

LATTICE DYNAMICS AND PHASE TRANSITIONS

Phase Transitions in the $(\text{NH}_4)_2\text{NbOF}_5$ Oxyfluoride

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Abstract—The thermal and dielectric properties of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride have been investigated. It has been established that the structural phase transitions $Cmc2_1 \rightarrow C2 \rightarrow Ia$ observed at the temperatures $T_1 = 258.0$ K and $T_2 = 218.9$ K exhibit a nonferroelectric nature. The hydrostatic pressure, which stabilizes the initial phase and destabilizes the low-temperature phase, hardly affects the temperature range of stability of the intermediate phase. The model of sequential ordering of the structural elements due to phase transitions has been analyzed using experimental data on the entropies of the phase transitions.

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1. INTRODUCTION

The symmetry of oxyfluorides $A_2^+ \text{MeO}_x\text{F}_{6-x}$ and $A_2^+(A')^+ \text{MeO}_x\text{F}_{6-x}$ with a structure containing quasi-octahedral anions with mixed ligands can exhibit a wide variety—from cubic to triclinic—depending of the valence of the central atom, the mutual arrangement of anions in the crystal lattice, and the composition of univalent cations. The same parameters are also responsible, to a large extent, for the physical properties manifested by these compounds, as well as for the nature and mechanism of the phase transitions occurring in them. Among the oxyfluorides of the general formula $A_2^+(A')^+ \text{MeO}_3\text{F}_3$ ($A, A' = \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$) with a structure of elpasolite ($A \neq A'$) or cryolite ($A = A'$), there exist a number of multiferroics that, owing to the loss of stability of the cubic phase, undergo structural distortions accompanied by the simultaneous appearance of the spontaneous polarization and deformation [1, 2]. Some compounds with a different ratio of the ligands F(O) also experience phase transitions. However, although the quasi-octahedra have a dipole moment due to the displacement of the central atom toward the oxygen atom, ferroelectric phases in the $A_2^+ \text{MeO}_x\text{F}_{6-x}$ and $A_2^+(A')^+ \text{MeO}_x\text{F}_{6-x}$ ($x = 1, 2$) compounds have not been found previously.

A significant role of the central atom in the $(\text{NH}_4)_2\text{MeO}_2\text{F}_4$ ($\text{Me} = \text{W}, \text{Mo}$) compounds was revealed using calorimetric, optical, and structural

methods [3–7]. At room temperature, both crystals belong to the orthorhombic crystal system with space group $Cmcm$ ($Z = 4$). The unit cell contains two crystallographically nonequivalent disordered ammonium groups and partially ordered quasi-octahedra $[\text{MeO}_2\text{F}_4]$, in which it has been possible to locate only the axial atoms of fluorine and oxygen. Upon cooling, the $(\text{NH}_4)_2\text{MeO}_2\text{F}_4$ oxyfluorides undergo two sequential phase transitions, which, as judged from the significantly different entropy changes $\Delta S_1 \sim R \ln 10$ and $\Delta S_2 \sim 0.2R$, are the order–disorder and displacive transformations, respectively. However, the similarities of the structures and properties of the tungstate and the molybdate end there.

The initial orthorhombic structure is substantially more stable with respect to variations in temperature and hydrostatic pressure in the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ tungstate ($T_1 = 200$ K, $dT_1/dp = 13.4$ K/GPa) as compared to the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ molybdate ($T_1 = 270$ K, $dT_1/dp = 92.8$ K/GPa). The low-temperature phases have different symmetries, namely, $P\bar{1}$ (tungstate) and $Pnma$ (molybdate). According to the results obtained from investigations of the optical and dielectric properties, the phase transitions at the temperature T_1 exhibit a ferroelectric nature in the tungstate and an antiferroelectric nature in the molybdate.

