LATTICE DYNAMICS
AND PHASE TRANSITIONS

Calorimetric and Optical Studies of Orthorhombic and Cubic CsLiCrO₄ Crystals

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Abstract—Careful calorimetric and polarization optical studies of a metastable cubic modification of a $CsLiCrO_4$ crystal (space group ($F\bar{4}3m$)) are performed. Anomalies of the heat capacity indicative of structural distortions at 92.4 and 69.1 K were revealed, and the values of the thermodynamic parameters of the phase transitions were determined. The crystal twinning in the intermediate phase was studied. A comparative analysis of the phase transitions occurring in a series of $ALiMO_4$ crystals (A = NH₄, Cs; M = S, Cr, Mo, W) was performed.

First studies of the monotropic structural transformation $F\bar{4}3m \longrightarrow Pmcn$ and the enantiotropic phase transition $Pmcn \rightleftharpoons P112_1/n$ were carried out using scanning calorimetry, and the thermodynamic parameters of these transitions were determined.

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1. INTRODUCTION

Among the crystals of the β-K₂SO₄ family, there are compounds existing in two crystallographic modifications under normal conditions [1, 2]. As a rule, the formation of a polymorphic modification is dictated by the conditions of crystal growth. The transition between polymorphic modifications is irreversible under thermal cycling, but sometimes a crystal can turn back to the metastable phase under the influence of other external factors, such as humidity and uniaxial pressure [3].

Among the crystals with the general formula $ALiMO_4$, there are likewise compounds having two crystallographic modifications, e.g., NH₄LiSO₄ [2] and CsLiCrO₄ [1]. The thermally stable modifications of these crystals are orthorhombic (space group *Pmcn*). However, their metastable phases differ significantly; they belong to space groups $Pca2_1$ [4] and $F\bar{4}3m$ [1], respectively. Both crystallographic modifications of the NH₄LiSO₄ crystal and the monotropic transition between them have been studied in detail [5, 6] using, in particular, thermal-physics methods [2].

The stable modification of the CsLiCrO₄ crystal (studied in sufficient detail by various methods, excluding calorimetric methods) is an analog of the CsLiSO₄ crystal [7] but, contrary to this crystal, has a distorted unit cell with $P112_1/n$ symmetry at room temperature [8]. The substitution S $\longrightarrow$ Cr leads to a substantial change in the temperature dependence of the monoclinicity angle $\Delta\gamma(T)$ (spontaneous shear deformation), the

rotation angle of the indicatrix $\varphi(T)$, and the rotation angle of tetrahedra in the low-symmetric phase [7–11]. The authors of [9–11] suggest that this difference in the behavior of $\Delta\gamma(T)$ can be described under the assumption that the crystal structure consists of two sublattices. One sublattice is formed by tetrahedra, and the other, by cesium atom pairs. During the phase transition (PT), the cesium pairs and tetrahedra are rotated. However, in the chromate, their rotations occur in antiphase, whereas in the sulfate they occur in phase. In [7, 8], this phenomenon was considered from the other point of view; more specifically, the unusual behavior of the monoclinicity angle was explained by a significant difference between the thermal expansion coefficients along the [110] and [1$\bar{1}$0] directions.

Earlier, calorimetric studies of the $Pmcn \rightleftharpoons P112_1/n$ transformations were performed only on CsLiSO₄ [12]. Up to now, the effect of the specific features of the CsLiCrO₄ structures mentioned above on the thermodynamic parameters of the structural transformation has not yet been studied.

