
LATTICE DYNAMICS
AND PHASE TRANSITIONS

Refinement of the Crystal Structure of the High-Temperature Phase G_0 in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ (Powder, X-Ray, and Neutron Scattering)

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Abstract—The $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ compound undergoes a series of phase transitions: $G_0 \rightarrow 201$, $K \rightarrow G_1 \rightarrow 160$, and $K \rightarrow G_2$, with a significant change in entropy ($\Delta S_1 \sim R \ln 10$ at the $G_0 \rightarrow G_1$ transition), which indicates significant orientational disordering in the G_0 phase and the order–disorder type of the phase transition. X-ray diffraction is used to identify the crystal structure of the G_0 phase as rhombohedral (sp. gr. $Cmcm$, $Z = 4$), determine the lattice parameters and the positions of all atoms (except hydrogen), and show that $[\text{WO}_2\text{F}_4]^{2-}$ ions can form a superposition of dynamic and static orientational disorders in the anionic sublattice. A determination of the orientational position of $[\text{NH}_4]^+$ ions calls for the combined method of elastic and inelastic neutron scattering. Inelastic neutron scattering is used to determine the state of hindered rotation for ammonium ions in the G_0 phase. Powder neutron diffraction shows that the orientational disorder of NH_4 ions can adequately be described within the free-rotation approximation.

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INTRODUCTION

An interesting feature of the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ compound is the manifestation of the barocaloric effect, which is due to the orientational lattice disorder of the tetrahedral $[\text{NH}_4]^+$ and octahedral $[\text{WO}_2\text{F}_4]^{2-}$ ions [1]. A study of the temperature dependence of the specific heat of this material revealed the presence anomalies at temperatures $T_1 = 201$ K and $T_2 = 160$ K, which correspond to the $G_0 \leftrightarrow G_1 \leftrightarrow G_2$ phase transitions; the change in entropy ΔS_i ($i = 1, 2$) at these critical points is $\Delta S_1 = 19.0$ J/(mol K) (or $\Delta S_1 \approx R \ln 10$) and $\Delta S_2 = 1.4$ J/(mol K) [2, 3].

The change in entropy $\Delta S_i \cong R \sum_i m_i(p, T) \ln(m_i(p, T))$ (m_i is the multipole moment in orientation i at a pressure p and temperature T in the G_0 phase) at the $G_0 \rightarrow G_1$ phase transition is estimated, on the one hand, from the change in the specific heat and, on the other hand, from the change in the orientational disorder of tetrahedral and octahedral ions in the complex study using X-ray and neutron scattering.

An X-ray analysis showed that at room temperature the crystal structure is described by the orthorhombic sp. gr. $Cmcm$ with $Z = 4$ and the lattice parameters $a = 5.9292(3)$ Å, $b = 14.3940(7)$ Å, and $c = 7.1351(3)$ Å [4].

The significant change in entropy at the critical temperature T_1 indicates a phase transition of order–disorder type due to the orientational disorder of tetrahedral and octahedral molecular ions. The results of an X-ray structural study [5, 6] indicate the possibility of superposition of the dynamic and static orientational disorders in the anionic sublattice of the G_0 phase. One oxygen atom and one fluorine atom of the octahedral ion $[\text{WO}_2\text{F}_4]$ are localized on the b axis. The other ligands occupy four equatorial positions with probabilities of 0.75 (F) and 0.25 (O); 86% octahedra are in dynamics and only 14% octahedra are in statics [2, 4–6].

The orientational disorder of tetrahedral ions (NH_4) was not determined; however, it was shown that the unit cell contains two crystallographically independent ammonium ions (N1H_4 and N2H_4), and the positions of their nitrogen atoms were determined. It was suggested that these ions make a significant contribution to the orientational disorder of the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ lattice.

The presence of tungsten in the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ compound hinders a determination of the orientational position of ammonium ions by X-ray diffraction. In this paper we report the results obtained with a complex method for determining the orientational disorder in the G_0 phase using X-ray powder and neutron scattering.

