Investigation of the Reconstructive Phase Transition between Metastable (α) and Stable (β) Modifications of the NH_4LiSO_4 Crystal

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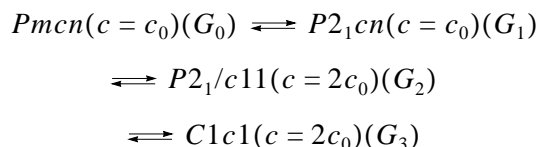*e-mail: msv@iph.krasn.ru*
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Abstract—Crystals of ammonium lithium sulfate NH_4LiSO_4 in α and β modifications are studied, and conditions of their nucleation and growth are determined. The α modification of NH_4LiSO_4 and α ⟶ β phase transitions are investigated using polarized light microscopy, x-ray diffraction, and differential scanning calorimetry in the temperature range 80–530 K. It is found that, depending on the conditions of growth and storage, there exist two temperature ranges ($T_{\alpha \to \beta} \approx 340$–350 and ≈440–450 K) in which the crystals can undergo an α ⟶ β reconstructive phase transition. The enthalpy of this transformation depends on the symmetry of the final phase. In the former case (340–350 K), the reconstructive phase transition leads to rapid destruction of the sample. In the latter case (440–450 K), the crystal structure undergoes a slow transformation (recrystallization) without noticeable distortions. The results obtained indicate that no structural phase transition occurs in the α modification of NH_4LiSO_4 at 250 K. © *2003 MAIK "Nauka/Interperiodica"*.

1. INTRODUCTION

Ammonium lithium sulfate NH_4LiSO_4 (NLS) has been extensively studied over many years. It is established that, during cooling, this compound undergoes the following sequence of symmetry changes:

$$Pmcn(c = c_0)(G_0) \rightleftharpoons P2_1cn(c = c_0)(G_1)$$

$$\rightleftharpoons P2_1/c11(c = 2c_0)(G_2)$$

$$\rightleftharpoons C1c1(c = 2c_0)(G_3)$$

at T_i = 460, 284, and 27 K, respectively [1–3]. The phase is ferroelectric with considerable spontaneous polarization at room temperature and ferroelastic below ~284 K. On the other hand, there have appeared works in which new phase transitions in NH_4LiSO_4 were revealed or previously determined symmetry groups of the known phases were subjected to question [4]. Certainly, polymorphism of the NH_4LiSO_4 compound is also responsible to a large extent for the discrepancy in the experimental results obtained by different authors.

The above sequence of transitions is observed for NH_4LiSO_4 crystals in the β modification (β-NLS). These crystals have a tridymite-like pseudohexagonal structure consisting of SO_4 and LiO_4 tetrahedra joined together by their vertices and forming six-membered rings perpendicular to the *c* axis. In the structure, free vertices of one half of these tetrahedra are directed upward and the tetrahedra themselves are bound to the upper layer of the tetrahedra, whereas the vertices of the other half of the tetrahedra are oriented downward

and the tetrahedra themselves are bound to the lower layer. The ammonium groups occupy cavities formed between the layers. The unit cell parameters of the β modification at room temperature are as follows: *a* = 5.280 Å, *b* = 9.140 Å, and *c* = 8.786 Å. A comprehensive review of the experimental data available in the literature for NH_4LiSO_4 crystals in the β modification was given by Polomska [5].

The α modification of the NH_4LiSO_4 compound (α-NLS) has been known for more than one hundred years. According to Pietraszko and Lukaszewicz [6] and Tomaszewski [7], the structure of the α modification is also composed of SO_4 and LiO_4 tetrahedra. However, in the α modification, unlike the β modification, the SO_4 and LiO_4 tetrahedra located in a layer perpendicular to the [001] direction can be joined not only by their vertices but also by their edges. The adjacent layers are bound to nitrogen atoms of the ammonium groups through hydrogen bonds and form a layered structure with the orthorhombic space group $Pbc2_1$ and the lattice parameters *a* = 4.991 Å, *b* = 10.196 Å, and *c* = 17.010 Å. It should be noted that, as a rule, samples of the α modification can involve several polytypes that differ in the lattice parameter *c*: $c_1 = c$, $c_2 = 2c$, and $c_3 = 3c$ [7].

