

LATTICE DYNAMICS
AND PHASE TRANSITIONS

Calorimetric and Dielectric Studies
of the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ Oxyfluoride

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Abstract—The temperature dependences of the heat capacity, dielectric properties, and response to an external pressure and an electric field for the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ oxyfluoride (space group *Cmcm*, $Z = 4$) have been studied. A comparative analysis of the data on the entropy of phase transitions, p – T phase diagrams, permittivity, and anomalous heat capacity in combination with the results of previous studies of the related compounds $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ and $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ has made it possible to establish that both $[\text{MO}_2\text{F}_4]^{2-}$ anions and ammonium groups play a substantial role in the mechanism and nature of the structural transformations.

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1. INTRODUCTION

One of the actively developed directions in the study of oxyfluorides is associated with the area in which interests of solid state chemistry, solid state physics, and materials science intersect each other. The eccentricity of fluorine–oxygen sixfold-coordinated anions due to the displacement of a metal atom from the center of an octahedron toward oxygen ligands can be responsible for the existence of the polar phase in the initial state of the crystal or the appearance of this phase with a change in external parameters, such as the temperature and pressure. Therefore, among oxyfluorides, there should exist many compounds promising from the standpoint of manifestation of piezoelectric, ferroelectric, and nonlinear optical properties. It is evident that both statistical ligand disordering, which leads to the appearance of the internal center of symmetry in a sixfold-coordinated anion, and the center of symmetry of the crystal lattice as a whole should be absent in these materials.

Extensive studies have been devoted to the search for modes of the ligand ordering that favors the appearance of polar phases in fluorine–oxygen materials, which contain, in particular, $[\text{MO}_2\text{F}_4]^{2-}$ ($M = \text{Mo}, \text{W}$) anions. It was revealed that the O(F) ligands in the crystal lattice of $A_2\text{MO}_2\text{F}_4$ compounds can be ordered ($\text{Na}_2\text{WO}_2\text{F}_4$ [1], $\text{K}_2\text{MoO}_2\text{F}_4$ [2]) and partially ($\text{Rb}_2\text{MoO}_2\text{F}_4$ [3]) or completely ($\text{Cs}_2\text{WO}_2\text{F}_4$ [4] and $\text{Rb}_2\text{WO}_2\text{F}_4$ [5]) dynamically disordered depending on

the composition of univalent atomic cations. The possibilities of varying the character and degree of disordering of F(O) atoms in the $[\text{MO}_2\text{F}_4]^{2-}$ anion were studied for crystals with complex organic cations, such as pyridine, pyrazine, etc. [6, 7]. The cation composition also influences the symmetry of the crystal lattice of oxyfluorides [1–7].

Until recently, possible phase transitions in such oxyfluorides were not studied. Only relatively recently, the structural transformations were revealed for the first time in the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ crystal with the initial orthorhombic symmetry (space group *Cmcm*) [8, 9]. X-ray diffraction studies performed on a single-crystal diffractometer allowed one to locate only one fluorine and one oxygen atoms lying on the fourfold pseudoaxis in the initial phase [9]. Other ligands in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ appeared to be statistically disordered over four equivalent positions. Thus, the sixfold-coordinated anion, first, has a *cis* configuration and, second, exhibits a dipole moment due to the displacement of the tungsten atom from the plane of the rectangle formed by the F(O) atoms. However, the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ crystal, as a whole, is nonpolar because of the centrosymmetric structure.

Studies of the physical properties showed that the above compound undergoes a sequence of two phase transitions at the temperatures $T = 201$ K and $T_2 = 160$ K [8, 9]. It turned out that the structural distortion at T_1 is associated with the first-order transition with

the temperature hysteresis $\delta T_1 = 1.4$ K and accompanied by a significant change in the entropy ($\Delta S_1 \approx R \ln 9.8$), which indicates an ordering of some structural units as a result of the transition. The refinement of the initial structure of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ [9] revealed that the thermal parameters of all atoms are small and the possibility of disordering the atoms was not considered. It was assumed that the ordering of tetragonal ammonium groups NH_4 is the main factor determining the large entropy of the high-temperature transition. A small variation in the entropy at T_2 ($\Delta S_2 = 0.17R$) was attributed to the displacive phase transition.

The recent precise studies of the structures of the initial and distorted phases of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ allowed one to obtain new important results [5]. First, the performed analysis of competing structural models made it possible to propose the model according to which the $[\text{WO}_2\text{F}_4]$ octahedron in the $Cmcm$ phase has two independent states that differ in ordered and disordered positions of the central atom. Second, the problem of the crystal twinning in the distorted phase was overcome and it was revealed that the crystal has a triclinic symmetry with space group $P\bar{1}$ characterized by the complete ordering of the W and F(O) atoms. The hydrogen atoms were not located in both phases; however, it was assumed that, as in [9], both crystallographically nonequivalent ammonium groups are orientationally disordered in the $Cmcm$ phase.

The centrosymmetric structure below T_1 is supported by the data of the optical and dielectric measurements [8, 10]: the phase transition has a ferroelastic origin.

