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LATTICE DYNAMICS  
AND PHASE TRANSITIONS

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## Effect of Deuteration on the Thermal Properties and Structural Parameters of the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ Oxyfluoride

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**Abstract**—The thermal properties and structure of  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  crystals are investigated. It is established that deuteration does not lead to a change in the symmetry of the initial phase *Cmcm* but considerably decreases the extent of its disordering, which, in turn, brings about a substantial decrease in the phase transition entropy. Apart from the anomalies associated with phase transitions characteristic of the protonic compound, the heat capacity exhibits two additional anomalies. Analysis of the phase diagram of the deuterated crystal reveals a triple point at a pressure  $p = 0.18$  GPa, which is predicted for  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  at about 0.7 GPa.

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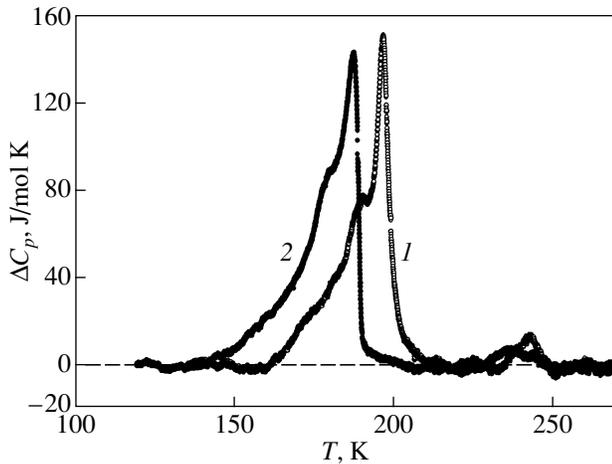
### 1. INTRODUCTION

Oxyfluorides with sixfold-coordinated anions that contain mixed F(O) ligands and are the main structural units are conventionally divided in two groups [1]. The first group includes oxide derivatives prepared by gradual continuous substitution of fluorine for oxygen. This substitution should naturally be accompanied by the corresponding partial replacement of the central cation by a cation with a lower valence; i.e., oxyfluorides of this type are solid solutions. Compounds of the second group are termed “true” oxyfluorides. These oxyfluorides retain the usual stoichiometry, and their F/O ratio, as a rule, is equal to or larger than 0.2. For a long time, primary attention had been focused on the effect of the O  $\rightarrow$  F substitution in various proportions on the stability of the ferroelectric and/or ferroelastic phase in perovskite-like oxyfluorides with atomic cations, which belong to one of the above two groups [2]. Later studies dealt with the stability of the initial cubic phase in true oxyfluorides with a nonspherical ammonium cation [3, 4]. Only quite recently, structural phase transitions were revealed in a crystal with a lower symmetry, namely, in  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  [5, 6]. It was established that this oxyfluoride has a rhombohedral structure at room temperature (space group *Cmcm*,  $Z = 4$ ) [6, 7] and, as the temperature decreases, undergoes a sequence of two phase transitions of ferroelastic nature at  $T_1 = 201$  K and  $T_2 = 160$  K [5, 6]. Observations with a light-polarizing microscope revealed that both distorted phases of the crystal belong to a triclinic crystal system. The absence of second optical harmonic generation in the intermediate phase argued for the  $\bar{1}$  sym-

metry [5]. The symmetry of the phase persisting at  $T < T_2$  remains an open question.

Comprehensive calorimetric studies showed that the major contribution to the large entropy change  $\Sigma\Delta S_i = 20.4$  J/mol K due to the two phase transitions comes from the structural transformation at  $T_1$  ( $\Delta S_1 = 19.0$  J/mol K [6]). Such a large change in the entropy ( $\Delta S_1 \approx R \ln 10$ ) clearly indicates that the high-temperature phase transition is associated with ordering of some structural elements.

In the refinement of the  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  structure, it was found that the isolated  $\text{WO}_2\text{F}_4$  octahedra contain one oxygen atom and one fluorine atom each in positions located on the  $b$  axis. The other ligands occupy four equatorial sites with probabilities of 0.75 (F) and 0.25 (O) [6] and, hence, are statistically disordered. However, since the local symmetry of the  $\text{WO}_2\text{F}_4$  octahedra corresponds to the lower ( $C_{2v}$ ) of the two possible symmetries, the probability of orientational disordering in the equatorial plane formed by the F(O) atoms is relatively low. The absence of orientational disorder of octahedral ionic groups in the initial phase was also indicated by the small thermal parameters of the F(O) atoms and by the character of the electron density distribution [6]. One did not succeed in obtaining precise data on the behavior of hydrogen atoms. However, it was reliably established that the ammonium tetrahedra occupying inequivalent crystallographic positions are disordered in varying degrees. The above experimental data led to the suggestion [6] that the major contribution to the entropy of the high-temperature transition can be due to ordering of the tetrahedral ammonium



**Fig. 1.** Tentative DSC curves measured for  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  under (1) heating and (2) cooling.

groups, whereas the second transition involves only slight atomic displacements.

