Inelastic Neutron Scattering Study of the Specific Features of the Phase Transitions in $(NH_4)_2WO_2F_4$

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Abstract—Oxyfluoride $(NH_4)_2WO_2F_4$ has been studied by the inelastic neutron scattering method over a wide temperature range 10–300 K at two initial neutron energies of 15 and 60 meV. The role of tetrahedral ammonium groups in the mechanism of sequential phase transitions at $T_1 = 201$ K and $T_2 = 160$ K has been discussed.

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1. INTRODUCTION

Oxyfluorides containing sixfold-coordinated (quasi-octahedral) anions as main elements of the structure are considered promising compounds for the preparation of polar materials [1]. Actually, depending on the proportions of fluorine and oxygen (F : O) in the polyhedron and mutual arrangement of ligands (*cis*, *trans*, and *fac* configurations), the local symmetry of the quasi-octahedra can be tetragonal, orthorhombic, and trigonal. The central atom in the polyhedron, as a rule, is displaced toward the oxygen atom, which brings about the appearance of a dipole moment. At present, we know a significant variety of chemical compounds that can be grouped into several series of oxyfluorides, e.g., with the general formulas $A_3MO_xF_{6-x}$ ($x = 1, 2, 3$; $M = $ Ti, Nb, W, Mo, etc.) and $A_2MO_2F_4$ ($M = $ W and Mo), where A is a univalent cation. The former compounds, despite the low local symmetry of the sixfold-coordinated anions and possible existence of a dipole moment in them, predominantly crystallize in a cubic perovskite-like structure of the elpasolite–cryolite type with symmetry $Fm\bar{3}m$ [2–5] and, naturally, do not possess a macroscopic polarization in this state. Such a high symmetry is explained by the possible existence of two types of disordering in the oxyfluorides. The first type is a disordering of F(O) atoms in a sixfold-coordinated anion, and the second type is due to the orientational disor-

dering in the anion arrangement relative to each other in the crystal lattice, in which the resultant dipole moment of the crystal is equal to zero. At the same time, it was established that, as the temperature decreases, many cubic oxyfluorides $A_3MO_xF_{6-x}$ undergo structural phase transitions, which are accompanied by the appearance of the ferroelectric and ferroelastic states [3–6].

The symmetry of oxyfluorides of the $A_2MO_2F_4$ group is dependent on the size and shape of the univalent cation A, and their structure is centrosymmetric in all the known cases. The disturbance of the stability of the initial phase with respect to the temperature was reliably established only for ammonium-containing crystals [7–9].

The oxyfluoride $(NH_4)_2WO_2F_4$, whose structure is characterized at room temperature by the orthorhombic symmetry (space group *Cmcm*, $Z = 4$) [9, 10] is one of the most extensively studied oxyfluorides. The study of the specific heat and birefringence over a wide temperature range shows that the crystal undergoes a sequence of two phase transitions at temperatures $T_1 = 201$ K and $T_2 = 160$ K [7, 9]. The shape of the temperature dependences of the permittivity along three principal crystallographic directions demonstrates the nonferroelectric nature of the structural transformations [6]. The existence of excess contributions of the orthorhombic phase [7, 9] to the birefringence and

specific heat of $(NH_4)_2WO_2F_4$ over a wide temperature range is indicative of a complex character of the phase transition at T_1. Changes in the entropy accompanying the phase transitions are substantially different: $\Delta S_1 = 19.0$ J/mol K ($\sim R\ln 10$) and $\Delta S_2 = 1.4$ J/mol K ($\sim R\ln 1.2$) [9]. Thus, it is evident that the high-temperature transition is due to the processes of ordering of some structural elements and the low-temperature transition is due to the small displacements of atoms in the already ordered phase. It was established that the temperature range of the stability of the intermediate phase narrows as the hydrostatic pressure increases.

The crystal structure of the initial phase of $(NH_4)_2WO_2F_4$ was refined at 293 K [9] and 297 K [10] using X-ray single-crystal diffractometry. As a whole, coinciding results of both studies show that the crystal structure consists of the isolated octahedra $[WO_2F_4]$ with the *cis* configuration and two crystallographically independent ammonium groups $N1H_4$ and $N2H_4$. The motion of the partially ordered octahedra is characterized by a dynamic orientational disorder related to their rotation around the axis in which the localized atoms $O = W-F$ lie. Unlike [9], where only the aniso-tropic motion of all the atoms was considered, in [10], a model of the structure was considered and justified including, to a high degree of reliability, the disordering of the central atoms over two sites, namely, 4c (the central atom W1 is on the pseudotetragonal axis of the sixfold-coordinated polyhedron) and 16h (disordering of W2 atom over four sites). Owing to the very short W1–W2 distance, the electron clouds of the atom in different sites overlap [10] and, most likely, that is why the electron density map of the W atoms [9] shows its homogeneous distribution without portions with increased density which are characteristic of disordered positions of the atoms. On the other hand, the electron density profile is a square with vertices oriented toward the sites of the F(O) atoms, which quite probably demonstrates the displacement of the W atom due to its motion providing a short W–O bond.

