

LATTICE DYNAMICS AND PHASE TRANSITIONS

Mechanism of Phase Transitions in the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ Ferroelastic

I. N. Flerov^a, V. D. Fokina^a, M. V. Gorev^a, A. D. Vasiliev^a,
A. F. Bovina^a, M. S. Molochev^a, A. G. Kocharova^a, and N. M. Laptash^b

^a Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia

e-mail: flerov@iph.krasn.ru

^b Institute of Chemistry, Far Eastern Division, Russian Academy of Sciences, pr. Stoletiya Vladivostoka 159, Vladivostok,
690022 Russia

Received June 29, 2005

Abstract—Precision studies of the thermophysical properties and structure of an $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ crystal have been performed. It was established reliably that there is a sequence of two phase transitions at $T_1 = 201$ K and $T_2 = 160$ K characterized by wedging out of an intermediate phase with an increase in pressure. The role of tetrahedral and octahedral ionic groups in the mechanism of the structural transitions was determined.

PACS numbers: 64.70.Kb, 65.40.De

DOI: 10.1134/S1063783406040238

1. INTRODUCTION

Crystals with the general formula $A_2\text{MO}_2\text{F}_4$ ($A = \text{Na}, \text{Rb}, \text{Cs}$, or a molecular cation and $M = \text{W}, \text{Mo}$) that contain octahedral ionic groups can have different symmetry, depending on the size and form of the cations. So far, there is no information on the stability of these structures with respect to variations in external factors (temperature, pressure). It has been shown just recently [1] that the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ compound, which has an orthorhombic lattice at room temperature (space group $Cmcm$, $Z = 4$) [2] undergoes at least one phase transition as the temperature decreases. Structural distortions in this oxyfluoride at $T_1 = 202$ K were reliably determined by optical and calorimetric research tests. The question as to whether there is a second phase transition remains open, because, despite an anomaly in the specific heat that has been repeatedly observed at lower temperatures ($T_2 \approx 170$ K) under temperature cycling, no peculiarities in the optical properties were observed in this temperature range. Optical second harmonic generation in the distorted phases has not been detected.

The experimental data obtained in [1, 2] are apparently insufficient to reliably establish the number of phase transitions in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$, much less their mechanisms. In order to answer this question, detailed heat capacity studies were performed in the present work using an adiabatic calorimeter. The unit cell parameters were measured with a powder x-ray diffractometer, and the T - p phase diagram was analyzed by differential thermal analysis (DTA) under hydrostatic pressure. The structure of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ at room temperature was established in [2]. Nevertheless, we repeated x-ray studies with a single-crystal diffracto-

meter in order to analyze the character of the electron density distribution of the fluorine and oxygen atoms. This information, in combination with the thermodynamic parameters, should help to determine what role these atoms play in the mechanisms of the phase transitions more accurately.

Samples were synthesized using the method described in [1].

2. COEFFICIENT OF EXPANSION, SPECIFIC HEAT, AND T - p PHASE DIAGRAM

As was mentioned in [1], no significant distinctions are found between the x-ray diffractograms of the initial and a distorted phase. In order to confirm that the specific heat anomalies of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ found in [1] are due to structural transitions, we examined single-crystal (600)-, (0140)-, and (006)-oriented plates in a wide temperature range using a DRON-2 x-ray diffractometer. The changes in the unit cell parameters a_i , even though they occurred at T_1 and T_2 , proved to be insignificant. The anomalous behavior is more obvious in the temperature dependences of the coefficients of linear thermal expansion $\alpha_i = a_i^{-1}(\partial a_i/\partial T)$ (Fig. 1). Thus, it has additionally been proved that the compound under study really undergoes a sequence of two structural phase transitions.

