LATTICE DYNAMICS
AND PHASE TRANSITIONS

Heat Capacity and Phase Transitions in NH_4LiSO_4, $Cs_x(NH_4)_{1-x}LiSO_4$, and $RbLiSO_4$

I. N. Flerov, A. V. Kartashev, and V. A. Grankina

Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia
e-mail: flerov@ksc.krasn.ru
Received June 25, 2004

Abstract—The heat capacity of NH_4LiSO_4, $RbLiSO_4$, and $Cs_x(NH_4)_{1-x}LiSO_4$ crystals and its behavior over a broad temperature range including the phase transition regions were studied. The entropy changes corresponding to structural transformations in these crystals were found not to be characteristic of straightforward ordering of structural blocks. The results obtained are discussed in terms of phenomenological theory and model concepts. © 2005 Pleiades Publishing, Inc.

1. INTRODUCTION

The numerous compounds with the general chemical formula $AA'CX_4$ (A, A', and C are cations, and X is an anion) form a representative family of crystals possessing a β-K_2SO_4-type structure (space group $G_1 = D_{2h}^{16}$–$Pmcn$, $z = 4$) over a certain temperature interval. The praphase of this structure is the hexagonal α-K_2SO_4 structure (space group $G_0 = D_{6h}^4$–$P6_3/mmc$, $z = 2$), which can exist only if the tetrahedral ionic groups CX_4 are disordered in orientation [1]. However, the hexagonal phase has not been observed experimentally in all crystals with the β-K_2SO_4 structure. The $\alpha \longrightarrow \beta$ phase transition has been reliably established to occur in several oxygen-containing compounds with identical A and A' cations, for instance, in K_2SO_4, K_2SeO_4, and K_2CrO_4 [1]. However, in many crystals with $A \neq A'$, either phase transitions to the hexagonal phase with space group $P6_3/mmc$ have not been observed up to the melting point or the space group of the hexagonal phase has not been established unambiguously. Considered, however, from the standpoint of model concepts, the praphase G_0 may also exist in crystals of this type [2].

As the temperature is lowered, the stable crystal modification β-K_2SO_4 frequently transforms into a ferroelectric, ferroelastic, or incommensurate phase in single or successive reversible phase transitions. The diversity of distorted phases depends, to a considerable extent, on chemical pressure, which can be varied through proper isovalent substitutions of cations and anions in the β-K_2SO_4 structure. This is convincingly illustrated by the crystal series $ALiSO_4$, whose symmetry within a certain temperature interval is orthorhombic with space group $Pmcn$ [1]. In these compounds, the SO_4 tetrahedral groups are linked together by the LiO_4 tetrahedra to form a network. Depending on the size of the A cation, phase transitions to the ferroelastic phase

with space group $G_2 = (C_{2h}^5)$–$P112_1/n$ and $z = 4$ occur under cooling either directly ($CsLiSO_4$–CLS) or via a series of intermediate structural forms including the incommensurate phase I: $Pmcn \longrightarrow I \longrightarrow P2_1/c11 \longrightarrow P11n \longrightarrow P112_1/n$ ($RbLiSO_4$–RLS). In NH_4LiSO_4 (NLS), the ferroelastic monoclinic phase $P112_1/n$ is not observed down to liquid-helium temperatures and the phase transition from $Pmcn$ is accompanied by the onset of a ferroelectric state (space group $P2_1cn$, $z = 4$) in the region of ~160 K. This transition is followed by a transition to the ferroelastic phase $P2_1/c11$ ($z = 8$). Recent studies of the $Cs_x(NH_4)_{1-x}LiSO_4$ (CNLS) have revealed that the $P112_1/n \longrightarrow P2_1cn$ phase transition occurs only in compounds corresponding to the narrow concentration region $x = 0.3$–0.5 [3].

The $TlLiSO_4$ crystal (TLS) has also been reported fairly recently to have an orthorhombic phase ($Pmcn$) at room temperature, which transfers, in a series of structural transformations under cooling, to a monoclinic phase with a still unknown space group [4–6]. When heated above 531 K, TLS transfers to a hexagonal phase; however, its space group, $P6_3$ ($z = 24$), does not fit with the α-K_2SO_4 structure.

As for the $KLiSO_4$ compound (KLS), it has been found to exist in a hexagonal and an orthorhombic phase, but their space groups have not yet been established unambiguously [1].

Some experimental data obtained, in particular, in structural studies suggest that the $G_0(P6_3/mmc) \longrightarrow G_1(Pmcn) \longrightarrow G_2$ phase transitions in $AA'CX_4$ and A_2CX_4 compounds are driven by ordering of the CX_4 tetrahedral ionic groups [1, 2, 7]. The fact that ordering of the NH_4 tetrahedra does not contribute noticeably to the mechanism of phase transitions in ammonium-containing crystals is supported convincingly by studies of ND_4LiSO_4 [8]. Data obtained in structural studies of

$A\mathrm{LiSO_4}$ crystals, however, are not always convincing enough to warrant unambiguous conclusions regarding the mechanism of the transitions involved. It would seem at first glance that arguments for the ordering of tetrahedra carry more weight and that the order–disorder model is preferable [9–11]. However, a comparative analysis of the structure of a number of crystals [12] has shown that the extent of ionic disorder depends on the relative cation size.

It is known that, as a fundamental thermodynamic property, the entropy of a phase transition ΔS makes it possible to describe the mechanism of structural distortions and that its magnitude depends not to a small degree on the anharmonicity of critical-ion vibrations [13]. In the limiting cases, i.e., for a weakly anharmonic (displacive phase transformations) and a strongly anharmonic potential (order–disorder transitions), the values of ΔS differ greatly; they are $\sim 0.1R$ and $\geq 0.7R$ ($R\ln 2$), respectively.

Although many of the physical properties of $A\mathrm{LiSO_4}$ crystals have been studied in considerable detail [1], the thermophysical aspects of phase transitions have not been probed adequately, in particular, using calorimetry. Reliable data on the entropy change associated with a second-order transition from the orthorhombic phase $Pmcn$ have been obtained for CLS only [14]. It has been found that $\Delta S \approx 0.2R$ is much closer to the value characteristic of displacive transitions. Calculations made with the model of stage-by-stage ordering of tetrahedra as a result of $P6_3/mmc \longrightarrow Pmcn \longrightarrow P112_1/n$ structural distortions [2] revealed that correlations in vibrations of critical ions can cause a substantial decrease in transition entropy. In this case, ΔS for CLS is $\sim 0.3R$ for each of the two phase transitions.