Until recently, the cubic metastable modification of the CsLiCrO₄ crystal had been studied only superficially. From studying the temperature dependence of the unit cell parameters, it is only known that a structural PT takes place near 89 K and a noticeable decrease in the intensities of the structural reflections and their broadening observed near 63 K indicate the possible occurrence of another PT [9]. Based only on these data, the authors of [9] proposed that the sequence
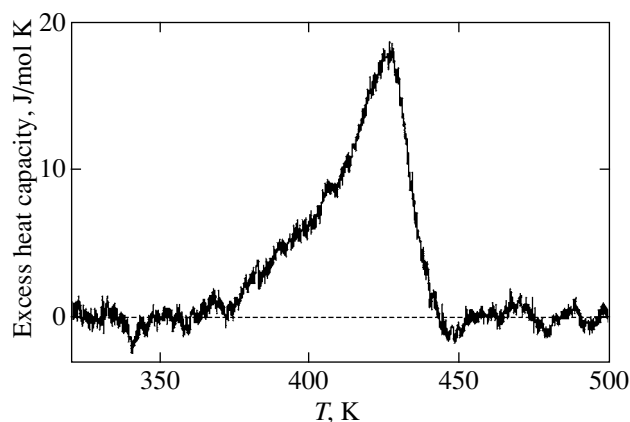
Fig. 1. Temperature dependence of the excess heat capacity of the orthorhombic CsLiCrO$_4$ crystal.

of PTs occurring in the cubic modification of CsLiCrO$_4$ crystals may be similar to that observed in CsLiMoO$_4$ and CsLiWO$_4$, which likewise have $F\bar{4}3m$ symmetry in the initial phase [13]. Optical studies showed that the cubic phase with $F\bar{4}3m$ symmetry in these compounds sequentially changes to a trigonal ($3m$) and then a monoclinic (m) phase. Calorimetric experiments [14] established that the entropies of the sequential PTs in these two compounds are approximately equal; namely, $\Delta S_1 = 0.34R$ and $\Delta S_2 = 0.28R$ for CsLiMoO$_4$ and $\Delta S_1 = 0.31R$ and $\Delta S_2 = 0.33R$ for CsLiWO$_4$. To a certain extent, the validity of the hypothesis proposed in [9] may be elucidated using polarization-optical and calorimetric methods, which are highly sensitive to changes in the symmetry and energy of a crystal.

X-ray diffraction studies [1] showed that, as the cubic modification of CsLiCrO$_4$ is heated, an irreversible phase transformation to a stable orthorhombic phase ($F\bar{4}3m \longrightarrow Pmcn$) occurs near $T_m \approx 573$ K. Based on the fact that the cubic modification has a lower density than the orthorhombic modification (3.22 and 3.47 g/cm^3, respectively), the authors of [1] assumed that the cubic phase is metastable and can be grown from solution only under certain conditions. From analyzing the properties of a series of CsLiMO_4 crystals (M = S, Se, Cr, Mo, W), the authors of [1] concluded that these compounds crystallize in derivatives of β cristobalite ($F\bar{4}3m$) in the case of large anion-forming elements (W, Mo) and in derivatives of β tridymite ($Pmcn$) in the case of smaller cations (S, Se). The compound with the Cr(VI) cation is intermediate and can crystallize in both structures. The thermodynamic parameters of the $F\bar{4}3m \longrightarrow Pmcn$ transformation in CsLiCrO$_4$ have not yet been studied.

In this work, we performed the first calorimetric heat capacity studies of both polymorphic modifications of CsLiCrO$_4$ and the monotropic PT between

them and polarization-optical studies of the metastable crystal modification. The results are analyzed in combination with the data from our earlier investigation into PTs in $ALiMO_4$ crystals (A = Cs, NH$_4$; M = S, Cr, Mo, W) [1, 7–9, 12–14].

2. EXPERIMENTAL

Cubic CsLiCrO$_4$ crystals in the form of tetrahedra with an edge of 0.5–3.0 mm were grown from solution only. As a rule, orthorhombic crystals in the form of plates grew simultaneously. The sample quality was controlled using an x-ray diffractometer.

Calorimetric studies were performed using a DSM-2M differential scanning microcalorimeter and an adiabatic calorimeter [15].

The adiabatic calorimetry studies were carried out in the temperature range 55–360 K. The measurement procedure was described in detail in [15]. A set of single crystals with a total mass of 0.848 g was placed in a copper capsule, which, in turn, was placed in an indium container filled with helium as a heat-exchanging gas. Thus, the measurements were performed on a sample + furniture (copper capsule, indium container, helium, heater, and aluminum foil shell) system.

The heat capacity was measured in the discrete (ΔT = 1.0–2.5 K) and continuous (dT/dt = 0.16–0.50 K/min) heating modes. Near the PT point, measurements were performed using the method of quasi-static thermograms with a heating rate of $\sim 3 \times 10^{-2}$ K/min.