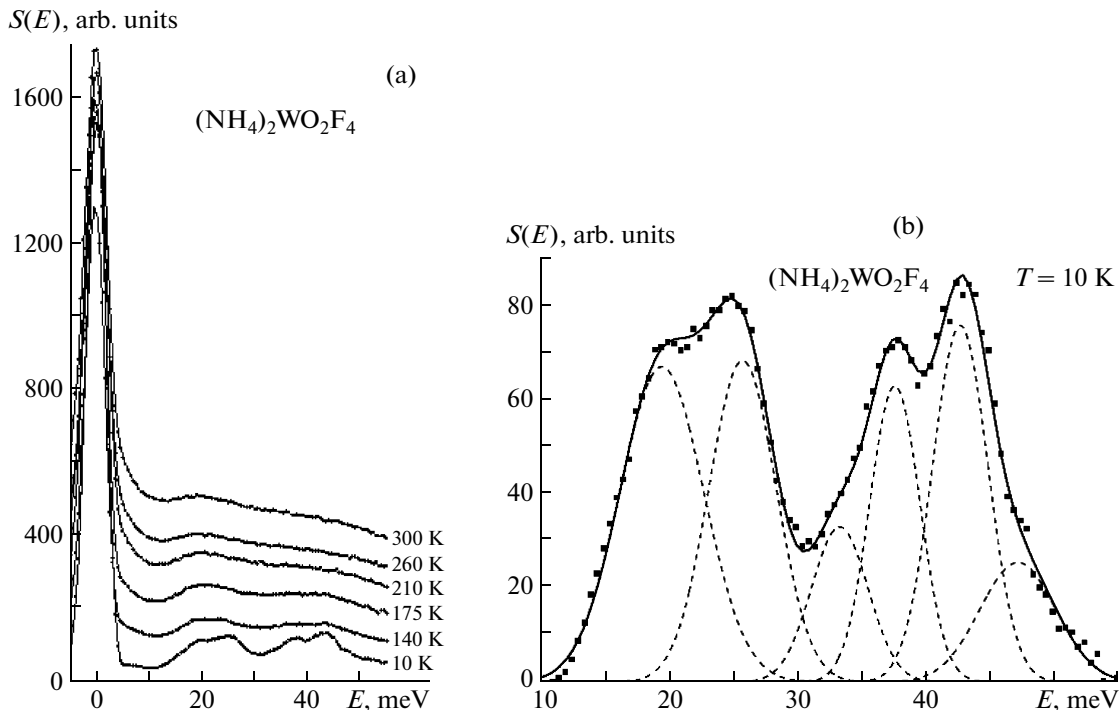


Fig. 1. $(\text{NH}_4)_2\text{WO}_2\text{F}_4$: (a) the IINS intensity $S(E)$, measured at an incident neutron energy of 60 meV and temperatures of 10, 140, 175, 210, 260, and 300 K, and (b) the 10-K $S(E)$ spectrum expanded in hydrogen modes.

EXPERIMENTAL DATA AND RESULTS

Inelastic Incoherent Neutron Scattering from $(\text{NH}_4)_2\text{WO}_2\text{F}_4$

Measurements of inelastic incoherent neutron scattering (IINS) were carried out in [7] to confirm the significant contribution of tetrahedral ammonium ions to the formation of orientational disorder in the high-temperature G_0 phase of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$. The cross section of incoherent neutron scattering from hydrogen atoms is known to significantly exceed a similar cross section for other atoms; this fact allows one to selectively study the motion of hydrogen atoms. The method used to synthesize an $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ sample was described in [2, 3].