The present communication reports on heat capacity measurements for the NLS, RLS, and CNLS crystals performed within a broad temperature interval including the regions of structural transformations. The measurements were carried out with the aim of broadening our understanding of possible values of the entropy and mechanisms of phase transitions in $A\mathrm{LiSO_4}$ crystals.

2. EXPERIMENTAL TECHNIQUES

CNLS ($x = 0.95$), NLS, and RLS crystals were grown from aqueous solutions by slow evaporation at 310 K. The identification and characterization of the samples were performed in three steps. Room-temperature x-ray diffraction studies allowed us to verify the absence of starting components as impurities and of foreign phases. The optical homogeneity of the samples was established using a polarization microscope. In the last stage of characterization, a DSM-2M differential scanning microcalorimeter was employed to perform calorimetric studies in the temperature range 120–520 K. Samples were in both crystal and powder form. The phase transition temperatures of the samples under study were found to coincide satisfactorily with available data obtained earlier by other techniques [1]. The same calorimetric method was used in more thorough thermophysical measurements carried out in the region of high-temperature phase transitions in NLS and RLS. The rate of temperature variation in both heating and cooling runs was 8 K/min in all experiments, and the sample mass varied in the range 0.10–0.15 g. A more detailed description of experimental factors regarding the determination of the phase transition enthalpy and entropy can be found in [15].

Although the high-temperature phase transition in NLS was studied by us earlier using differential scanning calorimetry (DSC) [15, 16], we repeated these experiments in this work on a large number of powder and single-crystal samples prepared under different crystallization conditions. These statistical data permitted us, first, to unambiguously determine the number of phase transitions in NLS and, second, to obtain more reliable information concerning the behavior of the heat capacity.

Below 373 K, the behavior of the heat capacity of NLS and CNLS crystals was investigated with adiabatic calorimetry. The samples were plane plates with masses of 1.288 g (NLS) and 1.585 g (CNLS). The measurements were conducted in a fixture similar to that employed in [17] for heat capacity measurements on uniaxial ferroelectrics. The heat capacity of the fixture was determined in a separate experiment. The heat capacity of samples was measured in discrete ($\Delta T = 1.0$–2.5 K) and continuous ($dT/dt = 0.16$–0.50 K min^{-1}) heating modes. In the immediate proximity of the low-temperature transition in NLS, quasi-static thermograms were obtained with a heating rate of 3×10^{-2} K min^{-1}.

3. EXPERIMENTAL RESULTS

3.1. NLS

Figure 1 presents experimental data on the specific heat $C_p(T)$ of an NLS crystal obtained within a broad temperature range with an adiabatic (110–373 K) and a differential scanning (350–520 K) calorimeter in continuous and discrete heating modes. DSC does not provide sufficient accuracy in determining the absolute values of heat capacity. Therefore, the data obtained using this method were referred to adiabatic calorimeter measurements in the range 355–373 K.

Two heat capacity anomalies associated with a sequence of phase transitions between the paraelectric ($Pmcn$), ferroelectric ($P2_1cn$), and ferroelastic ($P2_1/c11$) phases were detected.

The thermodynamic parameters of the high-temperature phase transition studied on a large series of samples proved reproducible to within acceptable limits. The location of the heat capacity maximum $T_1 = 460.5$ K varied from one sample to another within 1.5 K. To determine the magnitude of the excess specific heat ΔC_p and the temperature interval of its existence in the $P2_1cn$
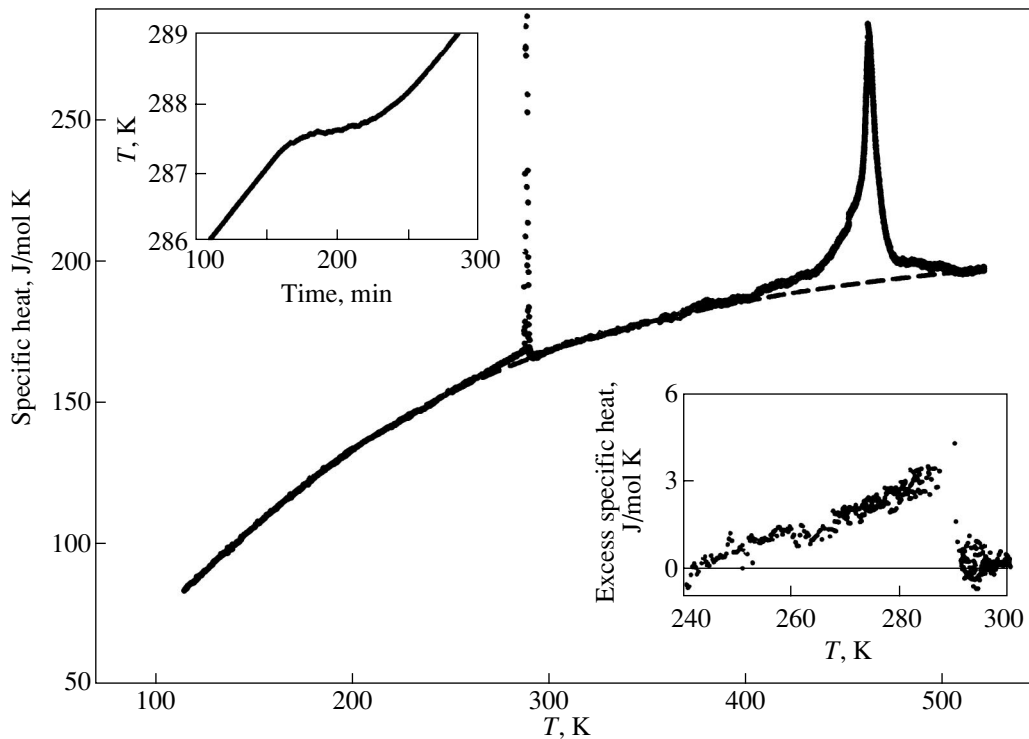
Fig. 1. Specific heat of NLS over a broad temperature interval. The dashed line is the lattice specific heat. The top inset shows a thermogram obtained in the heating mode near T_2. The lower inset shows the excess specific heat in the vicinity of T_2.