Orthorhombic CsLiCrO$_4$ crystals were grown from a melt by the Bridgman method. The temperature of the reversible PT for this modification is higher than the limiting operating temperature of the adiabatic calorimeter. Therefore, the heat capacity was measured using only a DSM–2M microcalorimeter. The same method was also used in studying the high-temperature monotropic transformation in the CsLiCrO$_4$ crystal. In all experiments, the heating rate was 8 K/min. The samples were ground to a fine-dispersed state and packed into a special aluminum container. The mass of the material under investigation was 150–200 mg.

3. EXPERIMENTAL RESULTS

Since we are interested only in the phase transformations in the crystals, we restricted our analysis to the anomalous portion of the heat capacity. The DSM data were processed in accordance with the procedures described in [15].

Figure 1 shows the temperature dependence of the excess heat capacity of an orthorhombic CsLiCrO$_4$ crystal, which has a peak with a maximum at a temperature $T_0 = 428 \pm 2$ K corresponding to the reversible $Pmcn \longleftrightarrow P112_1/n$ phase transition. By integrating the $\Delta C_p(T)$ dependence over the range 370–445 K covering
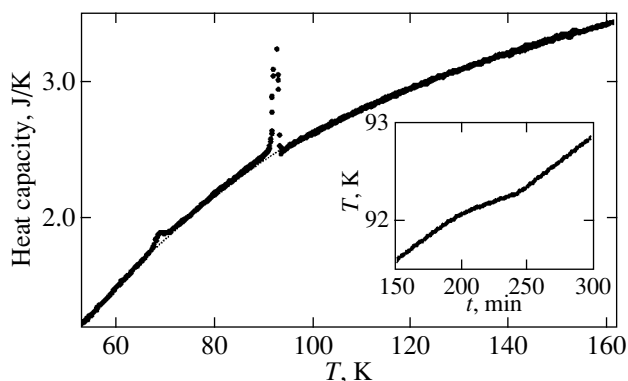
Fig. 2. Temperature dependence of the heat capacity of the CsLiCrO$_4$ ($F\bar{4}3m$) + furniture system. The dotted line is the background heat capacity. The inset shows the time dependence of the sample temperature at a constant heating power (thermogram).

Fig. 3. Temperature dependence of the excess heat capacity of CsLiCrO$_4$ ($F\bar{4}3m$) related to the sequence of phase transformations at T_1 and T_2.

the excess portion, we found the enthalpy change to be $\Delta H_0 = 550 \pm 100$ J/mol.

Figure 2 shows the temperature dependence of the heat capacity of the sample + furniture system for the cubic modification of CsLiCrO$_4$. Two anomalies of the heat capacity were reliably established at $T_1 = 92.4 \pm 0.1$ K and $T_2 = 69.1 \pm 0.1$ K. These anomalies indicate that the primary cubic phase of CsLiCrO$_4$ does undergo two sequential PTs, as proposed in [9].

Since the anomaly at T_1 has a shape characteristic of a first-order PT, we carried out a quasi-static thermography study in the vicinity of this temperature. The inset to Fig. 2 shows the time dependence of the sample temperature at a constant heating power. The rate of temperature variation in the vicinity of the PT point was ~0.01 K/min. Under the assumption that the latent heat is smeared over the range 92.13–92.26 K due to sample imperfection, we calculated its value to be $\delta H_1 = 120 \pm 10$ J/mol.

We were interested only in the anomalous thermal effects related to the PT and did not determine the temperature dependence of the heat capacity of the crystal over the entire temperature range studied. However, in order to obtain information on the integrated PT characteristics, it is necessary to subtract the background heat capacity from the total heat capacity of the system under study. In our case, the background is not due to the lattice heat capacity alone but also includes the furniture heat capacity.