To elucidate the role of ammonium tetrahedra in the mechanisms of phase transitions, the calorimetric studies of the $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ crystal were carried out in our earlier work [11]. The deuteration did not significantly change the phase transition temperatures characteristic of the protonated compound ($T_1 = 200$ K, $T_2 = 162$ K) but led to the appearance of two additional small anomalies of the heat capacity at $T_1' = 267.5$ K and $T_2' = 193.5$ K. The temperature hysteresis δT_1 remained unchanged, and the transformation at T_2' turned out to be the first-order transition ($\delta T_1 = 1.5$ K). A change in the entropy due to the transition at T_1 in the deuterated compound was substantially smaller ($\Delta S_1 \approx R \ln 4.9$) [11], which undeniably demonstrates the participation of the tetrahedra in this transition, at least, in the protonated oxyfluoride. The closeness of the values of ΔS_2 for the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ and $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ crystals suggests that the mechanism of the phase transition at T_2 is the same in both compounds.

Investigations into the effect of hydrostatic pressure [9, 11] demonstrated that the rates of shift in the

temperature T_1 under pressure are almost the same for the protonated and deuterated tungsten oxyfluorides. At the same time, the $D \rightarrow H$ substitution resulted in an increase in the quantity dT_2/dp by a factor of almost 2.5. That is why the triple point, which was only assumed for $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ near 0.7 GPa, was established in the p - T phase diagram of $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ at $p_{\text{tr}} = 0.18$ GPa and $T_{\text{tr}} = 202.6$ K.

The studies of the cryolite-type oxyfluorides (space group $Fm\bar{3}m$) $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ and $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ demonstrated that the replacement of the central atom leads to substantial changes in the physical properties and nature of phase transformations [10]. The study of the role of the central cation in the structure stability, nature, and mechanism of phase transitions in the $(\text{NH}_4)_2\text{MO}_2\text{F}_4$ ($M = \text{Mo}$ and W) crystals was of particular interest. It was recently established that the $\text{Mo} \rightarrow \text{W}$ substitution does not change the symmetry (space group $Cmcm$) of the initial phase of the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ crystal and the number of phase transition as compared to the tungsten compound [12, 13]. However, it was revealed that there are a number of specific features characteristic only of the molybdate.

- (1) The phase transition temperatures are substantially higher.
- (2) According to the preliminary structural studies, the character of the statistical ligand disordering in the initial phase does not completely agree with that observed in the tungstate.
- (3) The crystal twinning is absent in the distorted phases.
- (4) The orthorhombic symmetry is retained at temperatures below T_1 and T_2 (space group $Pnma$).
- (5) A number of ligands in the distorted phases remain statistically disordered.
- (6) The traces of hydrogen atoms belonging to both ammonium tetrahedra were revealed in the electron density syntheses for the $Pnma$ phase.

In this work, with the aim of elucidating the effect of the $\text{Mo} \rightarrow \text{W}$ substitution on the mechanism and nature of the phase transitions, we studied some thermodynamic properties of the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ compound, such as the heat capacity, permittivity, and response to the hydrostatic pressure and electric field.

2. HEAT CAPACITY AND p - T PHASE DIAGRAM

Colorless transparent single crystals $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ were prepared from a solution according to the technique described in [12].

The detailed measurements of the heat capacity of the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ crystal, as for the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ crystal in our previous work [9], were performed on an adiabatic calorimeter during discrete ($\Delta T = 2.0$ – 3.5 K) and continuous ($dT/dt = 0.14$ K/min) heatings.

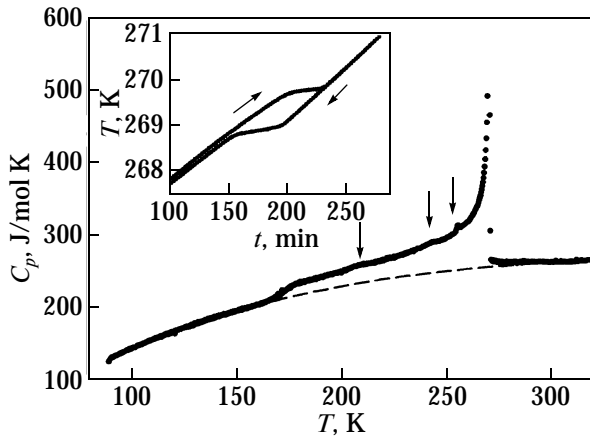


Fig. 1. Temperature dependence of the heat capacity of the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ oxyfluoride. The dashed line represents the lattice heat capacity. The inset shows the thermograms obtained during heating and cooling. Vertical arrows indicate the temperatures of additional anomalies of the heat capacity.

The range in the vicinity of the phase transition at T_1 was studied by the method of quasistatic thermograms in the course of heating and cooling ($dT/dt = (2-4) \times 10^{-2}$ K/min). The sample under study with a mass of 1.34 g was hermetically packed in an indium container. The heat capacity of the container was measured in a separate experiment.