and $P2_1/c11$ phases, the regular component, i.e., lattice specific heat (shown in Fig. 1 by a dashed line) was found. We used the combined Debye–Einstein function $C_{\mathrm{latt}}(T) = A_1 D(\Theta_D/T) + A_2 E(\Theta_E/T)$ to fit the experimental data obtained far from the phase transition points (114–203 and 308–373 K). The average deviation of the experimental points from the smoothed curve was approximately ±0.5%. This procedure revealed that an excess specific heat is present within a broad temperature interval both above and below T_1 (Fig. 1). These findings correlate with earlier data on the behavior of thermal expansion and birefringence [3, 18]. In this case, the increased change in the enthalpy due to the $Pmcn \longrightarrow P2_1cn$ transition obtained in the present measurements, $\Delta H_1 = 1300 \pm 150$ J mol^{-1}, as compared to the value of 1170 ± 200 J mol^{-1} derived from heat capacity measurements performed on NLS within a narrower temperature interval [15], appears natural. It should also be pointed out that none of the NLS samples studied by us revealed a splitting of the heat capacity anomaly at T_1 into two peaks, which was observed in [19] and assigned to the existence of a sequence of phase transitions within a range 2–3-K wide.

The position of the heat capacity peak maximum $T_2 = 287.7$ K, accepted in the first stage as the temperature of the second transition, agrees satisfactorily with the values reported, for instance, in [1]. No other heat capacity peaks were found between T_1 and T_2 and

below T_2 within the scatter of experimental points. Thus, our high-precision measurements performed using the very sensitive calorimetric method also argue convincingly against the existence of additional anomalies in the NLS heat capacity allegedly associated with phase transitions occurring in the temperature range 330–350 K [20], near 250 K [21], and at 225 K [22].

Studies of NLS using quasi-static thermography in the immediate vicinity of the phase transformation at T_2 are illustrated in the upper inset to Fig. 1. The pattern of the thermogram suggests heat absorption at the transition. The phase transition temperature ($T_2 = 287.6 \pm 0.1$ K) was refined, and the enthalpy jump (latent heat) was determined, $\delta H_2 = 310 \pm 15$ J mol^{-1}.

Isolation of the lattice component revealed that the excess specific heat of NLS below T_2, which is not connected in any way with the absorption of latent heat, though small ($\Delta C_p \approx 0.025 C_{\mathrm{latt}}$ near T_2), does nevertheless exist within a fairly broad temperature interval (40-K wide) near T_2 (see lower inset to Fig. 1). With inclusion of $\Delta C_p(T)$, the total enthalpy change associated with the $P2_1/c11 \longrightarrow P2_1cn$ phase transition and defined as $\Delta H_2 = \int \Delta C_p dT + \delta H_2$ was found to be 385 ± 35 J mol^{-1}.

Repeated measurements of $C_p(T)$ in the vicinity of the low-temperature phase transition performed in the continuous heating mode at different rates ($dT/dt =$
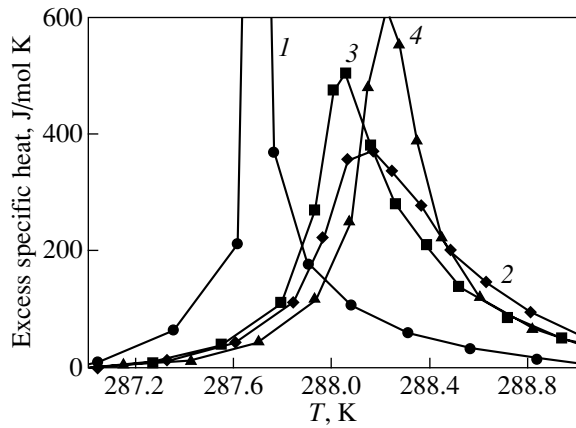
Fig. 2. Excess specific heat of NLS near T_2 measured in successive heating cycles. Numerals *1–4* label successive experiments.

0.28–0.47 K min^{-1}) revealed the influence of thermal cycling on the magnitude and position of the excess heat capacity peak maximum at T_2 (Fig. 2). The largest value of $(\Delta C_p)_{max}$ was measured in the first experiment, which is characteristic of clearly pronounced first-order phase transitions. Subsequent deviations of the magnitude of $(\Delta C_p)_{max}$ observed to occur from one experiment to another may be assigned, in particular, to degradation of the thermal contact between parts of the

crystal, which may form as a result of sample cracking caused by a noticeable jump in volume. However, the changes in transition enthalpy from one experiment to another turned out considerably smaller than the determination error. Under these conditions, the temperature of the maximum $(\Delta C_p)_{max}$ varied within 0.6 K. In view of a certain lack of reproducibility of the experimental data as a function of the sample heating rate, we should accept for the transition temperature the value obtained in the conditions closest to equilibrium, more specifically, that obtained in the quasi-static thermographic measurements.