The replacement of the central cation W^{6+} (or Mo^{6+}) by pentavalent niobium, which leads to a change in the ratio of the fluorine–oxygen ligands in

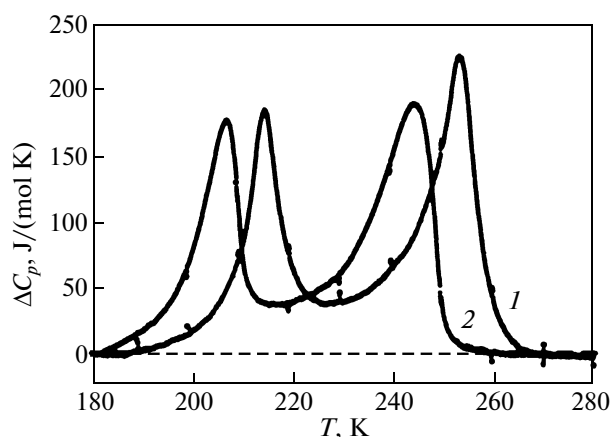


Fig. 1. Behavior of the excess heat capacity of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride according to the data obtained from measurements with a differential scanning microcalorimeter during (1) heating and (2) cooling.

the $[\text{MeVOF}_5]^{2-}$ quasi-octahedron, is accompanied by the formation of crystal lattices with different symmetries due to the change in the type of univalent cations, for example, in the $A_2\text{NbOF}_5$ compounds with $A = \text{Li}$ ($P\bar{3}/m$, $Z = 1$), Na ($Pcnb$, $Z = 4$), and K ($P4/nmm$, $Z = 2$) [8–10]. Information on phase transitions in these oxyfluorides is lacking. Only in his paper [8], Pinsker suggested the probability of occurrence of the structural transformation $P4/nmm \rightarrow P4/n$ in the K_2NbOF_5 compound due to the possible ordering of the $[\text{NbOF}_5]^{2-}$ complex, which is statistically disordered in the initial phase over two equivalent positions.

The presence of the ammonium cation in the structure of the oxyfluorides irrespective of their symmetry, as a rule, encourages a considerable disordering of the quasi-octahedral anions [2, 4, 6, 11], which, in turn, increases the probability of the structural transformations caused by the ordering processes. In this work, we have investigated the heat capacity, permittivity, and susceptibility with respect to the hydrostatic pressure for the $(\text{NH}_4)_2\text{NbOF}_5$ crystal. The structure of this oxyfluoride at room temperature was previously determined as orthorhombic; however, in contrast to the $(\text{NH}_4)_2\text{MeOF}_5$ compounds, it was interpreted as a noncentrosymmetric structure $Cmc2_1$, $Z = 4$ [12].

2. PRELIMINARY INVESTIGATIONS

Colorless transparent single crystals of the $(\text{NH}_4)_2\text{NbOF}_5$ compound in the form of tetragonal prisms or polyhedra were grown using the solution crystallization method. Niobium oxide Nb_2O_5 was dissolved in a boiling 40% HF acid in a platinum crucible with the subsequent filtration and addition of an NH_4F solution at the ratio $\text{NH}_4^+ : \text{H}_2\text{NbOF}_5 = 2.5$.

The stoichiometry of the composition of the $(\text{NH}_4)_2\text{NbOF}_5$ crystalline samples was checked using the chemical analysis. A satisfactory agreement was observed between the calculated and experimentally determined (in parentheses) contents of the elements (wt %): NH_4 , 15.0 (15.0 ± 0.3); Nb , 38.7 (38.3 ± 0.5); and F , 39.6 (39.4 ± 0.5).

The samples were structurally characterized at room temperature on a D8 ADVANCE X-ray diffractometer. The X-ray diffraction patterns did not reveal peaks corresponding to impurities of the initial components and foreign phases. The stability of the initial orthorhombic phase $Cmc2_1$ as a function of the temperature was investigated by measuring a powdered sample of the $(\text{NH}_4)_2\text{NbOF}_5$ compound on a DSM-10M differential scanning microcalorimeter (DSM). The experiments were performed during heating and cooling at a rate of 8 K/min in the temperature range 110–350 K. The weight of the samples was equal to 0.11–0.14 g.

Figure 1 presents the results of the measurements in the form of the temperature dependence of the excess heat capacity ΔC_p , which was determined as the difference between the total molar heat capacity of the compound and its lattice component. It can be seen from this figure that, during heating, the temperature dependence of the excess heat capacity exhibits an anomalous behavior in the form of two peaks with maxima at the temperatures $T_1 = 253$ K and $T_2 = 214$ K. A significant hysteresis in the temperatures of the maxima of the heat capacity ($\delta T_1 \approx 4$ K and $\delta T_2 \approx 7$ K) revealed in the thermal cycling experiments suggests that the revealed phase transitions are first-order transformations. The considerable excess heat capacity observed over the entire temperature range of the existence of the intermediate phase complicates the determination of the individual integral characteristics of the phase transitions at the temperatures T_1 and T_2 . The total enthalpy change $\sum \Delta H_i = 5200 \pm 500$ J/mol, which is associated with the sequence of structural transformations, was determined by integrating the function $\Delta C_p(T)$.