In order to obtain more comprehensive information on the behavior of the specific heat and thermodynamic parameters of the phase transitions in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$, we studied this compound in detail using an adiabatic calorimeter in the temperature range 80–320 K. A sample 1.915 g in mass was hermetically sealed in an

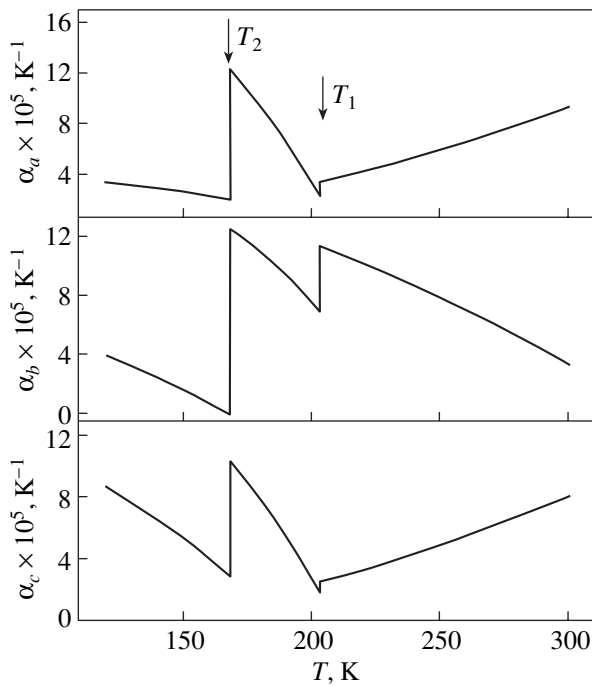


Fig. 1. Temperature dependences of the coefficients of linear thermal expansion of the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ crystal.

indium vessel in a helium atmosphere. Measurements were carried out in discrete ($\Delta T = 2.0\text{--}3.5$ K) and continuous ($dT/dt = 0.14$ K/min) heating regimes.

Figure 2 shows the temperature dependence of the molar specific heat of an $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ crystal. As in the differential scanning microcalorimetric (DSM) experiments [1], we observed two anomalies in the spe-

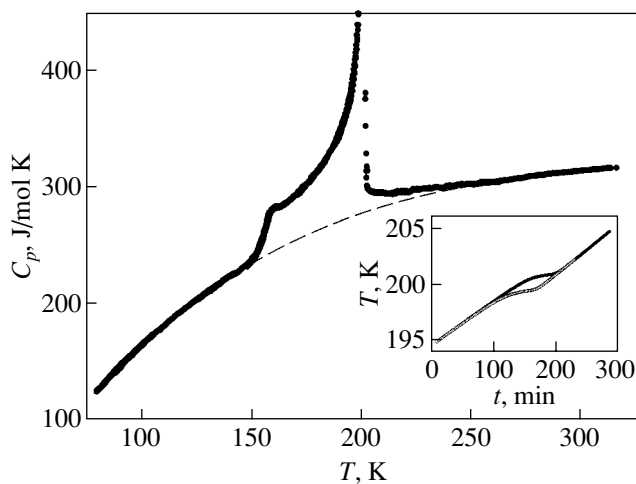


Fig. 2. Temperature dependence of the molar specific heat of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ over a wide temperature range. The dashed line corresponds to the lattice specific heat. Thermograms obtained in the heating and cooling regimes near T_1 are shown in the inset.

cific heat. The corrected temperatures of phase transitions were $T_1 = 201.2 \pm 0.1$ K and $T_2 = 160 \pm 1$ K.

By studying quasi-static thermograms obtained in the heating and cooling regimes ($dT/dt = 0.04$ K/min) in the vicinity of T_1 , it was established that the hysteresis of the transition temperature is $\delta T_1 = 1.4$ K (inset to Fig. 2). This value proved to be far smaller than that obtained in the DSM studies (9 K) performed at a significantly higher rate of temperature variation $dT/dt = 8$ K/min [1]. Such a strong dependence of δT_1 on dT/dt gives evidence that the phase transition at T_1 is of the first order. This dependence can be due to the fact that a higher rate leads to more nonequilibrium experimental conditions and, consequently, to more considerable superheating and overcooling effects. Based on the experiments under quasi-equilibrium conditions, we also determined the latent heat of transition at T_1 , which proved to be $\delta H_1 = 620 \pm 100$ J/mol.