3.2. CNLS

The behavior of the specific heat of CNLS with temperature was studied using adiabatic calorimetry and is displayed graphically in Fig. 3a. Also shown for comparison are earlier data on CLS obtained and reported in [14] (with the participation of one of the present authors). As expected, partial substitution of ammonium for cesium does affect the thermodynamic parameters, both far from and near the phase transition. The temperature of the heat capacity maximum, considered as the temperature of the $Pmcn \longrightarrow P112_1/n$ phase transition, rose in the solid solution by 5 K to become $T_0 = 207.2 \pm 0.7$ K. The regular specific heat determined using same approximating function as used earlier for NLS is shown in Fig. 3a by dashed lines. This
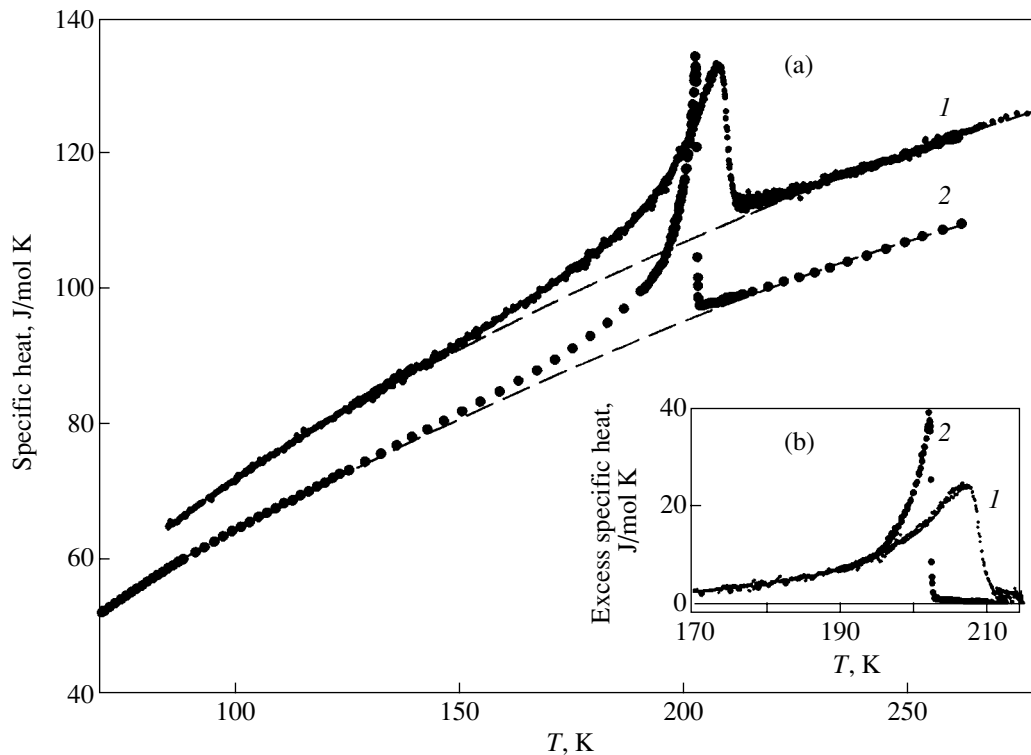

Fig. 3. Temperature dependence of (a) the specific heat and (b) excess specific heat of (*1*) CNLS and (*2*) CLS [14]. The dashed line is the lattice specific heat.
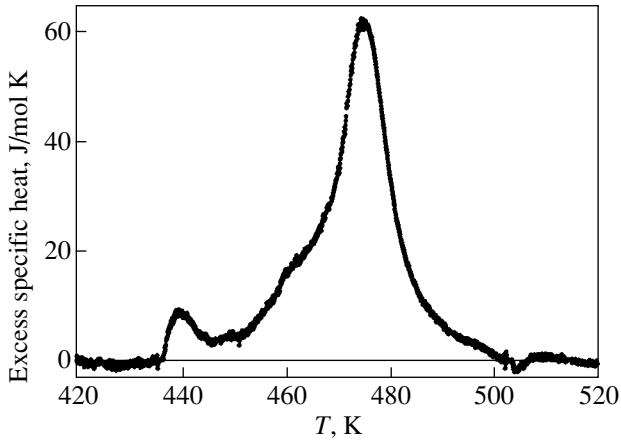
Fig. 4. Temperature dependence of the excess specific heat for RLS.

quantity turned out to be higher for the solid solution throughout the temperature interval studied. As for the excess specific heat, its behavior for CNLS changed markedly (Fig. 3b). The narrow $\Delta C_p(T)$ peak observed in CLS flattens out and becomes substantially smaller in magnitude at T_0. Note also that the regular specific heat was described in [14] by a polynomial. Both in CLS and CNLS, the $Pmcn \longrightarrow P112_1/n$ phase transition is a second-order transformation; therefore, the change in enthalpy was determined by integrating the $\Delta C_p(T)$ function. No noticeable effect was observed of the way in which $C_{latt}(T)$ was represented on the enthalpy of the $Pmcn \longrightarrow P112_1/n$ phase transition in CLS ($\Delta H_{CLS} = 335 \pm 25$ J mol^{-1}); indeed, the difference is within the accuracy of determining ΔH. In the case of CNLS, the enthalpy of the transition increased, as compared to CLS, to reach $\Delta H_{CNLS} = 460 \pm 50$ J mol^{-1}.

3.3. RLS

Since the phase transitions in RLS occur at temperatures above 370 K, the heat capacity of this crystal was studied using the DSC method only. Figure 4 plots the temperature dependence of the anomalous specific heat. Three heat capacity peaks can be clearly discerned, with the maxima lying at $T_1 = 475$ K, $T_3 = 460$ K, and $T_4 = 439$ K. As for the anomaly at T_2, it merges with the heat capacity peak at T_1. This is, however, not of any importance here, because we are interested primarily in changes in the thermodynamic parameters associated with the symmetry change $Pmcn \longrightarrow P112_1/n$. This distortion of the structure is a result of four successive phase transitions occurring in RLS and of the direct transformation to CLS. Therefore, our analysis of the $\Delta C_p(T)$ dependence for RLS was not aimed at answering questions regarding with the separation of the contributions from each of the successive $Pmcn \longrightarrow I \longrightarrow P2_1c11 \longrightarrow P11n$ transitions to the enthalpy change

$\Delta H_{1-3} = \Sigma(\Delta H_1 + \Delta H_2 + \Delta H_3) = 1030 \pm 150$ J mol^{-1}. As for the $P11n \longrightarrow P112_1/n$ transformation, the corresponding enthalpy change was small, $\Delta H_4 \approx 70$ J mol^{-1}. Thus, the total enthalpy change connected with the structural transition from $Pmcn$ to $P112_1/n$ in RLS is 1100 J mol^{-1}.

4. DISCUSSION OF THE RESULTS

The experimental results obtained in this work make it possible to determine and analyze the thermodynamic characteristics associated with the phase transitions in ALiSO$_4$ crystals, in particular, the magnitude and behavior of the anomalous specific heat ΔC_p and entropy ΔS, as well as to establish the applicability of some thermodynamic relations connecting the thermophysical properties and other properties. The total entropy changes in the case of first-order phase transitions are defined by the sum of two contributions, $\Delta S = \delta S + \int (\Delta C_p/T)dT$. The first term is due to the abrupt change in the transition parameter at the transformation point and is calculated from the latent heat, $\delta S = \delta H/T_i$. For second-order transformations, the quantity ΔS is naturally identified with the second term only.