We failed to localize the hydrogen atoms; however, according to the symmetry of the environment, we concluded that the tetrahedral $N1H_4$ and $N2H_4$ cations are most likely characterized by different degrees of the orientational disordering [9, 10].

Below T_2, the $(NH_4)_2WO_2F_4$ structure is characterized by the triclinic symmetry ($P\bar{1}$) and complete ordering of the W, F, and O atoms [10]. As for the ammonium tetrahedra, it is assumed that they are not completely ordered, if at all.

A complex analysis of the crystal structure and entropy [9, 10] allows the assumption that the mechanism of the phase transition at T_1 can involve ordering of both the octahedra (and, correspondingly, central atom) and the tetrahedra.

In this work, the mechanism of the phase transitions in $(NH_4)_2WO_2F_4$ has been studied using the incoherent inelastic neutron scattering. The incoherent cross section of neutron scattering by hydrogen atoms is very large and exceeds those for W, O, and F atoms by a factor of approximately 80. Thus, the incoherent inelastic neutron scattering spectra measured give the possibility of obtaining objective information on the ammonium-ion dynamics.

2. EXPERIMENTAL TECHNIQUE AND RESULTS OF MEASUREMENTS

The $(NH_4)_2WO_2F_4$ samples were synthesized by the technique described in [7].

The incoherent inelastic neutron scattering spectra were measured on a HRMECS high-resolution spectrometer at the Argonne National Laboratory (United States) [11]. Two initial energies $E_i = 15$ and 60 meV were used. The experiments were performed at six temperatures equal to 10, 140, 175, 210, 260, and 300 K with exposure for 16 h per measurement from the sample in a cell and for 8 h for the background measurement from an empty cell.

The results of measuring the incoherent inelastic neutron scattering spectra at $E_i = 15$ meV at different temperatures are presented in Fig. 1a. The incoherent inelastic neutron scattering spectrum measured at 10 K has no a contribution from the incoherent quasi-elastic neutron scattering, and the maxima observed on the transferred-energy scale approximately in the range from 2.5 to 12.0 meV are associated with the hydrogen modes. At the same time, even at 140 K, i.e., below the phase transition temperature T_2, a contribution of incoherent quasi-elastic neutron scattering appears and rather quickly increases at 175 K and higher temperatures. In the intermediate phase at 175 K and in the initial orthorhombic phase *Cmcm* at 210 K, the contributions of incoherent quasi-elastic neutron scattering to the incoherent inelastic neutron scattering spectra almost overlap with the intensities of the hydrogen modes.

The incoherent inelastic neutron scattering spectra measured at $E_i = 60$ meV at the same temperatures are shown in Fig. 1b. The spectrum measured at 10 K gives information on the partial density of vibrational states of the hydrogen modes in the range of the transferred energy approximately from 10 to 50 meV.

The maxima in the incoherent inelastic neutron scattering spectra measured at $E_i = 15$ and 60 meV and at a temperature of 10 K allow one to select and determine the energies of the ammonium groups. The decomposition of the incoherent inelastic neutron scattering spectra was performed by approximation of the peaks by Gaussians. The results obtained are given in the table.