The measured temperature dependence of the molar heat capacity of the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ crystal is plotted in Fig. 1. On the whole, the dependence $C_p(T)$ coincides with that observed for $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ [9]: two pronounced anomalies of the heat capacity occur at the temperatures $T_1 = 269.80 \pm 0.05$ K and $T_2 = 180 \pm 2$ K, which are fairly close to the phase transition temperatures revealed by measuring the birefringence [12]. However, in the temperature range between T_1 and T_2 , the curve $C_p(T)$ for the molybdate exhibits three additional anomalies, which are insignificant in magnitude as compared to the main heat-capacity peaks (Fig. 1).

The inset to Fig. 1 shows the results of the study of the range in the vicinity of the temperature T_1 by the method of quasistatic thermograms in the course of heating and cooling. The temperature hysteresis $\delta T_1 = 0.9$ K measured in these experiments agrees satisfactorily with that found in the optical measurements [12]. The enthalpy jump in the transition (latent heat of the phase transition) is $\delta H_1 = 560 \pm 60$ J/mol, and its temperature range is fairly narrow, namely, $T_1 \pm 0.07$ K.

To determine the integral characteristics of the phase transitions in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$, we divided the molar heat capacity into the regular component and the anomalous contribution related to the phase transitions. For this purpose, the experimental data on

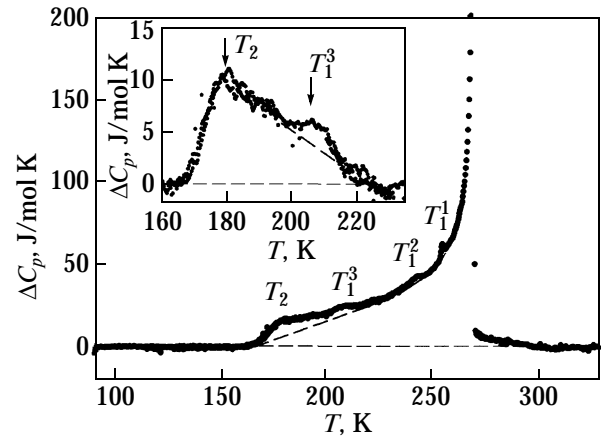


Fig. 2. Temperature dependence of the excess heat capacity of $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$. The inset shows the temperature range near T_2 .

$C_p(T)$ at temperatures considerably above T_1 and below T_2 were approximated by a combination of Debye and Einstein functions and then the interpolation was performed to the range of the anomalous behavior of the heat capacity. The regular contribution to the heat capacity is shown by the dashed line in Fig. 1, and the temperature dependence of the anomalous heat capacity is shown in Fig. 2. In the latter figure, the additional peaks of C_p at temperatures $T_1^1 = 256$ K, $T_1^2 = 245$ K, and $T_1^3 = 209$ K more clearly manifest themselves. In the initial phase, the excess heat capacity appears at $\sim(T_1 + 30$ K) and, hence, exists in the narrower temperature range ($T_1 + 60$ K) as compared to $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ and its deuterated analog [9, 11].

The integration of the function $\Delta C_p(T)$ over the temperature range of its existence (160–300 K) allowed us to determine the total change in the enthalpy $\sum \Delta H_i = 4800 \pm 330$ J/mol in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ due to the thermal effects observed at temperatures T_i .

To estimate the contributions of each of the effects to the quantity $\sum \Delta H_i$, the background heat capacities shown in Fig. 2 by the dashed lines were separated in an arbitrary form. The changes in the enthalpy (in J/mol) for all the heat-capacity peaks observed in the experiment are as follows: $\Delta H_1 = 4420 \pm 300$, $\Delta H_2 = 300 \pm 35$, $\Delta H_1^1 \approx 10$, $\Delta H_1^2 \approx 20$, and $\Delta H_1^3 \approx 50$. The values of ΔH_i at T_1^1 , T_1^2 , and T_1^3 appear to be within the error in the determination even for ΔH_2 . On the other hand, no features were revealed in the behavior of other physical quantities in the temperature range T_1-T_2 . Therefore, we can assume that the thermal

effects at T_1^1 , T_1^2 , and T_1^3 are not related to the phase transitions in the molybdate. Hereafter, these effects will be disregarded.

The response of $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ to the hydrostatic pressure was measured using a technique based on differential thermal analysis described in [14] and previously used in the study of the p - T phase diagrams for other oxyfluorides and fluorides. The single-crystal sample was cemented to one of the junctions of the high-sensitive Cu-Ge thermocouple element placed in a high-pressure chamber filled with a transformer oil. The results of the studies are presented in the form of the pressure-temperature phase diagram in Fig. 3. In the experiments performed at normal and high pressures, we recorded only one anomaly of the heat capacity, which corresponds to the phase transition at T_1 . An increase in the pressure is accompanied by an increase in the transition temperature at the rate $dT_1/dp = 92.8 \pm 3.5$ K/GPa. As the pressure increases, the heat-capacity anomaly is rather rapidly smeared and almost completely disappears at $p > 0.3$ GPa. In the pressure range under study, we did not reveal triple points and high-pressure phases. No phase transition at T_2 was recorded in spite of the larger enthalpy ΔH_2 as compared to those for tungstates [9, 11]. This is predominantly associated with the significant smoothness of the heat-capacity anomaly (Fig. 2).