The thermodynamic description of the phase transition sequence in the NLS crystal is outlined in [23]. The free energy F was presented as a function of the transition parameters ξ and η corresponding to librations of the tetrahedral groups and macroscopic polarization P_s:

$$\Delta F = \alpha\xi^2 + \beta\xi^4 + \gamma\xi^6 + \varepsilon\xi P_s + aP_s^2$$
$$+ A(\eta_1^2 + \eta_2^2) + B_1(\eta_1^2 + \eta_2^2)^2 + B_2\eta_1^2\eta_2^2 \quad (1)$$
$$+ C(\eta_1^2 + \eta_2^2)^3 + \mu\xi^2(\eta_1^2 + \eta_2^2) + \dots$$

Because both transitions in NLS are first-order transformations, the following relations were suggested in [23]: $\alpha = \alpha_T(T - T_1)$, $A = A_T(T - T_2)$, $T_1 > T_2$, $\beta < 0$, and $B_1 < 0$. The condition of the minimum $\partial\Delta F/\partial P = 0$ implied that $\xi = -(a/\varepsilon)P_s$, in which case the free energy can be written as a function of two variables, $\Delta F(P, \eta)$:

$$\Delta F = \alpha(a/\varepsilon)^2 P_s^2 + \beta(a/\varepsilon)^4 P_s^4 + \gamma(a/\varepsilon)^6 P_s^6$$
$$+ A(\eta_1^2 + \eta_2^2) + B_1(\eta_1^2 + \eta_2^2)^2 + B_2\eta_1^2\eta_2^2 \quad (2)$$
$$+ C(\eta_1^2 + \eta_2^2)^3 + \mu(a/\varepsilon)^2 P_y^2(\eta_1^2 + \eta_2^2) + \dots$$

Because only the coefficients α and A are temperature-dependent, the total entropy change associated with the phase transition sequence $Pmcn \longrightarrow P2_1cn \longrightarrow P2_1/c12$ will be

$$\partial\Delta F/\partial T = -\Delta S = \alpha_T(a/\varepsilon)^2 P_s^2 + A_T(\eta_1^2 + \eta_2^2). \quad (3)$$

In accordance with [23], the conditions of stability of the NLS phases can be written as

$$Pmcn: \quad P_s = \xi = \eta_i = 0; \quad \alpha > 0, a > 0, A > 0,$$

$$P2_1cn: \quad P_s \neq 0; \quad \xi \neq 0; \quad \eta_1 = \eta_2 = 0, \quad (4)$$

$$P2_1/c11: \quad P_s = 0; \quad \xi = 0; \quad \eta_1^2 = \eta_2^2 = \eta^2.$$

Hence, the entropy change at the $Pmcn \longrightarrow P2_1cn$ phase transition can be identified with the first term on the right-hand side of Eq. (3). The corresponding relation connecting the jump in entropy δS_1 with the jump in polarization δP at the transformation point T_1 can be cast as

$$\delta S_1 = \alpha_T (a/\varepsilon)^2 \delta P_s^2. \quad (5)$$

A specific feature of the DSC technique employed by us in high-temperature studies, in particular, on NLS, consists in that it does not permit separation of the contributions to enthalpy (and entropy) associated with the jump in the order parameter at a first-order phase transition point and the gradual approach of the order parameter to the saturation level. In other words, DSC data cannot always provide a reliable conclusion concerning the nature of a transition. The studies reported in [16, 24] did not reveal any clearly pronounced jumps in the birefringence Δn or polarization P_s at T_1. However, a study [18] carried out with the participation of one of the present authors showed that the pattern of the strain behavior and of the quasi-static thermogram argue persuasively for the presence of jumps in volume and enthalpy at the $Pmcn \longrightarrow P2_1cn$ transition point. It seems appropriate to quote a conclusion made in [25] on the determination of the order of a transition in controversial cases, which we believe to be correct: "…*the observation of latent heat (a jump in a transition parameter) in at least one of a set of samples indicates the transformation in a given substance to be a first-order transition.*" Thus, according to experimental evidence [18], the transition occurring in NLS at T_1 can be unambiguously assigned to first-order transformations. At the same time, it is known that the polarization [24], birefringence [16], and thermal expansion coefficients [18] of NLS undergo a change within a broad temperature interval between T_1 and T_2. These facts imply that the parameter of the transition increases gradually with decreasing temperature. Because the entropy change, according to Eq. (3), scales as the square of the transition parameter, there should also be excess specific heat in a broad temperature interval below T_1. Experimental data convincingly demonstrate that the $Pmcn \longrightarrow P2_1cn$ phase transition is fairly close to the tricritical point. This conclusion follows from the relative magnitude of the jump in enthalpy and its total change, $\delta H_1/\Delta H_1 = 0.2$, which turned out to be substantially smaller than 1. It seems appropriate at this point to recall the studies of the anomalous part of birefringence in NLS below T_1 [16], which led to a similar conclusion

concerning the position of the transition with respect to the tricritical point.

In view of the above, the calorimetric data presented in [19], where the excess specific heat was found to exist in NLS only within a narrow temperature region $\Delta T \approx 5$ K near T_1, cannot be considered reliable. In this case, most likely, the part of the anomalous heat capacity associated only with the absorption of latent heat was detected. Indeed, integrating the $\Delta C_p(T)$ function yielded $\Delta H_1 = 2.9$ J g^{-1} [19], which is close to the enthalpy jump $\delta H_1 = 2.2 \pm 0.9$ J g^{-1} determined and reported by us in [18].

Taking the value of δH_1 and the Curie–Weiss constant $C = 5.6$ K [24], we can use Eq. (5) to estimate the polarization jump at T_1 assuming the relation $\alpha_1(a/\varepsilon)^2 = (2\pi/C)T_1$ [26] to be valid. The calculated value $\delta P_s \approx 0.1$ μC cm^{-2} correlates satisfactorily with the figure 0.05–0.10 μC cm^{-2} corresponding to the fastest variation of polarization near T_1 [24]. The reliability of the experimental values is also corroborated by the results of fitting the changes in the enthalpy δH_1 and the relative volume $\delta V_1/V = 4 \times 10^{-4}$ [18], as well as of the parameter characterizing the response of the crystal to pressure, $dT_1/dp = 0.6$ K GPa^{-1} [1], to the Clapeyron–Clausius relation $dT_1/dp = T_1\delta V_1/(V\delta H_1)$. The calculated enthalpy jump $\delta H_1 = 1.5$ J g^{-1} agrees with the experimental value to within attainable accuracy [18].