The data obtained in searching for phase transitions and determining their temperatures were used by Udoenko and Laptash [12] in the refinement of the structure of the $(\text{NH}_4)_2\text{NbOF}_5$ compound. They established the following sequence of structural phase transitions with decreasing temperature: $Cmc2_1 \rightarrow C2 \rightarrow Ia$.

3. HEAT CAPACITY

In the subsequent analysis of the models describing the possible ordering of the structural elements, we will need more reliably determined integral characteristics of the phase transitions. In this respect, we undertaken detailed investigations of the temperature

dependence of the heat capacity of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride under considerably more equilibrium conditions using adiabatic calorimetry.

The sample under investigation in the form of a set of small crystals ($\sim 2 \times 2 \times 2$ mm) with a total weight of 1.1 g was packed in a copper container. The system as a whole was hermetically sealed in an inert helium atmosphere into an indium capsule, which, in turn, was placed in a furnace with a heater. The heat capacity of the system was measured in the regimes of continuous ($dT/dt = 0.15$ K/min) and discrete ($\Delta T = 2.5$ – 3.0 K) heatings. In the immediate vicinities of the phase transition temperatures, the investigations were performed using the method of quasi-static thermograms at mean rates of heating and cooling $|dT/dt \approx 0.02|$ K/min. The heat capacity of the furnace consisting of the heater, the copper capsule, and the indium capsule was measured in a separate experiment.

The measured temperature dependence of the molar isobaric heat capacity of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride is plotted in Fig. 2. In addition to the fairly significant changes in the heat capacity at the corresponding refined temperatures of the two phase transitions ($T_1 = 258.00 \pm 0.05$ K and $T_2 = 218.90 \pm 0.05$ K), we revealed small peaks of the heat capacity at temperatures of 297, 261, and 246 K.

The lattice heat capacity in the range of phase transitions is determined by fitting the experimental data $C_p(T)$ outside the temperature region of the existence of the heat capacity anomalies with the use of the Debye–Einstein functions and shown by the dashed line in Fig. 2. It can be seen from this figure that the heat capacity anomalies, which are associated with the phase transitions at the temperatures T_1 and T_2 , are overlapped in an approximately the same manner as is observed in the experiments on a differential scanning microcalorimeter at high rates of change in the temperature. The enthalpy change $\sum \Delta H_i = 7500 \pm 600$ J/mol for the $(\text{NH}_4)_2\text{NbOF}_5$ compound due to the sequential structural transformations significantly exceeds the value determined using a differential scanning microcalorimeter. The discrepancy between the data obtained by different calorimetric methods is predominantly caused by the difficulties encountered in determining the temperature region of the existence of the anomalous heat capacity in measurements on a differential scanning microcalorimeter. As can be seen from Figs. 1 and 2, the integration is performed for temperatures in the range from 190 to 265 K in the former case and over a substantially wider range (from 150 to 300 K) in the latter case. The problem regarding the possibility of determining individual integral thermal effects will be considered below when we will analyze the set of experimental data obtained in our present investigations.

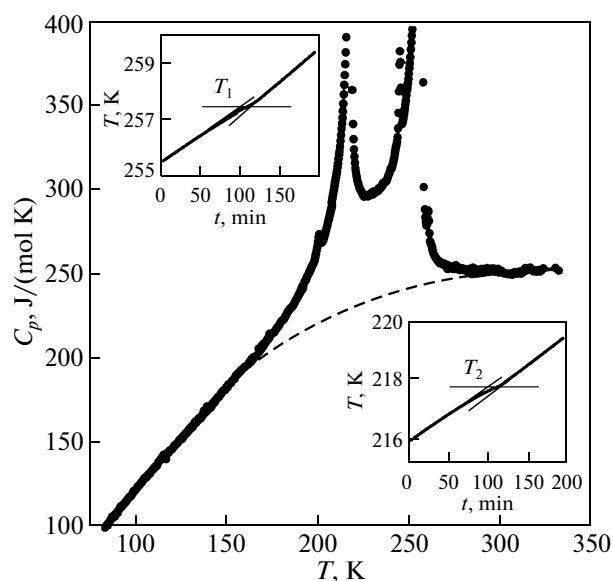


Fig. 2. Temperature dependence of the heat capacity of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride. The dashed line represents the lattice heat capacity. The insets show the thermograms obtained during heating and cooling in the ranges near the temperatures T_1 and T_2 .