The differences in the structure and properties of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ and $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$, which were revealed in [12, 13] and noted in Introduction, suggest that the nature and mechanism of the phase transitions in these crystals can exhibit specific features.

3. PERMITTIVITY AND EFFECT OF THE ELECTRIC FIELD

To obtain information on the nature of the phase transformations in the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ compound, we measured the temperature dependence of its permittivity for plates ($\sim(0.6-1.0)$ mm thick) cut parallel to the (100), (010), and (001) planes. Copper and gold electrodes were deposited by vacuum evaporation. The dependence $\varepsilon(T)$ was measured on an E 7-20 immittance meter at a frequency of 1 kHz in the temperature range 100–320 K. The rates of variation in the temperature during the heating and cooling were ~ 0.7 K/min.

It can be seen from the measured results presented in Fig. 4 that the permittivity exhibits a pronounced anomalous behavior at the temperature of the phase transition from the $Cmcm$ phase. The dependences $\varepsilon(T)$ for the (001) and (100) directions are similar to each other: the anomalies represent substantially asymmetric peaks with maximum values that differ by a factor of almost two. The permittivity ε_b is characterized by another behavior: during the heating, this quantity abruptly increases at the phase transition

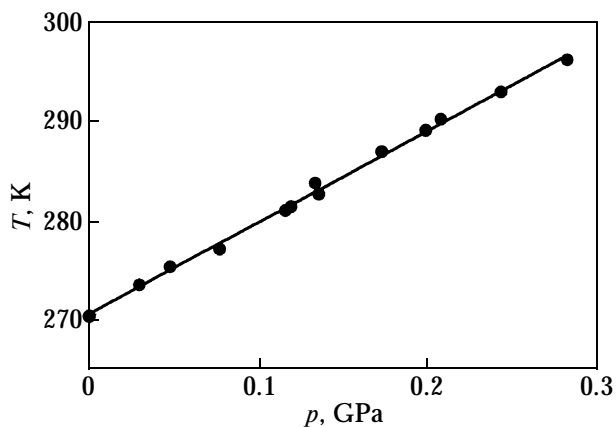


Fig. 3. The p - T phase diagram of the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ oxyfluoride.

temperature and remains almost constant above T_1 . The dielectric loss tangent also exhibits an anomalous behavior, but the maxima of $\tan\delta$ for all directions are located at temperatures below T_1 .

At T_2 , the curves $\varepsilon_a(T)$ and $\varepsilon_b(T)$ have only insignificant kinks (insets to Figs. 4a and 4c). In the range of the other aforementioned temperatures T_1^1 , T_1^2 , and T_1^3 , there are no any features in the behavior of the permittivity and $\tan\delta$.

Since the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ compound underwent a pronounced first-order phase transition $Cmcm \rightarrow Pnma$, the effect of the electric field on the temperature T_1 was studied by the method that, in essence, was similar to the thermography method used to measure the latent heat and temperature hysteresis. Owing to the considerable enthalpy jump δH_1 , the phase transition can be recorded at a fairly high rate of heating of the oxyfluoride under study, which was $dT/dt \approx 0.25$ K/min. The experiments were performed with the same samples that were used in the measurements of $\varepsilon(T)$. The samples were placed in a device that provided adiabatic conditions of the experiment by maintaining almost zero difference between the temperatures of the sample and the surrounding temperature screen. The thermocouple measuring the temperature was cemented directly to the sample electrode. The measurements were carried out in the electric fields $E = 0, 2.0, \text{ and } 3.4$ kV/cm.

The results of one of the experiments are presented in Fig. 5a, which shows the graph of the sample temperature as a function of the time near the phase transition. The temperature T_1 decreases under the action of the electric field. For more clarity of the effect of the shift in T_1 , the experimental data are presented in the form of the dependences $dT/dt(T)$ at different field strengths (Fig. 5b and inset to it). The relative shift in