In order to validate the hypothesis of the dominant role played by tetrahedra in the mechanism of at least the high-temperature phase transition, we carried out calorimetric and structural studies of the deuterated  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  crystal. It could be expected that the replacement of protons by heavier deuterium atoms would bring about a change in the character of thermal vibrations of the ammonium tetrahedra and, accordingly, a change in the phase transition entropy.

## 2. SYNTHESIS AND TENTATIVE STUDIES

We succeeded in synthesizing the deuterated compound  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  only in the form of fine crystal powder, which was prepared from the initial protonic oxyfluoride by multiple recrystallization in heavy water. The sample was characterized by NMR and powder x-ray diffractometry. The degree of deuteration, which was found to be 85%, was determined by comparing the integrated  $^1\text{H}$  NMR absorption lines of the protonic and deuterated compounds. The structural studies revealed that, first, the sample was single phase, and, second, deuteration did not change the symmetry (space group  $Cmcm$ ) of the crystal at room temperature.

In the first stage, we performed tentative studies of the stability of the  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  rhombohedral phase with a DSM-2M differential scanning microcalorimeter within the temperature range 120–370 K under heating and cooling at a rate of 8 K/min. The sample weight was  $\sim 0.22$  g.

The temperature dependence of the DSM signal exhibited four features in the form of peaks with maxima at  $243 \pm 5$ ,  $196 \pm 1$ ,  $190 \pm 1$ , and  $174 \pm 1$  K. Figure 1 plots the results of the studies in the form of the temperature dependence of  $\Delta C_p$ . The good reproducibility of all the four anomalies obtained under thermal cycling

and in measurements on different samples suggested that, in contrast to  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  with two transformations [6], the  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  crystal undergoes a sequence of four phase transitions. Because both crystals reveal characteristic transitions near  $\sim 200$  and  $\sim 170$  K, and to simplify the comparison and analysis of the results, we chose the following notation for the transition temperatures in the order of their decrease:  $T_1'$ ,  $T_1$ ,  $T_2'$ , and  $T_2$ .

The change in the enthalpy at the first transition was found to be  $\Delta H_1' = 100 \pm 10$  J/mol. For the remaining three transitions, we did not succeed in isolating in this stage of the study the corresponding contributions, and the total enthalpy turned out to be  $\Delta H_1 + \Delta H_2' + \Delta H_2 = 2000 \pm 200$  J/mol.

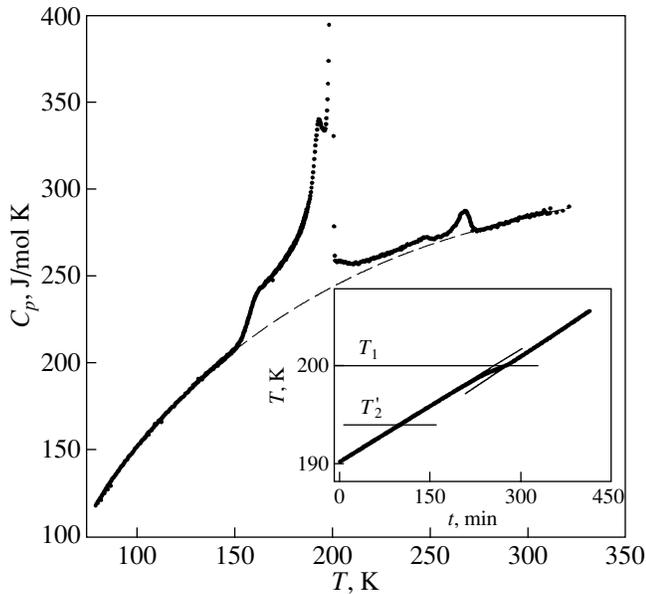
As in the study of the protonic compound, it was established that structural distortions of the deuterated analog are apparently fairly small because the low-temperature x-ray powder diffraction patterns did not exhibit any noticeable changes as compared to the initial rhombohedral phase.

## 3. HEAT CAPACITY AND THE $p$ - $T$ PHASE DIAGRAM

We carried out comprehensive measurements of the heat capacity of  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  by adiabatic calorimetry in the temperature range 80–320 K. A sample 1.9 g in weight was sealed in an air-tight indium container in a helium atmosphere. The measurements were performed under discrete ( $\Delta T = 2.0$ – $3.5$  K) and continuous ( $dT/dt = 0.14$  K/min) heating. The temperature was measured with a platinum resistance thermometer.

Figure 2 plots the temperature dependence of the heat capacity of  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ . As in the DSM experiments, four anomalies in the heat capacity were found. The refined phase transition temperatures turned out to be  $T_1' = 267.4 \pm 1.0$  K,  $T_1 = 200.0 \pm 0.3$  K,  $T_2' = 193.4 \pm 0.4$  K, and  $T_2 = 162.0 \pm 1.0$  K. Thus, the deuteration did not bring about noticeable changes in the temperatures of the transitions characteristic of the protonic compound  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  ( $T_1 = 201.2 \pm 0.1$  K,  $T_2 = 160.0 \pm 1.0$  K [6]), on the one hand, and two additional thermal anomalies appeared, on the other hand.