The thermal effects, which correspond to the aforementioned weak anomalies in the heat capacity at temperatures different from T_1 and T_2 , are very small (≤ 100 J/mol) as compared to the total enthalpy of the phase transitions. Moreover, no specific features have been revealed in the behavior of the other physical properties at the temperatures under consideration. Therefore, we will ignore these anomalies in the subsequent analysis.

The results of the investigations performed in the vicinities of the phase transitions by the method of quasi-static thermograms (see insets to Fig. 2) have made it possible to refine the magnitudes of the temperature hysteresis $\delta T_1 = 0.63$ K and $\delta T_2 = 1.04$ K, which proved to be considerably less than those determined in the preliminary investigations using a differential scanning microcalorimeter. Undeniably, such a large difference in the magnitudes of δT_i is associated with the different degrees of the equilibrium state achieved under the conditions used in the measurements. In the same experiments, we determined the magnitudes of the enthalpy jumps (latent heats of transformations) $\delta H_1 = 710$ J/mol and $\delta H_2 = 480$ J/mol and the entropy jumps $\delta S_1 = \delta H_1/T_1 = 2.8$ J/(mol K) and $\delta S_2 = \delta H_2/T_2 = 2.2$ J/(mol K).

4. PHASE DIAGRAM AND PERMITTIVITY

The influence on the hydrostatic pressure on the temperatures and the sequence of the phase transitions in the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride was investigated

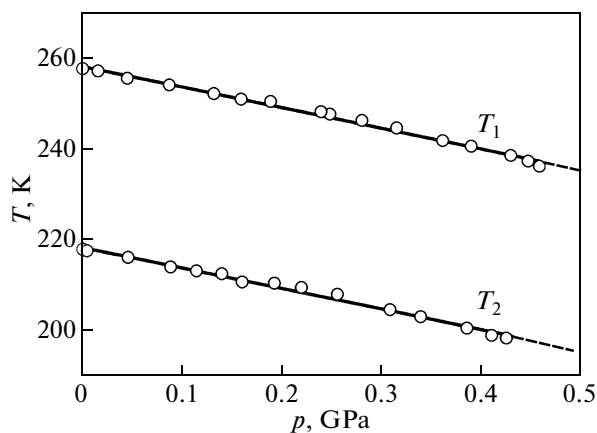


Fig. 3. Pressure dependences of the phase transition temperatures of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride.

using the differential thermal analysis under pressure. A sensitive element of the differential thermocouple consisted of copper–germanium–copper electrodes connected in series. A single-crystal sample was cemented to one thermoelectric junction of this thermocouple, and a quartz reference sample was cemented to the other junction. The system thus mounted was placed in a cylinder–piston-type chamber connected to a multiplier. This made it possible to perform measurements up to a pressure as high as ~ 0.5 GPa. A transformer oil was used as the pressure-transferring medium. The pressure in the chamber was measured on a manganin resistance pressure gauge, and the temperature of the sample under investigation was measured using a copper–constantan thermocouple. The errors in these measurements were equal to $\pm 10^{-3}$ GPa and ± 0.3 K, respectively. The reliability of the experimental results was confirmed by the coincidence of the positions of the phase boundaries in the pressure–temperature phase diagram determined with an increase and a decrease in the pressure.

The pressure–temperature phase diagram constructed using experimental data on the shift in the phase transition temperatures under hydrostatic pressure is depicted in Fig. 3. As the pressure increases, the temperatures of both transitions decrease almost linearly at the same rate. In this case, the pressure coefficients are found to be as follows: $dT_1/dp = -45.4 \pm 1.5$ K/GPa and $dT_2/dp = -45.2 \pm 1.5$ K/GPa; i.e., they prove to be equal to each other within the limits of their determination. Thus, the intermediate phase C2, for which the temperature range of the existence under pressure remains unchanged, appears to be less susceptible to external actions.

