PHASE TRANSITIONS

Specific Heat, Cell Parameters, Phase T–p Diagram, and Permittivity of Cryolite $(NH_4)_3Nb(O_2)_2F_4$

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Abstract—The temperature dependences of the specific heat, unit cell parameters, susceptibility to hydrostatic pressure, and permittivity of cryolite $(NH_4)_3Nb(O_2)_2F_4$ have been studied. Phase transitions of nonferroelectric nature have been detected. Entropy parameters point to the relation of structure distortions to ordering processes.

1. INTRODUCTION

One of the characteristic features of oxyfluorides $A_2^+ (A')^+ MeO_xF_{6-x}$ ($x = 1, 2, 3$) and $A_2^+ MeO_xF_{6-x}$ ($x = 1, 2$) is the ability to form centrosymmetric structures, despite the low local symmetry (trigonal, tetragonal, orthorhombic) of main structural elements, i.e., six-coordinated polyhedra $[MeO_xF_{6-x}]$. Anions inhomogeneous in ligand composition have a dipole moment, which is caused by displacement of the central atom Me toward the oxygen atoms. However, studies of physical properties showed that the ferroelectric state in oxyfluorides is by no means always achieved even if the structure is distorted due to phase transitions [1–3].

Polyhedra containing the same central atom can quite often be six- and seven-coordinated and, hence, have different symmetries depending on the ligand composition. Illustrative examples are compounds with titanium and niobium: $(NH_4)_3TiOF_5$, $(NH_4)_3Ti(O_2)F_5$, A_2NbOF_5 (A = Li, Na, K, NH4), A_3NbOF_6 (A = K, NH4). Both titanium compounds at room temperature have the Na_3AlF_6 cryolite-type cubic structure (space group $Fm\overline{3}m$, $Z = 4$) characterized by disordering of both ammonium tetrahedra and fluorine–oxygen octahedra [4–7]. For $(NH_4)_3TiOF_5$, as a result of analysis of competing models, disordering of F and O atoms over mixed positions $24e + 96j$

was chosen as an optimum version [4]; however, there is no common opinion about the disorder nature in the $[Ti(O_2)F_5]$ polyhedron. In [5], it was assumed that ligands of both types are disordered over four positions, occupying the $96j$ crystallographic site. According to the opinion of other researchers [6, 7], such a disorder type is characteristic of only closely spaced oxygen ligands forming a "dumbbell," whereas the fluorine atoms, although significant vibration anisotropy is inherent in them, more probably occupy $24e$ sites. Ammonium tetrahedra, occupying at least the $4b$ site, are considered as disordered in both $(NH_4)_3TiOF_5$ and $(NH_4)_3Ti(O_2)F_5$.

The stability of the cubic phase of both titanium compounds is violated upon cooling due to phase transitions associated with ordering of structural units [8, 9]. Calorimetric studies showed that the presence of the "oxygen dumbbell" as one of ligands in $(NH_4)Ti(O_2)F_5$, causing an increase in the degree of polyhedron coordination, results in a significant decrease in the transition entropy $\Delta S \approx 9$ J/mol K $\approx R\ln 3$ [9] in comparison with $(NH_4)_3TiOF_5$, $\Delta S \approx 18$ J/mol K $\approx R\ln 9$ [8]. At the same time, since a comparison of the degree of disordering of six- and seven-coordinated polyhedra in different structure types is not certainly quite correct, nevertheless, it should be noted that successive phase transitions in oxyfluorides $(NH_4)_3NbOF_6$ (space group $Fm\overline{3}m$) and $(NH_4)_2NbOF_5$ (space group $Cmc2_1$) are
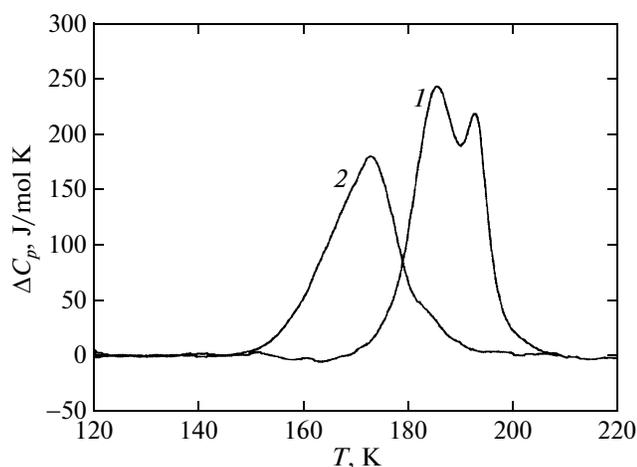
Fig. 1. Temperature dependence of the anomalous specific heat of $(NH_4)_3Nb(O_2)_2F_4$ according to the DSM studies under conditions of (1) heating and (2) cooling.