The quasi-static thermograms were obtained under heating and cooling ( $|dT/dt| = 0.04$  K/min) in the vicinity of  $T_1$  and  $T_2'$ . The time dependence of the temperature (see the inset to Fig. 2) measured throughout the temperature range covered reliably indicates only the phase transition at  $T_1 = 199.79 \pm 0.12$  K, which is characterized by a latent heat absorption  $\delta H_1 = 370 \pm 50$  J/mol in the range  $\sim 0.3$  K. At  $T_2' = 193.20 \pm 0.12$  K, no clear indications of latent heat absorption were revealed, and the singular point was detected only from



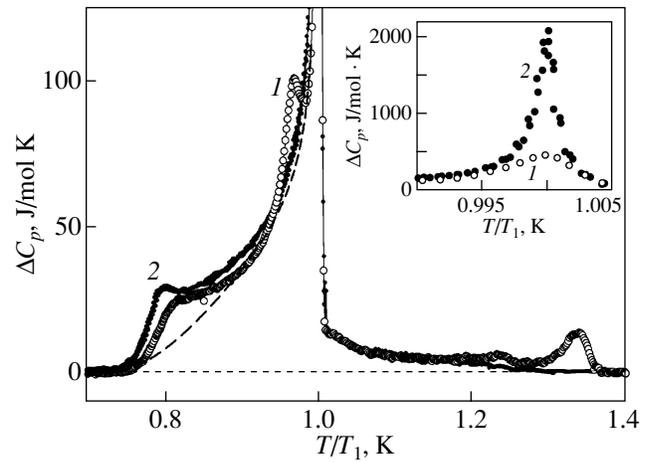
**Fig. 2.** Temperature dependence of the molar heat capacity of the  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  compound over a wide temperature range. The dashed line corresponds to the lattice heat capacity. The inset shows the thermogram measured under heating in the vicinity of  $T_1$  and  $T_2'$ .

a very small jump in the  $dT/dt$  derivative. A comparison of thermal cycling data made in thermographic mode permitted us, however, to establish the existence of a temperature hysteresis ( $\delta T_1 = 1.4$  K and  $\Delta T_2' = 1.5$  K), which argues for the corresponding phase transitions being first order.

The considerable diffuseness of the heat capacity anomalies associated with the other two transitions did not permit us to perform the corresponding thermographic measurements. However, a comparison of the data obtained with the differential scanning microcalorimeter and the adiabatic calorimeter at substantially different rates of temperature variation gives grounds, as in the case of  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ , to believe that the heat capacity anomalies at  $T_1'$  and  $T_2$  are likewise associated with first order transitions.

The lattice heat capacity  $C_L$  of  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  (dashed line in Fig. 2) was determined by the polynomial approximation of the experimental data on  $C_p(T)$  far from the transition temperatures. For comparison, the excess heat capacities of the protonic [6] and deuterated compounds are shown in Fig. 3. We readily see that the anomalous heat capacity exists in both crystals within virtually the same region, with the exception of the peak at  $T_1'$ .

The enthalpy changes at the phase transitions were found by integration of the  $\Delta C_p(T)$  function within the corresponding temperature ranges. The enthalpy of the

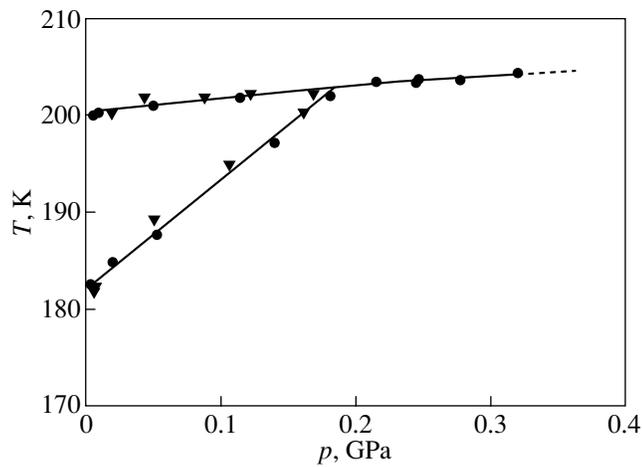


**Fig. 3.** Temperature dependence of the excess heat capacities of (1)  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  and (2)  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  over a wide temperature range and in the vicinity of  $T_1$  (inset).

high-temperature phase transition  $\Delta H_1' = 100 \pm 10$  J/mol compares satisfactorily with the value derived from DSM measurements. The total change in the enthalpy associated with the excess heat capacity in the range 150–260 K,  $\Delta H_1 + \Delta H_2' + \Delta H_2 = 2800 \pm 100$  J/mol, was found to be substantially larger than that following from the DSM data. This does not come as a surprise, because scanning calorimetry has a lower sensitivity and, besides, it cannot include the contribution due to the latent heat of the transition.