The negative sign of the pressure coefficients indicates that the volume of the $(\text{NH}_4)_2\text{NbOF}_5$ phase decreases upon the structural phase transitions $Cmc2_1 \rightarrow C2 \rightarrow Ia$ during heating. Since the quan-

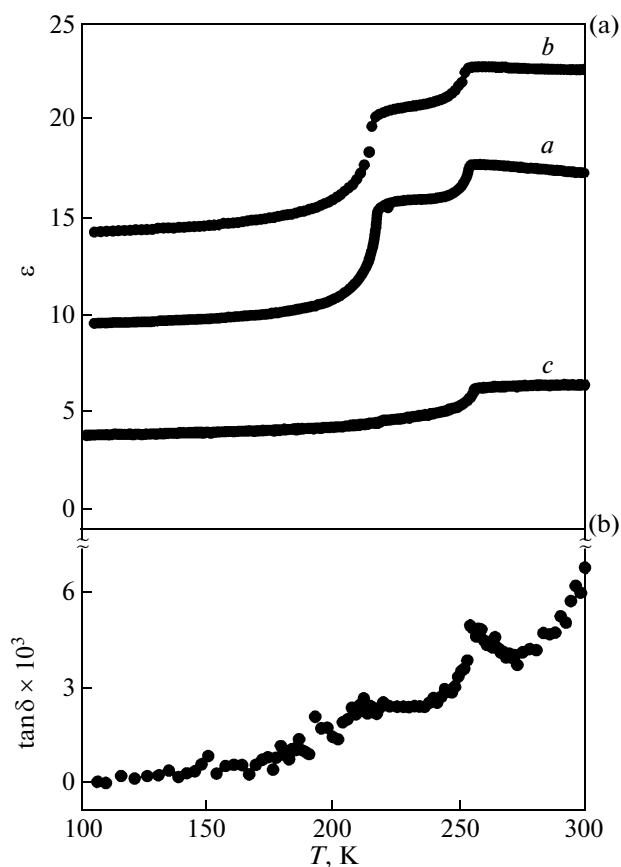


Fig. 4. Temperature dependences of (a) the permittivity ϵ of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride measured along the directions parallel to the (a) (100), (b) (010), and (c) (001) planes and (b) the dielectric loss tangent $\tan \delta$ measured along the a direction.

ties δS_i and dT_i/dp are close to each other, the relative changes of the volume $\delta V/V$ are also approximately identical in accordance with the Clausius–Clapeyron relationship $dT/dp = (\delta V/V)\delta S^{-1}$.

For the permittivity measurements, the samples were prepared in the form of single-crystal plates (~ 1 mm thick) cut out parallel to the (100), (010), and (001) planes of the $(\text{NH}_4)_2\text{NbOF}_5$ crystal. Copper electrodes were deposited on the samples through vacuum evaporation. The temperature dependences of the permittivity and the dielectric loss tangent were measured on an E7-20 immittance meter at a frequency of 1 kHz in the temperature range from 100 to 300 K during heating and cooling at a rate of ~ 1 K/min. Figure 4 presents the relevant experimental data that correspond to the heating regime.

The anomalous behavior of the dependence $\epsilon(T)$ in the form of a stepwise increase observed at the phase transition temperatures most clearly manifests itself along the a and b axes (Fig. 4a). The permittivity ϵ undergoes considerably less pronounced changes along the c axis at the temperature T_1 and exhibits only

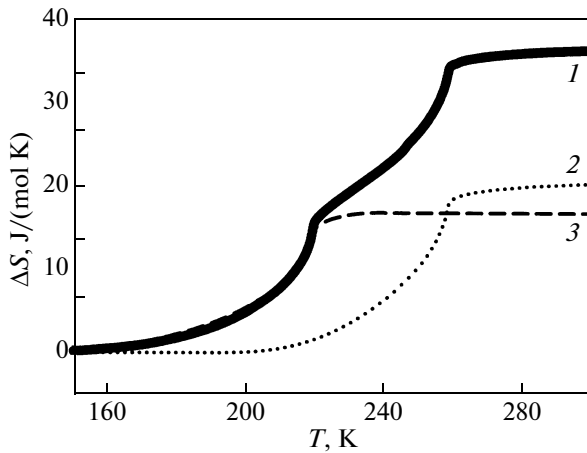


Fig. 5. Temperature dependences of (1) the total anomalous entropy change $\sum \Delta S_i$ and (2, 3) its constituent contributions (2) ΔS_1 and (3) ΔS_2 due to the phase transitions at the temperatures T_1 and T_2 .

an insignificant kink at the temperature T_2 . The anomalies of the dielectric loss tangent in the temperature range of the phase transitions are substantially weaker, as can be clearly seen from Fig. 4b, which shows the temperature dependence of the dielectric loss tangent $\tan \delta(T)$ along the a direction.

