The thermodynamic quantities were calculated in the usual way (Landau 1976, Binder 1979):

$$\begin{aligned}
 U &= \sum_{m=1}^N \sum_{s=1}^6 V_{ih}(s, m) \\
 C &= \frac{N^2}{kT^2} (\Delta U)^2 \\
 \chi_i &= \frac{N^2}{kT} (\Delta \eta_i)^2
 \end{aligned} \tag{6}$$

where U is the internal energy, C is the heat capacity, η_i are order parameters which will be determined below, χ_i is the susceptibility and $(\Delta A)^2 = \langle A^2 \rangle - \langle A \rangle^2$.

One MC step per 'spin' was $N \times N \times N_1$ 'spin' turning trials. The first 500–1000 MC steps were discarded and not used in computing averages. The average was carried out in two steps; after p MC steps, subaverages were determined for the group of states (usually $p = 50$) and then, after a number of subaverages (usually 85), final averages were computed. The calculations are repeated at another temperature and so on.

The structure of the ordered phase which resulted from MC simulation at a low temperature had the following occupation numbers:

$$\begin{aligned}
 n_1^I(R=0) &= n_4^I(R=a) = n_3^{II}(R=b) = n_2^{II}(R=c) = 1 \\
 n_2^I(R=0) &= n_3^I(R=a) = n_4^{II}(R=b) = n_1^{II}(R=c) = 0 \\
 n_3^I(R=0) &= n_1^I(R=a) = n_1^{II}(R=b) = n_3^{II}(R=c) = 0 \\
 n_4^I(R=0) &= n_2^I(R=a) = n_2^{II}(R=b) = n_4^{II}(R=c) = 0
 \end{aligned} \tag{7}$$

where $a = a_0$, $b = \sqrt{a_0^2/3 + c_0^2/4}$, $c = \sqrt{4a_0^2/3 + c_0^2/4}$. The values $n_i^k(R)$ are determined from MC data at the temperature $T/T_{c2} = 0.6$. At lower temperatures the metastability problem arises, when the system is quenched from a disordered state. The results (7) coincide with the exact result of the ground-state structure of the finite system with periodic boundary conditions (Zamkova and Zinenko 1992). The ordered phase has monoclinic symmetry with the space group C_{2h}^5 and with four molecules in the unit cell.

The order parameters in the MC procedure are computed as

$$\begin{aligned}
 \eta_1 &= |n_1^I(R=0) + n_2^I(R=0) - n_3^I(R=0) - n_4^I(R=0)| \\
 &\quad + |n_3^I(R=a) + n_4^I(R=a) - n_1^I(R=a) - n_2^I(R=a)| \\
 &\quad + |n_3^{II}(R=b) + n_4^{II}(R=b) - n_1^{II}(R=b) - n_2^{II}(R=b)| \\
 &\quad + |n_1^{II}(R=c) + n_2^{II}(R=c) - n_3^{II}(R=c) - n_4^{II}(R=c)| \\
 \eta_2 &= |n_1^I(R=0) - n_2^I(R=0) + n_3^I(R=0) - n_4^I(R=0)| \\
 &\quad + |n_2^I(R=a) - n_1^I(R=a) + n_4^I(R=a) - n_3^I(R=a)| \\
 &\quad + |n_1^{II}(R=b) - n_2^{II}(R=b) + n_3^{II}(R=b) - n_4^{II}(R=b)| \\
 &\quad + |n_2^{II}(R=c) - n_1^{II}(R=c) + n_4^{II}(R=c) - n_3^{II}(R=c)|
 \end{aligned} \tag{8}$$

where an equivalence of the unit-cell parameters a_0 and b_0 of the hexagonal phase is taken into account.

The program, written in FORTRAN, required about 0.2 ms per 'spin' (included for determining the averages) on an AT-486/50 computer.

4. Results

The results of the calculations of the thermodynamic quantities are presented in figures 4–7 and in table 2. The transition temperatures are calculated from the peak in the specific heat. Typical error bars near the critical points and far from the critical points are 9.7% and 3%, respectively (Sobol 1973, Landau 1976).