Unfortunately, the method of using an adiabatic calorimeter does not allow specific-heat measurements to be performed in the cooling regime in a wide temperature range. Therefore, we could not study the behavior of the anomaly at T_2 under cooling of the crystal.

The dashed line in Fig. 2 indicates the temperature dependence of the lattice specific heat C_L , which was obtained by fitting the experimental $C_p(T)$ dependence far from the transition temperature with a polynomial function. The excess specific heat ΔC_p is the difference between the total molar and lattice specific heats (Fig. 3). As is seen, the anomaly in the specific heat exists in a rather wide temperature range (~ 60 -K wide) above T_1 . This suggests that pretransition phenomena occur in the initial crystal phase, which is also confirmed by the temperature dependence of the birefringence [1].

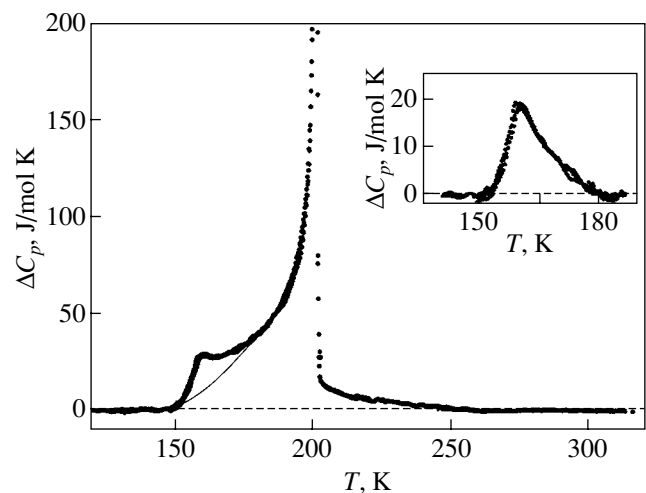


Fig. 3. Temperature dependence of the excess specific heat of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$. The inset shows the anomaly in the specific heat at T_2 .

In the intermediate phase, the excess specific heat related to the high-temperature transition decreases smoothly and in the region of T_2 it can be regarded as a background specific heat for the low-temperature transition (Fig. 3). This allowed us to determine the integrated characteristics of both of the phase transitions. The changes in enthalpy related to the structural transitions were determined by integrating the corresponding $\Delta C_p(T)$ functions in the temperature range 150–260 K for the high-temperature transition and in the range 150–180 K for the low-temperature transition (Fig. 3). These parameters are $\Delta H_1 = 3420 \pm 170$ J/mol and $\Delta H_2 = 235 \pm 15$ J/mol, respectively.

In order to study the stability of the initial phase under excess hydrostatic pressure, calorimetric tests of the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ compound were performed by DTA in a high-pressure bomb. The experimental technique employed was the same as that in [3]. Figure 4 shows the T - p phase diagram. It is seen that the temperatures of both phase transitions increase nonlinearly with pressure. The initial slopes of the phase boundaries are $dT_1/dp = 13.4 \pm 0.4$ K/GPa and $dT_2/dp = 41.7 \pm 1$ K/GPa. Therefore, as the hydrostatic pressure increases, the domains of existence of the initial orthorhombic phase and the intermediate phase narrow. Triple points and pressure-induced phases were not found up to 0.5 GPa. However, the character of the phase diagram suggests that a triple point may exist in the region of 0.7 GPa, where the intermediate distorted phase wedges out.

It should be noted that the temperature T_1 coincides sufficiently well with that determined experimentally by using an adiabatic calorimeter. However, the domain of existence of the intermediate phase as determined in the DTA measurements was 15-K narrower. At this stage, the only possible reason that could somehow explain the significant distinction between the values of T_2 obtained in the experiments in question is that this temperature depends on the rate of sample temperature variation, which in the calorimetric experiments is an order of magnitude lower than in the DTA measurements. As was already mentioned in the discussion about δT_1 , this phenomenon is typical of first-order phase transitions.