5. ANALYSIS AND DISCUSSION OF THE RESULTS

Thus, as it has been frequently observed in ammonium-containing oxyfluorides with different symmetries of the crystal lattice and the fluorine–oxygen anion [2–6], the $(\text{NH}_4)_2\text{NbOF}_5$ niobate, unlike the related compounds with monoatomic cations [8–10], undergoes phase transitions. The results obtained from the permittivity investigations indicate that the structural transformations observed upon the phase transitions have a nonferroelectric nature. Actually, the changes revealed in the permittivity at the temperatures T_1 and T_2 are equal to only a few unities, whereas, for example, the antiferroelectric transition between two orthorhombic phases in the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ oxyfluoride is accompanied by a change in the permittivity along the a and c axes by a factor of three. In order to answer the question as to whether the structural transformations observed in the niobate have a ferroelastic nature, it is necessary to perform investigations using a light-polarizing microscope.

The analysis of the mechanism responsible for the structural distortions occurring in the crystal due to the phase transition and the proper choice of an optimum model describing atomic displacements and ionic rotations require the knowledge of detailed data

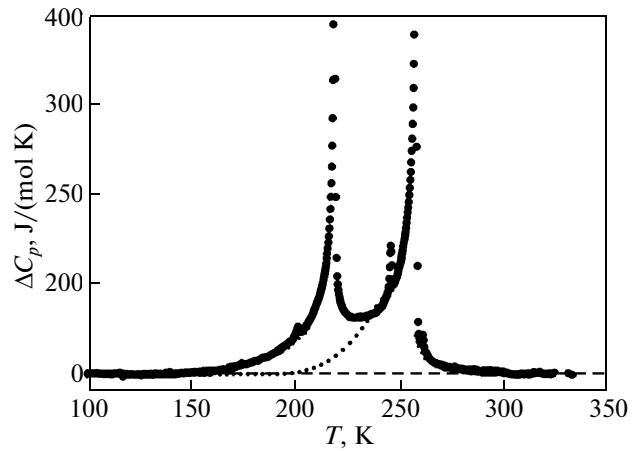


Fig. 6. Temperature dependence of the anomalous heat capacity due to the phase transitions in the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride. The dashed line represents the results of the extrapolation of the heat capacity ΔC_p due to the $Cm2_1 \rightarrow C2$ phase transition.

on the corresponding entropy change and the structure of the initial and distorted phases.

The total entropy change due to the sequential phase transitions is presented in Fig. 5; at saturation, it is determined to be $\sum \Delta S_i = \int (\Delta C_p/T) dT = 37.2 \pm 1.9$ J/(mol K). In order to determine the contributions to the total entropy change from each of the phase transitions, it is necessary to separate the corresponding contributions to the heat capacity.

A priori reasoning for using a specific physical model describing the dependences $\Delta C_p(T)$ for each of the distorted phases of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride is lacking. Therefore, the integral characteristics corresponding to each of the structural transformations are separated using the following approach. We cannot rule out that a particular parameter (or a component of a parameter) of the structural transition, which appears at the temperature T_1 , can reach saturation both in the intermediate phase and at a temperature $T < T_2$. Therefore, the extrapolation of the excess heat capacity, which is related to this parameter of the phase transition and observed in the $C2$ phase near the temperature T_1 , to the region of the overlap of the anomalies and/or to the region of the existence of the low-temperature phase Ia was performed using the method of smoothing splines by varying the temperature of vanishing of the excess heat capacity ΔC_p (or the temperature of saturation of the transition parameter) over wide ranges. Figure 6 shows the temperature dependence of the excess heat capacity, in which the dotted line corresponds to the averaged results of the extrapolation.

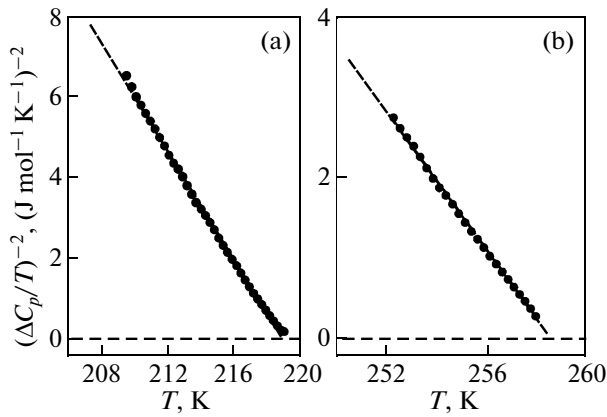


Fig. 7. Thermal behavior of the anomalous heat capacity of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride according to relationship (1) at temperatures (a) $T < T_2$ and (b) $T < T_1$.