In order to determine the enthalpies of each transition separately, we followed the same approach as employed in [6] to analyze the data for the protonic compound. The total excess heat capacity below the temperature  $T_1'$ , except for the phase transition ranges at  $T_2'$  and  $T_2$ , was approximated with a polynomial, with the results of the fitting illustrated in Fig. 3 by the dashed line. In this case, the transition enthalpies were found to be  $\Delta H_2' = 150 \pm 30$  J/mol and  $\Delta H_2 = 170 \pm 30$  J/mol. The values of  $\Delta H_2$  for  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  and  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  ( $235 \pm 15$  J/mol [6]) turned out close in magnitude within experimental error. Thus, the decrease in the total enthalpy change in the deuterated compound (for  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ ,  $\Delta H_1 + \Delta H_2 = 3655$  J/mol [6]) should be assigned to the substantial decrease in the contribution due to the transition at  $T_1$ . This difference between the enthalpies is shown pictorially in the inset to Fig. 3.

The pressure–temperature phase diagram for the  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  crystal was studied by the DTA method in a high-pressure chamber equipped with a multiplier by the technique described in [8] and used by us earlier in the investigation of  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  [6]. The results of the experiments are displayed in Fig. 4. Because of the



**Fig. 4.** Pressure–temperature phase diagram for the  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  crystal.

lower sensitivity of the DTA method as compared to adiabatic calorimetry, we succeeded in detecting, just as with  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ , only two anomalies in the DTA signal that correspond to the phase transitions occurring at  $T_1$  and  $T_2$ . Incidentally, just as with the protonic compound, the temperature range  $T_1$ – $T_2$  in these experiments turned out substantially narrower than the range determined by adiabatic calorimetry under close-to-equilibrium conditions. Note that the rates of pressure-induced displacement of  $T_1$  were found to be virtually the same for the two compounds,  $dT_1/dp = 13.3 \pm 0.3$  K/GPa ( $\text{ND}_4$ ) and  $13.4 \pm 0.4$  K/GPa ( $\text{NH}_4$ ) [6]. At the same time, the H  $\rightarrow$  D substitution brought about a faster rise of  $T_2$ :  $dT_2/dp = 112.3 \pm 3.3$  K/GPa ( $\text{ND}_4$ ) and  $41.7 \pm 1$  K/GPa ( $\text{NH}_4$ ) [6]. It is this that permitted one to detect in the  $p$ – $T$  diagram of  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  the

**Table 1.** Data collection and structure refinement parameters for the  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  and  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  compounds

Characteristics	$(\text{NH}_4)_2\text{WO}_2\text{F}_4$	$(\text{ND}_4)_2\text{WO}_2\text{F}_4$
Space group	<i>Cmcm</i>	<i>Cmcm</i>
$a$ , Å	5.9442(1)	5.9423(1)
$b$ , Å	14.4272(2)	14.4211(1)
$c$ , Å	7.1472(1)	7.1402(1)
$V$ , Å <sup>3</sup>	612.93(2)	611.88(1)
2 $\theta$ range, deg	11.00–110.00	11.00–110.00
Number of Bragg reflections	238	238
Number of parameters refined	11	12
$R_p$	9.57	14.5
$R_{wp}$	11.3	16.5
$R_B$	4.02	6.08

triple point with the parameters  $p_{tr} = 0.18$  GPa and  $T_{tr} = 202.6$  K, which in  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  was assumed to lie about 0.7 GPa [6]. No noticeable change in the slope of the boundary between the *Cmcm* phase and the triclinic phase was found at the triple point (8.2 K/GPa).

#### 4. STRUCTURAL INVESTIGATIONS

The structure of  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  was refined from x-ray measurements performed for a single-crystal sample [6, 7]. Unfortunately, as was already pointed out, we succeeded in synthesizing the deuterated analog only in a powdered form. To make the investigation of the effect of pressure on the structure of  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  as accurate as possible, we studied both the protonic and deuterated compounds. The x-ray diffraction patterns were recorded at room temperature on a D8-ADVANCE powder diffractometer ( $\text{CuK}_\alpha$  radiation,  $\theta$ – $2\theta$  scan mode), with the subsequent Rietveld refinement of the structure. The scan step in  $2\theta$  was  $0.02^\circ$ , and the exposure at each point was 15 s. In order to reduce the effect of the texture on the reflection intensity, the samples were rotated at a rate of  $0.5$  s<sup>–1</sup>.

The determination of the cell parameters and their refinement by the reflection profile fitting were performed according to procedures similar to those used in [9]. The peak shape was approximated by the Pearson VII function with FWHM = 6.0 for profile refinement, and with FWHM = 20.0 for final refinement of the structure. The first stage in the structure refinement of both samples was profile fitting, which was performed in several steps. In the second stage, the structure was refined. The main parameters of data collection and structure refinement are presented in Table 1. The space group *Cmcm* was derived from disappearance of the reflections.