characterized by almost the same and rather significant total entropy $\Sigma\Delta S_i \approx 38$ J/mol K $\approx R\ln 96$ [10, 11].

The structure of oxyfluoride with eight-coordinated niobium anion $(NH_4)_3Nb(O_2)_2F_4$ was also characterized as the cubic cryolite-like one [7]. X-ray studies of the single crystal showed that fluorine and oxygen atoms occupy 24e and 96j crystallographic sites. The partial site occupation by ligands (0.667 and 0.167 for F and O) is caused by their statistical disordering over all polyhedron vertices, which, in turn, causes disordering of ammonium tetrahedra. Preference is given to the parallel arrangement of "oxygen dumbbells" at opposite polyhedron vertices, which corresponds to the trans-configuration. This circumstance contradicts the data on correction of the $Fm\overline{3}m$ structure of related oxyfluoride $(NH_4)_3Ta(O_2)_2F_4$ for which the cis-configuration corresponding to a polyhedron shaped as a square antiprism was assumed [12].

Taking into account the experimentally determined disordering of cations and anions in cubic oxyfluorides with an eight-coordinated anion polyhedron [7, 12], the presence of phase transitions associated with ordering of structural units could be expected. The study of the conditions causing destabilization of such structures is of doubtless interest to determine the degree of polyhedra coordination on the structural disorder nature, ways for its elimination, and physical properties of oxyfluorides. However, to our knowledge, such detailed studies of such structures have not yet been performed. Only in [12], it was reported on the absence of changes in a powder X-ray pattern corresponding to the cubic phase $(NH_4)_3Ta(O_2)_2F_4$, at least to 120 K.

In this paper we present the results of the study of some physical properties and parameters of the cryolite $(NH_4)_3Nb(O_2)_2F_4$ unit cell in a wide temperature and pressure range.

2. SYNTHESIS, CHARACTERIZATION, AND SEARCH FOR PHASE TRANSITIONS

Ammonium peroxyfluoroniobate $(NH_4)_3Nb(O_2)_2F_4$ was synthesized by dissolving oxide Nb_2O_5 in concentrated (40%) HF followed by adding 30% H_2O_2 solution and leading the obtained solution to pH = 6 by adding 25% ammonia solution (all concentrations are given in weight percent). The obtained precipitate was filtered, and desired crystals were obtained by slow evaporation of a mother liquor in air. The complex composition was monitored by determining the peroxide group $(O_2)^{2-}$ concentration using permanganatometry. The experimentally determined value of 20.3 wt % $(O_2)^{2-}$ appeared smaller than the calculated one (22.3 wt %). The ~2 wt % deficiency of $(O_2)^{2-}$ in relation to the above stoichiometry indicates the presence of O^{2-} in the complex, which corresponds to the actual composition $(NH_4)_3NbO_{0.2}(O_2)_{1.8}F_4$.

In the first stage, the synthesized compound was certified at room temperature using a DRON-2 X-ray diffractometer. As expected, the $(NH_4)_3Nb(O_2)_2F_4$ crystal appeared to be cubic (space group $Fm\overline{3}m$, $Z = 4$) with the unit cell parameter $a_0 = 0.9450$ nm which is in good agreement with the data of [7] ($a_0 = 0.9444$ nm). Powder X-ray diffraction patterns showed no reflections corresponding to foreign phases.

