LATTICE DYNAMICS
AND PHASE TRANSITIONS

Thermophysical Studies of the Phase Transitions in $(NH_4)_3NbOF_6$ Crystals

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Abstract—The thermophysical properties of oxyfluoride $(NH_4)_3NbOF_6$ were studied in detail over wide ranges of temperatures and pressures. At atmospheric pressure, a sequence of four structural phase transitions was established with the following changes in entropy: $\Delta S_1 = R \ln 2.7$, $\Delta S_2 = R \ln 38.3$, $\Delta S_3 = 0.08R$, and $\Delta S_4 = 0.17R$. An external hydrostatic pressure was found to narrow the region of existence of the initial cubic phase. A triple point was detected in the p–T diagram; at a pressure above 0.07 GPa, the transition between the tetragonal and monoclinic phases occurs through a distorted high-pressure phase.

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1. INTRODUCTION

Oxyfluoride compounds with six-coordinated anions and with the general formula $A_2A'MO_xF_{6-x}$ ($x = 1, 2, 3$) in the initial high-temperature phase are characterized with the cubic elpasolite structure $Fm\bar{3}m$ ($z = 4$) formed by quasi-octahedral anions $A'O_xF_{6-x}$ and MO_xF_{6-x} [1]. Recent studies of the physical properties of the oxyfluorides with $x = 1$ and 3 have revealed ferroelastic and ferroelectric phase transitions in them [2–4]. The mechanism of the structural distortions has been discussed in terms of the entropy of the phase transformations and the structural characteristics (electron density distribution, thermal parameters of atoms) [5, 6].

Studying the structure of $(NH_4)_3ZrF_7$ [7] and $(NH_4)_3Ti(O_2)F_5$ [8, 9] crystals has shown that the cubic symmetry $Fm\bar{3}m$ of the crystal lattice in the compounds with seven-coordinated anions can likewise be preserved due to statistical disordering of the anions. The anion in this case can be either a pentagonal bipyramid [7, 8] or a quasi-octahedron [9] at whose apex there is a pair of closely spaced ligands, which are necessarily disordered and occupy the position $96k$ or $96j$.

The thermophysical investigations in [6] revealed that the presence of an "oxygen dumbbell" among the ligands in $(NH_4)_3Ti(O_2)F_5$ significantly decreases the entropy of the phase transition from the cubic phase in comparison with that in $(NH_4)_3TiOF_5$, which is strong

evidence of a lower degree of disordering of this building block.

As for the other oxyfluorides with seven-coordinated anions, the K_3NbOF_6 and $(NH_4)_3NbOF_6$ compounds have also been found to have the cubic $Fm\bar{3}m$ structure [10–12]. At present, no data are available in the literature on the stability of niobates to external influences, such as temperature and pressure.

In this work, the thermodynamic properties and structural parameters of the $(NH_4)_3NbOF_6$ compound were studied in order to investigate possible loss of stability of the cubic structure containing the seven-coordinated polyhedron OF_6.

2. SAMPLE SYNTHESIS AND THE SEARCH FOR PHASE TRANSITIONS

Samples of the $(NH_4)_3NbOF_6$ compound were obtained by slow evaporation in air of a solution of niobium pentoxide in concentrated HF with addition of a large excess (no less than 200%) of a concentrated (40%) NH_4F solution. As a result, we obtained small single crystals of the octahedral form with an octahedron edge of about 500 µm.

Using an x-ray powder diffractometer, we established that the compound obtained possesses a cubic structure at room temperature. The unit cell parameter $a_0 = 9.326$ Å is close to that reported in [11] ($a_0 = 9.31$ Å).

Preliminary heat capacity studies of $(NH_4)_3NbOF_6$ for detecting phase transitions were performed on a DSM-2M differential scanning microcalorimeter in the temperature range 110–340 K in the heating and cooling modes at a rate of 8 K/min. The sample mass was 0.14 g.