The coordinates of the atoms (except for hydrogen), isotropic thermal parameters, and occupancies of the positions are presented in Table 2. As can be seen from a comparison of the results of refinement, substitution of the deuteron for the proton has no noticeable effect on the structural characteristics of the crystal, in particular, on the thermal parameters of all atoms, which were satisfactorily refined in the isotropic approximation.

In place of the increase in the cell volume due to deuteration, it slightly decreased. A comparison of the bond lengths demonstrated that this circumstance was caused by the decrease of some interatomic distances in the deuterated crystal, in particular, by the decrease in the distance between the nitrogen atoms N1 and N2.

#### 5. DISCUSSION OF THE RESULTS

In view of the incomplete H  $\rightarrow$  D isotope substitution and of the lack of data on hydrogen atom coordinates, we have not succeeded in establishing the ratio in which the  $(\text{NH}_4)^+$  and  $(\text{ND}_4)^+$  cations occupy the

inequivalent crystallographic positions. Because, however, a cell contains an equal number of positions of two types for the nitrogen atoms, it can be suggested that their occupation by the tetrahedral cations of different species is equally probable.

Let us consider some aspects of the manifestation of the isotopic effect.

First, the symmetry of the initial phase did not change as a result of deuteration (*Cmcm*).

Second, in the temperature ranges far from the phase transitions, the regular heat capacity decreased. At 100 and 300 K, it was found to be 162 and 314 J/mol K for the protonic [6], and 153 and 285 J/mol K for the deuterated compound. Because the heat capacity of ammonium compounds always contains a contribution due to the degrees of freedom of the tetrahedral cation, the pronounced difference between the values of  $C_p$  revealed experimentally suggests clearly slowed down motion (vibrations) of the tetrahedra in the lattice of the deuterated crystal.

Third, the temperatures  $T_1$  and  $T_2$  of the phase transitions observed in the protonic compound ( $T_1 = 201$  K,  $T_2 = 160$  K) [6] virtually did not change, but new heat capacity anomalies appeared at  $T'_1$  and  $T'_2$ . The appearance itself of intermediate phases induced by deuteration does not cause surprise. Similar effects were observed in other ammonium-containing structures with a sixfold-coordinated anion, for instance, antiferrofluorites  $(\text{NH}_4)_2\text{MCl}_6$  ( $M = \text{Pb}, \text{Te}$ ) [10, 11]. Incidentally, transitions induced by isotope substitution occurred in the distorted rather than the initial phase. In this respect, detection in the present study of a new phase in  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  in the temperature range  $T_1 - T'_2$  can be considered reliable.

$(\text{NH}_4)_2\text{WO}_2\text{F}_4$  and  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  share features in the excess heat capacity, common in the magnitude and behavior with temperature, over a wide temperature range above  $T_1$  (Fig. 3), as well as in the pattern of the pressure dependence of this temperature (Fig. 4 and data in [6]).

All this suggests that in both crystals the *Cmcm* phase persists below room temperature down to  $T_1$ . In this connection, we believe that the heat capacity anomaly in the vicinity of  $T'_1$  can be due to the presence in the samples of small amounts of the growth solution. A comparison of the thermal effect in the sample (100 J/mol) with the enthalpy of melting of  $\text{H}_2\text{O}$  led us to  $\sim 1.7 \times 10^{-3}$  g, i.e.,  $\sim 0.1$  wt % as a possible amount of the solution in the sample.

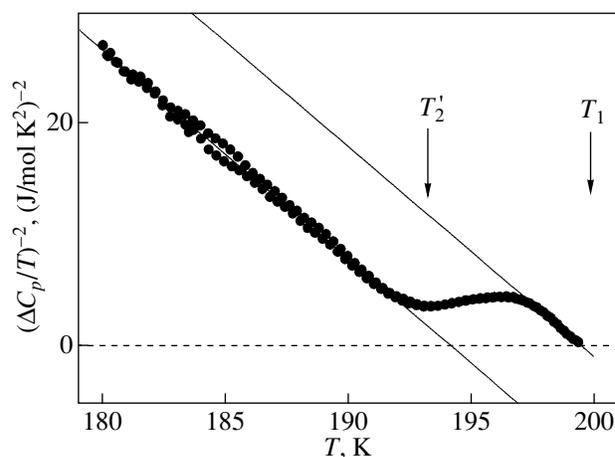
Fourth, the pressure range within which intermediate phases exist has been narrowed; indeed, the triple point in the  $p$ - $T$  diagram of  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  is observed at a substantially lower pressure.