3. STRUCTURE OF THE INITIAL PHASE

The crystal structure of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ was studied at 238 K with a SMART APEX II CCD x-ray single-crystal automated diffractometer (Bruker, FRG). The sample was an ellipsoid with a maximum dimension of

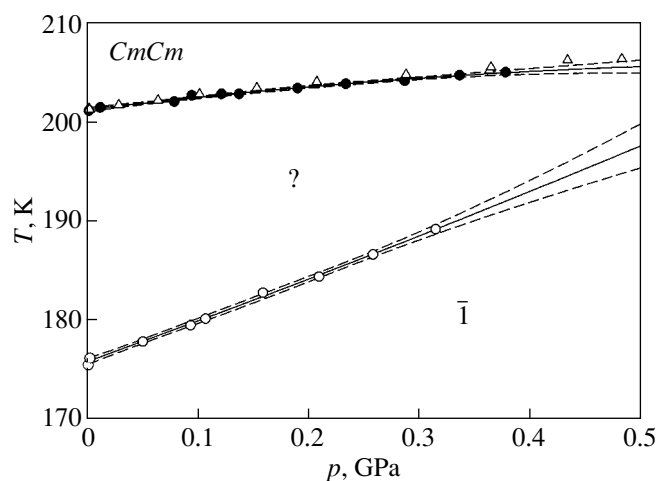


Fig. 4. T - p phase diagram of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$.

~0.25 mm. The reflection intensities were measured at $2\theta < 65^\circ$, in which case the indices varied within the following intervals: $-6 \leq h \leq 5$, $-9 \leq k \leq 21$, and $-8 \leq l \leq 10$. By analyzing the systematic extinction of the reflections and the unit cell parameters, it was established that the crystal has orthorhombic symmetry and a C -centered lattice. Three possible symmetry groups, namely, $Cmcm$, $Cmc2_1$, and $C2cm$, were examined to determine and refine the structure. The structure model was obtained in all three cases. The final R factors were close to each other after the refinement, but the refining in the $Cmcm$ group had advantageous characteristics, namely, 31 refined parameters (in contrast to 50 in the noncentrosymmetric crystal groups), the absence of a degenerate ellipsoid of thermal oscillations of atoms, and good averaging parameters of the equivalent reflections. Moreover, it was impossible to determine the absolute configuration in terms of the $Cmc2_1$ and $C2cm$ groups. Consequently, there is a good reason to decide in favor of the $Cmcm$ crystal group. The main experimental and refined characteristics are listed in Table 1, and the atomic coordinates and thermal parameters are listed in Table 2.

The structure of the compound under study (Fig. 5) consists of two isolated WO_2F_4 octahedra in which two positions are occupied by oxygen or fluorine atoms separately and four equivalent positions are occupied by fluorine and oxygen atoms in a 75 to 25% proportion (line F(O) in Table 2). The W-O distance is smaller than W-F (Table 3), whereas the O-F(O) distance is

Table 1. Crystallographic and experimental x-ray diffraction data on $(\text{NH}_4)_2\text{WO}_2\text{F}_4$

T , K	Radiation	Total number of reflections	Independent reflections	Reflections with $F_{hkl} \geq 4\sigma_F$	$R_{int}/R\sigma$	a , Å	b , Å	c , Å	$R_1; wR_2$ for all reflections	Goof (refining quality)
238	MoK α	1453	498	471	0.0186/0.0211	5.9292(3)	14.3940(7)	7.1351(3)	0.0264; 0.0573	1.031

Table 2. Relative coordinates and equivalent thermal parameters of atoms in the $(\text{NH}_4)_2\text{WO}_4$ structure.