We fitted the background component $C(T)$ by using different functions and varying the temperature range (excluded from the fitting procedure) over which the anomalous contribution $\Delta C_p(T)$ to the heat capacity was assumed to be nonzero. The temperature range where $\Delta C_p(T)$ was nonzero was found to extend from 60 to 94 K (Fig. 3). The Debye and Einstein approximations did not prove to be adequate, most probably because the heat capacity contains many components. Thus, further
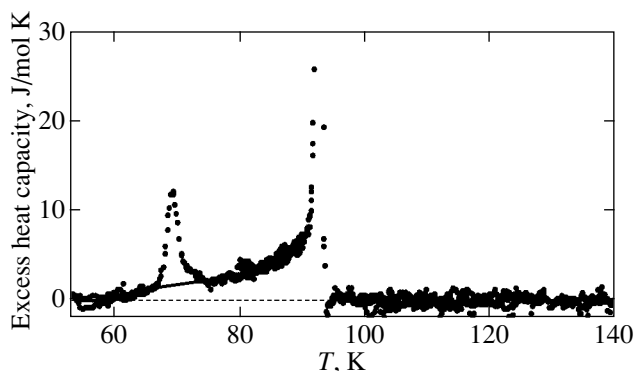
processing of the background component was carried out using a polynomial of the form $C(T) = a_1 T^{-3} + a_2 T^{-2} + a_3 T^{-1} + a_4 + a_5 T + a_6 T^2 + a_7 T^3$ [16]. The background heat capacity is shown in Fig. 2 by a dotted line. The scatter of points about the fitted line is ±0.25%.

Figure 3 shows the temperature dependence of the excess heat capacity determined as the difference between the total measured heat capacity and the background component. It is seen that the anomalous contribution to the heat capacity associated with the PT at T_1 does not vanish even below T_2. To separate the anomalous contributions from both PTs to the total $\Delta C_p(T)$, we constructed the basis line corresponding to the excess heat capacity related to the PT at T_1 (heavy line in Fig. 3). This line was fitted with a polynomial of the same form as that used in determining the background heat capacity $C(T)$.

The total enthalpy change was obtained by integrating the function $\Delta C_p(T)$ and including the latent heat and was found to be $\Delta H_1 = \int \Delta C_p(T) dT + \delta H_1 = 400 \pm 35$ J/mol. The quantity $\delta H_1/\Delta H_1 \approx 0.7$ is relatively large, which indicates that the PT is far from the tricritical point.

The enthalpy change ΔH_2 related to the PT at T_2 is 26 ± 2 J/mol.

Polarization-optical investigations into the cubic modifications of CsLiCrO$_4$ were performed only on (111)-oriented plates cut parallel to the growth faces of single crystals. We could not study other cuts of crystals due to the small volume of the tetrahedral single crystals. The samples are optically isotropic at room temperature and retain this property under cooling to $T_{1\downarrow} \approx 91$ K (Fig. 4a). Below this temperature, the samples exhibit optical anisotropy and a clear lamellar twin structure with boundaries inclined to each other at an angle of 60° (Fig. 4b). The pattern has the highest contrast at liquid-nitrogen temperature (Fig. 4c). Extinc-
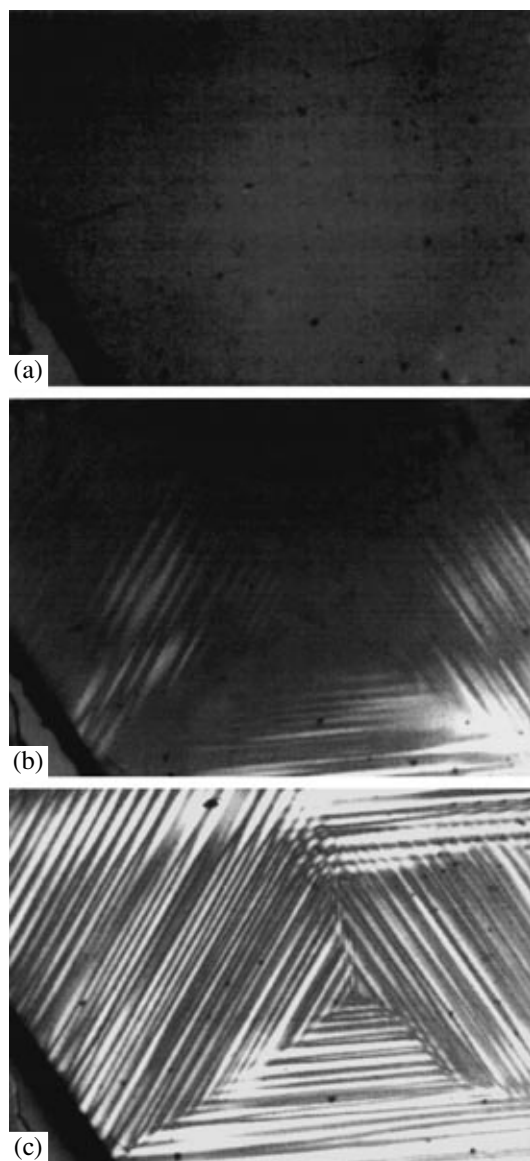
(a)