The behavior of the heat capacity of the protonic compound below  $T_1$  is satisfactorily described by the

**Table 2.** Atomic coordinates, isotropic thermal parameters  $B_{\text{iso}}$ , and occupancies of the  $p$  positions

Atom	$p$	$X$	$Y$	$Z$	$B_{\text{iso}}, \text{\AA}^2$
$(\text{NH}_4)_2\text{WO}_2\text{F}_4$					
W	1.0	0.5	0.1307(2)	0.25	1.79(2)
F1	0.75	0.2783(7)	0.1221(3)	0.4331(6)	1.9(1)
O1	0.25	0.2783(7)	0.1221(3)	0.4331(6)	1.9(1)
O2	1.0	0.5	-0.0129(7)	0.25	1.5(3)
F2	1.0	0.5	0.2458(6)	0.25	1.7(2)
N1	1.0	0.5	0.4492(6)	0.25	1.0
N2	1.0	0.5	0.2212(8)	0.75	1.0
$(\text{ND}_4)_2\text{WO}_2\text{F}_4$					
W	1.0	0.5	0.10908(5)	0.25	2.22(3)
F1	0.75	0.2621(8)	0.1179(3)	0.4310(7)	1.0(1)
O1	0.25	0.2621(8)	0.1179(3)	0.4310(7)	1.0(8)
O2	1.0	0.5	-0.0207(8)	0.25	2.5(4)
F2	1.0	0.5	0.2447(8)	0.25	3.8(4)
N1	1.0	0.5	0.4379(9)	0.25	1.2(3)
N2	1.0	0.5	0.221(1)	0.75	1.2(3)

Landau theory [6] over a wide temperature range  $T_1 - 25$  K. As evident from Fig. 5, the magnitude and the behavior of the excess heat capacity of  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  and  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  between  $T_1$  and  $T_2$  are virtually identical (with the exclusion naturally of the immediate vicinity of  $T'_2$  for the deuterated compound). This prompted an analysis of the heat capacity of  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  in the frame of the theory of Landau within the temperature range specified. Figure 5 shows that the temperature dependence of the squared reciprocal excess heat capacity of this crystal, in full agreement with Eq. (1) of [6], does indeed remain linear at



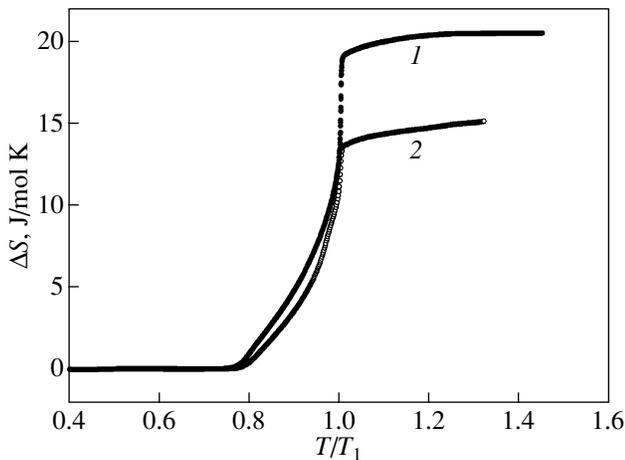
**Fig. 5.** Temperature dependence of the square of the inverse excess heat capacity for the  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  crystal.

**Table 3.** Thermodynamic parameters of the phase transitions in the  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  and  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  compounds

Parameter	$(\text{NH}_4)_2\text{WO}_2\text{F}_4$	$(\text{ND}_4)_2\text{WO}_2\text{F}_4$
$A_T^3/C, \text{J}^2/\text{mol}^2 \text{K}^3$	11.5	6.4
$A_T^2/B, \text{J}/\text{mol K}^2$	-2.19	$\sim\infty$
$T_1^*, \text{K}$	201.4	199.65
$N$	0.063	$\sim 0$
$\delta H_1/\Delta H_1$	0.18	0.15
$\Delta S_1, \text{J}/\text{mol K}$	18.9	13.2

Note:  $A_T$ ,  $B$ , and  $C$  are coefficients of the potential  $\Delta\Phi = A_T(T - T_C)\eta^2 + B\eta^4 + C\eta^6$ ; and  $T_1^*$  is the temperature at which the quantity  $(\Delta C_p/T)^{-2}$  vanishes.

temperatures considerably lower than  $T_1$ , but the two linear parallel sections in the ranges 180–192 and 197.5–199.5 K are displaced, which should be attributed to the presence of the anomaly at  $T_2'$ . Table 3 lists data derived from the temperature dependence of  $(\Delta C_p/T)^{-2}$  that characterize the thermodynamic parameters of the transition at  $T_1$  occurring in  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  [6] and  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ . We readily see that deuteration gave rise to a considerable change in the ratios of the coefficients  $A_T^3/C$  and  $A_T^2/B$  of the thermodynamic potential  $\Delta\Phi(p, T, \eta) = A_T(T - T_C)\eta^2 + B\eta^4 + C\eta^6$ . The phase transition in the deuterated compound turned out a much less pronounced first-order transformation, which is apparently very close to the tricritical point. This is evidenced by the very near coincidence of the



**Fig. 6.** Temperature dependences of the excess entropy of (1)  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  and (2)  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  due to the sequence of phase transitions.

phase transition point with the temperature  $T_1^*$  at which the quantity  $(\Delta C_p/T)^{-2}$  vanishes and, as a consequence, vanishes  $N = \pm\sqrt{B^2/3A_TCT_C}$ . In the case of interest to us here, one could suggest the following relation among the characteristic temperatures:  $T_C$  (the Curie temperature) =  $T_1 = T_1^*$ . Despite the closeness of the transition to the tricritical point, latent heat was detected thermographically, but was found to be substantially smaller than that for the protonic compound (Table 3). The relative value of  $\delta H_1/\Delta H_1$  also decreased after deuteration.

