LATTICE DYNAMICS
AND PHASE TRANSITIONS

A Study of the Effect of Gradual Substitution NH$_4$ ⎯ Cs on Phase Transitions in NH$_4$LiSO$_4$ Crystals

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Abstract—Solid solutions in the $Cs_x(NH_4)_{1-x}LiSO_4$ ($0 \leq x \leq 0.35$) system are grown and investigated. The birefringence ($n_a - n_b$) and the heat capacity are measured in the temperature range 100–530 K. The (x–T) phase diagram is constructed. It is demonstrated that the substitution of cesium for ammonium in the NH_4LiSO_4 crystal affects the transition temperatures in such a way that the region of the ferroelectric phase increases and the ferroelastic phase disappears at $x > 0.22$. The character of the high-temperature transition remains unchanged ($2\beta = 0.24 \pm 0.01$ for all compositions), but the birefringence anomaly and enthalpy decrease. As the concentration x increases, the low-temperature transition becomes more similar to a first-order transition: the birefringence jump δn and the temperature hysteresis ΔT increase. © 2002 MAIK "Nauka/Interperiodica".

1. INTRODUCTION

Crystals of the $ALiSO_4$ (A = K, NH$_4$, Rb, and Cs) family contain LiO$_4$ and SO$_4$ tetrahedral groups that are linked into a framework structure of the tridymite type (cations A occupy large-sized holes). These crystals are characterized by various sequences of changes in the symmetry upon phase transitions due to step-by-step orientational ordering of the structural groups. Structural transformations in these compounds are primarily associated with changes in the orientation of sulfate groups [1]. In order to elucidate the subtle mechanisms responsible for the specific features of ordering in different compounds of this family, it is expedient to investigate mixed systems. A gradual replacement of cations in the A position by cations of another size induces local distortions that do not provide transformations of long-range environment but are sufficient to change the transition temperature. Eventually, this can lead to a change in the mechanism of phase transition.

There are many works concerned with the investigation of solid solutions belonging to the above family. The phase diagrams and the possibility of forming a vitreous phase have been studied in $Cs_xRb_{(1-x)}LiSO_4$ [2–6] and $K_xRb_{(1-x)}LiSO_4$ [7, 8] solid solutions. Kawamura *et al.* [9] performed an x-ray structural investigation of the NH_4LiSO_4–$RbLiSO_4$ system. For these compounds, the (x–T) regions of existence of structures with different symmetries were determined in the temperature range from the melting point to liquid-nitrogen temperatures. It was demonstrated that a change in the degree of substitution for the A^+ cation can result in the stabilization of particular phases, the disappearance of already existing phases, and the formation of new phases.

Ammonium lithium sulfate NH_4LiSO_4 has been extensively studied to date and remains a subject of investigation. It was established that this compound is characterized by the following sequence of changes in the symmetry: $Pmcn(c = c_0)$ ⟵⟶ $P2_1cn(c = c_0)$ ⟵⟶ $P2_1/c11(c = 2c_0)$ ⟵⟶ $C1c1(c = 2c_0)$ at $T_{0i} = 460$, 284, and 27 K, respectively [10–12]. The phase is ferroelectric with considerable spontaneous polarization at room temperature and ferroelastic below 284 K. On the other hand, there appear works in which new phase transitions in NH_4LiSO_4 are revealed or previously determined symmetry groups of the known phases are subjected to question [13].

Kruglik *et al.* [14] studied $CsLiSO_4$ crystals and observed only one ferroelastic phase transition from the initial phase with the symmetry $Pmcn(c = c_0)$ to the phase with the monoclinic symmetry $P112_1/n(c = c_0)$ at $T_0 \approx 201$ K.

The aim of the present work was to elucidate how the gradual replacement of ammonium cations by considerably larger-sized cations Cs^+ affects the temperature and the character of phase transitions in the NH_4LiSO_4 crystal. For this purpose, we measured the heat capacity and birefringence.

The NH_4LiSO_4 compound was investigated earlier by differential scanning calorimetry (DSC) [13, 15] and differential thermal analysis [16] at temperatures above room temperature, i.e., in the range of the high-temperature phase transition. The experimental data are contradictory. This is particularly true for the number of phase transitions and the corresponding changes in the enthalpy. In this respect, we studied not only the solid solutions but also the NH_4LiSO_4 compound over a wide

range of temperatures, including the low-temperature and high-temperature phase transitions. It should be noted that the temperature behavior of the birefringence of the NH_4LiSO_4 crystal in the ranges of the ferroelectric and ferroelastic phase transitions is sufficiently well understood [17, 18].