$$U_{\text{equi}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

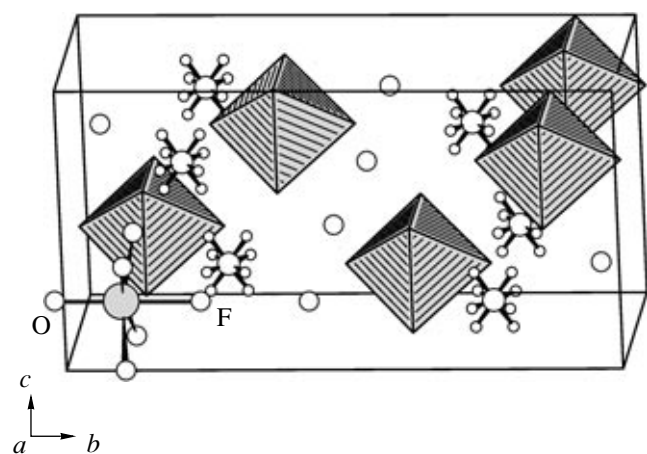
Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{equi}}, \text{\AA}^2$
W	0	0.10757(3)	0.25	0.0279(2)
O	0	-0.0132(4)	0.25	0.030(2)
F	0	0.2475(4)	0.25	0.045(2)
F(O)	0.2280(6)	0.1209(2)	0.0656(4)	0.0338(7)
N1	0.5	0.2753(6)	0.25	0.028(2)
N2	0	0.4427(6)	0.25	0.028(2)

Table 3. Angular and linear parameters of the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ structure

Atoms	Length, \AA	Atoms	Angle, deg
W–O	1.738(6)	O–W–F(O)	95.8(1)
W–F(O)	1.896(3)	F–W–F(O)	84.2(1)
W–F	2.014(6)	F(O)–W–F(O)	87.9(2)
O–F(O)	2.699(5)		91.0(2)
F–F(O)	2.622(5)		168.6(2)
F(O)–F(O)*	2.699(6)		
F(O)–F(O)**	2.631(6)		

Note: F(O)* has coordinates $(-x, y, z)$, and F(O)** has coordinates $(x, y, 1/2 - z)$.

larger than F–F(O), which is a result of a tungsten atom coming out of the plane of the rectangle formed by the F(O) atoms. Thus, due to the fact that a fraction of the ligands is localized, it was established that the configuration of the oxygen and fluorine atoms corresponds to the cis configuration. This case corresponds to a lower

**Fig. 5.** Unit cell of the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ crystal. Nitrogen atom N1 is shown as surrounded by hydrogen atoms belonging to a tetrahedron disordered in two positions.

local symmetry (C_{2v}) of the WO_2F_4 octahedron. Consequently, there is a low probability of F(O) atoms disordering in the plane of the rectangle.

The nitrogen atoms that belong to NH_4 tetrahedra were localized on the line of intersection of the mirror planes.

4. DISCUSSION

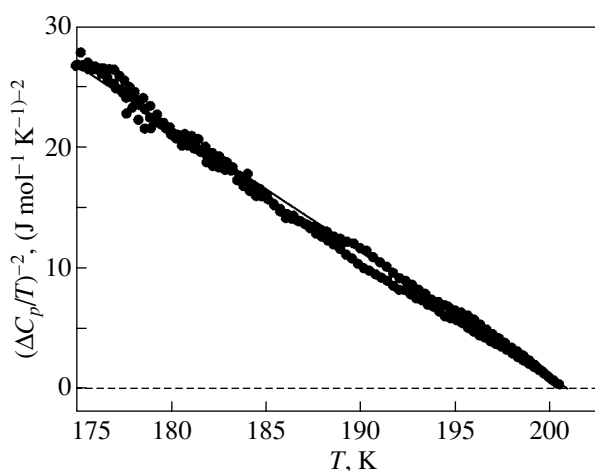
In the compound under study, both phase transitions are, as has been shown above, first-order phase transitions. However, only the high-temperature phase transition exhibits a significant excess specific heat over a wide temperature range below T_1 . Therefore, it is reasonable to analyze the $\Delta C_p(T)$ dependence for this transition only.