(b)

(c)

Fig. 4. Results of polarization-optical studies of (111)-oriented plates of the cubic CsLiCrO$_4$ at various temperatures: (a) $T = 293$ K, (b) $T \leq 91$ K, and (c) $T = 80$ K.

tions in individual twins are observed in the [100]-type directions and, hence, likewise differ by 60° in direction. On heating, the twin structure gradually loses brightness and finally disappears at $T_{1\uparrow} \approx 93$ K. Thus, the thermal hysteresis of the PT is $\delta T_1 \approx 2$ K.

As noted above, the temperature of the transition from the cubic to orthorhombic modification in CsLiCrO$_4$ crystals is substantially below the temperature that can be achieved in the adiabatic calorimeter. Thus, we studied this transition only using the DSM-2M microcalorimeter.

Figure 5 shows the temperature dependence of the excess heat capacity of a sample measured in two sequential heating runs. In the first heating run (dashed
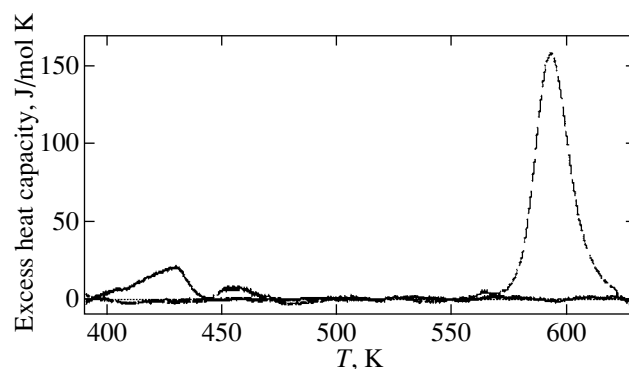

Fig. 5. Temperature dependences of the excess heat capacity of a CsLiCrO$_4$ crystal measured during the first (dashed line) and second (solid line) heating runs.

line in Fig. 5), a heat-capacity anomaly at $T_m = 592 \pm 2$ K is clearly observed, which agrees well with the data from [1]. By integrating the anomalous portion, the PT enthalpy is found to be $\Delta H_m = 2860 \pm 400$ J/mol. Calorimetric studies on independently grown crystals show that the temperature T_m varies from sample to sample through a 20- to 30-K-wide range. However, the enthalpy of the monotropic PT remains constant to within the determination error indicated above.

During the next heating (solid line in Fig. 5), the anomaly near T_m does not appear, but a heat-capacity peak at $T_0 = 429 \pm 2$ K (which is absent in the first heating) is clearly observed. This peak is reproduced during thermal cycling. The temperature of the heat-capacity maximum coincides with the PT temperature measured for the CsLiCrO$_4$ crystals grown in the orthorhombic phase from a melt. Thus, the results obtained allow us to conclude that the CsLiCrO$_4$ crystals undergo an irreversible transformation from the metastable cubic phase to a stable orthorhombic phase near 600 K.

4. DISCUSSION OF THE RESULTS

In [12], the results of adiabatic calorimetry studies of CsLiCrO$_4$ were analyzed in terms of the mechanism of the structural transformation and a possible description of the anomalous heat capacity in terms of the phenomenological theory of PTs was discussed. Unfortunately, we failed to compare in detail the thermodynamic parameters of the $Pmcn \rightleftarrows P112_1/n$ phase transitions in CsLiCrO$_4$ and CsLiSO$_4$ crystals, since the experimental data obtained for CsLiCrO$_4$ using the DSM-2M microcalorimeter are not sufficiently accurate to analyze the $\Delta C_p(T)$ dependence. Therefore, we consider only the PT entropy ΔS using the available structural data and theoretical concepts regarding the mechanism of structural distortions in the crystals under study.