2. EXPERIMENTAL TECHNIQUE

The single crystals used in our measurements were obtained by two methods: (1) slow evaporation of the appropriate mixtures of NH_4LiSO_4 and $CsLiSO_4$ aqueous solutions at $T \approx 310$ K and (2) growth from a mixture of NH_4LiSO_4 and $CsLiSO_4$ solutions in caustic ammonia taken in required proportion. The initial compounds $CsLiSO_4$ and NH_4LiSO_4 were prepared according to the reactions

$$Cs_2SO_4 + Li_2SO_4 = 2CsLiSO_4,$$

$$(NH_4)_2SO_4 + Li_2SO_4 = 2(NH_4)LiSO_4.$$
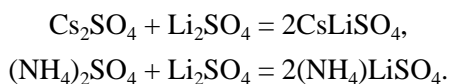
The polycrystalline compounds synthesized were examined using x-ray powder diffraction analysis prior to dissolution in water [method (1)] or 25 wt % ammonia [method (2)].

The largest and most perfect single crystals in the form of hexagonal prisms were grown from mixtures of aqueous solutions. The quantitative composition of these crystals was determined by atomic absorption analysis. Analysis showed that, as a rule, the cesium content in the crystals is less than that in the as-batched composition. For example, single crystals with $x = 0.15$ were obtained at the as-batched composition with $x = 0.4$. The chemical composition of the crystals grown by the second method was closer to the as-batched composition, which made it possible to prepare the crystals with $x = 0.2$–0.35. For optical investigations, samples in the form of plates with different orientations and thicknesses were oriented on a URS x-ray instrument.

The plates prepared were used in polarization-optical investigations and measurements of the birefringence in the range from the liquid-nitrogen temperature to temperatures corresponding to the decomposition of the studied compounds (~530 K). The birefringence was measured on plates of the (001) section ($c \approx 8.7$ Å). The measurements were performed on a Berec compensator with an accuracy of $\cong 10^{-5}$ and a Senarmont compensator with a sensitivity of no less than 10^{-7}. The former compensator made it possible to investigate small-sized samples and to determine the birefringence magnitude.

The thermodynamic properties were studied on a DSM-2M differential scanning microcalorimeter modified for recording and processing of measured signals on a computer. This appreciably increased the amount of information obtained with the microcalorimeter. The measurements were carried out in the temperatures ranges 150–390 K with a low-temperature unit and in the range 340–510 K with a high-temperature unit. The upper limit of measurements was determined by the temperature of the onset of the NH_4LiSO_4 decomposition.

For the most part, calorimetric experiments were performed with powder samples. In a number of cases, when the solid solutions were studied in the form of crystals, close thermal contact between the sample and the cell was ensured by a KPT-8 organosilicon paste. The cesium concentrations (x) in the $Cs_x(NH_4)_{1-x}LiSO_4$ solid solutions were equal to 0, 0.045, 0.065, 0.09, 0.125, 0.15, and 0.22. The sample weight was approximately equal to 0.1 g.

In each experiment, the data on the DSM signals as functions of time were converted into the temperature dependence of the heat capacity for the studied compound with the use of the heat capacity of corundum as a reference. The enthalpy changes ΔH_i due to phase transitions were determined by integrating the function $\Delta C_p(T)$, where ΔC_p is the excess heat capacity. In order to increase the reliability of the results, we carried out four or six series of measurements with one or two solid-solution samples of each composition. In different series, the temperatures of phase transitions for the same sample and for different samples of the same solid solution differed by no more than 0.5–1.0 K. The enthalpy change was determined accurate to within 10–15%.

Finally, it should be noted that the polarization-optical observations revealed that the grown crystals contain extended regions of inhomogeneous stresses that disappear upon annealing. Moreover, the low-temperature transition at T_{02} in compounds with a sufficiently high cesium content (for example, at $x = 0.15$) was observed only after annealing. For this reason, prior to optical and thermal investigations, the samples were necessarily annealed at a temperature of approximately 470 K for 2 h.