The stability of the initial structure to temperature changes was tested in calorimetric experiments using a DSM-2M differential scanning microcalorimeter (DSM). Measurements were performed in the temperature range of 110–310 K under conditions of temperature decrease and increase with a rate of 8 K/min on several samples of mass 0.10–0.15 g. Upon heating, a reproducible specific heat anomaly with two peaks at 185 and 193 K was observed. The experimental results are shown in Fig. 1 as the excess specific heat $\Delta C_p(T)$. Upon cooling, "merging" of peaks into a single one with a maximum ~20 K below the temperature of the high-temperature peak observed upon heating. These experimental facts suggest that oxyfluoride $(NH_4)_3Nb(O_2)_2F_4$ exhibit two pronounced first-order phase transitions characterized by different values of the temperature hysteresis. The enthalpy related to two phase transitions was determined by integrating the function $\Delta C_p(T)$ as $\Sigma\Delta H_i = 4000 \pm 500$ J/mol.

X-ray studies performed in a wide temperature range showed a change in the lattice symmetry due to
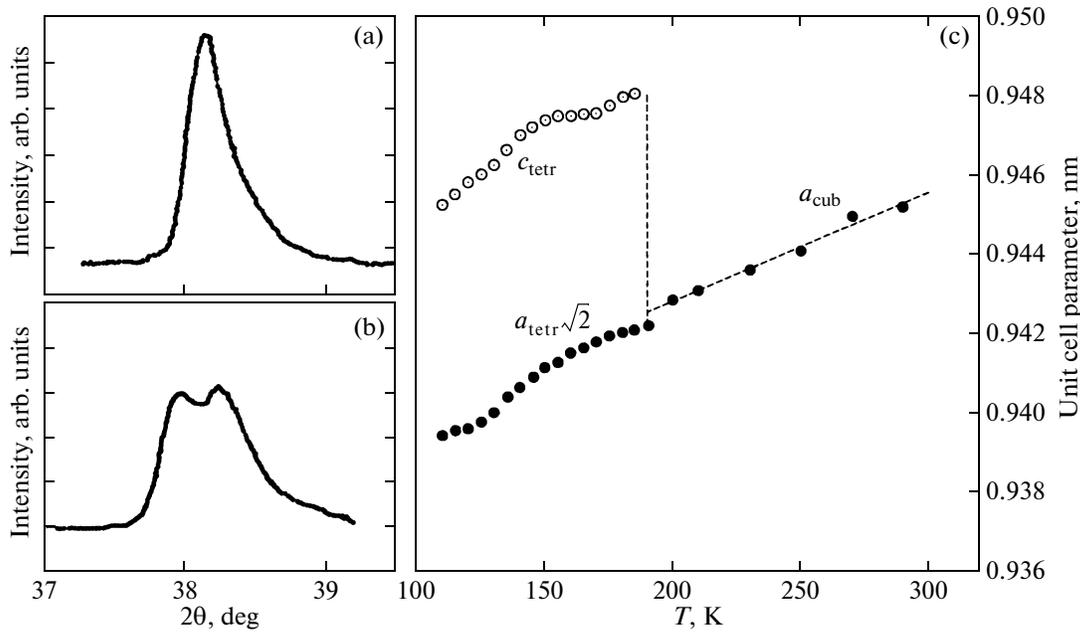
Fig. 2. Results of X-ray studies of $(NH_4)_3Nb(O_2)_2F_4$: (a, b) the (400) reflection at 293 and 115 K, respectively; (c) the temperature dependence of unit cell parameters.

phase transitions. Figures 2a and 2b show the (400) reflection at 293 and 115 K: the structure distortion appeared in its splitting.

In the low-temperature phase, reflections were satisfactorily identified in the approximation of a pseudo-tetragonal cell with the following relations of parameters $a_{tetr} \approx a_{cub}/\sqrt{2}$ and $c_{tetr} \approx a_{cub}$. In the temperature dependence of the cell parameters, shown in Fig. 2c, we can see that X-ray experiments reliably detected only one particular temperature point at which splitting and an abrupt change in a_0 are observed. It is quite probable that this is because of a small temperature interval between two specific heat anomalies detected in the study using the DSM.