The change in the entropy of the $Pmcn \rightleftarrows P112_1/n$ phase transition in CsLiCrO$_4$ was determined from the

formula $\Delta S = \int (\Delta C_p (T)/T) dT$ and was found to be $\Delta S_0 = 0.16R$, which agrees satisfactorily with the PT entropy in $CsLiSO_4$ ($0.2R$) [12], in spite of the substantial difference in the behavior of the shear strain in these crystals [9–11]. Low experimental values of the PT entropy are characteristic of displacive PTs. In compounds with a β-K_2SO_4-type structure, such PTs can be related to small-angle rotations of the tetrahedra. For a long time, the experimental data on PTs in these compounds were believed to indicate the order–disorder character of the PTs [9]. However, in comparatively recent studies, this approach to describing structural distortions in these compounds was revised on the basis of an analysis of the electron-density maps for oxygen atoms [17]. It has been revealed that, although the temperature factors of the oxygen atoms are relatively large, these atoms do not show clear evidence of being disordered in the orthorhombic phase.

In [18], the Monte Carlo method was used to calculate the temperature dependences of the heat capacity and some thermodynamic parameters of the $CsLiSO_4$ and $CsLiCrO_4$ crystals. In the mean-field approximation, the values of the entropy change due to the $Pmcn \rightleftharpoons P112_1/n$ phase transition in both crystals were found to be $R \ln 2$, which is characteristic of order-disorder PTs, although the PT temperatures differ substantially in these crystals. On the other hand, the inclusion of strong short-range correlations of the $S(Cr)O_4$ octahedra led to a significantly decreased entropy $\Delta S_0 = 0.3R$.

Thus, at the present time, it is impossible to make a final conclusion about the PT mechanism in $CsLiSO_4$ and $CsLiCrO_4$ crystals. It should be noted, however, that the entropy change due to PTs in $ALiMO_4$ crystals is often small [19], although, for example, $TlLiSO_4$ undergoes a clear order–disorder PT for which $\Delta S_1 \approx R \ln 2$ [20].

Based on the calorimetric studies of the cubic modification of $CsLiCrO_4$, we analyzed the behavior of the heat capacity below T_1 in terms of the Landau theory. According to this theory, the temperature dependence of the heat capacity in the distorted phase is described by the equation [21]

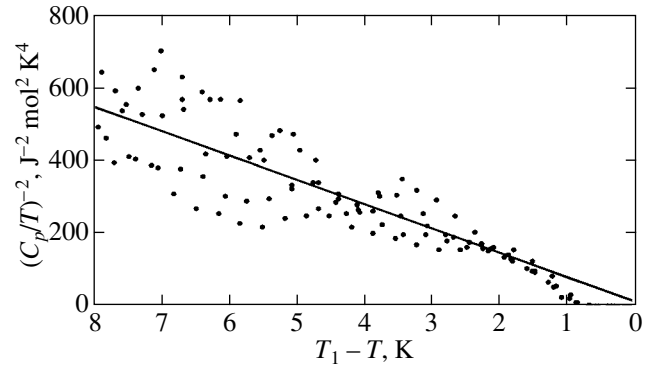$$\left(\frac{\Delta C_p(T)}{T} \right)^{-2} = \frac{B^2}{A_T^4} + \frac{12C}{A_T^3}(T_1 - T),$$

Fig. 6. Temperature dependence of the square of the reciprocal excess heat capacity for a $CsLiCrO_4$ ($F\bar{4}3m$) crystal.

where A_T, B, and C are the coefficients of the invariants containing the order parameter to the second, fourth, and sixth powers, respectively, in the thermodynamic potential. As seen from Fig. 6, the reciprocal of the excess heat capacity squared does indeed depend linearly on temperature over a rather wide temperature range, down to $T_1 - 8$ K. Using these data, we found that $A_T^2/B = 0.2$ J/(mol K^2), $A_T^3/C = 0.19 \times 10^{-2}$ J^2/(mol^2 K^3), and $T_1 - T_c = B^2/4A_T C = 1$ K. The degree of proximity of the first-order transition ($B > 0$) to the tricritical point [21] is found to be $N = -(B^2/3A_T CT_c)^{1/2} = -0.13$.