3. RESULTS

Experimental calorimetric data in the form of temperature dependences of the excess heat capacities associated with high- and low-temperature phase transitions are shown in Fig. 1. An increase in the cesium concentration leads to a considerable decrease in the temperatures of both structural transformations and in the excess heat capacity at a maximum. This results in an increase in the error in determining the phase transition temperatures T_{0i} and the enthalpy changes ΔH_i. The data on T_{0i} and ΔH_i are listed in the table. It is seen that, as the cesium content in the solid solutions increases, the enthalpy of the high-temperature phase transition decreases substantially, whereas the enthalpy of the low-temperature phase transition remains constant to within the limits of the estimation error.

Figure 2 depicts the experimental temperature dependences of the birefringence $\Delta n_c = n_a - n_b$ for $Cs_x(NH_4)_{1-x}LiSO_4$ solid solutions with different
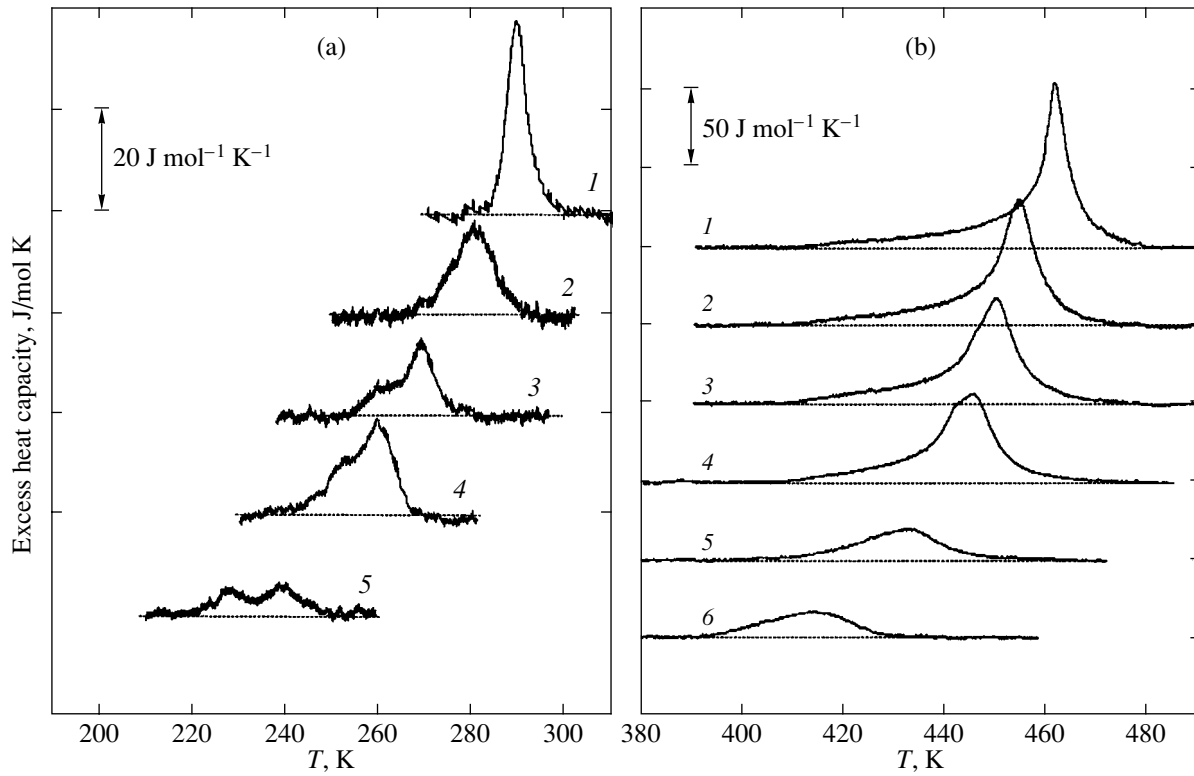
Fig. 1. Temperature dependences of the excess heat capacity for $Cs_x(NH_4)_{1-x}LiSO_4$ solid solutions in the vicinity of (a) low-temperature and (b) high-temperature phase transitions at different concentrations x: (*1*) 0, (*2*) 0.045, (*3*) 0.065, (*4*) 0.09, (*5*) 0.15, and (*6*) 0.22.
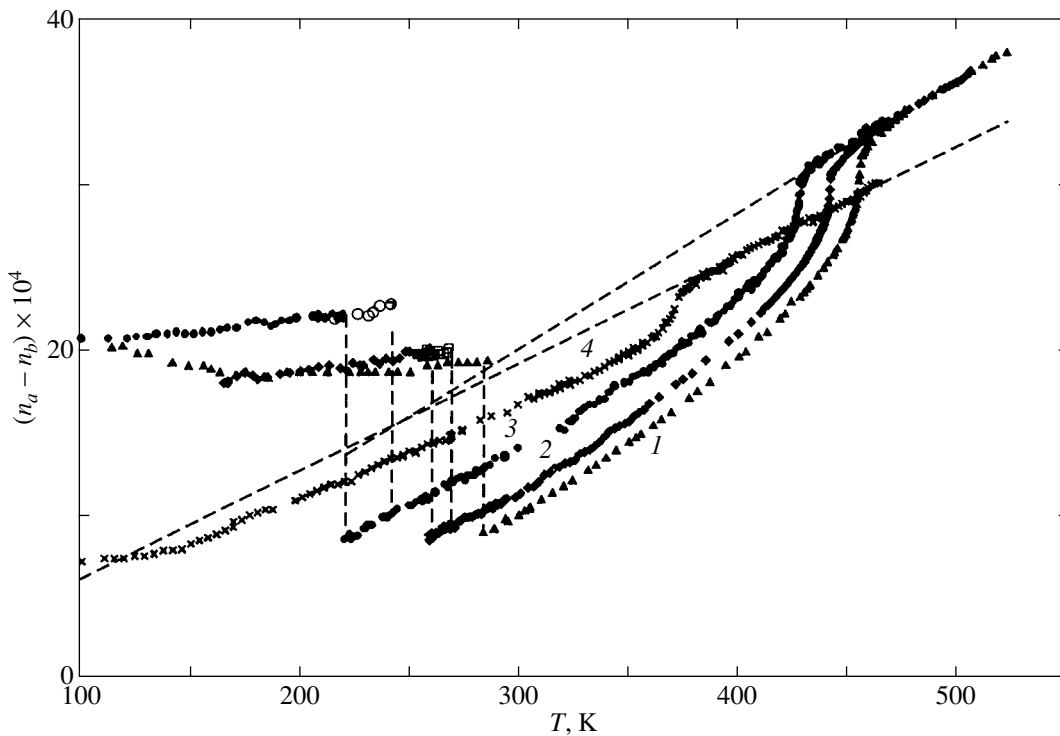