The above data also make it possible to determine the electric field–induced temperature shift of the $Pmcn \longrightarrow P2_1cn$ phase transition with the use of the "electrical" Clapeyron–Clausius relation $dT_1/dE = -(\delta P_y/\delta H_1)T_1$ [26]. Unfortunately, we are not aware of any experimental study of the $T_1(E)$ dependence. A comparison of the calculated data (for T_1) with experimental data (for T_2) suggests, however, that the high-temperature phase transition (for which we have $dT_1/dE = 1 \times 10^{-7}$ K m V^{-1}) is more stable against an electric field than the $P2_1cn \longrightarrow P2_1/c12$ transformation ($dT_2/dE = 20 \times 10^{-7}$ K m V^{-1} [27]).

X-ray diffraction measurements performed on NLS show the SO$_4$ tetrahedra in the ferroelastic phase of NLS to be completely ordered. Thus, the $P2_1cn \longrightarrow P2_1/c11$ structural transformation is actually a transition between ordered phases, so the corresponding change in the entropy should be substantially smaller than $R\ln2$. However, since both space groups are subgroups of the $Pmcn$ phase, they are not connected with each other through a group–subgroup relation; therefore, this structural transformation occurs between two irreducible representations and should be a clearly pronounced first-order transition [1]. The experimental data obtained by us agree with the structure transformation model. The total entropy change $\Delta S_2 = 1.33 \pm 0.04$ J mol^{-1} K^{-1} (0.16 R) did turn out to be small and characteristic of displacive transformations. As for the relation connecting the
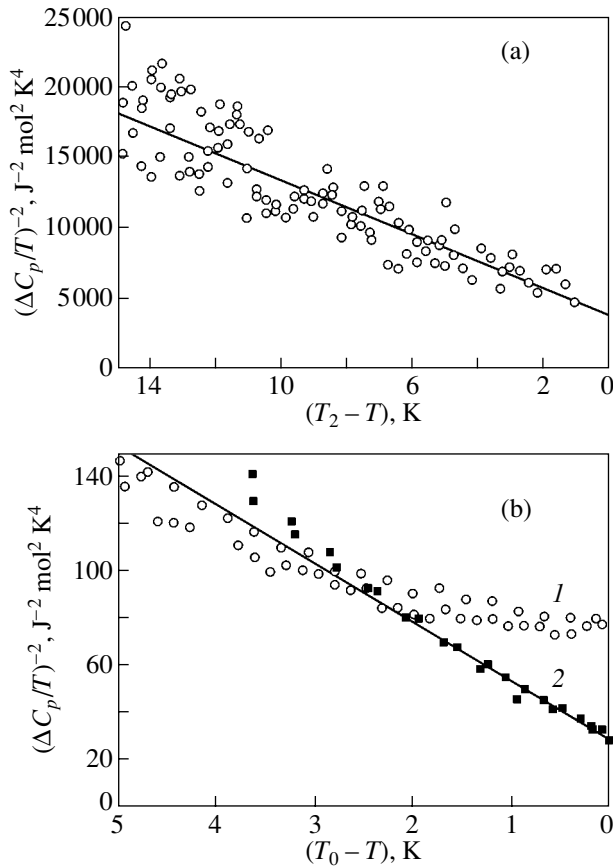
Fig. 5. Temperature dependence of the square of the inverse excess specific heat of (a) NLS and (b) (*1*) CNLS and (*2*) CLS.

enthalpy change at the transition point with its total change, $\delta H_2/\Delta H_2 = 0.81$, it argues for the $P2_1cn \longrightarrow P2_1/c11$ transition (unlike the transition at T_1) being fairly far from the tricritical point.

In accordance with [28], the excess specific heat below T_2 should satisfy, as follows from Eq. (1), the relation

$$\left(\frac{\Delta C_p}{T}\right)^{-2} = \left(\frac{2\sqrt{B^2 - 3A'C}}{A_T^2}\right)^2 + \frac{12C}{A_T^3}(T_2 - T). \quad (6)$$

Here, in accordance with Eq. (4), $B = (4B_1 + B_2)$ and $A' = A_T(T_2 - T_c)$. As seen from Fig. 5a, the excess specific heat squared is indeed a linear function of temperature over a fairly broad interval (15-K wide) near T_2. This fact allowed us to derive expressions relating the coefficients of the potential in Eq. (1) $A_T^2/B = 1.7 \times 10^{-2}$ J mol^{-1} K^{-2} and $A_T^3/C = 1.2 \times 10^{-2}$ J^2 mol^{-2} K^{-3} and the quantity $T_2 - T_c = B^2/4A_TC = 10$ K. The degree of proximity of the first-order ($B < 0$) transition to the tricritical point was established using the expression [28] $N = (B^2/(3A_TCT_C))^{1/2} = -0.22$.

In accordance with Eqs. (3) and (4), the entropy change δS_2 is connected with the abrupt appearance of a new transition parameter, $\eta_1^2 + \eta_2^2$, at T_2. The corresponding jump in volume, $\delta V_2/V = -4.6 \times 10^{-4}$, is calculated from the Clapeyron–Clausius equation using the data on the effect of hydrostatic pressure, $dT_2/dp = -26$ K/GPa [1]. Thus, at the phase transitions $Pmcn \longrightarrow P2_1cn$ ($\delta V_1/V = -4.0 \times 10^{-4}$) and $P2_1cn \longrightarrow P2_1/c11$, the unit cell volume of NLS undergoes changes in volume which are similar in magnitude and opposite in sign.

Studies of the elasticity and optical properties showed the $Pmcn \longrightarrow P112_1/n$ transition in CLS to be satisfactorily described in terms of the Landau phenomenological theory [29]. We carried out a similar analysis for the temperature dependence of the heat capacity of this crystal. The behavior of the square of the inverse excess specific heat of CLS near T_0 turned out to be in agreement with Eq. (6) (Fig. 5b). As seen from Fig. 5b, this relation is not met for CNLS. The reason for these discrepancies is most probably associated with the fact that, although CNLS was characterized as a crystalline compound, the ammonium ion could play the part of an impurity that makes the phase transition diffuse and distorts the real behavior of the excess specific heat.

As for the entropies of the phase transitions in CLS ($\Delta S_{CLS} = 1.66 \pm 0.13$ J mol^{-1} K^{-1}) and CNLS ($\Delta S_{CNLS} = 2.24 \pm 0.23$ J mol^{-1} K^{-1}), the difference between them is seen to be larger than the experimental error of their determination. One of the reasons for the increase in ΔS may be associated with the fact that the transition in the solid solution approaches the tricritical point lying on the $T(x)$ line [3], which governs the stability of the $Pmcn$ phase.