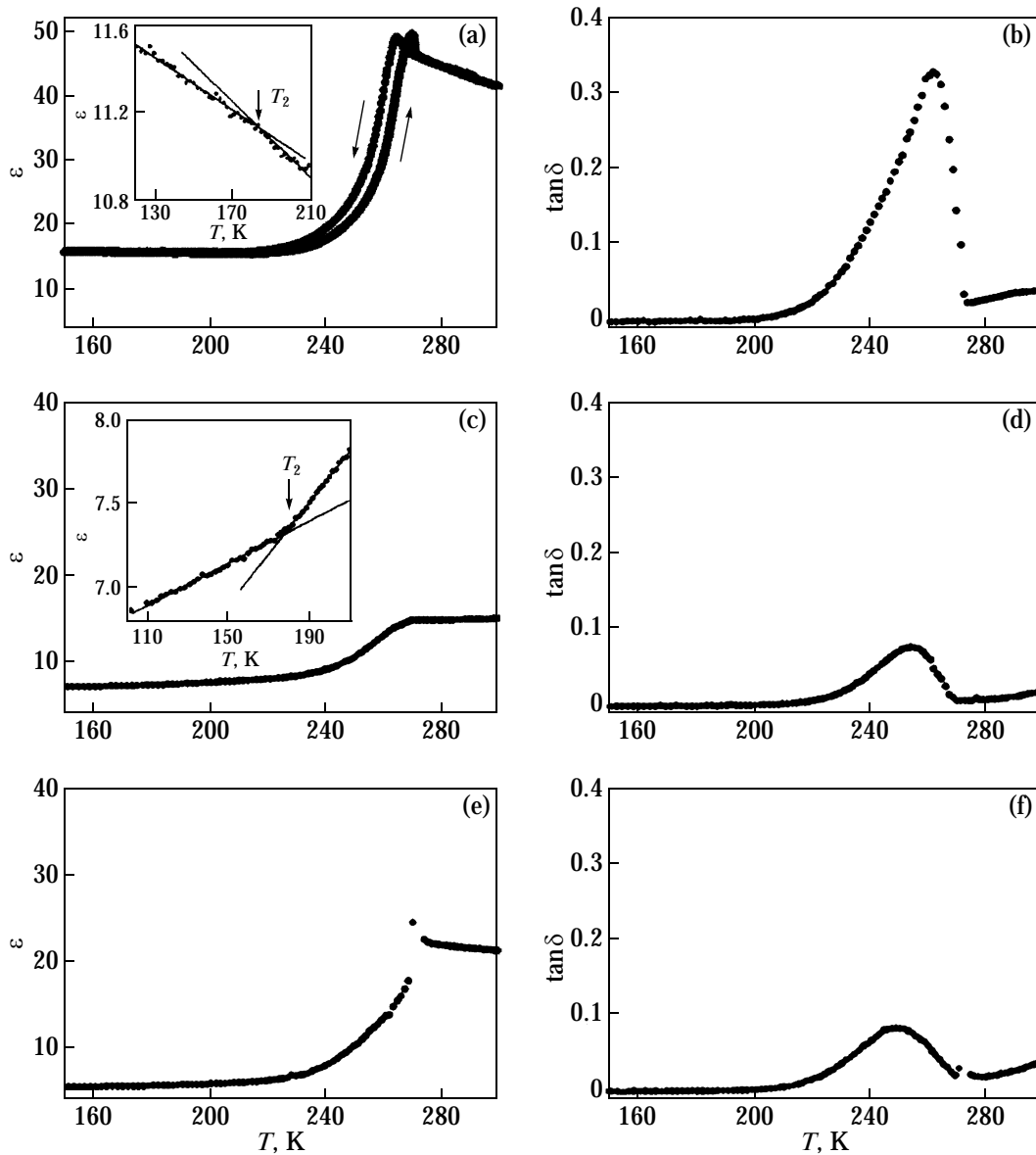


Fig. 4. Temperature dependences of (a, c, e) the permittivity ϵ and (b, d, f) the dielectric loss tangent $\tan\delta$ of $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ along the (a, b) *a*, (c, d) *b*, and (e, f) *c* crystallographic axes. Insets show the behavior of ϵ at T_2 .

the phase transition temperature is quite insignificant: $dT_1/dE = -0.026 \text{ K/kV cm}^{-1}$.

Attempts to open the dielectric-hysteresis loop in the *Pnma* phase were unsuccessful at least up to 1.5 kV/cm.

4. DISCUSSION

As a result of the studies performed in [5, 8, 12, 13], it was established that the structures of the initial and distorted phases and optical properties of the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ and $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ crystals somewhat differ from each other. The data presented in the table clearly demonstrate the relation between the type of

the central atom and a number of the thermodynamic properties of these oxyfluorides.

Despite an insignificant difference between the ionic radii of W (0.60 Å) and Mo (0.59 Å), the initial phase *Cmcm* as a result of the $\text{Mo} \rightarrow \text{W}$ substitution becomes less stable to variations in the external parameters (temperature, pressure). This manifests itself in both the considerable increase in the temperature T_1 and its anomalously large pressure coefficient dT_1/dp , which exceeds the value previously determined for $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ [9] by a factor of seven. However, the range of existence of the intermediate phase between T_1 and T_2 is substantially extended from 40 to 90 K due to the significantly smaller change in T_2 .

Unfortunately, the question as to the stability of this phase in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ subjected to hydrostatic pressure remains open. In our opinion, the problem can be indirectly solved, e.g., from the results of the study of the thermal expansion in the vicinity of T_2 , because the sign of the pressure coefficient is determined by the sign of the change in the volume and volume expansion coefficient for first-order and second-order phase transitions, respectively.