Fig. 2. Temperature dependences of the birefringence Δn_c upon heating (open circles and squares) and cooling (closed circles and squares) for samples at different cesium concentrations x: (*1*) 0, (*2*) 0.065, (*3*) 0.09, and (*4*) 0.35.

cesium concentrations x. It can be seen that the temperatures of the high-temperature (T_{01}) and low-temperature (T_{02}) transitions gradually decrease with an increase in the cesium content in the crystal. It is worth noting that the high-temperature phase transition does not change in character and only the anomalous component of the birefringence decreases progressively, which is in agreement with the above behavior of the enthalpy. The effect of the substitution on the phase transition temperature T_{02} is much more pronounced. An increase in the concentration x leads to an increase in the birefringence jump δn and in the temperature hysteresis ΔT_{02}: $\delta n \approx 10 \times 10^{-4}$ and $\Delta T_{02} = 2$ K at $x = 0$, $\delta n \approx 12 \times 10^{-4}$ and $\Delta T_{02} = 8.5$ K at $x = 0.065$, and $\delta n \approx 15 \times 10^{-4}$ and $\Delta T_{02} = 18$ K at $x = 0.15$. Only the high-temperature phase transition is observed in the solid solution with $x = 0.35$. Observations made under a microscope in polarized light indicate that, upon gradual substitution of cesium for ammonium, the sequence of changes in the symmetry of phases in the studied compounds remains identical to that in pure NH_4LiSO_4. Clear-cut and direct absences are observed in the range from 500 K to the temperature T_{02} of the transition to the monoclinic phase $P2_1/c11$. Below the T_{02} temperature, the twinning typical of this phase [18] is observed in the (100) section ($a \approx 5.2$ Å).