The table also lists the results of studying the vibrational modes of $(NH_4)_2WO_2F_4$ at room temperature by infrared (IR) spectroscopy [12]. The vibrational modes determined using IR spectroscopy differ from
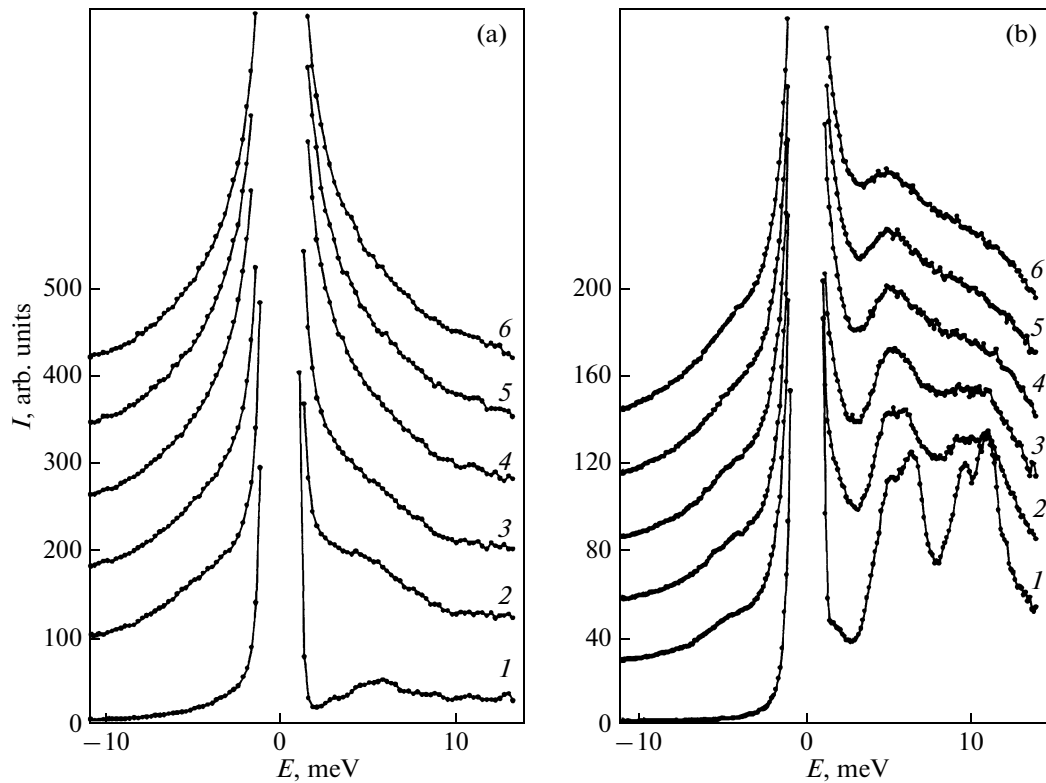
Fig. 1. Incoherent inelastic neutron scattering spectra of $(NH_4)_2WO_2F_4$ measured using neutrons with the initial energies $E_i =$ (a) 15 and (b) 60 meV at temperatures of (*1*) 10, (*2*) 140, (*3*) 175, (*4*) 210, (*5*) 260, and (*6*) 300 K.

the hydrogen modes. The symmetric designation of the vibrational modes found from the IR studies corresponds to the anion complex $[WO_2F_4]^{2-}$ [12]. The hydrogen modes with energies of 36.1 and 43.4 meV can be ascribed to the vibrational modes of the ammonium ions. It is natural that the vibrational modes of the anion complex are not observed in the incoherent inelastic neutron scattering spectra.

The factors entering into the expression for the incoherent inelastic neutron scattering intensity can be estimated by dividing of the incoherent neutron scattering cross section σ_{inc}^i for the ith atom by the atomic mass M_i: $\Sigma_{inc}^i = \sigma_{inc}^i / M_i$ [13]. The quantities Σ_{inc}^i determine the partial contribution of each atom to the intensity of the incoherent neutron scattering. These parameters for N, W, O, and F atoms are 0.80, 0.03, 0.53, and 0.45, which are very small as compared to the value characteristic of H atom (81.7).

Thus, incoherent inelastic neutron scattering preferably gives only the hydrogen modes and the IR experiments detect only the internal modes of the $[WO_2F_4]^{2-}$ complex.

3. DISCUSSION

As a result of the measurement of incoherent inelastic neutron scattering, we have obtained information on the hydrogen modes in $(NH_4)_2WO_2F_4$ at a temperature of 10 K. As the temperature increases, the incoherent quasi-elastic neutron scattering makes, at 140 K, a significant contribution to the incoherent inelastic neutron scattering intensity, overlapping with the hydrogen-mode peaks. At low transferred energies (2–10 meV), already at a temperature above T_2, the incoherent quasi-elastic neutron scattering is predominantly observed over the temperature range from 175 to 300 K. The significant contribution of incoherent quasi-elastic neutron scattering is indicative of a decrease in the height of the rotational barrier, which prevents the reorientation of the ammonium ions over the temperature range of the phase transition at temperatures T_2 and T_1.

The incoherent inelastic neutron scattering by the orientational degrees of freedom of the ammonium ions with increasing temperature is accompanied by a faster broadening of the hydrogen mode peaks as compared to the incoherent inelastic neutron scattering by the translational degrees of freedom of the hydrogen modes. As the temperature increases, the peaks of the hydrogen vibrational modes the energies of 36.1 and 43.4 meV disappear earlier as compared to the peaks

from the hydrogen translational modes with energies of 18.9 and 25.6 meV (see Fig. 1b).

Thus, the study of the vibrational properties of $(NH_4)_2WO_2F_4$ using the incoherent inelastic neutron scattering demonstrates a significant participation of the ammonium ions during both phase transitions. However, a more complete understanding of these phase transitions needs a detailed study of the crystal structures of the initial and distorted phases by neutron diffraction, which allows the determination of the coordinates and degree of disordering of the hydrogen atoms.