According to the data obtained in [5, 13], there are no noticeable structural differences between the intermediate ($T_2 < T < T_1$) and low-temperature ($T < T_2$) distorted phases in the molybdate and tungstate. The existence of these phases was reliably established by the optical and calorimetric measurements performed in [8, 9, 11–13] and our work. At T_1 , ligands and, correspondingly, central atoms in both crystals become ordered (completely in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ and partially in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$); namely, the central atoms are displaced by a fairly large distance (Mo by ~ 0.3 Å and W by 0.2 Å) [5, 13]. The ammonium groups, which are assumed to be disordered in the $Cmcm$ phase, can most likely remain somewhat disordered in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ below T_1 [5]. In $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$, the $Cmcm \rightarrow Pnma$ phase transition most likely results in the ordering of tetrahedra, because the electron density syntheses for the $Pnma$ phase contain traces of hydrogen atoms of both ammonium groups [15].

Let us consider the entropies of the phase transitions $\Delta S_1 = 18.2 \pm 1.3$ J/mol K and $\Delta S_2 = 1.70 \pm 0.25$ J/mol K, which were determined by integration $\Delta S_i = \int (\Delta C_p/T) dT$. Although the phase transition enthalpies considerably increase as a result of the Mo \rightarrow W substitution, the corresponding values of the entropy are either unchanged (ΔS_2) or even decrease (ΔS_1) (see table). This circumstance is explained by the substantial increase in the phase transition temperatures T_1 and T_2 . This increase, in principle, was expected reasoning from the data of the studies of fluorine–oxygen tungstates and molybdates with a perovskite-like structure [10, 16, 17]. As in the related tungsten compounds [9, 11], the main change in the entropy of $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ is due to the transformation at T_1 .

Therefore, the analysis of the data on the phase transition temperatures, their response to the hydrostatic pressure, values of the entropy, and character of structural changes allows us to make some conclusions regarding the general and specific features of the mechanism of the phase transitions in the related compounds $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ [9], $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ [11], and $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$.

Judging from the ordering (complete or partial) of the ligands in the distorted phases of protonated oxyfluorides, some contribution to the entropy of the transition can be due to processes of the statistical

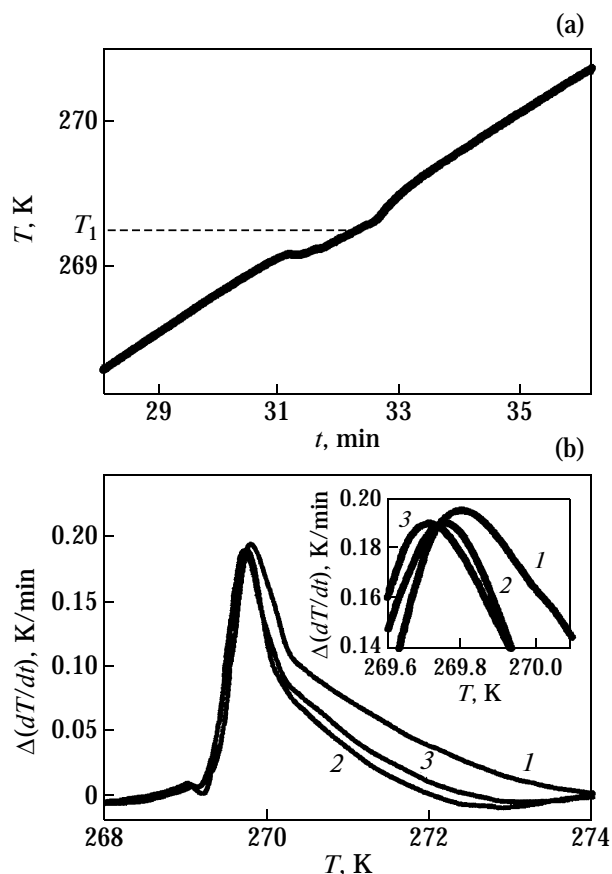


Fig. 5. Results of the investigation into the effect of the electric field on the temperature T_1 : (a) temperature of the sample as a function of the time and (b) temperature dependences of the derivative dT/dt over a wide temperature range and in the immediate vicinity of the $Cmcm \rightarrow Pnma$ phase transition (in the inset). Curves 1, 2, and 3 correspond to the measurements at electric field strengths of 0, 2.0, and 3.4 kV/cm, respectively.

ordering of the F(O) atoms and, hence, the central atoms. According to the model proposed in [5] for the $Cmcm$ structure of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$, the central atom in the $[\text{WO}_2\text{F}_4]$ polyhedron is disordered between the special (4c) and general (16h) positions, which are characterized by different occupation probabilities, namely 0.143 and 0.214, respectively. The complete ordering of the central atom brings about the change in the entropy $R \ln 3.42 = 10.2$ J/mol K. The same mechanism of structural distortion but from the standpoint of ligand ordering leads to $R \ln(4/1) = 11.5$ J/mol K. Therefore, the change in the entropy of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ in the course of ordering of quasioctahedra at T_1 is considerably smaller than the value of ΔS_1 found experimentally (see table). The deuteration of the tungstate brings about a decrease in the corresponding entropy by a factor of about 1.5: $\Delta S_1 = 13.2$ J/mol K = $R \ln 4.9$ [11]. The significant difference between the entropies is equal to 5.7 J/mol K $\approx R \ln 2$, which, in our