4. DISCUSSION

Figure 3 displays the phase diagram of the $Cs_x(NH_4)_{1-x}LiSO_4$ solid solutions with $x \leq 0.35$, which was constructed using the results of optical and calorimetric measurements. The introduction of cesium ions into NH_4LiSO_4 decreases both the T_{01} temperature of the high-temperature structural phase transition from the orthorhombic phase $Pmcn$ to the orthorhombic
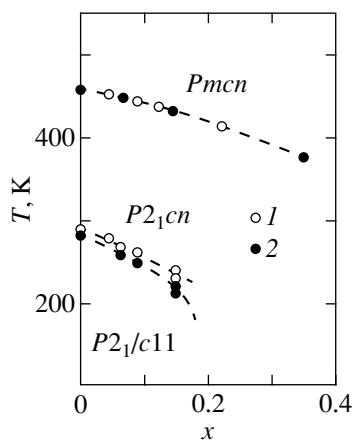

Fig. 3. Phase (x–T) diagram of the $Cs_x(NH_4)_{1-x}LiSO_4$ solid solutions in the concentration range $x = 0$–0.35: (*1*) DSC data obtained upon heating and (*2*) optical data obtained upon cooling.

polar phase $P2_1cn$ and the T_{02} temperature of the transition to the monoclinic phase $P2_1/c11$. Note that the T_{02} temperature changes considerably more strongly, so that the phase transition in the solution with the cesium concentration $x = 0.22$ is not observed above the liquid-nitrogen temperature and, hence, the region of existence of the ferroelectric phase becomes more extended. Chekmasova *et al.* [19] analyzed the influence of hydrostatic pressure on the phase transitions in pure NH_4LiSO_4 and revealed that the pressure appreciably affects the phase transition temperatures: the temperature of the high-temperature transition increases drastically ($dT_{01}/dp = 90$ K/GPa), whereas the temperature of the low-temperature transition decreases ($dT_{02}/dp = -26$ K/GPa). Our measurements demonstrate that, compared to hydrostatic pressure, the replacement of ammonium ions by larger-sized Cs ions in the structure has the opposite effect. This replacement favors the loosening of the structure and leads to a decrease in the T_{01} temperature of the $G_0 \longleftrightarrow G_1$ transition. At the same time, the compression and loosening of the structure identically affect the $G_1 \longleftrightarrow G_2$ transition and drastically decrease the region of existence of the G_2 phase. Therefore, it can be concluded that the G_2 phase is unstable.

The temperature dependences of the anomalous component of the birefringence in the range below the T_{01} temperature is plotted in Fig. 4. These dependences were obtained by subtracting the linear dependences of the birefringence (extrapolated from the initial phase) from the dependences displayed in Fig. 2. As can be seen, the pretransitional effects are observed in the range 5–10 K above the phase transition, which masks the weak first-order nature of this transition [17]. Moreover, it is seen that the birefringence anomaly accompanying the phase transition gradually decreases with an increase in x. Indeed, the maximum deviation of the birefringence from a linear dependence for pure NH_4LiSO_4 ($x = 0$) is determined as $\delta(n_a - n_b) = 10 \times 10^{-4}$, whereas the value of $\delta(n_a - n_b)$ for the sample with $x = 0.35$ is four times less ($\approx 2.5 \times 10^{-4}$).