The measurements in the heating mode revealed an anomaly in the heat capacity (Fig. 1) in the form of a peak with a maximum at a temperature $T_1 = 258.6 \pm 1.0$ K. On cooling, this anomaly splits into two anomalies at temperatures $T_1 = 251 \pm 1$ K and $T_2 = 245.8 \pm 1.0$ K. The reproducibility of the results of repeated thermocycling suggests that the compound under study undergoes a sequence of two phase transitions. The fact that the second heat capacity anomaly is not observed on heating can be explained by a difference in the thermal hysteresis of the transitions. The existence of thermal hysteresis shows that the oxyfluoride under study undergoes first-order phase transitions.

The measurement results were used to determine the integrated characteristics of the phase transitions, namely, the excess enthalpy $\sigma\Delta H = 5600 \pm 400$ J/mol and the change in entropy $\Sigma\Delta S = 22.0 \pm 1.4$ J/mol K. Since we failed to separate the contributions from the different transitions, we only present the total values for the two sequential transitions. However, the observed large change in entropy is undeniably a result of ordering processes that occur during structural distortions.

The existence of the sequence of the two structural phase transitions in a narrow temperature range near 260 K was confirmed by polarization-optical measurements, which revealed that these transitions are accompanied by crystal twinning and the following changes in symmetry: cubic ⟷ tetragonal ⟷ monoclinic.

Structural studies were carried out using a DRON-2 x-ray powder diffractometer. We did not observe any noticeable differences between the x-ray diffraction patterns of the cubic and distorted phases. The phase transitions were detected only when studying the temperature dependence of the unit cell parameter (Fig. 2); this parameter exhibits an anomalously rapid decrease over the range from 261 to 242 K. We also observed a stepwise decrease in $a(T)$ over the temperature range 180–210 K. However, the DSM measurements over this temperature range did not reveal any specific features of the heat capacity to within the accuracy of this method.

3. THE HEAT CAPACITY AND THE p–T PHASE DIAGRAM

To refine the thermodynamic parameters of the phase transitions in $(NH_4)_3NbOF_6$, we studied in detail the heat capacity of this compound using the adiabatic-calorimeter method, which has a higher sensitivity to small thermal effects than the DSM method does. A sample 0.49 g in mass was hermetically sealed in an indium container in a helium atmosphere. The mea-
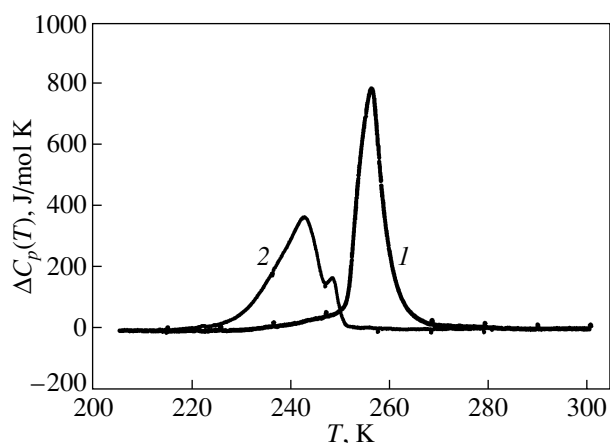

Fig. 1. Temperature dependence of the excess specific heat of the $(NH_4)_3NbOF_6$ compound obtained by the DSM method under (*1*) heating and (*2*) cooling.

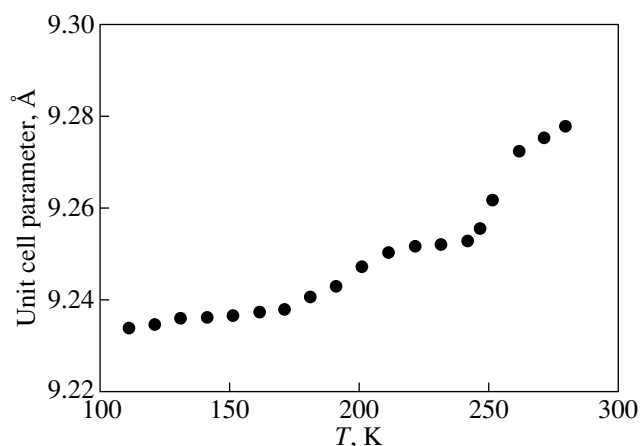**Fig. 2.** Temperature dependence of the unit cell parameter of $(NH_4)_3NbOF_6$.

surements were carried out under discrete ($\Delta T = 2.5$–4.0 K) and continuous ($dT/dt = 0.14$ K/min) heating. The temperature was measured using a platinum resistance thermometer.