Some thermodynamic parameters of the phase transitions in the oxyfluorides $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ (T_1^* is the temperature at which the quantity $(\Delta C_p/T)^{-2}$ according to relationship (1) becomes zero, T_C is the Curie temperature, and N is the degree of closeness of the phase transition to the tricritical point)

Parameter	$(\text{NH}_4)_2\text{WO}_2\text{F}_4$ [9]	$(\text{NH}_4)_2\text{MoO}_2\text{F}_4$
T_1 , K	201	270
$\Delta S_1/R$	$\ln 9.8$	$\ln 8.9$
$\delta S_1/\Delta S_1$	0.18	0.11
dT_1/dp , K GPa ⁻¹	13.5	93
A_7^2/B , J/mol K ²	-2.2	-0.7
A_7^3/C , J ² /mol K ³	11.5	16.4
$T_1^* - T_1$, K	0.2	1.4
$T_1 - T_C$, K	0.6	4.2
N	-0.06	-0.18
T_2 , K	160	180
$\Delta S_2/R$	$\ln 1.2$	$\ln 1.2$
dT_2/dp , K GPa ⁻¹	42	?

opinion, can be due to the fact that the tetrahedron disordered over two positions in the *Cmcm* phase of the protonated tungstate is ordered as a result of the $D \rightarrow H$ substitution. Almost identical temperatures T_1 and pressure coefficients dT_1/dp for $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ [9] and $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ [11] are most likely associated with the absence of N–H...F(O) hydrogen bonds in the *Cmcm* phase. The deuteration in the presence of these bonds can lead to an increase in the phase transition temperature by several tens of degrees, as is the case with KDP and DKDP [18].

According to the aforesaid, the entropies of the phase transitions at T_1 in the tungstates can be represented as those consisting of the following contributions:

$$\begin{aligned} & (\text{NH}_4)_2\text{WO}_2\text{F}_4 - R\ln 9.8 \\ &= R(\ln(4/1) + \ln(2/1) + \ln 1.2), \\ & (\text{ND}_4)_2\text{WO}_2\text{F}_4 - R\ln 4.9 \\ &= R(\ln(4/1) + \ln(1/1) + \ln 1.2). \end{aligned}$$

The changes in the entropy $R\ln(4/1)$ and $R\ln(2/1)$ are due to the orientational ordering of the fluorine–oxygen and ammonium polyhedra, respectively, and the value of $R\ln 1.2$ can be due to the displacements of individual atoms.

The specific feature of the disordering of the *Cmcm* structure in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ is that the F atom was located in one of the polar vertices of the $[\text{MoO}_2\text{F}_4]$ polyhedron and the other vertex was occupied by the F and O atoms with an occupancy ratio of 1/9 [15]. As a

result of the transition, the structure is ordered only partially: we succeeded in locating only three F atoms forming the face of the $[\text{MoO}_2\text{F}_4]$ polyhedron, and the other ligands occupy three vertices of the opposite face with an equal probability. The incomplete ordering of the F(O) atoms in the *Pnma* phase suggests that phase transitions can occur in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ with a further cooling of the crystal. It is unlikely that the anomaly of $C_p(T)$ at T_2 is related to the ligand ordering, because the entropy ΔS_2 is small and coincides with the corresponding entropies in both tungstates. The heat capacity was measured on a Physical Properties Measurement System at temperatures below the lowest temperature of the experiments performed on the adiabatic calorimeter. No anomalies were revealed down to 4 K. Therefore, we can assume that the ligand disordering in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ is gradually frozen.

At first glance, the distorted phase model proposed in [15] complicates the direct calculation of the entropy related to the ligand ordering. However, we can assume that, in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$, there can exist a praphase G_0 in which all ligands are completely disordered, as, e.g., in $\text{Rb}_2\text{WO}_2\text{F}_4$ [5], and from which phase transitions ($G_0 \rightarrow \text{Cmcm}$ and $G_0 \rightarrow \text{Pnma}$) can occur. In this case, the first-order phase transition $\text{Cmcm} \rightarrow \text{Pnma}$ between the subgroups is possible, so that the occupancy of the polyhedron with the F(O) atoms or the number of positions of the Mo atom is changed so unusually (4/3) as compared to tungstates. According to [15], both NH_4 tetrahedra are ordered upon the transition. In this case, the entropy ΔS_1 is the sum of the contributions corresponding to those considered above for the tungstates; that is,

$$\begin{aligned} & (\text{NH}_4)_2\text{MoO}_2\text{F}_4 - R\ln 8.9 \\ &= R(\ln(4/3) + 2\ln(2/1) + \ln 1.7). \end{aligned}$$