The anomalous component of the birefringence $\delta(n_a - n_b)$ and the transition parameter η are related by the quadratic expression $\delta(n_a - n_b) \sim \eta^2 \sim (T - T_0)^{2\beta}$. With this relationship, it is possible to determine the critical exponent β and to fit the phase transition temperature T_{01} in such a way as to fulfill the above quadratic dependence. The determination of the phase transition temperature from birefringence curves is problematic, especially when the transition is smeared under the influence of any factor. In our case, the substitution leads to an increase in the fluctuation anomalies in the range of the T_{01} temperature. There are many techniques of determining the T_{01} temperature. In the present work, the phase transition temperature was fitted using linear dependences of the type shown in Fig. 4 according to the technique proposed by Kim
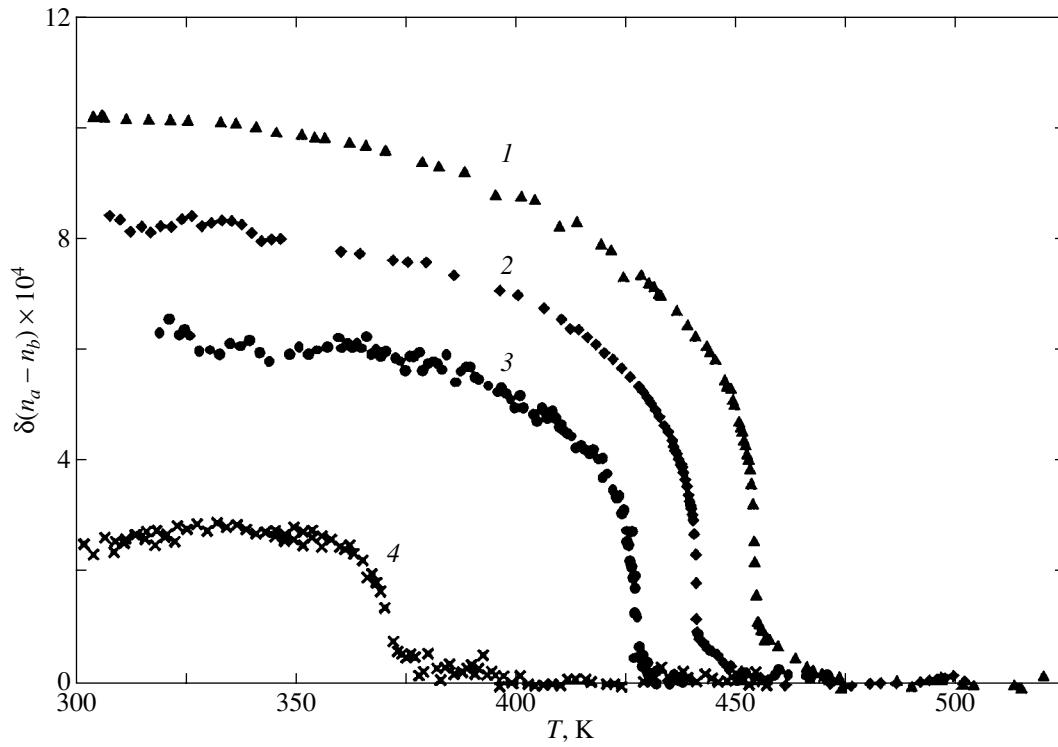
Fig. 4. Temperature dependences of the anomalous component $\delta(n_a - n_b)$ of the birefringence in the ferroelectric phase of the $Cs_x(NH_4)_{1-x}LiSO_4$ solid solutions at different concentrations x: (*1*) 0, (*2*) 0.065, (*3*) 0.09, and (*4*) 0.35.
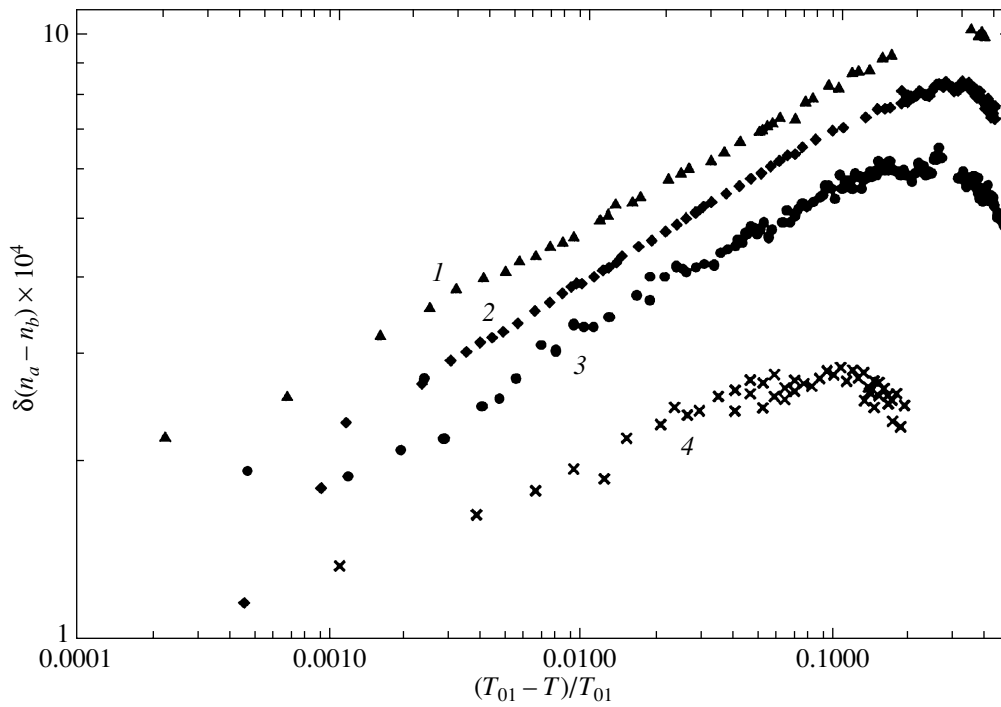