Figure 3 shows the specific heat of $(NH_4)_3NbOF_6$ measured over a wide temperature range. The relatively large spread of the experimental points is due to the small contribution of the sample heat capacity to the total heat capacity of the sample–furniture system under study. Nevertheless, it is seen that, in addition to the heat capacity anomalies revealed in the DSM measurements, there are two additional anomalies of $C_p(T)$ in a low-temperature range (Fig. 3a). Since the rate of change in temperature in the adiabatic-calorimeter experiments was significantly lower then that in the DSM measurements, the splitting of the heat capacity anomalies in the narrow temperature range corresponding to the sequence of two phase transitions was
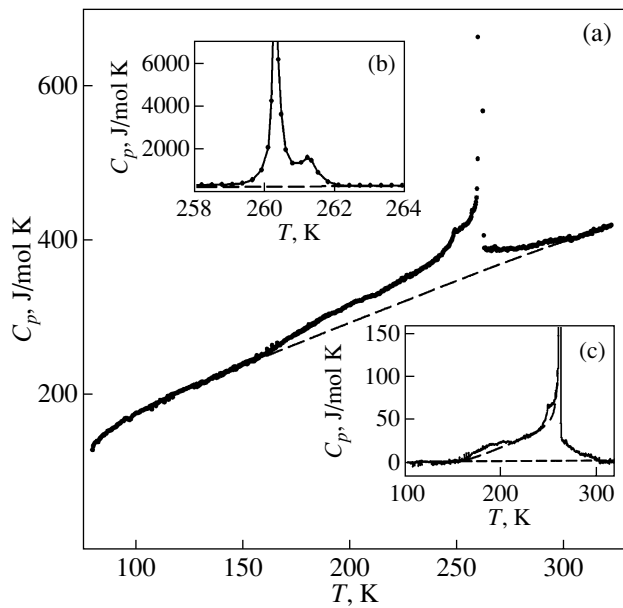
Fig. 3. (a, b) Molar heat capacity of the $(NH_4)_3NbOF_6$ compound measured (a) in a wide temperature range and (b) in the vicinity of the phase transitions at T_1 and T_2 and (c) the excess heat capacity obtained by adiabatic calorimetry.
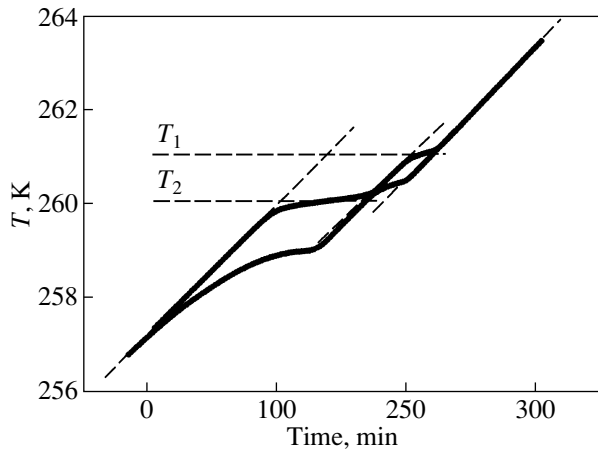
Fig. 4. Thermogram of the oxyfluoride $(NH_4)_3NbOF_6$.

observed even under heating (Fig. 3b). The refined phase transition temperatures are $T_1 = 261.09 \pm 0.03$ K, $T_2 = 260.08 \pm 0.03$ K, $T_3 = 248.6 \pm 0.5$ K, and $T_4 = 188 \pm 1$ K. From comparing these data with the measured $a(T)$ dependence, it follows that a significant change in the unit cell parameter over the temperature range 261–242 K (Fig. 2) is related to the sequence of the phase transitions at T_1, T_2, and T_3. The heat capacity anomaly at T_4 lies in the temperature range in which the anomalous behavior of the unit cell parameter $a(T)$ was detected.

The dashed line in Fig. 3a shows the lattice heat capacity determined by fitting the experimental $C_p(T)$ data to a polynomial outside the region of the anomalous behavior. The excess heat capacity $\Delta C_p(T)$ was obtained by subtracting the regular contribution from the total heat capacity, and its temperature dependence is shown in Fig. 3c. It is seen that $\Delta C_p(T)$ exists over a sufficiently wide temperature range, $\sim(160–300)$ K.