The behavior of the change in entropy associated with the sequence of three phase transitions with temperature is plotted in Fig. 6. The total entropy, determined by integrating the  $\Delta C_p(T)/T$  function in the temperature range 150–260 K, turned out equal to  $\Sigma\Delta S = 15.0 \pm 0.8 \text{ J}/\text{mol K}$ , which is less by close to 25% than  $20.4 \pm 1.1 \text{ J}/\text{mol K}$ , the figure found in [6] for the protonic compound (Fig. 6). It can be maintained that the structural elements of the deuterated compound in the initial phase remained disordered, although to a lesser extent. Note also that these relative magnitudes of the transition entropies fit well the experimentally observed considerable difference between the molar heat capacities of  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  and  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$ .

As can be seen from the refined structure (Table 2), deuteration virtually did not change the thermal parameters of the fluorine-oxygen ligands. That the pattern of motion of the atoms forming the  $\text{WO}_2\text{F}_4$  octahedra in the crystal lattices of  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  and  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  did not change is evidenced also by a comparison of their electron density maps (Fig. 7). The absence of a clearly pronounced anisotropy in their vibrations bears out the ordered state of both localized and statistically distributed F(O) atoms. Thus, the decrease in the entropy associated with the phase transition sequence is most likely the result of the change in the disorder pattern of the ammonium tetrahedra.

The failure in our attempt at growing bulk single crystals did not permit us to use optical techniques to determine the symmetry of the distorted phases, as this was done for the protonic crystal [6]. But the fact that the phase transition temperatures  $T_1$  and  $T_2$  in both crystals turned out only insignificantly different and that the temperature dependences of the heat capacities are identical does not suggest any other symmetry for the distorted phase below  $T_1$ , i.e., the structure of the  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  crystal in this phase is also apparently completely ordered.

The separation of the anomalous contributions to the heat capacity performed earlier for each of the transitions permitted determination of the corresponding changes in the entropy:  $\Delta S_1 = 13.2 \pm 0.2 \text{ J}/\text{mol K}$ ,  $\Delta S_2' = 0.80 \pm 0.16 \text{ J}/\text{mol K}$ ,  $\Delta S_2 = 1.0 \pm 0.2 \text{ J}/\text{mol K}$ .