The NH_4LiSO_4 compound in the α modification has an unstable structure and transforms into the β modification upon heating. According to the differential thermal analysis (DTA) performed by Polomska *et al.* [8], the as-grown crystals undergo a reversible phase transition at a temperature of approximately 250 K and an

irreversible ($\alpha \longrightarrow \beta$) phase transition at temperatures close to 350 K. These authors revealed a steplike anomaly in the DTA curves at 350 K and assigned this feature to the coexistence of different polytypes in the sample. Moreover, they investigated variations in the frequencies of librational and translational vibrations of SO_4^{2-}, NH_4^+, and Li^+ ions upon the $\alpha \longrightarrow \beta$ phase transition with the use of far-infrared spectroscopy [8].

The main objectives of the present work were as follows: (i) to elucidate the influence of the growth conditions of NH_4LiSO_4 crystals on the formation of the α and β modifications, (ii) to investigate the reversible phase transition to the α modification at 250 K, (iii) to examine the kinetics of the $\alpha \longrightarrow \beta$ reconstructive phase transition, and (iv) to analyze the thermodynamic parameters of the phase transitions in NH_4LiSO_4 crystals.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

In order to solve the problems formulated above, we used the techniques of measuring the heat capacity and birefringence and also observations in polarized light. The α and β phases in the studied samples were identified from the x-ray powder diffraction patterns recorded on a DRON-2 diffractometer. For optical investigations, the single-crystal samples were oriented with a URS-1 x-ray instrument.

Observations in polarized light and measurements of the birefringence of the crystals grown were performed in the range from ~80 K to temperatures corresponding to the decomposition of the studied compound (~530 K). The birefringence was measured on the (001) cleavage surfaces ($c = 17.01$ 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 thin samples and to determine the birefringence magnitude. It should be noted that the temperature behavior of the birefringence of β-NLS crystals in the ranges of the ferroelectric and ferroelastic phase transitions is sufficiently well understood [9–11].

The thermodynamic properties were examined on a DSM-2M differential scanning microcalorimeter. The measurements were carried out in the temperatures range 150–370 K with a low-temperature unit and in the range 340–550 K with a high-temperature unit. The calorimetric experiments were conducted using, for the most part, single-crystal and, with rare exception, powder samples. In the case when the compound was studied in the form of a single crystal, close thermal contact between the sample and the cell was ensured by a KPT-8 organosilicon paste. The sample weight was approximately equal to 0.1–0.2 g. In order to determine the confidence intervals of the thermodynamic parameters
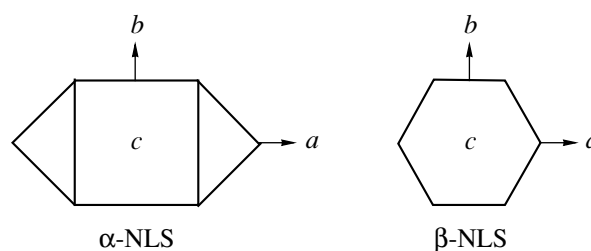

**Fig. 1.** Crystal habit of NH_4LiSO_4 in α and β modifications.

under investigation, the measurements were performed with several samples for each crystallization. The weight of the samples was checked prior to and after heating in each experiment. In all the main experiments, the samples were heated or cooled at a rate of 8 K/min.

With the aim of determining the formation conditions for NH_4LiSO_4 single crystals in the α and β modifications, we performed five crystallizations from a solution under different conditions at temperatures of 281, 283, 293, and 303 K. Crystallizations at temperatures of 281 and 293 K proceeded through spontaneous growth without stirring of the solution (crystallizations *1*, *2*). All other crystallizations (crystallizations *3–5*) occurred through slow growth with stirring of the solution at temperatures of 283, 293, and 303 K.