According to the Landau phenomenological theory, $(\Delta C_p/T)^{-2}$ is a linear function of temperature below the phase transition point [4]:

$$\left(\frac{\Delta C_p}{T}\right)^{-2} = \left(\frac{2\sqrt{B^2 - 3A'C}}{A_T^2}\right)^2 + \frac{12C}{A_T^3}(T_0 - T), \quad (1)$$

where $A = A' + A_T(T - T_0)$, B , and C are the coefficients in the thermodynamic potential $\Delta\Phi(p, T, \eta) = A\eta^2 + B\eta^4 + C\eta^6$.

Figure 6 shows the squared magnitude of the inverse excess specific heat of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ for several runs of measurements. It is seen that Eq. (1) holds true over a wide temperature range (~ 25 -K wide) below T_1 . This allows us to find the following relations between the coefficients of the thermodynamic potential: $A_T^3/C = 11.54 \text{ J}^2 \text{ mol}^{-2} \text{ K}^{-3}$ and $A_T^2/B = -2.19 \text{ J mol}^{-1} \text{ K}^{-2}$. Judging by the value of $N = \pm\sqrt{B^2/3A_TCT_C} = -0.063$ (where $T_C = T_0 - B^2/4A_T^3C$ is the Curie temperature) [4],

**Fig. 6.** Temperature dependence of the squared inverse excess specific heat of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$.

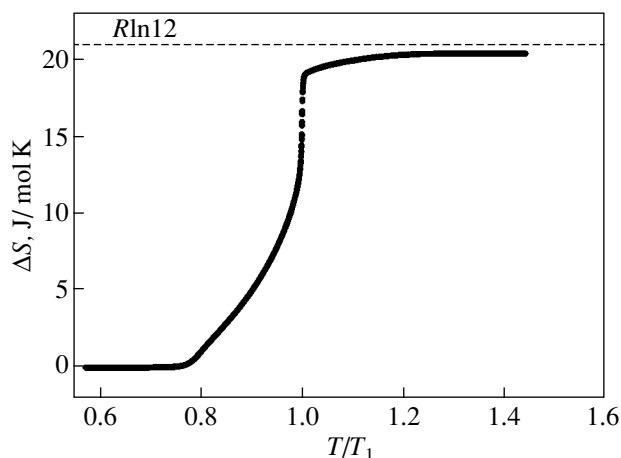


Fig. 7. Temperature dependence of the excess entropy of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ related to the sequence of phase transitions.

the high-temperature transition in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ is close to the tricritical point. This is also confirmed by the value of the difference between T_1 and the temperature at which $(\Delta C_p/T)^{-2}$ becomes zero, which is as small as 0.2 K.

Since the phase transitions under study are ferroelastic [1], the distorted phase of a crystal divides into domains (structural twins). This circumstance poses problems in determining the crystal symmetry of the distorted phases using the x-ray technique. However, polarization-optical studies revealed that the low-temperature phase is characterized by extremely low (triclinic) symmetry. Thus, it can be stated that all structural elements in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ are ordered below T_2 . Since studies of second harmonic generation have shown that the distorted phases of this crystal do not

exhibit ferroelectricity, the most probable symmetry of the low temperature phase is $\bar{1}$.

When discussing the mechanisms of structural distortions in the crystals, one argument in favor of one or another model is the change in the entropy caused by a transition. The values of the entropy related to the successive transitions in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ are $\Delta S_1 = 19.0 \pm 1.1$ J/mol K and $\Delta S_2 = 1.40 \pm 0.07$ J/mol K, respectively. This significant difference in the entropy of the transitions confirms that they definitely have different mechanisms of structural distortions. The first case corresponds to ordering processes, while the second case relates to a displacive phase transition. Figure 7 shows the total excess entropy associated with both phase transitions in the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ crystal as a function of temperature reduced to T_1 .

Since the O and F atoms lying on the b axis in the structure under study are definitely localized, they could be expected to be ordered. However, the statistical disorder of the F(O) atoms in the plane normal to the b axis does not exclude the possibility that they are orientationally disordered.