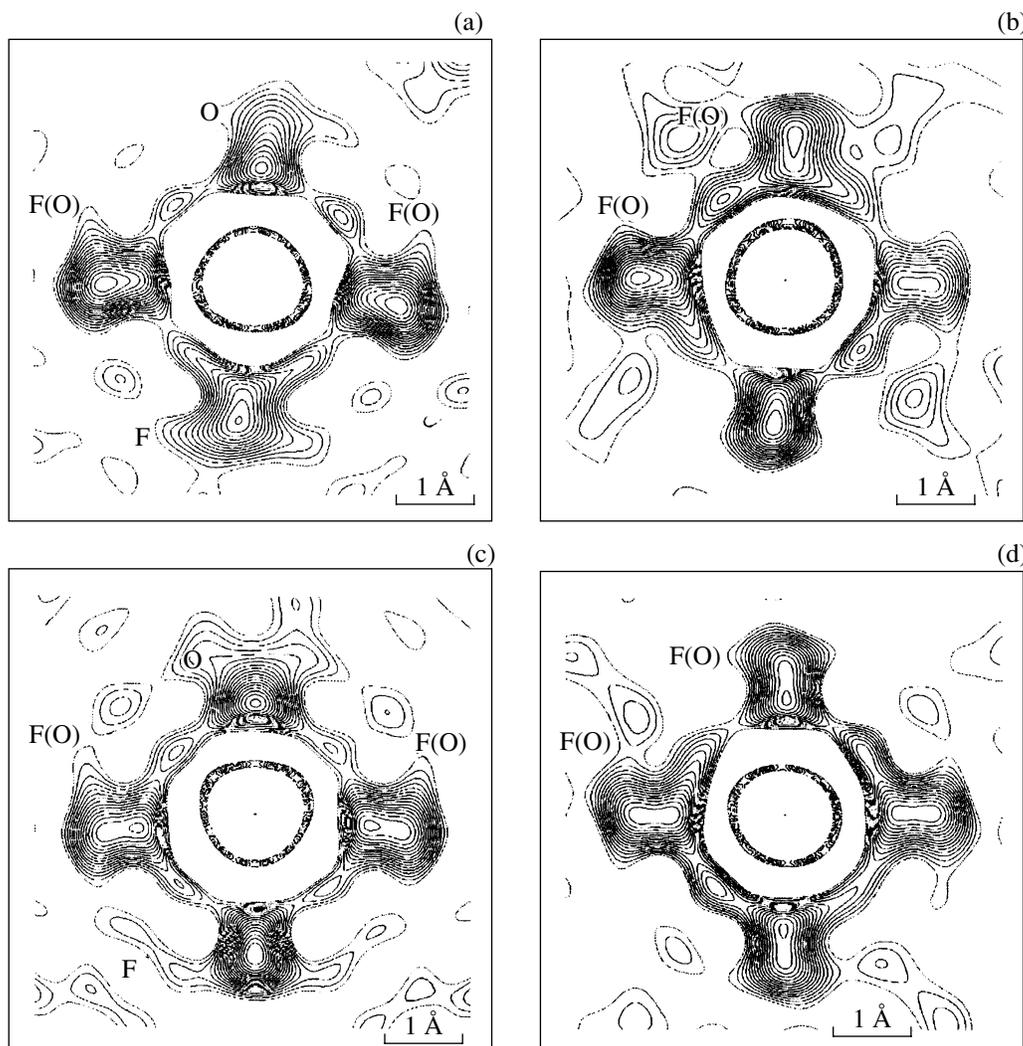


Fig. 7. Electron density maps of the  $\text{WO}_2\text{F}_4$  octahedron in the planes (a, c) passing through the O-F(O)-F-F(O) atoms and (b, d) containing only nonlocalized F(O) atoms for (a, b)  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  and (c, d)  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  crystals.

The closeness of the values of  $\Delta S_2$  for  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  (1.4 J/mol K [6]) and  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  suggests that the phase transition occurring at  $T_2$  in the deuterated compound is likewise not connected with ordering of any structural elements.

Consideration of the results of the x-ray, calorimetric, and optical studies of  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  culminated in the formulation of a model of disordering for ammonium tetrahedra of two types, which differ in the extent of disorder in accordance with the electron density maps [6]. One of them (with atom N1) had in the  $Cmcm$  phase two possible orientations, and the other (with N2), four. It was assumed that the phase transition at  $T_1$  ( $\Delta S_1 \approx R \ln 10$ ) involves complete ordering of both types of the tetrahedra ( $R \ln 2 + R \ln 4$ ), and that the additional contribution to the phase transition entropy ( $R \ln 1.25 = 0.22 R$ ) comes from the lattice distortion associated with displacement of other atoms.

The heat capacity anomaly in  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  at  $T_2'$  can, on the one hand, indicate in the deuterated analog that these processes are separated in temperature. Indeed, the slight displacement of atoms at  $T_2'$  is argued for by the entropy  $\Delta S_2' = R \ln 1.1$ , which is close to  $R \ln 1.25$ . On the other hand, the change in entropy at  $T_1$  would in this case be associated only with ordering and would be a multiple of  $R \ln 2$ . Experiment revealed a considerable decrease in the phase transition entropy at  $T_1$  in the deuterated compound ( $R \ln 5$ ) is compared to its protonic analog, which indicates a decrease in the extent of disorder of tetrahedral cations in the initial phase. Because x-ray powder structural data cannot yield information on the deuterons, one cannot pinpoint the tetrahedron (with N1 or N2) which had been ordered, completely or partially, by deuteration; the more so that the symmetry of the initial phase does not

preclude a configuration with the H(D) atoms located on mutually perpendicular planes. The entropy  $\Delta S_1$  can be represented in the form of sums  $R\ln 5 = R\ln 2 + R\ln 2.5$  or  $R\ln 5 = R\ln 1 + R\ln 5$ , i.e., the contribution to the entropy  $R\ln 1.25$  due to the assumed displacement of other atoms remained the same as in the protonic compound. Therefore, the heat capacity peak at  $T_2'$  in  $(\text{ND}_4)_2\text{WO}_2\text{F}_4$  is more likely to be related with a new displacive phase transition induced by deuteration. The above considerations concerning the change in entropy at  $T_1$  were made assuming total H  $\rightarrow$  D substitution. Taking into account the real extent of deuteration (85%) brings about a difference between the calculated entropies within 0.1R, which is less than the experimental error of determination of  $\Delta S_1$ .

## 6. CONCLUSIONS

The deuteration of  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  did not lead to a change in the range of stability of the *Cmcm* phase but caused a substantial decrease in the entropy of the transition from this phase and brings it closer to the tricritical point. As in the protonic compound, no indications of disordering in the octahedral subsystem were revealed in the deuterated analog. Thus, we obtained supportive evidence for the hypothesis put forward in [6] that the mechanism of phase transitions in  $(\text{NH}_4)_2\text{WO}_2\text{F}_4$  is associated with tetrahedral ions.

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