3. RESULTS AND DISCUSSION

The crystals grown in the α and β modifications can easily be distinguished by their habit. Single crystals of NH_4LiSO_4 in the α modification have the shape of rectangular plates with perfect cleavage planes (001). In the course of their growth, platelike crystals transform into hexahedra with an angle of 90° (Fig. 1). Single crystals in the β modification have the shape of hexagonal prisms. It is worth noting that crystallization at a temperature of 281 or 283 K results in the formation of the α modification alone, crystallization at 293 K leads to the formation of crystals in both modifications with an equal probability, and crystallization at 303 K brings about the formation of crystals only in the β modification. An analysis of the results obtained in our investigations demonstrated that, in [8], the scheme of the crystallographic axes of the unit cell in the α modification of the NH_4LiSO_4 crystal is invalid. The correct orientation of the crystallographic axes with respect to the growth faces is given in Fig. 1.

As was shown in numerous experiments, single crystals of NH_4LiSO_4 in the α modification slightly differ from one another. In the case when an as-grown crystal obtained through crystallization *1* or *2* (spontaneous growth without stirring of the solution) is held in a dry air atmosphere at room temperature, its transparency rapidly (either totally or partially) disappears. The x-ray powder diffraction pattern taken from the opaque
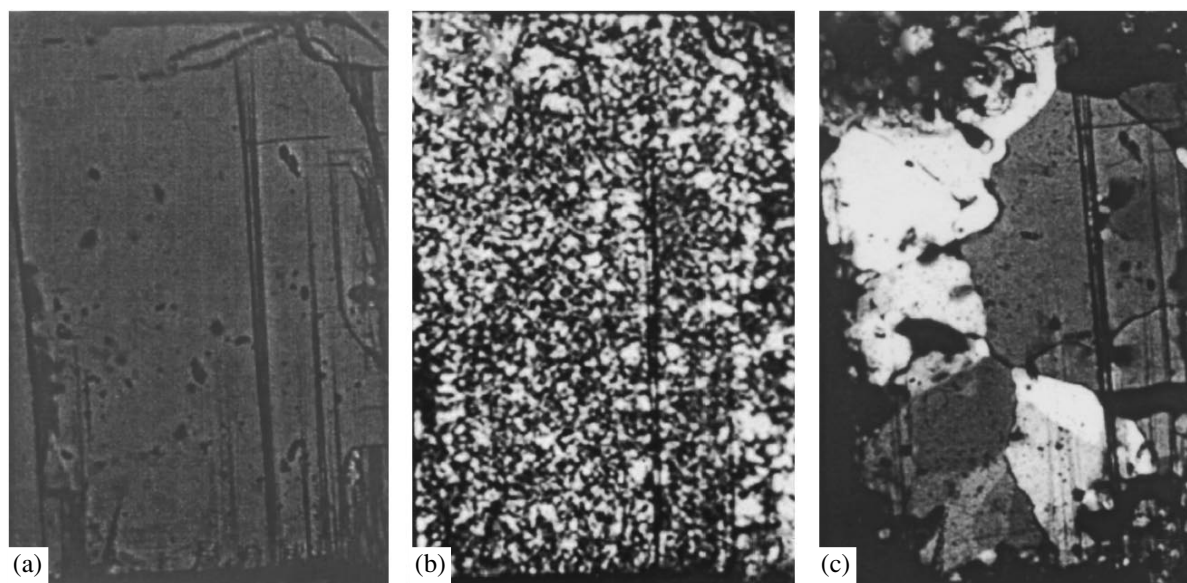
Fig. 2. Micrographs of the (001) cleavage surfaces of α-NLS crystals in polarized light: (a) $T = 293$ K, clear-cut extinctions; (b) $T = 446$ K, extinctions are absent; and (c) $T = 446$ K (exposure, 35 min), well-defined regions of the β phase.