As already pointed out, the assignment of heat effects in RLS to particular phase transitions is complicated by their being close in temperature. However, the structure of RLS contains, within certain temperature intervals, ferroelastic phases $P2_1/c11$ and $P112_1/n$, which also occur in NLS and CLS, respectively. While the entropy changes due to the same $P2_1/c11$ monoclinic distortion are relatively small, the total value for NLS ($\Delta S_1 + \Delta S_2 = 4.24 \pm 0.42$ J mol^{-1} K^{-1}) is substantially larger than that for RLS ($\Delta S_1 + \Delta S_2 + \Delta S_3 = 2.08 \pm 0.20$ J mol^{-1} K^{-1}). Also, the difference between the entropies greatly exceeds the error of their determination. However, the entropy changes due to the formation of the $P112_1/n$ monoclinic phase in CLS (1.66 ± 0.16 J mol^{-1} K^{-1}) and RLS $\Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = 2.25 \pm 0.22$ J mol^{-1} K^{-1}) are closer in magnitude.

The mechanisms of the phase transitions occurring in crystals with an α-K$_2$SO$_4$ or β-K$_2$SO$_4$ structure have been considered in several experimental and theoretical studies [1, 2, 7]. In many cases, the researchers were inclined to believe that the SO$_4$ tetrahedra, which are

disordered over four positions in the α-K_2SO_4 phase and over two positions in the β-K_2SO_4 phase, become ordered after phase transitions and occupy only one position in different distorted phases of symmetry lower than *Pmcn*; in other words, transitions from the α and β phases should be of the order–disorder type. Straightforward model concepts suggest that the sequence of these transitions should be accompanied by changes in the entropy of $R(\ln2 + \ln2)$.

However, available experimental data do not always agree with the expected large value of ΔS. As established reliably by repeated measurements [1], only for K_2SO_4 undergoing a single transition $G_0 \longrightarrow G_1$ (*Pmcn*) is ΔS indeed equal to $R\ln4$. The situation is different for K_2SeO_4, where the same phase transition involves one-half the above entropy change, $\Delta S = R\ln2$ [2], and is apparently accompanied by partial ordering of the tetrahedra. As the temperature decreases further, however, this crystal undergoes three successive phase transitions [1], for which the changes in entropy are very small (<0.1 R) and argue rather for the mechanism of slight atomic displacement than for ordering in the case where the symmetry is lower than *Pmcn*. This suggestion is also substantiated by the observation of a soft mode in the β phase of this crystal [1].

As already mentioned, the α phase does not form in $ALiSO_4$ up to the melting or decomposition temperature. The entropy changes due to the phase transitions from the *Pmcn* orthorhombic phase in the crystals studied in [4, 14] and the present work are summed up in the table. The main point to mention is that, except for TLS, all the entropy changes ΔS determined by various methods are substantially smaller than the expected value $R\ln2 \approx 0.7R$, if we assume that the SO_4 tetrahedra occupy two equivalent positions in the *Pmcn* phase.

It would be instructive to point out that the kind of phase transition that occurs and its proximity to the tricritical point for different $ALiSO_4$ compounds turned out to be different. The *Pmcn* structure suffers distortions as a result of a second-order transformation in CLS and CNLS and of a first-order transition in the other crystals. Note also that, according to [4], the total entropy change of $R\ln2$ occurs in TLS in a narrow region near T_0; therefore, the distance of the transition from the tricritical point is quite large (at least as compared to NLS).

It is known [13] that second-order transitions may give rise to strong correlations, which appear in the initial phase long before the transition temperature is reached. The analysis of CLS in [9] was based on the structural model of disordered tetrahedra, because inclusion of the anisotropy of thermal vibrations resulted in an improvement of the magnitude of the R factor. Monte Carlo studies of the order–disorder model (four-state model [1]) were applied in [2] to $P6_3/mmc \longrightarrow Pmcn \longrightarrow P112_1/n$ successive phase transitions in CLS under the assumption that the crystal has a hexagonal

Thermodynamic parameters of the phase transition (PT) from the *Pmcn* phase in $ALiSO_4$ crystals

Crystal	T_1, K	$\Delta S_1/R$	PT order	Reference
NLS	461	0.35	I	This work
RLS	475	0.25	I	"
CNLS	207	0.27	II	"
CLS	202	0.20	II	[14]
TLS	288	0.69	I	[4]

phase, which has not been observed experimentally. It was established that the presence of strong short-range tetrahedron correlations (caused by competitive interactions among the tetrahedra) in the disordered hexagonal and the partially ordered orthorhombic phases results in a decrease in the transition entropy by a factor of more than 2 with respect to $R\ln2$. This conclusion is in satisfactory agreement with the experimental value of the entropy change for CLS (see table).

The above reasoning no longer seems convincing when one invokes data obtained by other researchers who analyzed competing models of the structure of $ALiSO_4$ crystals. It was found in [11], for instance, that for RLS the model that considers anharmonic vibrations of the tetrahedra is the most appropriate. Preference was given, however, to the model assuming their disorder over two positions, in accordance with the observation of two maxima in the electron density distribution for oxygen atoms. However, the data reported in [12], where, as we believe, the structure was most carefully analyzed, seems more substantiative. Evidence for the vibrations of SO_4 tetrahedra in the *Pmcn* phase of NLS, RLS, and RCLS being characterized by different degrees of anharmonicity was presented. Electron density maps for NLS indicate that the oxygen atom does indeed have two equilibrium positions coupled by tilting of the SO_4 group. After the transition to the G_2 phase, the oxygen atom orders in one of these positions. The rubidium analog reveals the same situation, although less clearly pronounced. However, small additions of cesium (~9 mol %) radically change the electron density distribution around the oxygen atom in the RCLS structure [12] and the double-peak pattern corresponding to two oxygen positions disappears. The structural data obtained were used to calculate the parameters of the two-minimum potential confining the vibrations of a regular rigid tetrahedron. It turned out that the height of the potential barrier $1.2k_BT_1$ permits assignment of the transition from the *Pmcn* phase to "pure" order–disorder transformations only in NLS. In the ferroelectric phase, the potential becomes asymmetric, with the stable tetrahedron configuration corresponding to one of the disordered phase configurations. The barrier height in RLS is only $0.75k_BT_1$, which indicates a considerable decrease in tetrahedron vibration anharmonicity as a result of the tetrahedral cation being