The preliminary polarization–optical observations on an unoriented $(NH_4)_3Nb(O_2)_2F_4$ sample showed that optical anisotropy appears upon cooling and disappears upon heating at ~178 and ~190 K, respectively. Thus, these experiments also detected a significant temperature hysteresis of ~12 K.

3. SPECIFIC HEAT STUDY

Detailed studies of the $(NH_4)_3Nb(O_2)_2F_4$ specific heat were performed by adiabatic calorimetry in the temperature range of 90–320 K. The sample of mass 0.6 g to be studied was packed into a copper container. Then the entire system in an inert helium atmosphere was sealed into a gas-tight indium capsule which was placed into a furniture with heater. Calorimetric

experiments were carried out under conditions of continuous ($dT/d\tau$ = 0.18–0.32 K/min) and discrete (ΔT = 1.8–2.0 K) heatings. The furniture (heater, copper and indium cells) specific heat was measured in an independent experiment. Methodical features of the experiment are described in more detail in [13].

Figure 3 shows the results of calorimetric studies of $(NH_4)_3Nb(O_2)_2F_4$ in the form of the temperature dependence of the isobaric molar specific heat, which, in general, confirm the data obtained by the DSM
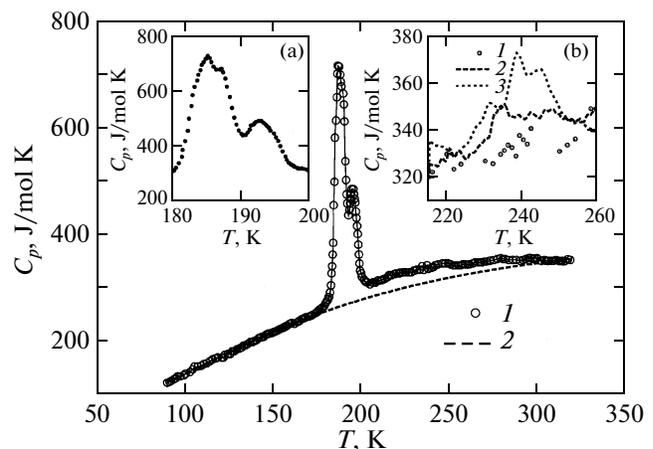
Fig. 3. Temperature dependences of (*1*) molar and (*2*) lattice specific heats of $(NH_4)_3Nb(O_2)_2F_4$. The insets show the specific heat (a) in the vicinity of the phase transitions and (b) in the range of 220–260 K at heating rates $dT/d\tau$ = (*1*) 0.04, (*2*) 0.18, and (*3*) 0.32 K/min.
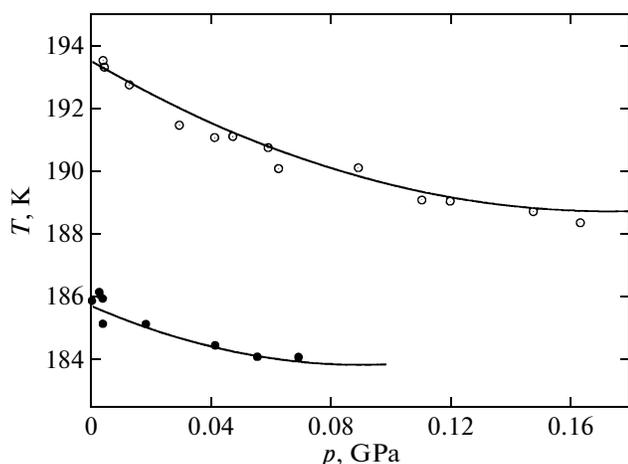
Fig. 4. Dependences of the phase transition temperatures of $(NH_4)_3Nb(O_2)_2F_4$ on the hydrostatic pressure.

method (Fig. 1). The specific heat anomaly in the region of phase transitions is characterized by two pronounced maxima at ~193 and ~185 K. However, close examination of the results of multiple measurement series showed that the low-temperature peak is structured, i.e., contains two maxima at 187.5 and 185.5 K (inset a of Fig. 3). Thermal cycling resulted in an insignificant redistribution of temperatures and peak areas. The temperatures of maxima can finally be characterized as $T_1 = 193.00 \pm 0.15$ K, $T_2 = 187.00 \pm 0.15$ K, and $T_3 = 185.40 \pm 0.15$ K.