part of the sample corresponds to the β-NLS structure. The transparent part of the sample remains in the α modification. Therefore, the α $\longrightarrow$ β phase transition can occur at room temperature. When the samples prepared under the same conditions are kept in a hermetically closed vessel for a certain amount of time (two or three months), the process described above is not observed. This process is also not revealed in samples produced by crystallizations *3* and *4*, i.e., in the crystals grown, as might appear at first sight, under "ideal" conditions: very slow growth (within two months) with careful stirring of the solution. Consequently, all crystals grown in the α modification can be divided into two groups, namely, the group *A* (as-grown crystals that are prepared through the spontaneous crystallization without stirring of the solution and can undergo an α $\longrightarrow$ β monotropic transition in a dry air atmosphere) and the group *B* (crystals grown either under ideal conditions or through any one of the above crystallizations and then held in a hermetically closed vessel during a sufficiently long period of time). Subsequently, the latter crystals keep quite well in a dry atmosphere. As will be shown below, the results of optical and calorimetric experiments performed with crystals of these groups differ significantly.

Upon gradual heating, samples of the *A* group undergo rapid destruction in the temperature range 330–350 K and become totally or partially opaque, as is the case with samples prepared through crystallization *1* or *2* and then held in a dry atmosphere at room temperature.

Crystals of the *B* group upon heating remain transparent and exhibit clear-cut extinctions at temperatures from 100 K to the range 440–450 K, in which there

occurs an α $\longrightarrow$ β phase transformation. As follows from numerous experiments, the α $\longrightarrow$ β phase transition in the temperature range 440–450 K proceeds very slowly and, under isothermal conditions, does not necessarily lead to destruction of the sample. Figure 2 displays the micrographs obtained for the (001) cleavage surfaces of α-NLS crystals with the use of a polarizing microscope upon heating. It can be seen from Fig. 2a that, at room temperature, the sample is transparent and exhibits clear extinctions. Upon heating of the sample, extinctions become less pronounced at a temperature of 440 K and disappear at 446 K. As a result, the sample turns a speckled gray, which gives the impression that it is optically isotropic. This color is provided by small regions (with a size of the order of several microns) that exhibit extinctions upon rotation of the plate through different angles (Fig. 2b). After isothermal holding for 30 min, part of these regions rapidly grow (Fig. 2c) and transform into transparent regions of β-NLS with clear-cut extinctions. The regions thus formed are relatively large in size and frequently occupy the whole volume of the sample. Judging from the geometry of the optical indicatrices, the crystallographic directions in these regions are random and their orientation is in no way related to the initial crystallographic directions of the α phase. The formation of the β phase can proceed both at a constant temperature and during heating or cooling of the sample but, in all cases, only after the crystal experiences a pseudoisotropic state. However, the regions of the β phase formed upon heating or cooling are considerably larger in size.

The temperature dependences of the birefringence $\Delta n_c = (n_a - n_b)$ for NH_4LiSO_4 crystals in different modifications are shown in Fig. 3. Curve *1* is depicted for comparison and represents the temperature dependence

of the birefringence $\Delta n_c(T)$ for β-NLS crystals with an anomalous behavior in the range of two phase transitions [11]. Experimental data on the birefringence $\Delta n_c(T)$ for the two samples of α-NLS are shown by curves *2*. As can be seen from Fig. 3, the birefringences for different modifications of NH_4LiSO_4 in the [001] direction have opposite signs: $n_a > n_b$ for β-NLS [12] and $n_a < n_b$ for α-NLS. The temperature dependence of the birefringence for α-NLS exhibits linear behavior in the range 250–440 K. At temperatures below 250 K, the straight line smoothly becomes curved without a specific feature that could be assigned to a phase transition. This shape is typical of birefringence "tails" associated with pretransition phenomena (e.g., for $CsLiSO_4$ [13]). We believe that, in this case, the phase transition can occur at temperatures below 100 K. However, the temperature dependence of the birefringence $\Delta n_c(T)$ can deviate from linearity, for example, due to the freezing of a small amount of interlayer water, which, in turn, brings about macroscopic deformation of the sample. Most likely, this is the reason why the temperature dependences of the birefringence for the two samples slightly differ at temperatures below 250 K (Fig. 3). As the temperature increases to higher than 440 K, the birefringence magnitude rapidly decreases to zero and the crystal becomes optically pseudoisotropic, as described above. Note that the birefringence of the studied samples goes to zero at different temperatures. The experiments demonstrated that this point for different samples lies in the temperature range 440–450 K.