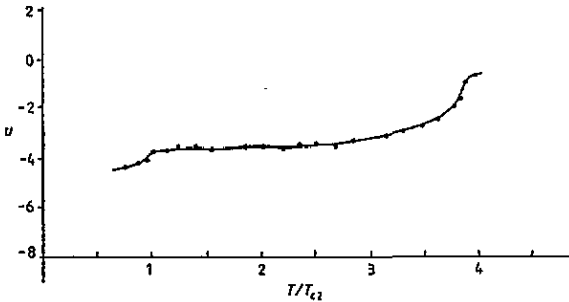


Figure 4. The temperature dependence of the internal energy U (in I_3^2/a_0^3 units).

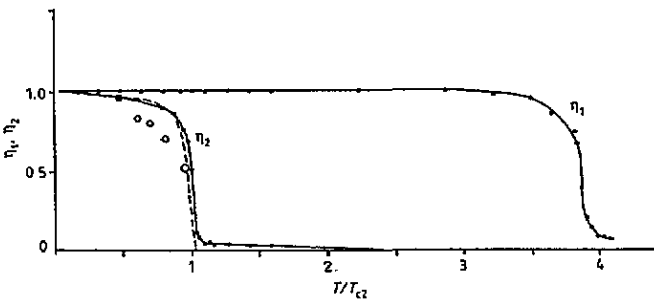


Figure 5. The temperature dependences of the order parameters η_1 and η_2 : —, MC simulation; O, experimental data for CsLiSO₄ (Aleksandrov *et al* 1980); ●, experimental data for CsLiCrO₄ (Aleksandrov *et al* 1988).

Table 2. The phase transition temperatures and the entropy changes.

	T_{c2} (K)		$\Delta S_2/R$	
	Calculation	Experiment	Calculation	Experiment
CsLiSO ₄	T_{c2exp}	202	0.3	0.2
CsLiCrO ₄	370 ± 35.89	427	0.3	—
	T_{c1} (K)		$\Delta S_1/R$	
	Calculation	Experiment	Calculation	Experiment
CsLiSO ₄	768 ± 74.5	—	0.2	—
CsLiCrO ₄	1405 ± 136.3	—	0.2	—

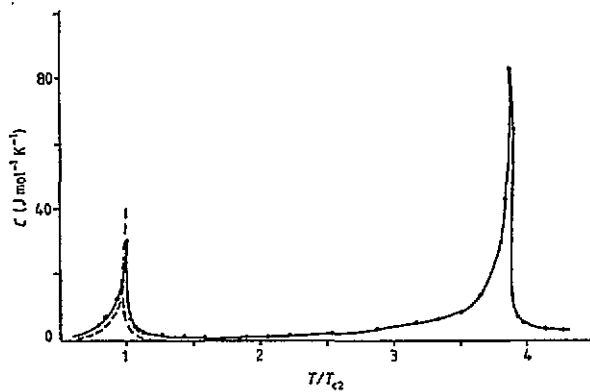


Figure 6. The temperature dependence of the specific heat: —, MC simulation; ●, experimental data (Aleksandrov *et al* 1980).

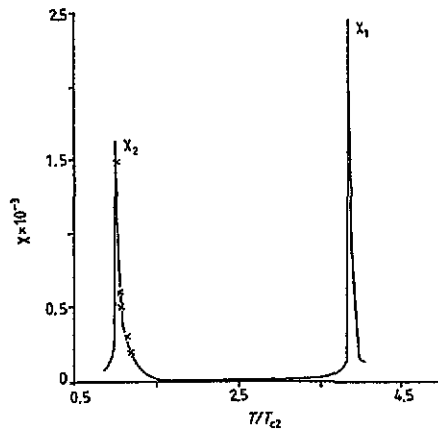


Figure 7. The temperature dependence of susceptibility ($\chi_0 = 0.4 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$): —, MC simulation; ×, experimental data (Zamkov and Anistratov 1982).