The significant increase in the pressure coefficient dT_1/dp upon the $\text{Mo} \rightarrow \text{W}$ substitution undoubtedly indicates that the transitions occurring in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ and $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ differ substantially. One more confirmation of this difference is provided by the behavior of the permittivity. The dependences $\varepsilon(T)$ for the tungstate [10] suggest a radically nonferroelectric origin of structural distortions at T_1 [19]. The situation for the molybdenum oxyfluoride appears to be more complex. On the one hand, its distorted phase is not ferroelastic. On the other hand, it is not ruled out that the antiferroelectric state can exist in the *Pnma* phase, as can be judged from the following experimental facts: (1) the appearance of the superstructure as a result of the *Cmcm* \rightarrow *Pnma* transition (the primitive-cell volume is doubled), (2) the first-order phase transition and large entropy ΔS_1 , (3) the negative shift in T_1 in the electric field, (4) the substantial difference between the values of ε in the initial and distorted phases and the increase in ε as the temperature T_1 is approached, and (5) the absence of hysteresis

loops at $T < T_1$. According to [20, 21], the aforementioned properties correspond to indications characteristic of antiferroelectrics that undergo order–disorder phase transitions, e.g., NH_4HPO_4 and $(\text{NH}_4)_2\text{H}_3\text{IO}_6$.

The significant role of the ammonium groups in the mechanism of the transition at T_2 is evidenced by a substantial influence of the deuteration on the stability of this temperature to the pressure [11]. Recall that the intermediate phase in $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ appears at a relatively low pressure < 0.2 GPa due to the increase in the quantity $dT_2/dp = 112$ K GPa $^{-1}$ by several factors as compared to that for $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ (see table). On the other hand, according to small values of ΔS_2 (see table), any ordering processes in the course of this transformation are absent. As regards the nature of this transition, judging from the behavior of ε and $\tan\delta$, we can believe with confidence that the phase transition has a nonferroelectric nature in both $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ [10] and $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$.

Previously, we showed that the behavior of the heat capacity of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ and $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ in the intermediate phase between T_1 and T_2 is satisfactorily described in terms of the phenomenological Landau theory of phase transitions. Judging from the value of $\delta S_1/\Delta S_1$ (see table), which characterizes the ratio between the entropy jump at T_1 and the total change in the entropy in the range $T_1 - T_3$, the transition from the *Cmcm* phase in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ is also fairly close to the tricritical point. The representation of the excess heat capacity of the molybdate according to the relationship [22]

$$\left(\frac{\Delta C_p}{T}\right)^{-2} = \left(\frac{2\sqrt{B^2 - 3A'C}}{A_T^2}\right) + \frac{12C}{A_T^3}(T_1 - T) \quad (1)$$

obtained from the analysis of the thermodynamic potential $\Delta\Phi(p, T, \eta) = A\eta^2 + B\eta^4 + C\eta^6$ shows that the quantity ΔC_p is linearly dependent on the temperature over a fairly wide temperature range (Fig. 6). The data in the table demonstrate how the Mo \rightarrow W substitution affects the relationship between the coefficients of the potential ($A = A_T(T_1 - T_C) + A_T(T - T_1) = A' + A_T(T - T_1)$). Moreover, the quantities $T_1^* - T_1$, $T_1 - T_C$, and $N = \pm\sqrt{B^2/3A_TCT_C}$, which characterize the closeness of the transition to the tricritical point, indicate that, in the molybdate, the phase transition from the *Cmcm* phase acquires features of a more pronounced first-order transformation.

5. CONCLUSIONS

A comparison of the data obtained in this work for the $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ oxyfluoride and the related compound $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ demonstrates that the changes

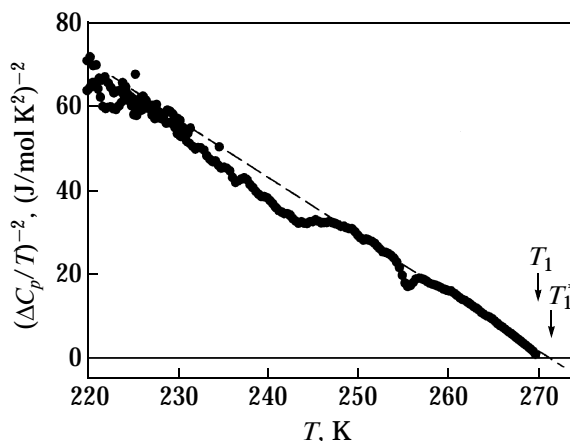


Fig. 6. Temperature dependence of the square of the inverse excess heat capacity of $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$.

associated with the Mo \rightarrow W substitution can be summarized as follows.

- (1) The phase transition entropies at T_1 and T_2 change within the limits of error in their determination.
- (2) The instability of the initial *Cmcm* phase with respect to the hydrostatic pressure increases substantially.
- (3) It is not ruled out that there can appear an antiferroelectric state at $T < T_1$.
- (4) The analysis of the structure and entropy suggests that the high-temperature transition is associated with the ordering of both ammonium groups and only with partial ordering of ligands.
- (5) Within the approximation of the phenomenological theory, the phase transition from the orthorhombic phase moves away from the tricritical point.

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