Fig. 5. Dependences $\delta(n_a - n_b)(T)$ below the T_{01} transition temperature on the logarithmic scale at different concentrations x: (*1*) 0, (*2*) 0.065, (*3*) 0.09, and (*4*) 0.35.

Thermodynamic parameters of phase transitions in $Cs_x(NH_4)_{1-x}LiSO_4$ solid solutions

x	T_{01}, K	ΔH_1, J/mol	T_{02}, K	ΔH_2, J/mol
0	460.5	1170	289	205
0.045	453	1045	280	190
0.065	449	990	268.5	200
0.09	445	930	260	230
0.15	431.5	530	229, 241	100
0.22	414.6	400	–	–

et al. [20]. The T_{01} temperatures obtained agree well with the results of thermal measurements.

Figure 5 shows the dependences of $\delta(n_a - n_b)$ on $(T_{01} - T)/T_{01}$ on the logarithmic scale for samples with different concentrations x. From the slopes of the straight lines, we obtain the "nonclassical" critical indices $2\beta = 0.24 \pm 0.01$ for all the studied samples. The dependence is linear in the temperature range $(T_{01} - T)$ from 0.5 to 90 K below the phase transition temperature. The small critical index can be associated with the closeness of the transition to a tricritical point and the effect of higher-order terms in the thermodynamic potential. It should be noted that a similar small critical index for the high-temperature phase transition in NH_4LiSO_4 was obtained earlier in [17]. The constant value of 2β for different compositions suggests that the transition remains unchanged in character with an increase in the degree of substitution of cesium for ammonium.

The enthalpy change ΔH_1 determined in our work for the high-temperature transformation in the NH_4LiSO_4 compound (see table) is nearly twice as large as that obtained by Solans *et al.* [13] ($\Delta H_1 = 610$ J/mol) also with the use of the DSC technique. This considerable difference in the enthalpy change ΔH_1 can, most likely, be explained by the different approaches used to determine the anomalous heat capacity ranges. The function $\Delta C_p(T)$ was integrated in the temperature range 410–480 K in our work and only in a range of 6.2 K in the vicinity of the T_{01} temperature in [13]. However, the anomalous heat capacity over a wide temperature range below the T_{01} temperature is indicated by the data on the thermal expansion [21, 22] and the birefringence (Figs. 2, 4). It should be noted that our experimental data on the enthalpy change is in reasonable agreement with the change $\Delta H_1 = 1305$ J/mol calculated by Tomaszewski and Pietraszko [22] from the Clausius–Clapeyron equation with the use of data on the volume change and dT_{01}/dp.

As far as we know, the calorimetric investigation of the low-temperature phase transition in NH_4LiSO_4 was performed for the first time in the present work. Since this transition is a pronounced first-order phase transformation, it can be assumed that the determined enthalpy change ΔH_2 predominantly corresponds to the latent heat. Using the data on the effect of hydrostatic pressure on the T_{02} temperature ($dT_{02}/dp = -26$ K/GPa [19]), the volume jump $\Delta V_2/V = 0.02\%$ at T_{02} was calculated from the Clausius–Clapeyron equation $(\Delta V_2/V)(T_{02}) = \Delta H_2(dT_{02}/dp)$.

Recently, it was found that there is one more heat capacity anomaly (at 335 [13] or 350 K [16]) which is unrelated to the known phase transitions in NH_4LiSO_4. Solans *et al.* [13] noted that this anomaly was revealed at the rate of change in the sample temperature $dT/dt = 5$ K/min and was not observed at $dT/dt = 20$ K/min. We performed measurements in the range between the T_{01} and T_{02} temperatures at a rate of 8 K/min. No anomalous changes in the heat capacity were observed at 335 K or at 350 K. It should be noted that the enthalpy change (120 J/mol) determined in [13] for the above anomaly is only half as large as the change ΔH_2 (see table). To put it differently, we can state with assurance that the additional anomaly in our experiments could be recorded quite reliably. Furthermore, the necessity of annealing the samples should be taken into account, especially as the samples used in [13] were grown by the short-cut method at a high temperature. For this reason, we are inclined to believe that, at least in our NH_4LiSO_4 sample, there occur only two phase transitions in the above temperature range.