In order to study the character of the disorder of fluorine and oxygen atoms, maps of the electron density distribution of the atoms comprising the ionic group WO_2F_4 were plotted (Fig. 8). The electron density distributions of almost all fluorine and oxygen atoms are almost identical in character and confirm that there is no pronounced anisotropy in their oscillations; therefore, these atoms are in a virtually ordered state. Thus, it can be concluded that, according to the electron density distribution of the F, O, and F(O) atoms, these atoms are not actively involved in structural distortions and, consequently, cannot contribute to the entropy of a phase transition.

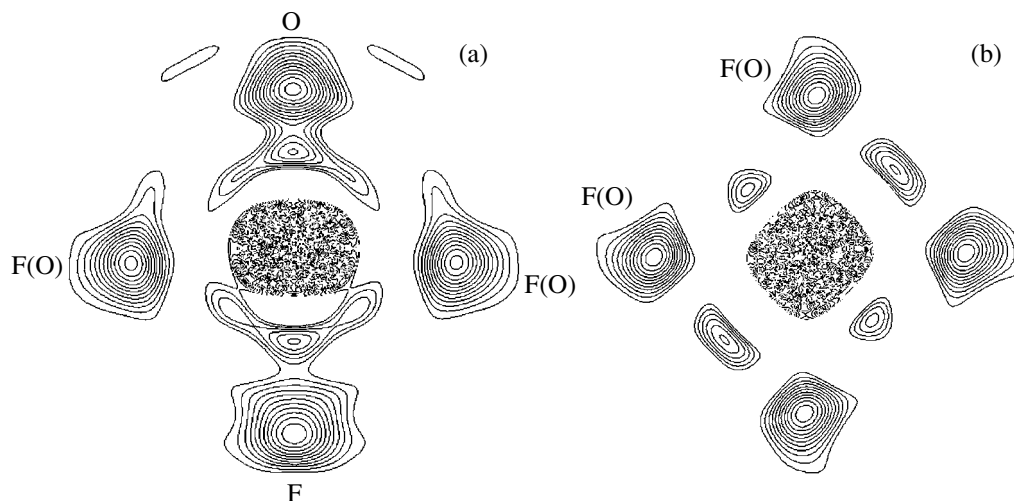


Fig. 8. Cross sections of the electron density of the WO_2F_4 octahedron by the planes formed by (a) O-F(O)-F-F(O) atoms and (b) by the planes containing only nonlocalized F(O) atoms.

As regards the ammonium groups, the nitrogen atoms occupy the intersection line of the mirror planes and, therefore, we should consider above all the configuration in which the hydrogen atoms belong to these planes. However, an analysis of the formation of electron densities suggests that this arrangement occurs only for the N1 atom. And in this case, it is difficult to say whether the tetrahedron is disordered in the two positions. Indeed, refining the variants does not yield an unambiguous answer. Weak maxima are observed in the electron density map near the N2 atom. It is impossible to relate these maxima unambiguously to the tetrahedral configuration of the hydrogen atoms, which prevents one from drawing a conclusion regarding the orientation of the corresponding tetrahedron. However, this particular result favors the suggestion that this tetrahedron is also disordered (maybe even to a greater extent than is the tetrahedron with N1).