The thermodynamic parameters ($T_1 = 460 \pm 2$ K, $T_2 = 289 \pm 2$ K, $\Delta H_1 = 1170 \pm 200$ J/mol, $\Delta H_2 = 280 \pm 50$ J/mol) for the phase transitions observed in β-NLS crystals grown at a temperature above 300 K were obtained in our previous study [11]. In the present work, these values will be used as reference data in order to determine the state of the studied samples. In the subsequent discussion, we will focus only on the phase transitions occurring in crystals and, hence, will analyze graphic data only on the anomalous heat capacity.

Figure 4 shows the temperature dependences of the excess heat capacity measured in two experiments for as-grown samples of α-NLS (group *A*) crystallized at $T = 281$ K. The solid line represents the results obtained upon the first heating. As is clearly seen, the excess heat capacity has no anomalies at temperatures of 250 and 289 K, which correspond to the reversible phase transitions in α-NLS [8] and β-NLS ($G_1 \longrightarrow G_2$) [11], respectively. At the same time, the excess heat capacity exhibits an anomaly with a maximum at a temperature of 341 ± 2 K. This is in reasonable agreement with the previously determined temperature of the phase transition between the α and β modifications of NH_4LiSO_4 [8]. The change in the enthalpy associated with this anomaly is estimated as $\Delta H_{\alpha \rightarrow \beta} = 2400 \pm 300$ J/mol.

The excess heat capacity measured during the second heating (dashed line in Fig. 4) is characterized by
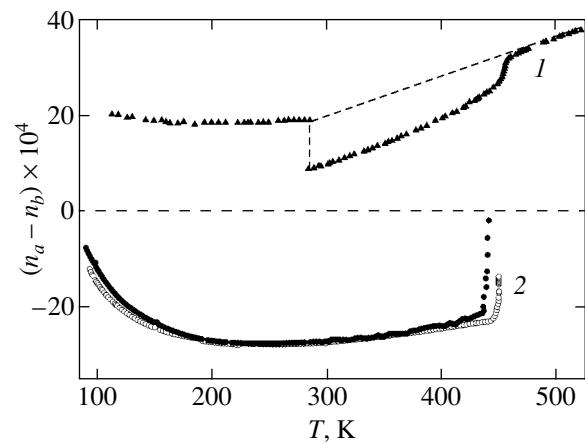

Fig. 3. Temperature dependences of the birefringence $\Delta n_c = (n_a - n_b)$ for NH_4LiSO_4 crystals in the (*1*) β and (*2*) α modifications.

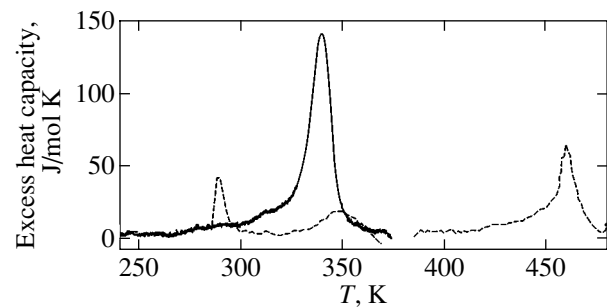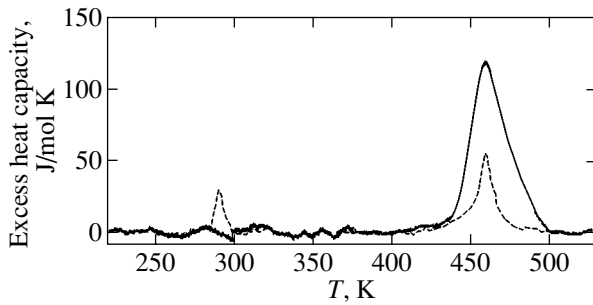**Fig. 4.** Temperature dependences of the excess heat capacity for as-grown crystals of α-NLS (group *A*) upon the first heating (solid line) and the second heating (dashed line).