The measurements detected a rather extraordinary fact, i.e., the specific heat in the region of ~(230−250 K) appeared strongly dependent on the temperature variation rate (inset b of Fig. 3). At rates $dT/d\tau > 10^{-1}$ K/min, a broad peak was observed in the curve $C_p(T)$. Figure 3 shows the results for the most equilibrium measurement process corresponding to the rate $dT/d\tau > 4 \times 10^{-2}$ K/min.

The regular specific heat C_L was determined by approximating experimental $C_p(T)$ outside the range of the existence of the anomalous specific heat using the Debye and Einstein functions. The difference between the total and regular specific heats corresponded to the excess specific heat $\Delta C_p(T)$. Its maximum values appeared very high and significantly, almost threefold exceeded the lattice specific heat (Fig. 3). However, in the vicinity of particular points, the peaks are rather smeared, which did not allow thermographic studies to determine the latent heat.

Above the phase transition temperature from the cubic phase, the anomalous contribution to the specific heat exists in a very wide temperature range, i.e., from 205 to 300 K (Fig. 3).

The total excess enthalpy of $(NH_4)_3Nb(O_2)_2F_4$ was determined by integrating the function $\Delta C_p(T)$ over the entire range of the excess specific heat, i.e., 175−300 K, as $\Sigma\Delta H = 6000 \pm 400$ J/mol. The closeness of the phase transition temperatures did not allow separation of the contributions corresponding to individual phase transitions. However, assuming that the anomalous specific heat associate with transitions exists in the range of ~175−205 K, the corresponding enthalpy change is $\Sigma\Delta H_i = 4500$ J/mol. This value is in quite satisfactory agreement with DSM measurements that confirms the first order of observed phase transitions at which all energy changes occur in a narrow temperature range. Thus, the excess enthalpy existing between 205 and 300 K, which is unrelated to the detected first-order phase transitions, appears high enough, i.e., ~$0.25\Sigma\Delta H$.

4. SUSCEPTIBILITY TO PRESSURE AND PERMITTIVITY

The $(NH_4)_3Nb(O_2)_2F_4$ susceptibility to high hydrostatic pressures was studied by the differential thermal analysis method recording the transition temperatures and their changes with pressure. The measuring cell represented a germanium−copper thermocouple to whose junctions a copper container with a sample of mass ~0.15 g and a quartz reference sample were attached. The sample temperature was measured with an error of ±0.3 K by a copper−constantan thermocouple glued to a germanium thermoelectrode. The cell was placed into a cylinder−piston pressure chamber filled with a silicon oil−pentane mixture. The pressure was measured by a Manganin resistance pressure gage with an error no more than $\pm 10^{-3}$ GPa. The reproducibility of experimental data was tested by measurements under conditions of pressure increase and decrease.

One can see in Fig. 4 that only two phase boundaries were detected due to the closeness of temperatures T_2 and T_3 and the small difference between corresponding specific heat peaks in pressure experiments. The pronounced nonlinear pressure dependence of transition temperatures was detected, which is described by the equations $T_1 = 192.6 - 57.4p + 160p^2$ and $T_2 = 185.4 - 44.4p + 228p^2$. According to the values of the coefficients at p and p^2 in both equations, the temperature range of the intermediate phase existence narrows with pressure.

The permittivity and loss tangent were determined using an E 7-20 immittance meter at a frequency of 1 kHz in the temperature range of 100−310 K. The $(NH_4)_3Nb(O_2)_2F_4$ sample heating and cooling rate was $dT/d\tau \approx |0.6|$ K/min. The study was performed on

a ceramic sample shaped as a pellet (8 mm in diameter, 2 mm high) prepared from finely divided powder only by pressing without annealing. Copper electrodes were made by vacuum deposition. The possibility of obtaining reliable results for such samples was illustrated previously [14].