Supposing that, in the case of both N1 and N2, the hydrogen atoms are placed in the symmetry planes, we considered the interatomic bond lengths in the surrounding of the NH₄ tetrahedra. It appeared that, in this case, there are hydrogen bonds, such as N–H...F (and N–H...F(O)), with the H...F distances in them ranging from 2.4 to 2.8 Å. Depending on the orientation of the tetrahedra, each hydrogen atom is involved in several bonds, the number of which changes with the rotation of a tetrahedron. Thus, it can be suggested that both tetrahedra in the orthorhombic phase are disordered, though probably to a different extent, which is confirmed by an analysis of the formation of the electron density near the nitrogen atoms. Each tetrahedron has at least two energetically equivalent states, where the hydrogen atoms are located in two mutually perpendicular mirror planes. In this case, if there occurs complete ordering due to a phase transition, the change in entropy should be at least $2R\ln 2$. However, because in the structural studies the hydrogen atoms were not localized around N2, it is possible that the corresponding tetrahedron can have a greater number of equally probable orientations. In this case, the value of ΔS_1 should be higher than $2R\ln 2$. Using calorimetric data, we experimentally found that the entropy due to the transition at T_1 is large, $\Delta S_1 \approx R\ln 10$, which can be expressed, for example, as a sum $\Delta S_1 = R\ln 10 = R\ln 2 + R\ln 5$. The first term corresponds to ordering of the tetrahedron with N1. The value of the second term favors the above assumption that the tetrahedron with N2 is more disordered. However, when a building block is disordered, all positions (orientations) that it occupies do not necessarily have to be energetically equivalent, in which case the entropy can be calculated from the simple expression $\Delta S = R\ln(N_1/N_2)$. Here, N_1 and N_2 are the numbers of equivalent positions in the initial and distorted phases, respectively. Indeed, taking into account the above-mentioned variation in the number and lengths of hydrogen bonds with the orientation of the tetrahedra, we have probably encountered a similar situation in the case of the (NH₄)₂WO₂F₄ crystal. Thus,

the quantity $\Delta S = R\ln 5$ can be interpreted in two ways. First, $R\ln 5 = R\ln 4 + R\ln 1.25$ is the entropy of the N2 tetrahedron disordered in the four positions plus the excess contribution due to additional distortions of the structure caused, for example, by the displacements of the other atoms. Second, the value $R\ln 5$ can be caused by the nonequivalence of the orientations of the N2 tetrahedron considered above.

5. CONCLUSIONS

Thus, joint analysis of the structure and entropy has brought us to the conclusion that the critical building blocks in the transition at T_1 are the NH₄ tetrahedra.

In view of the insignificant variations in entropy ($\Delta S_2 = 0.17R \ll R\ln 2$) at T_2 , it is obvious that the corresponding structural distortion is not caused by ordering processes and most likely can be caused by small displacements of some atoms. It is just an assumption at this stage, because data on the structure of the low-temperature phases are not available. In view of the twinning of the crystal mentioned above caused by the ferroelastic nature of the phase transition, powder diffraction methods of analysis are preferable.

ACKNOWLEDGMENTS

The authors are grateful to I.A. Baïdina and A.V. Virovets (Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences) for their assistance in performing the x-ray diffractometry experiment.

This work was supported by the National Science Support Foundation, the Krasnoyarsk Regional Science Foundation, the Russian Foundation for Basic Research (project no. 05-02-97707-r_Eniseï), and the Council on Grants from the President of the Russian Federation for Support of Leading Scientific Schools (project no. NSh 939.2003.2).

REFERENCES

1. S. V. Mel'nikova, V. D. Fokina, and N. M. Laptash, *Fiz. Tverd. Tela (St. Petersburg)* **48** (1), 110 (2006) [*Phys. Solid State* **48** (1), 106 (2006)].
2. N. M. Laptash, A. A. Udovenko, A. B. Slobodyuk, and V. Ya. Kavun, in *Abstracts of the 14th European Symposium on Fluorine Chemistry, Poznan, Poland, 2004* (Poznan, 2004), p. 253.
3. I. N. Flerov, M. V. Gorev, V. D. Fokina, A. F. Bovina, and N. M. Laptash, *Fiz. Tverd. Tela (St. Petersburg)* **46** (5), 888 (2004) [*Phys. Solid State* **46** (5), 915 (2004)].
4. K. S. Aleksandrov and I. N. Flerov, *Fiz. Tverd. Tela (Leningrad)* **21** (2), 327 (1979) [*Sov. Phys. Solid State* **21** (2), 195 (1979)].

Translated by E. Borisenko