The entropy changes ΔS_i due to phase transitions were determined from the obtained calorimetric data by integrating the function $(\Delta C_p/T)(T)$. These changes for both phase transitions in NH_4LiSO_4 turned out to be small ($\Delta S_1 = 2.5$ J/mol K and $\Delta S_2 = 0.62$ J/mol K) and comparable to the entropy change upon the phase transition in $CsLiSO_4$ ($\Delta S = 1.66$ J/mol K) [23]. Therefore, reasoning from our experimental data, the phase transitions in NH_4LiSO_4 cannot be treated as pure order–disorder transformations.

In the immediate future, the heat capacity of the NH_4LiSO_4 compound will be measured on an adiabatic calorimeter with a higher sensitivity and accuracy compared to the DSM calorimeter. This will make it possible to determine more reliably the entropy changes and to solve the problem of the additional heat capacity anomaly in the temperature range from 330 to 350 K.

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REFERENCES

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

2. S. V. Mel'nikova, V. A. Grankina, and V. N. Voronov, Fiz. Tverd. Tela (St. Petersburg) **36** (4), 1126 (1994) [Phys. Solid State **36**, 612 (1994)].

3. S. V. Mel'nikova, A. D. Vasil'ev, V. N. Voronov, and A. F. Bovina, Fiz. Tverd. Tela (St. Petersburg) **37** (8), 2529 (1995) [Phys. Solid State **37**, 1387 (1995)].

4. S. V. Mel'nikova, V. A. Grankina, and V. N. Voronov, Fiz. Tverd. Tela (St. Petersburg) **36** (4), 1126 (1994) [Phys. Solid State **36**, 612 (1994)].

5. S. V. Melnikova, A. D. Vasiliev, V. A. Grankina, *et al.*, Ferroelectrics **170**, 139 (1995).

6. K. Hasebe and T. Asahi, Ferroelectrics **96**, 63 (1989).

7. S. V. Mel'nikova, M. V. Gorev, and V. A. Grankina, Fiz. Tverd. Tela (St. Petersburg) **40** (7), 1341 (1998) [Phys. Solid State **40**, 1219 (1998)].

8. R. L. Moreira, P. Bourson, U. A. Leitao, *et al.*, Phys. Rev. B **52** (17), 12591 (1995).

9. K. Kawamura, A. Karamashi, N. Nakamura, *et al.*, Ferroelectrics **105**, 279 (1990).

10. A. I. Kruglik, M. A. Simonov, and K. S. Aleksandrov, Kristallografiya **23**, 494 (1978) [Sov. Phys. Crystallogr. **23**, 274 (1978)].

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

12. A. Dollase, Acta Crystallogr. B **25**, 2298 (1969).

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

14. A. I. Kruglik, M. A. Simonov, and E. P. Zhelezin, Dokl. Akad. Nauk SSSR **247** (7), 1384 (1979) [Sov. Phys. Dokl. **24**, 596 (1979)].

15. G. M. Loiacono, M. Delfino, W. A. Smith, *et al.*, Ferroelectrics **23** (1), 89 (1980).

16. M. Polomska, B. Hilczer, and J. Baran, J. Mol. Struct. **325**, 105 (1994).

17. V. N. Anisimova and N. R. Ivanov, Kristallografiya **31** (5), 1018 (1986) [Sov. Phys. Crystallogr. **31**, 605 (1986)].

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

19. T. I. Chekmasova, I. S. Kabanov, and V. I. Yusvak, Phys. Status Solidi A **44**, K155 (1977).

20. D.-Y. Kim, J.-G. Yoon, and S.-I. Kwun, J. Phys. Soc. Jpn. **67** (3), 903 (1998).

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

22. P. E. Tomaszewski and A. Pietraszko, Phys. Status Solidi **56**, 467 (1979).

23. K. S. Aleksandrov, L. I. Zherebtsova, I. M. Iskornev, *et al.*, Fiz. Tverd. Tela (Leningrad) **22**, 3673 (1980) [Sov. Phys. Solid State **22**, 2150 (1980)].

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