The results of $\varepsilon(T)$ and $\tan\delta(T)$ measurements are shown in Fig. 5. The permittivity exhibits an anomalous behavior such as a sharp increase in the rise rate in the range of $\sim(170–205)$ K coinciding with the temperature range in which the anomalous specific heat associated with phase transitions was observed. The dielectric loss peak exists approximately in the same temperature range (see Fig. 5b). Due to the significant decrease in the temperature variation rate in comparison with DSM experiments, the hysteresis decreased; nevertheless, it remained rather significant, $\delta T \approx 8$ K (Fig. 5).

The increase in the derivatives $d\varepsilon/dT$ and $d(\tan\delta)/dT$ above 260 K is caused, most likely, by the loss in the not annealed sample. Thus, no features associated with individual phase transitions were detected in the behavior of dielectric properties; and the stepwise variation of ε from 9 to 15 in the range of structural changes indicate their non-ferroelectric nature [15].

5. DISCUSSION

It is known that the data on the temperature dependence of the specific heat can yield information on phase transitions associated with the appearance or variation of order parameters of any physical nature; however, it is almost impossible to directly determine the nature of transformations. Furthermore, specific heat anomalies slightly differing in temperature can be associated not with different transitions, but, e.g., with the fact that the sample consists of growth units with different temperatures of the same transition, in particular, due to different mechanical stresses in them. Therefore, the problem of the number of phase transitions in $(NH_4)_3Nb(O_2)_2F_4$ cannot be considered as finally solved. In our opinion, the following experimental facts argue in favor of the existence of at least two structural transformations. First, these are different temperature hystereses corresponding to two specific heat anomalies observed in DSM measurements; second, their different pressure coefficients dT/dp suggesting the possibility of intermediate phase wedging-out. Insignificant changes in the permittivity point to the ferroelectric nature of phase transitions. Thus, additionally taking into account the relation between specific heat peaks, it can be reliably argued that specific heat anomalies at $T_1 = 193$ K and $T_2 = 185.4$ K correspond to phase transitions. In view of the insig-
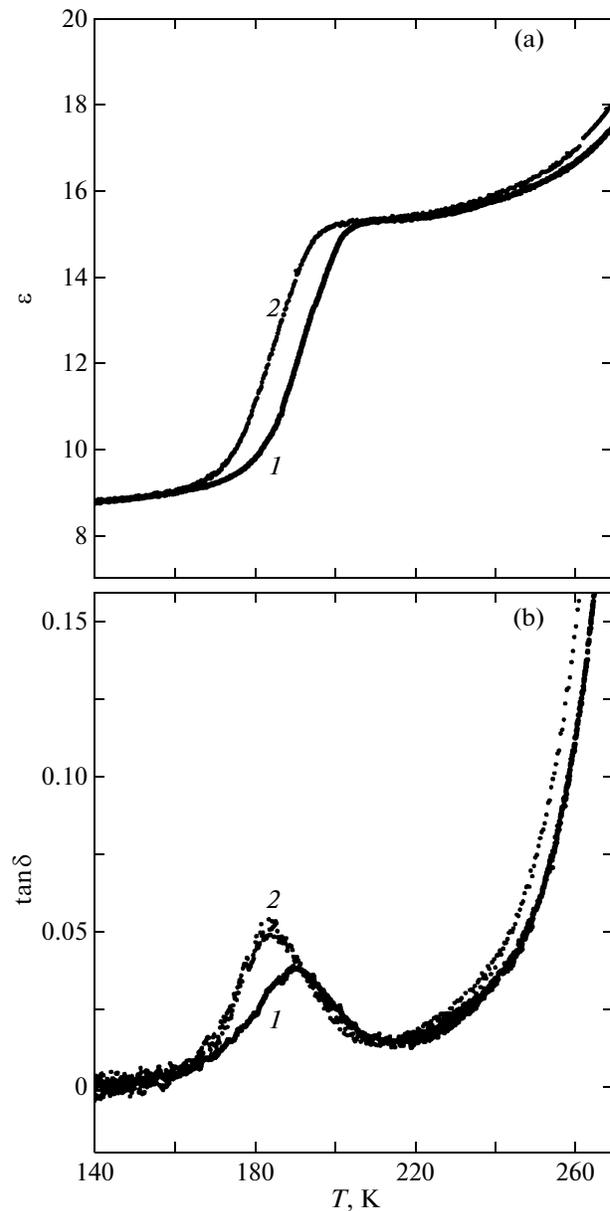
Fig. 5. Behavior of the (a) permittivity and (b) loss tangent during (*1*) heating and (*2*) cooling of $(NH_4)_3Nb(O_2)_2F_4$.