The changes in enthalpy on the phase transitions were determined by integrating the function $\Delta C_p(T)$. The total enthalpy associated with the sequence of the four phase transitions is $\Sigma \Delta H_i = 10\,170 \pm 500$ J/mol and is significantly larger than that determined from the DSM measurements. To determine the changes in enthalpy associated with each of the transitions at T_3 and T_4, we used the same approach as that in [13]; namely, the excess heat capacity below T_2, excluding the regions of the two transitions, was fitted by a polynomial (dashed line in Fig. 3c). The changes in enthalpy are found to be $\Delta H_3 = 160 \pm 25$ J/mol and $\Delta H_4 = 260 \pm 40$ J/mol.

With this method, we failed to reliably separate the contributions to the excess enthalpy coming from the transitions at T_1 and T_2. However, it is seen from Fig. 3b that the main contribution is due to the phase transformation at T_2.

The temperature range near T_1 and T_2 was studied using the quasistatic thermogram method under heating and cooling at a rate of $|dT/dt| = 0.03$ K/min. It is seen from Fig. 4 that both the structural transformations are accompanied by absorption (release) of a latent heat, as follows from the very small values of the derivative dT/dt observed at the phase transition points over a certain period of time. This fact, as well as the observation of thermal hysteresis of the phase transitions ($\delta T_1 = 0.65$ K, $\delta T_2 = 1.10$ K; Fig. 4), confirms that both the transitions are of first order. Using the results of the studies, we determined the latent heats for both the transitions. Since the power released in the heater of the sample–furniture system was constant, the latent heat absorbed by the sample during a phase transition is determined by the product of the power by the time of its absorption in the isobaric–isothermal process. In our crystal, as in all real samples, the latent heat spreads over a certain temperature range due to the crystal imperfection. To determine the time of the latent-heat absorption, the linear portions of the thermograms are extrapolated to the corresponding transition temperatures (dashed lines in Fig. 4). Using this method, we found that $\delta H_1 = 780 \pm 80$ J/mol and $\delta H_2 = 3300 \pm 160$ J/mol.

The effect of a hydrostatic pressure on the temperatures and sequence of the phase transitions in $(NH_4)_3NbOF_6$ was studied using differential thermal analysis (DTA) under pressure. The experimental technique was analogous to that described in [4]. At atmospheric pressure, we recorded two anomalies of the
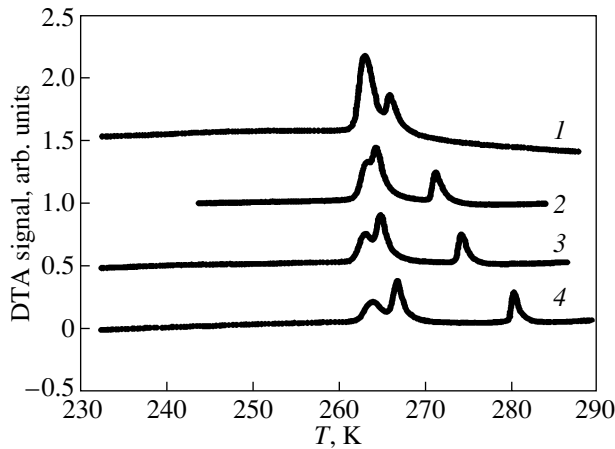
Fig. 5. Temperature dependence of the DTA signal at pressures of (*1*) 0.06, (*2*) 0.18, (*3*) 0.26, and (*4*) 0.32 GPa.

Fig. 6. p–T phase diagram of $(NH_4)_3NbOF_6$.

DTA signal corresponding to the phase transitions at $T_1 = 261 \pm 1$ K and $T_2 = 260 \pm 1$ K. No anomalies were observed at T_3 and T_4, which is likely due to the lower sensitivity of this method as compared with that of the adiabatic calorimeter method.