two anomalies at temperatures $T_1 = 460 \pm 2$ K and $T_2 = 290 \pm 2$ K, which correspond to the successive phase transitions $G_0 \longrightarrow G_1 \longrightarrow G_2$ in β-NLS. The enthalpy changes upon these transitions are as follows: $\Delta H_1 = 900 \pm 200$ J/mol and $\Delta H_2 = 280 \pm 60$ J/mol. These results are also in good agreement with the parameters obtained in our recent work [11] for the NH_4LiSO_4 crystal in the β modification. Therefore, the studied sample of α-NLS undergoes a monotropic phase transition at a temperature $T_{\alpha \rightarrow \beta} = 341 \pm 2$ K.
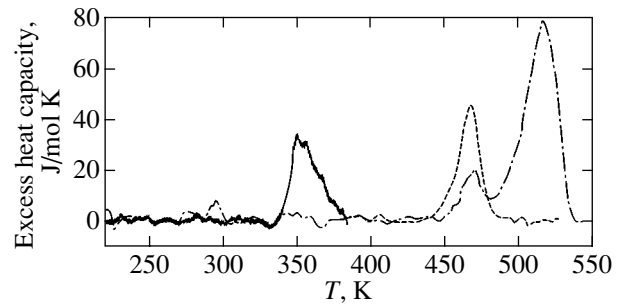
The temperature dependence of the excess heat capacity for a single crystal of α-NLS (group *B*) upon the first heating after prolonged holding at room temperature in a hermetically closed vessel is depicted by the solid line in Fig. 5. It can be clearly seen that, as in the preceding case, the excess heat capacity does not exhibit anomalies at temperatures of ~250 and ~289 K. However, we also did not reveal the anomaly attributed to the α $\longrightarrow$ β phase transition at a temperature close to 341 K, which was observed for the as-grown sample of α-NLS upon the first heating. With a further increase in the temperature, there appears an anomaly in the

Fig. 5. Temperature dependences of the excess heat capacity for single crystals of α-NLS (group *B*) upon the first heating (solid line) and the second heating (dashed line).

Fig. 6. Temperature dependences of the excess heat capacity for as-grown crystals of α-NLS (crystallization *3*) upon the first heating to 380 K (solid line), the second heating (dot-dashed line), and the third heating after cooling to ~370 K (dashed line).

excess heat capacity with a maximum at a temperature of 460 ± 2 K, which coincides with the temperature of the $G_0 \longrightarrow G_1$ phase transition in β-NLS [11]. It could be assumed that, in the course of ageing, the sample undergoes a monotropic phase transformation at room temperature, as in the situation described above. However, the change in the enthalpy associated with the observed anomaly in the heat capacity was found to be $\Delta H = 3600 \pm 500$ J/mol; this value substantially exceeds the enthalpy change characteristic of the $G_0 \longrightarrow G_1$ phase transition in β-NLS [11]. Such a large change in the enthalpy agrees satisfactorily with the sum of the enthalpies of the $\alpha \longrightarrow \beta$ monotropic phase transition ($\Delta H_{\alpha \rightarrow \beta} \approx 2400$ J/mol) and the $G_0 \longrightarrow G_1$ enantiotropic phase transition in β-NLS ($\Delta H_1 \approx 1000$ J/mol). Upon repeated heating, the sample is characterized by two anomalies in the excess heat capacity (dashed line in Fig. 5) with thermodynamic parameters ($T_1 = 459 \pm 2$ K, $T_2 = 290 \pm 2$ K, $\Delta H_1 = 920 \pm 200$ J/mol, $\Delta H_2 = 220 \pm 50$ J/mol) typical of phase transitions in β-NLS single crystals.