The PT entropies at T_1 and T_2 calculated from the formula $\Delta S_i = \Delta H_i/T_i$ are $0.510R$ and $0.045R$, respectively. The substantial difference between the entropy changes due to the sequential PTs in $CsLiCrO_4$ ($F\bar{4}3m$) demonstrates that the mechanisms of these PTs are significantly different, whereas in molybdates and tungstates (having analogous structures) the numerical values of the entropies of the sequential PTs are close to each other and the anomalous heat capacities are identical in behavior [14].

Our polarized-light studies suggest that the cubic $CsLiCrO_4$ crystal undergoes a structural PT at T_1, accompanied by loss of the threefold symmetry axis. The sharpness of the twin pattern (Fig. 4c) indicates that the symmetry elements along the [100] direction are most likely retained during the PT. Otherwise, additional twins would have blurred the observed pattern. From above, it follows that at T_1 the $\bar{4}3m \rightleftharpoons \bar{4}2m$ phase transition is most likely to occur in the crystal.

Thermodynamic parameters of monotropic phase transitions (PTs) in crystals of the β-K_2SO_4 family

Crystal	PT	T_m, K	ΔH, J/mol	$\Delta S/R$	References
$CsLiCrO_4$	$F\bar{4}3m \longrightarrow Pmcn$	590–615	2800	0.58	This work
NH_4LiSO_4	$Pca2_1 \longrightarrow Pmcn$	350–515	2400	0.56–0.82	[2]
Cs_2CdI_4	$P2_1/n \longrightarrow Pnma$	418–428	4200	1.15	[3]

Unfortunately, there is no direct evidence supporting this conclusion; such evidence could be obtained by studying the (100) cuts. Another (less probable) symmetry change at T_1 could be $\bar{4}3m \rightleftharpoons mm2$, as is the case in some representatives of the family of boracites [22]. Thus, the polarized-light studies showed that CsLiCrO$_4$ does not have a phase with $3m$ symmetry like crystals of the families of molybdates and tungstates [13].

Summing the optical and calorimetric data, we can conclude with confidence that the sequence of PTs observed in this crystal is not analogous to that occurring in the CsLiMoO$_4$, CsLiWO$_4$, RbLiMoO$_4$, and RbLiWO$_4$ crystals [13].

The table lists the parameters of the monotropic PT in CsLiCrO$_4$ and, for comparison, data on analogous PTs in some crystals of the β-K$_2$SO$_4$ family investigated earlier [2, 3]. In the table, a range of values of the PT temperature T_m is given, since this temperature does not have a certain value but rather varies depending on the sample prehistory. The range of experimental values of T_m is especially wide for NH$_4$LiSO$_4$. On the other hand, for all crystals, the value of the enthalpy change does not vary from sample to sample to within the determination error. For this reason, the entropy change due to a PT varies substantially only for NH$_4$LiSO$_4$. This can be understood by referring to the enthalpy differential $dH = TdS + Vdp$ at a constant pressure, which was observed in the calorimetric experiments.

In accordance with [23], the monotropic PTs in crystals cannot be treated as classical PTs, since they are accompanied by kinetic phenomena. Thus, the entropy presented in the table is not the only reliable characteristic of the mechanism of the structural PT in question. However, it is obvious that a monotropic transition is accompanied by a radical reconstruction of the structure and, hence, should cause a large change in the entropy, as is observed in all the crystals under study. It is unclear whether a reverse transition to the metastable phase can occur. For example, in [3], the reverse transition in a Cs$_2$CdI$_4$ crystal was observed to occur when the stable phase was exposed to a moist atmosphere. We performed similar procedures for CsLiCrO$_4$ and, in [2], for NH$_4$LiSO$_4$ crystals but failed to induce a reverse transition.

ACKNOWLEDGMENTS

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