As the pressure increases, the temperature of the transition from the cubic phase increases rapidly and the anomaly near T_2 splits into two anomalies (Fig. 5), which corresponds to the triple point in the phase diagram (Fig. 6). The triple-point parameters are found to be $p_{tr} = 0.07 \pm 0.01$ GPa and $T_{tr} = 261.5 \pm 2.0$ K. Thus, we established that, at pressures above p_{tr}, the compound under study has a pressure-induced intermediate distorted phase ($G1'$); i.e., the transition between the tetragonal ($G1$) and the monoclinic ($G2$) phases may occur in steps. All the phase boundaries are nonlinear and can be described by the following equations: $T_{G0-G1} = 261 + 54p - 15p^2$, $T_{G1-G2} = 260.7 + 16p - 77p^2$, $T_{G1-G1'} = 260.3 + 19p - 27p^2$, and $T_{G1'-G2} = 261.3 + 6p - 20p^2$. The reliability of the obtained data is supported by the reproducibility of the position of the phase boundaries in the phase diagram under increasing and decreasing pressures.

4. DISCUSSION

One of the parameters characterizing the mechanisms of phase transitions is the change in entropy due to the transitions, which is determined by integrating the function $\Delta C_p(T)/T$ over temperature. The entropy values corresponding to the structural distortions at T_3 and T_4 are found to be $\Delta S_3 = 0.7 \pm 0.1$ J/mol K and $\Delta S_4 = 1.4 \pm 0.2$ J/mol K, respectively. These small values indicate that the phase transitions are displacive, i.e., that ordering processes do not occur in the structure at these temperatures.
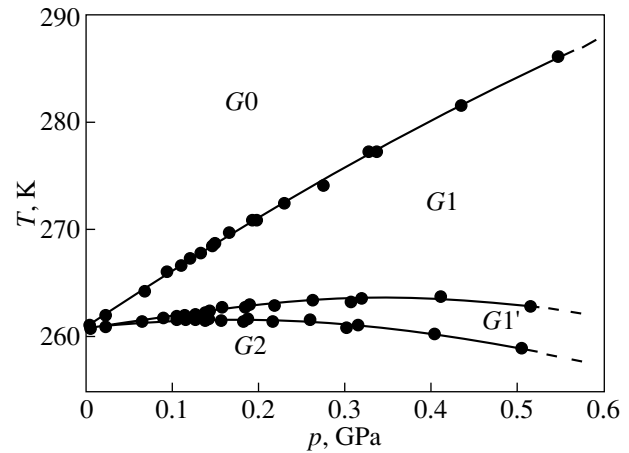
Since we failed to separate the anomalies associated with the phase transitions at T_1 and T_2 even using the adiabatic calorimeter method, we determined the entropies of the structural distortions from the DTA data obtained under pressure. As the pressure increases, the temperature of the first phase transition increases more rapidly. As a result, the heat capacity anomalies corresponding to the different phase transitions are completely separated at pressures above 0.3 GPa. Since the DTA signal is proportional to the heat capacity of the compound under study, the changes in entropy at T_1 and T_2 can be calculated using the adiabatic calorimetry data. The result is $\Delta S_1 = 8.5 \pm 0.9$ J/mol K ($R \ln 2.7$) and $\Delta S_2 = 30.3 \pm 3.0$ J/mol K ($R \ln 38.3$). The latter quantity can be represented as the sum of the entropies of the sequential phase transitions under pressure, $\Delta S_{G1 \to G1'} + \Delta S_{G1' \to G2} \approx R(\ln 3.3 + \ln 11.1)$. Thus, it is evident that the maximum contribution to the entropy of the structural transitions from the cubic to monoclinic lattice is due to the loss of the symmetry elements corresponding to the tetragonal phase.

As mentioned above, the cubic phase of the $(NH_4)_3NbOF_6$ crystal belongs to space group $Fm\bar{3}m$. Thus, it is of interest to compare the phase transition entropies obtained in this work with the data on elpasolite oxyfluorides with six- and seven-coordinated anions. The only phase transition occurring in $(NH_4)_3NbOF_6$ has an entropy close to $R\ln 3$ [6]. This transition was associated with the rotation of the quasi-octahedra by small angles (shifts of the F(O) ligands) resulting in ordering of the tetrahedra in interoctahedral voids (position $8c$), which were disordered in the $Fm\bar{3}m$ phase over three positions.