Within this approach, including a certain arbitrariness in the choice of the temperature at which the excess heat capacity vanishes ($\Delta C_p \rightarrow 0$) for the $Cmc2_1 \rightarrow C2$ phase transition, the entropies for each of the sequential phase transformations are characterized by a larger relative error of their determination as compared to the total entropy change $\sum \Delta S_i$ and amount to $\Delta S_1 = 21.6 \pm 2.1$ J/(mol K) and $\Delta S_2 = 16.6 \pm 1.6$ J/(mol K), respectively (Fig. 5). Such large values of ΔS_i conclusively confirm that the aforementioned two structural distortions in the $(\text{NH}_4)_2\text{NbOF}_5$ crystal are associated with the processes of ordering of the structural elements.

Since the phase transitions under consideration are structural (and, quite possibly, ferroelastic) transformations, the behavior of the physical properties of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride can correspond to that predicted from the phenomenological Landau theory. One of the consequences from the analysis of the thermodynamic potential $\Delta\Phi(p, T, \eta) = [A_T(T_i - T_C) + A_T(T - T_i)]\eta^2 + B\eta^4 + C\eta^6$ indicates that the quantity $(\Delta C_p/T)^{-2}$ linearly depends on the temperature [13]:

$$\left(\frac{\Delta C_p}{T}\right)^{-2} = \frac{2\sqrt{B^2 - 3A_T(T_i - T_C)C}}{A_T^2} + \frac{12C}{A_T^3} + (T_i - T). \quad (1)$$

The temperature dependence of the square of the inverse excess heat capacity of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride in the $C2$ and Ia phases is shown in Fig. 7. It is evident from this figure that relationship (1) satisfactorily describes the experimental results over rather wide temperature ranges of the existence of the two distorted phases. This indirectly proves that the approach proposed in the present study to the separa-

tion of the anomalous heat capacities for different phase transitions is fairly justified. The ratios between the coefficients of the potential are as follows: $A_T^3/C = 25.4$ J² mol⁻² K⁻³ and $A_T^2/B = -2.3$ J mol K⁻² for the $Cmc2_1 \rightarrow C2$ phase transition and $A_T^3/C = 18.1$ J² mol⁻² K⁻³ and $A_T^2/B = -5.2$ J mol K⁻² for the $C2 \rightarrow Ia$ phase transition. The quantity $N = \pm\sqrt{B^2/3A_TCT_C}$ characterizes the degree of closeness of the phase transition to the tricritical point. The Curie temperature T_C is related to the phase transition temperature T_i through the expression $T_C = T_i - B^2/(4A_T C)$. The values of $N_1 = -0.077$ and $N_2 = -0.033$ calculated for the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride unambiguously indicate that both transitions, even though exhibit obvious indications of first-order phase transitions ($\delta T_i \neq 0$, $\delta S_i \neq 0$), are very close to the tricritical point. This is also evidenced by two circumstances. First, these are small contributions from the entropy jumps to the total entropy change due to the phase transitions, i.e., $\delta S_1/\Delta S_1 = 0.13$ and $\delta S_2/\Delta S_2 = 0.13$. Second, these are small differences between the phase transition temperatures and the temperatures of vanishing of the quantity $(\Delta C_p/T)^{-2}$, which are equal to 0.39 and 0.06 K for the temperatures T_1 and T_2 , respectively.