replaced by a spherical one. The most remarkable observation is that, as the Rb ion is partially replaced by the larger Cs in the RCLS compound ($Rb_{0.9}Cs_{0.1}LiSO_4$), the potential barrier decreases in height by nearly four times ($<0.2k_BT_1$). This convincingly shows that the vibrations of critical ions in each of the crystals are anharmonic to different degrees, which should naturally manifest itself in the entropy of a phase transition. As seen from the table, the variation in ΔS from one sample to another correlates with this hypothesis; indeed, the transition entropy decreases with increasing cation size. Thus, the increase in the cation ionic radius in the ALiSO$_4$ series [(NH$_4^+$ (1.43 Å) $\longrightarrow$ Rb$^+$ (1.48 Å) $\longrightarrow$ Cs$^+$ (1.65 Å))] is apparently capable of suppressing disordering of the SO$_4$ tetrahedra.

ACKNOWLEDGMENTS

REFERENCES

1. K. S. Aleksandrov and B. V. Beznosikov, *Structural Phase Transitions in Crystals (Potassium Sulfate Family)* (Nauka, Novosibirsk, 1993) [in Russian].

2. N. G. Zamkova and V. I. Zinenko, J. Phys.: Condens. Matter **6** (43), 9043 (1994).

3. S. V. Mel'nikova and V. A. Grankina, Fiz. Tverd. Tela (St. Petersburg) **46** (3), 500 (2004) [Phys. Solid State **46**, 515 (2004)].

4. H. Mashiyama, J. Wu, F. Shimizu, and M. Takashige, J. Phys. Soc. Jpn. **67** (1), 359 (1998).

5. A. Elfakir, J.-P. Souron, G. Wallez, M. Quarton, and M. Touboul, Solid State Ionics **110**, 145 (1998).

6. H. Kasano, Sh. Tsuchiyama, Y. Kawamura, and H. Mashiyama, Ferroelectrics **217**, 121 (1998).

7. V. I. Zinenko and N. G. Zamkova, Phys. Rev. B **57** (1), 211 (1998).

8. G. M. Loiacono, M. Delfino, W. A. Smith, M. I. Bell, A. Shaulov, and Y. H. Tsuo, Ferroelectrics **23**, 89 (1980).

9. A. I. Kruglik, M. A. Simonov, E. P. Zhelezin, and N. V. Belov, Dokl. Akad. Nauk SSSR **247** (6), 1384 (1979) [Sov. Phys. Dokl. **24**, 596 (1979)].

10. K. Itoh, H. Ishikura, and E. Nakamura, Acta Crystallogr. B **37**, 664 (1981).

11. W. Steurer, H. Wittmann, H. Jagodzinski, and A. Pietraszko, Acta Crystallogr. B **42**, 11 (1986).

12. K. Hasebe and T. Asahi, Phys. Rev. B **41** (10), 6794 (1990).

13. V. G. Vaks, *Introduction to the Microscopic Theory of Ferroelectrics* (Nauka, Moscow, 1973) [in Russian].

14. A. I. Kruglik, K. S. Aleksandrov, O. V. Rozanov, I. M. Iskornev, L. I. Zherebtsova, and I. N. Flerov, Fiz. Tverd. Tela (Leningrad) **22** (12), 3673 (1980) [Sov. Phys. Solid State **22**, 2150 (1980)].

15. S. V. Mel'nikova, A. V. Kartashev, V. A. Grankina, and I. N. Flerov, Fiz. Tverd. Tela (St. Petersburg) **45** (8), 1497 (2003) [Phys. Solid State **45**, 1572 (2003)].

16. S. V. Mel'nikova, V. A. Grankina, and A. V. Kartashev, Fiz. Tverd. Tela (St. Petersburg) **44** (2), 365 (2002) [Phys. Solid State **44**, 379 (2002)].

17. I. N. Flerov and I. M. Iskornev, Metrologia, No. 1, 21 (1979).

18. I. M. Iskornev and I. N. Flerov, Fiz. Tverd. Tela (Leningrad) **19** (4), 1040 (1977) [Sov. Phys. Solid State **19**, 605 (1977)].

19. M. Gaafar, M. E. Kassem, and S. H. Kandil, Solid State Commun. **115**, 509 (2000).

20. X. Solans, J. Mata, M. T. Calvet, and M. Font-Bardia, J. Phys.: Condens. Matter **11**, 8995 (1999).

21. M. L. Martinez Sarrion, L. Mestres, A. A. Bakkali, and E. H. Bocanegra, Mater. Res. Bull. **33** (2), 269 (1998).

22. J. E. Diosa, G. M. Aparicio, R. A. Vargas, and J. F. Jurado, Phys. Status Solidi B **220**, 651 (2000).

23. V. I. Torgashev, V. Dvorak, and F. Smutny, Phys. Status Solidi B **126**, 459 (1984).

24. T. Mitsui, T. Oka, Y. Shiroishi, M. Takashige, K. Ito, and Sh. Sawada, J. Phys. Soc. Jpn. **39** (3), 845 (1975).

25. S. R. Garber and L. A. Smolenko, Zh. Éksp. Teor. Fiz. **55** (6), 2031 (1968) [Sov. Phys. JETP **28**, 1072 (1969)].

26. A. Smolenskiĭ, V. A. Bokov, V. A. Isupov, N. N. Kraĭnik, R. E. Pasynkov, and M. S. Shur, *Ferroelectrics and Antiferroelectrics* (Nauka, Leningrad, 1971) [in Russian].

27. N. R. Ivanov and L. F. Kirpichnikova, Izv. Akad. Nauk SSSR, Ser. Fiz. **51** (12), 2216 (1987).

28. K. S. Aleksandrov and I. N. Flerov, Fiz. Tverd. Tela (Leningrad) **21** (2), 327 (1979) [Sov. Phys. Solid State **21**, 195 (1979)].

29. A. T. Anistratov, A. V. Zamkov, L. A. Kot, I. N. Stolovitskaya, and L. A. Shabanova, Fiz. Tverd. Tela (Leningrad) **24** (9), 2763 (1982) [Sov. Phys. Solid State **24**, 1565 (1982)].

Translated by G. Skrebtsov