A set of the structural data [9, 10] and the results of study of the dynamics of $(NH_4)_2WO_2F_4$ using incoherent inelastic neutron scattering permit us to propose the explanation of the contribution from the ammonium tetrahedra to an anomalous behavior of the specific heat based on the Pauling theory [14]. The existence of the two crystallographically nonequivalent $N1H_4$ and $N2H_4$ groups allows the assumption that both ions with a different environment of the nearest neighbors are in different potential fields, which provides the existence of two librational modes with different energies belonging to different ammonium ions. At a relatively high temperature, namely, above the first critical temperature $T_1 = 201$ K, the rotational barrier to the reorientation or the activation energy does not exceed both energies of the librational modes. According to the Pauling theory, in this case, both ammonium ions perform the reorientation jumps, which are detected using the incoherent quasi-elastic neutron scattering. As the temperature decreases, the crystal lattice parameters decrease, which is accompanied by an increase in the rotational barrier. At the temperature T_1, the rotational barrier becomes larger than a librational-mode energy of 36.1 meV of one of the ammonium ions, which ceases to perform the reorientation jumps and becomes disordered. One can assume that the ordering of the octahedron is a primary reason of the structure distortion and is the trigger mechanism for ordering the $N1H_4$ groups. According to [10], one can assume that, in the low-temperature phase, the $N2H_4$ ion with a librational-mode energy of 43.4 meV remains disordered. Its ordering can gradually occur with further decreasing temperature irrespectively of the phase transitions. Such a circumstance occurs frequently; for example, it is observed in ammonium fluorides NH_4MF_3 ($M =$ Mn, Co) with a perovskite structure [15].

The proposed model of the anomalous behavior of the specific heat in $(NH_4)_2WO_2F_4$ in the temperature range 160–201 K is confirmed by the following approximate estimates. On the one hand, the difference between the critical temperatures is ~40 K; on the other hand, the difference between the energies of two librational modes corresponding to two ammonium ions is approximately 7 meV, which is about 70 K on the temperature scale. Thus, the crystallographi-

Vibrational modes in $(NH_4)_2WO_2F_4$

Energy, meV		Hydrogen modes
Incoherent inelastic neutron scattering, $T = 10$ K	IR, $T = 300$ K [12]	
2.9		NH_4, lattice
4.5		NH_4, lattice
5.9		NH_4, lattice
7.7		NH_4, lattice
10.8		NH_4, lattice
18.9		NH_4, ν_5
25.6		NH_4, ν_5
	30.9	B_1, ν_{11}
	32	A_1, ν_5
	35	B_2, ν_{14}
36.1		NH_4, ν_6
43.4		NH_4, ν_6
	47.8	A_1, ν_4

cally independent ammonium ions are, due to the nearest environment, in the potential wells with different activation energies and reorientation barriers, which determines the relationship between the phase transition temperatures, librational-mode energies, and the sequence of ordering during transformation from the high-temperature phase into the low-temperature phase.

Return to consideration of the values of the entropy in the phase transitions, its character in the intermediate phase, and also a change in the entropy at the transformation point at the temperature T_1, i.e., the entropy jump δS_1 [9]. The latter quantity is easily determined from the data on the study of $(NH_4)_2WO_2F_4$ by the method of the quasi-static thermograms, which allowed one to find the latent heat of the transition $\delta H_1 = 620$ J/mol [9]. Using the relationship $\delta S_1 = \delta H_1/T_1$ relating the latent heat and the entropy jump, we find $\delta S_1 = 3.1$ J/mol K $\approx R$ln1.5. Since δS_1 is smaller than the value Rln 2, we can believe with a fair degree of confidence that, at the high-temperature transition point, neither the tetrahedral cation with a lower librational energy nor the octahedral anion are completely ordered.

A smooth variation in the entropy in the intermediate phase [9] can be interpreted as a change related to a smooth gradual increase in the value of the potential barriers, which are accompanied by a gradual change in the probability of occupation of the sites corresponding to disordered states of the $[WO_2F_4]^{2-}$ and NH_4^+ groups. The small value of ΔS_2 demonstrates the absence of any processes of ordering in the

$(NH_4)_2WO_2F_4$ structure at this temperature and is most likely due to the small displacement of some atoms. One can assume that such atoms are the nitrogen atoms changing their equilibrium position as a result of the complete or partial ordering of the tetrahedra.

4. CONCLUSIONS

The studies of $(NH_4)_2WO_2F_4$ were performed by the incoherent inelastic neutron scattering method. The increasing contribution of the incoherent quasielastic neutron scattering to the intensity of incoherent neutron scattering as the temperature increases from 10 to 300 K due to the ammonium ions confirms the validity of the hypothesis [9] on the decisive contribution of ordering of the tetrahedral cations to the entropy of the high-temperature phase transition. To more deeply understand the mechanisms of both phase transitions, investigations into the structures of the initial and distorted phases of both hydrogen and deuterated compounds by the elastic neutron scattering method are necessary.

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