In the refinement of the structure of the high-temperature phase of the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride, Udovenko and Laptash [12] considered several possible space groups, in particular, the space group $Cmcm$, which was proposed earlier for the related oxyfluorides with a hexavalent central atom, i.e., $(\text{NH}_4)_2\text{MeO}_2\text{F}_4$ [5, 7]. The choice of a different space group ($Cmc2_1$) for the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride was motivated by a smaller (even though, insignificantly) value of the reliability factor R as compared to that for the space group $Cmcm$, as well as by more reliable values of the Nb–F(O) distances [12]. One of the main arguments for choosing the structure of the intermediate phase (space group $C2$) is that the initial lowest-temperature phase (space group Ia) is noncentrosymmetric. It is worth noting that the space groups chosen for all phases in [12] are not connected by the group–subgroup relationship. This means that, for the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride, there can also exist a particular high-symmetry parent phase for which the space groups $Cmc2_1$, $C2$, and Ia are the subgroups and the phase transitions $Cmc2_1 \rightarrow C2 \rightarrow Ia$ are possible only in the form of first-order transformations. The above analysis of the heat capacity has demonstrated that the $(\text{NH}_4)_2\text{NbOF}_5$ compound actually undergoes two first-order phase transitions but in the immediate vicinity of the tricritical point.

In [12], it was established that the structural elements in the Ia phase are completely ordered, which leads to the formation of several types of crystallographically nonequivalent $[\text{NbOF}_5]$ quasi-octahedra and $[\text{NH}_4]$ tetrahedra. By using detailed data on the coordinates of all atoms in the Ia phase, we will analyze a possible sequential disordering of the aforementioned polyhedra with a change in the symmetry as a result of the phase transitions and the corresponding entropy change due to these processes.

Two types of quasi-octahedra, which are rotated in the low-temperature phase at a small angle with respect to each other, become identical in the intermediate phase. Therefore, it can be assumed that, upon the phase transition to the $C2$ phase, the quasi-octahedron is dynamically disordered over just these two positions. During this phase transition, the number of types of nonequivalent tetrahedra decreases from four to two. Making allowance for the fact that the primitive cell contains two ammonium cations, the disordering of two types of polyhedra due to the symmetry change $Ia \rightarrow C2$ should lead to the entropy change $R\ln 2 + 2R\ln 2 = R\ln 8 = 17.3 \text{ J}/(\text{mol K})$.

During the $C2 \rightarrow Cmc2_1$ phase transition, the number of orientations of the quasi-octahedron increases by a factor of three. This is accompanied by a disordering of both types of nonequivalent tetrahedra with the simultaneous increase in the number of orientations of each polyhedron by a factor of no more than two. Therefore, the entropy change due to the phase transition under consideration should be as follows: $R\ln 3 + 2R\ln 2 = R\ln 12 = 20.7 \text{ J}/(\text{mol K})$.

The reliability of the above reasoning is confirmed by the fact that both entropies of the phase transitions are in satisfactory agreement with the experimentally determined values of $\Delta S_1 = 21.6 \pm 2.1 \text{ J}/(\text{mol K})$ and $\Delta S_2 = 16.6 \pm 1.6 \text{ J}/(\text{mol K})$.

The proposed model of ordering of structural elements in the $(\text{NH}_4)_2\text{NbOF}_5$ crystal, of course, needs to be refined in detailed structural investigations, for example, using neutron scattering methods.

It should be noted that the composition of the fluorine–oxygen anion substantially affects the degree of disordering of the quasi-octahedron and the ammonium tetrahedra in the orthorhombic structure. This circumstance most clearly manifests itself in a comparison of the entropies of the phase transitions in the oxyfluorides $(\text{NH}_4)_2\text{NbOF}_5$ and $(\text{NH}_4)_2\text{MeO}_2\text{F}_4$ ($Me = \text{W}, \text{Mo}$) [4, 6]. In the latter compounds, the phase transition from the initial orthorhombic phase is also associated with the ordering processes and the entropy change $\Delta S_1 \approx R\ln 9$ is close to the entropy determined in the present work for the niobate. However, the low-temperature phase transition in the tungstate and molybdate, unlike the phase transition in the niobate, is accompanied by insignificant entropy changes and represents a displacive transformation.

The related structural changes, most likely, are so small that this transition is not revealed by X-ray diffraction investigations [5, 7].

6. CONCLUSIONS

The above investigations of the heat capacity, permittivity, and susceptibility with respect to high pressures have revealed that the $(\text{NH}_4)_2\text{NbOF}_5$ oxyfluoride undergoes two phase transitions of the nonferroelectric nature. The entropy changes observed upon sequential structural transformations have clearly demonstrated that they are associated with the order–disorder processes. A combined analysis of the structure of the $(\text{NH}_4)_2\text{NbOF}_5$ compound and the calorimetric data has made it possible to construct a model describing the ordering processes due to the phase transitions.

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