There are two successive phase transitions in both crystals CsLiSO_4 and CsLiCrO_4 . We assume that these phase transitions are second order. The first to appear, as the temperature decreases, is caused by partial ordering of the BX_4 tetrahedra. The partially ordered phase is described by the next occupation numbers (at the temperature when the value of the order parameter η_1 is equal to 1):

$$\begin{aligned}
 n_1^I(R=0) &= n_2^I(R=0) = n_3^I(R=a) = n_4^I(R=a) = \frac{1}{2} \\
 n_3^I(R=0) &= n_4^I(R=0) = n_1^I(R=a) = n_2^I(R=a) = 0 \\
 n_3^{II}(R=b) &= n_4^{II}(R=b) = n_1^{II}(R=c) = n_2^{II}(R=c) = \frac{1}{2} \\
 n_1^{II}(R=b) &= n_2^{II}(R=b) = n_3^{II}(R=c) = n_4^{II}(R=c) = 0.
 \end{aligned}
 \tag{9}$$

The symmetry of the partial ordered phase is orthorhombic with the space group D_{2h}^{16} and with four molecules in the unit cell. This phase is observed experimentally at high temperatures.

The $D_{6h}^4 \rightarrow D_{2h}^{16}$ phase transition is not observed for CsLiSO_4 and CsLiCrO_4 but, as is seen from table 2, the calculated temperatures of the $D_{6h}^4 \rightarrow D_{2h}^{16}$ phase transition exceed the decomposition temperatures of both compounds. The temperature dependences of the internal energy, order parameter η_1 , heat capacity and susceptibility χ_1 at the phase transition from the hexagonal to the orthorhombic phase are shown in figures 4–7.

As the temperature decreases further, the second phase transition is connected with full ordering of the BX_4 groups. This ordered phase is monoclinic with the space group C_{2h}^5 and with four molecules in the unit cell. The $D_{2h}^{16} \rightarrow C_{2h}^5$ ferroelastic phase transition is observed experimentally for the CsLiSO_4 and CsLiCrO_4 crystals (Aleksandrov *et al* 1980, 1988). The spontaneous deformation u_{xy} in the monoclinic phase is proportional to the order parameter η_2 in the model under consideration and the corresponding susceptibility χ_2 is proportional to the elastic compliance S_{66} of the orthorhombic phase (Zamkov and Anistratov 1982).

The calculated temperature dependences of the thermodynamic quantities at the $D_{2h}^{16} \rightarrow C_{2h}^5$ phase transition together with the available experimental data are shown in figures 4–7. Changes in the entropy were found by integration of the areas under the curves $C(T)/T$. The computed and experimental values of the entropy change are presented in table 2. A comparison of the computed results with experimental data (Aleksandrov *et al* 1980, 1988, Zamkov and Anistratov 1982) shows that they are in a very good agreement. The higher value of the phase transition temperature for CsLiCrO_4 in comparison CsLiSO_4 is naturally described by the higher value of the octupole moment of CrO_4 group. The results of the calculation of the entropy changes ΔS_1 and ΔS_2 and the experimental value of ΔS_2 are quite interesting (see table 2). These values are much lower than calculated in the mean-field approximation ($\Delta S_1 + \Delta S_2 = 2 \ln 2$). The results reveal the presence of strong short-range correlations of the BX_4 groups in the disordered hexagonal and partially ordered orthorhombic phases. These correlations exist owing to the competitive nature of the effective interactions between the BX_4 tetrahedra, as seen from table 1.

5. Conclusion

We have applied the MC method to study the order–disorder phase transitions in CsLiSO_4 and CsLiCrO_4 . The effective constants of interactions between SO_4 (CrO_4) groups were calculated in the framework of the electrostatic approximation. The results obtained show that treatment of the model by the MC method yields a quantitative description of the thermodynamic properties of CsLiSO_4 and CsLiCrO_4 . The temperature dependences of the specific heat and susceptibility and a value for the entropy change for the crystal CsLiCrO_4 are predicted by the theory. The experimental verification of these characteristics seems desirable.

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