nificant temperature range $T_2–T_3$, there is no sufficient certainty that any other method could simple enough relate the specific heat anomaly at $T_2 = 187$ K to the phase transition or sample "mosaicity."

As noted in Section 1, there are different viewpoints on relative positions of "oxygen dumbbels" in eight-coordinated anion polyhedra of oxyfluorides $A_3Me(O_2)_2F_4$ ($A =$ K, NH$_4$; $Me =$ Nb, Ta). On the one hand, in [7], preference is given to the D_{2h} symmetry (trans-configuration) of the polyhedron which, due to the presence of the symmetry center, has no dipole moment. On the other hand, the analysis of structural
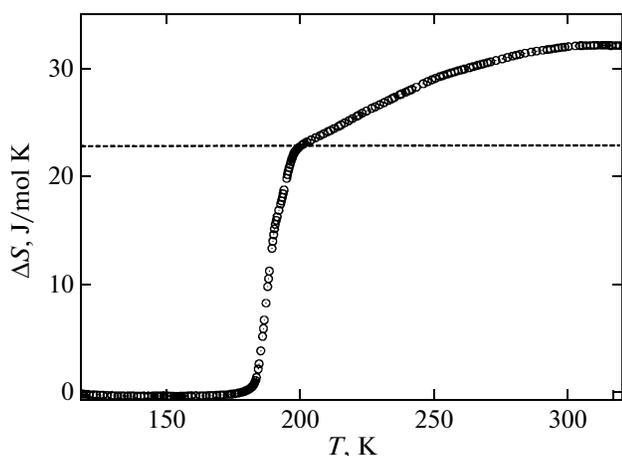
Fig. 6. Temperature dependence of the excess entropy ΔS. The dashed line indicates the entropy $\Sigma \Delta S_i$ associated with phase transitions.

and spectroscopic data and their consideration within various theoretical approximations showed that the cis-configuration (C_{2v} symmetry), according to which the polyhedron has a dipole moment caused by the central atom displacement to oxygen atoms, is more stable [12, 16]. Exactly in this case, there is the highest probability of the appearance of macroscopic polarization caused, e.g., by structure distortion due to a phase transition. The experimental data on the permittivity behavior, obtained in this study, indicate the absence of polar phases in $(NH_4)_3Nb(O_2)_2F_4$. However, certainly, it is impossible to finally solve the problem of the anionic polyhedron symmetry only by the $\varepsilon(T)$ behavior.

For example, in studying the cubic oxyfluoride Rb_2KTiOF_5 whose six-coordinated anion with C_{4v} symmetry undoubtedly has a local dipole moment; no ferroelectric phases were also detected [17].

According to [7, 12, 16], the cubic symmetry of the oxyfluoride $(NH_4)_3Nb(O_2)_2F_4$ lattice can exist only in the presence of at least two structural disorder types. First, this is statistical disordering of ligands (24e and 96j sites, respectively, for F and O atoms), resulting in the cubic polyhedron symmetry in the $Fm\bar{3}m$ phase. Second, this is orientational disordering over two positions of the [NH$_4$] tetrahedron at the polyhedron center (4b site), caused by the necessity of matching its local symmetry with the symmetry of the site occupied by it.

As was already noted, by the time of the present study, the data on the structure of distorted phases and possible phase transitions in structures with eight-coordinated anion polyhedron were absent. However, if we consider that the detected transformations cause complete ordering of various structural elements, we

can estimate the corresponding $(NH_4)_3Nb(O_2)_2F_4$ entropy change. The contributions of ammonium tetrahedron ordering at the 4b site and ligand ordering to the total entropy are $\Delta S = R\ln 2$ and $R\ln 8$, respectively.