Analysis of the results obtained in the calorimetric investigations of as-grown samples prepared through slow growth under isothermal conditions with careful stirring of the solution (crystallizations *3*, *4*) demonstrated that the structure of bulk samples can contain crystal blocks of both groups *A* and *B* simultaneously. The experimental temperature dependences of the excess heat capacity for these samples are displayed in Fig. 6. The behavior of the excess heat capacity during the first heating to 380 K is illustrated by the solid line. As can be seen, no anomalies in the heat capacity are observed at temperatures of 250 and 289 K. However, as is the case with the sample prepared through crystallization at 281 K, there appears a small anomaly at a temperature of 347 ± 2 K due to the phase transition to the ferroelectric phase β-NLS. The enthalpy change (≈ 720 J/mol) proves to be considerably less than the predicted value and amounts to approximately 1/3 of the total enthalpy change $\Delta H_{\alpha \rightarrow \beta}$. Upon the second heating (dot-dashed line in Fig. 6), as could be

expected, the excess heat capacity has an anomaly at a temperature of 293 ± 2 K, which is attributed to the $G_1 \longrightarrow G_2$ phase transition in β-NLS. It is worth noting that, in this case, the enthalpy change (≈ 100 J/mol) also amounts to approximately 1/3 of the total value ΔH_2. In the high-temperature range, the excess heat capacity measured during the second heating exhibits two more peaks, at temperatures of 465 ± 2 and 515 ± 2 K. The first temperature corresponds to the $G_0 \longrightarrow G_1$ phase transition in β-NLS, and the enthalpy change is also approximately equal to 1/3 of the total value ΔH_1. Integration with respect to the area under the peak in the heat capacity at $T = 515$ K gives an enthalpy change of ≈ 2200 J/mol, which amounts to approximately 2/3 of the sum $\Delta H_{\alpha \rightarrow \beta} + \Delta H_1$. Upon the third heating (dashed line in Fig. 6) after cooling to ≈ 370 K, the excess heat capacity is characterized by only one anomaly with thermodynamic parameters ($T_1 = 465 \pm 2$ K, $\Delta H_1 = 860 \pm 150$ J/mol) typical of the $G_0 \longrightarrow G_1$ phase transition in β-NLS. The observed change in the enthalpy indicates that, after the second heating, the sample completely transforms into the β-NLS modification. Therefore, it can be concluded that the studied sample initially consisted of two parts with different temperatures of the $\alpha \longrightarrow \beta$ phase transition. The shift in the maxima of the heat capacity anomalies toward the high-temperature range above 450 K due to the $\alpha \longrightarrow \beta$ phase transition can be explained in terms of the kinetics of the process. According to observations made under a microscope, the time required to accomplish this phase transition is considerably longer than the time it takes for the studied sample to be heated in the course of a differential scanning microcalorimetric experiment at rates of 2–8 K/min.

An examination of the other samples prepared through crystallization *3* revealed that the percentage ratio between crystal parts with different temperatures of the $\alpha \longrightarrow \beta$ phase transition changes from case to case. For example, we obtained a sample in which only 5% of the entire volume was occupied by the crystal

undergoing a monotropic phase transition in the temperature range 340–350 K (group *A*).

Moreover, we made an attempt to establish a correlation between the existence of polytypes in the structure of α-NLS crystals [7] and the phase transition temperatures or the shape of the heat capacity anomaly discussed in [8]. It turned out that the x-ray diffraction patterns of the (001) single-crystal plates contain a large number of reflections. In addition to the (0 0 *h*) reflections (*h* is an even index), which are characteristic of all polytypes, the x-ray diffraction patterns exhibit reflections corresponding to the lattice parameters $c_2 \approx$ 34 Å or $c_3 \approx$ 51 Å. The intensities of the latter reflections also change from sample to sample. Hence, we believe that polytypes actually exist in the structure of α-NLS crystals; however, their influence on the experimental results was not revealed.