However, up to now, large entropies such as ΔS_2 for $(NH_4)_3NbOF_6$ have not been observed in oxyfluorides. The maximum value $(NH_4)_3TiOF_5 - \Sigma \Delta S_i = R\ln 24$ has been observed for the phase transitions from the

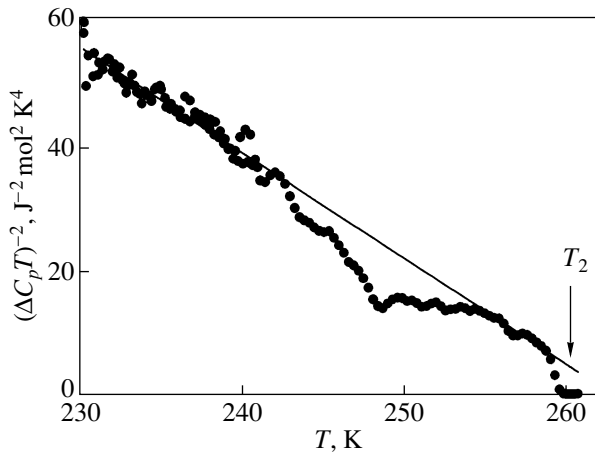**Fig. 7.** Temperature dependence of the reciprocal of the excess specific heat squared of $(NH_4)_3NbOF_6$ below T_2.

$Fm\bar{3}m$ phase in $(NH_4)_3TiOF_5$ under pressure [4]. The observation in the optical experiments of the tetragonal phase in $(NH_4)_3NbOF_6$ between the temperatures T_1 and T_2 does not exclude the possibility that the cubic structure of this crystal also belongs to space group $Fm\bar{3}m$. Then, based on the analysis of the possible versions of ordering of this structure, for which the maximum entropy is $R\ln 432$ [5], we may assume that the tetrahedral ionic groups occupying the positions $8c$ and $4b$ make a significant contribution to the entropy ΔS_2 of $(NH_4)_3NbOF_6$.

The calorimetric studies showed that both the phase transitions are of first order. The degree of proximity of the transitions to the tricritical point can be estimated from the ratio of the change in entropy at the transition point to the total change in entropy, $\delta S_i/\Delta S_i$. The values of this ratio for the transitions at T_1 and T_2 are found to be close, namely, 0.35 and 0.42, respectively.

The fairly small thermal hysteresis and the small ratios of the entropies demonstrate that both the phase transitions are close to the tricritical point. It is of interest to use the Landau thermodynamic theory to describe the heat capacity of the compound under study. We were able to analyze the behavior of the heat capacity for the transition at the temperature T_2 only. As is seen from Fig. 7, the temperature dependence of the reciprocal of the square of the excess heat capacity $(\Delta C_p/T)^{-2}$ obeys a linear law, in accordance with Eq. (1) from [13], at temperatures significantly below T_2. The only exclusion is the temperature range 243–255 K, over which the anomalous behavior of the heat capacity is observed near T_3. The fact that the excess heat capacity below T_2 and T_3 is described by a single equation indicates that this quantity is associated with the phase transition at T_2 and that our approach to determining the value of ΔH_3 is valid.

Using the data from Fig. 7, we find that the degree of proximity of the phase transition to the tricritical point is characterized by the quantity $N = \pm\sqrt{B^2/3A_TCT_C} = -0.21$, where $T_C = T_0 - B^2/4A_TC$ is the Curie temperature [5].

5. CONCLUSIONS

We have performed detailed studies of the thermal properties of the $(NH_4)_3NbOF_6$ crystal and established that this compound with cubic symmetry at room temperature undergoes four sequential phase transitions under cooling. These transitions differ significantly in terms of entropy. The anomalously large contribution to the entropy of the total structural distortion is due to the phase transition from the tetragonal phase both at atmospheric pressure and at a pressure higher than p_{tr}. This fact, in combination with the absence of differences between the diffraction patterns of the cubic and distorted phases, demonstrates that the tetrahedral ammonium ionic groups most likely play a significant role in the mechanism of the structural distortion. A hydrostatic pressure has been found to widen the temperature ranges of stability of the tetragonal and pressure-induced phases.

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