Thus, the total entropy change would be $\Sigma \Delta S = R\ln 16 = 23$ J/mol K.

The entropy change in the entire temperature range of the existence of the anomalous specific heat was determined by integrating the temperature dependence of $\Delta C_p/T$ as $\Sigma \Delta S = 32 \pm 1.5$ J/mol K (Fig. 6). As noted above, the measuring mode rate has a significant effect on the behavior and value of the specific heat in a wide temperature range ($\sim$100 K) of the cubic phase, but does not affect its temperature dependence in the phase transition region. Therefore, it can be undoubtedly considered that the anomalous specific heat in the temperature range of 205–300 K is unrelated to phase transitions. It can be assumed that this feature is caused, e.g., by the motion kinetics of some structural elements. In this sense, of obvious interest is the study of $(NH_4)_3Nb(O_2)_2F_4$, e.g., by the nuclear magnetic resonance method.

In view of the foregoing, to estimate the entropy of phase transitions, we restricted the analysis to the same temperature range of 175–205 K as in calculating the anomalous enthalpy $\Sigma \Delta H_i$ (see Section 3). The corresponding value was $\Sigma \Delta S_i = 23 \pm 2$ J/mol K. In the absence of reliable structural models allowing the description of ordering processes in $(NH_4)_3Nb(O_2)_2F_4$, the relation between experimental data and the estimates of the possible entropy change can be considered as satisfactory.

The substitution of seven-coordinated polyhedra with eight-coordinated ones in the cryolite structure resulted in the entropy decrease caused by successive phase transitions, from $\Sigma \Delta S_i \approx R\ln 96$ in $(NH_4)_3NbOF_6$ [10] to $\Sigma \Delta S_i \approx R\ln 16$ in $(NH_4)_3Nb(O_2)_2F_4$. As noted in Section 1, a similar phenomenon was observed for titanium cryolites with six- and seven-coordinated polyhedra [8, 9]. Thus, it can be assumed that an increase in the number of ligands in the "quasi-octahedron" at the same central atom results in a decrease in the degree of disordering of structural elements in the $Fm\bar{3}m$ lattice.

As noted above, the latent heats of phase transitions were not determined in this study. However, the large hysteresis of transition temperatures, observed in the DSM, dielectric, and optical measurements, and the significant abrupt change in the unit cell parameters (Fig. 2c) suggest that the structural transformations in $(NH_4)_3Nb(O_2)_2F_4$ are the first-order phase transitions far from the tricritical point. This is also supported by the impossible representation of the anomalous spe-

cific heat of the low-temperature distorted phase by the linear function $(\Delta C_p/T)^{-2}(T)$ corresponding to consequences of the phenomenological Landau theory even near the temperature T_3 [18].

The significant nonlinearity of phase boundaries in the $T-p$ diagram and the trend toward a sign change of dT_1/dp and dT_2/dp indicate possible changes in the degree of the transition closeness to the tricritical point and the volume change sign at transition points with increasing pressure. In this case, it is also not improbable that transitions in $(NH_4)_3Nb(O_2)_2F_4$ can become the second-order phase transition at a certain pressure. Similar phenomena were also observed and analyzed in the framework of the thermodynamic theory in the study of the effect of the hydrostatic pressure on phase transitions in perovskite-related ferroelastics with six-coordinated homogeneous anion polyhedra [19].

6. CONCLUSIONS

Phase transitions in cubic oxyfluoride with eight-coordinated anion polyhedron were detected and studied for the first time. The determined values of the anomalous entropy suggest with a high degree of confidence that $(NH_4)_3Nb(O_2)_2F_4$ exhibits a sequence of structural transformations associated with ordering of anion and cation polyhedra. The analysis of the temperature–pressure phase diagrams showed the possibility of changes in signs of pressure coefficients of transition temperatures and the possibility of intermediate phase wedging-out. According to the behavior of dielectric properties, the detected phase transitions are unrelated to the appearance of the ferroelectric state.

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