It seems likely that the origin of the α ⟶ β phase transition at room temperature can be explained in terms of the structural features inherent in the α modification. The crystal structure of α-NLS is composed of widely spaced tetrahedral layers with ammonium ions between them [6, 7]. Consequently, the solvent can be adsorbed in interlayer cavities during the crystal growth. The adsorption of the solvent most probably occurs in the course of a rapid growth, even without stirring of the solution, when the salt concentration decreases in the vicinity of the growing facet of the crystal. If the as-grown crystal is placed in a dry atmosphere, the water involved evaporates, thus initiating the α ⟶ β phase transformation of the structure. This process proceeds more vigorously in the region of intensive vaporization. Under the conditions where the crystal grows slowly or when the sample is held in a closed vessel, there occurs diffusional relaxation of impurities along the layers toward the crystal edges.

In order to verify the above assumption, we examined the behavior of a saturated solution under a microscope in the temperature range 200–350 K. It was found that the studied solution solidifies at a temperature of 250 K and undergoes melting at 256 K. The most intensive evaporation of the water from a saturated solution during heating is observed at temperatures above 330 K. For the same purpose, we performed a calorimetric investigation of the sample in the α modification prepared through the crystallization at a high rate (3–4 days). As can be seen from Fig. 7, the excess heat capacity of α-NLS crystals exhibits an anomaly with the maximum at a temperature of 255 ± 2 K (upon heating), which is in reasonable agreement with the results obtained in [8]. This anomaly was reproduced only in the case when the sample was not preliminarily heated to a temperature above 340–350 K, for which the mass loss of the sample reached approximately 2%.
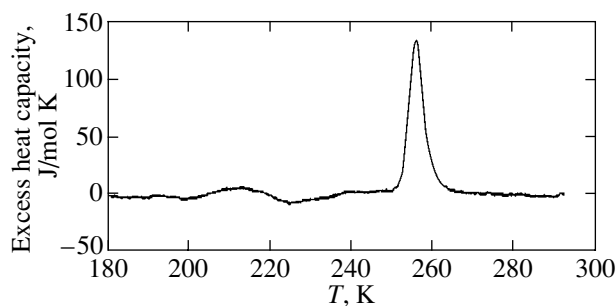

Fig. 7. Temperature dependence of the excess heat capacity for α-NLS prepared through crystallization at a high rate (3–4 days).

4. CONCLUSIONS

Thus, the experimental investigations of the birefringence and heat capacity demonstrated that no structural phase transition occurs in α-NLS crystals at a temperature of 250 K. The anomaly observed in the heat capacity in this range of temperatures was attributed to the incorporation of a large amount of water into the studied sample.

It was established that, depending on the conditions of growth and storage of NH_4LiSO_4 crystals, the temperature of the α ⟶ β monotropic phase transition can vary from room temperature to the boiling point of the salt solution (crystals of the *A* group). This transition is accompanied by complete destruction of the sample. Under the conditions where the crystals slowly grow with stirring or when the samples are held in a moist air atmosphere over a sufficiently long period of time (crystals of the *B* group), the α ⟶ β phase transition occurs in the temperature range 440–450 K. The crystal structure of these samples undergoes a slow transformation (recrystallization) without noticeable distortions. It was assumed that, in the temperature range 340–350 K, the reconstructive phase transition is initiated by the evaporation of a small amount of the water incorporated into the interlayer cavities (crystals of the *A* group). With time, the water molecules diffuse toward the crystal edges (crystals of the *B* group). The enthalpies of this transformation, which can proceed at different temperatures, also differ significantly. This can be explained by the fact that the NH_4LiSO_4 compound undergoes a phase transition to the G_1 ferroelectric phase of the β modification at $T = 340$–350 K and a phase transition to the G_0 paraelectric phase at $T \geq 460$ K. The investigations performed did not reveal a unique correspondence between the existence of polytypes in the structure of the α modification and the phase transition temperature $T_{\alpha \to \beta}$.

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