The IINS spectra from $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ were measured on a high-resolution HRMECS spectrometer

Table 1. $(\text{NH}_4)_2\text{WO}_2\text{F}_4$: the energies of hydrogen modes found using IINS at 10 K and by calculation [9] (the energies are in meV)

Mode	IINS	Calculation [9]	Hydrogen modes
1	19.5		$\nu_5^1 - (\text{NH}_4)^+$
2	26.0		$\nu_5^2 - (\text{NH}_4)^+$
3	34.2	32.7	$\nu_5^{\text{ridden}} - [\text{WO}_2\text{F}_4]^{2-}$ [9]
4	37.9		$\nu_6^1 - (\text{NH}_4)^+$
5	42.9		$\nu_6^2 - (\text{NH}_4)^+$
6	47.5	47.6	$\nu_4^{\text{ridden}} - [\text{WO}_2\text{F}_4]^{2-}$ [9]

(Argonne National Laboratory, United States) [8]. To study the lattice vibrations in the librational range, incident neutrons with an energy $E_{in} = 60$ meV were used. The measurements were performed in a wide temperature range from 10 to 300 K, with a 16-h exposure per measurement for a sample in a capsule and 8-h exposure per measurement from an empty capsule [7].

The IINS spectra $S(E)$ are shown in Fig. 1a in the energy-transfer range $\Delta E > 0.0$ meV (the range of generation of elementary excitations). The measurement temperatures are indicated in the caption to Fig. 1a: 10, 140, 175, 210, 260, and 300 K.

The $S(E)$ spectrum at 10 K, which corresponds to the low-temperature G_2 phase, contains two doublets; the profiles of the components can be described by Gaussians (see Fig. 1b). Their centroids determine the energies of lattice hydrogen modes. The doublet with energies of 19.5 and 26.0 meV corresponds to the optical translational modes of ammonium ions (ν_5^1 and ν_5^2), while the doublet with energies of 37.7 and 42.8 meV corresponds to the librational modes of ammonium ions (ν_6^1 and ν_6^2). Two hydrogen modes with energies of 33.4 and 47.3 meV, which are due, respectively, to the ν_5^r and ν_4^r modes of the $[\text{WO}_2\text{F}_4]^{2-}$ octahedral ion [9], were also selected; they were referred to as riddened modes. The hydrogen modes selected in the spectrum $S(E)$ are listed in Table 1.

At a temperature of 140 K, the contribution of the rise in the anharmonicity of translational and libra-

tional modes becomes significant in the G_2 phase; this rise is accompanied by an increase in the width of their peaks and leads to a much larger overlap of single-mode peaks in each doublet. Note that the peak of the librational mode at 37.7 meV undergoes a larger broadening than the peak of the librational mode at 42.8 meV. Another distinctive feature of the 140-K spectrum is the presence of a contribution from quasi-elastic incoherent neutron scattering (QENS) to the IINS spectrum.

The 175-K IINS spectrum $S(E)$ in Fig. 1a corresponds to the intermediate G_1 phase. The peaks of translational and librational modes have a form of wide maxima due to the complete overlap of the doublet-component profiles in view of the broadening of the corresponding unitary peaks.

The $S(E)$ spectra in the G_0 phase, which were measured successively at 210, 260, and 300 K, contain a single wide maximum corresponding to the doublet of optical translational hydrogen modes and the QENS contribution; they extend to high energies and overlap with the IINS spectrum.

Two groups of ammonium ions ($N1H_4$ and $N2H_4$) differ in the nearest environments and, hence, are located in potential wells with different rotational potential barriers to reorientations and have different librational-mode energies. The rotational potential barrier (E_{lib}) to reorientation decreases with an increase in temperature and, when the librational-mode energy starts exceeding the potential barrier to reorientation, this ammonium ion passes to the hindered-rotation state. This interpretation of the observed change in the intensity $S(E)$ in the region of scattering from librational modes can be presented based on the Pauling model [10].

Powder X-Ray Study of the $(NH_4)_2WO_2F_4$ Crystal Structure

The orientational state of molecules in the lattice is known to affect the intensity of Bragg reflections [11, 12]. Diffraction methods are widely used to determine orientational disorder in molecular crystals. The crystal structures of different phases of the $(NH_4)_2WO_2F_4$ compound were initially identified using the methods of powder and single-crystal X-ray diffraction [2, 4–6]. These techniques made it possible to determine only the positions of tungsten, oxygen, fluorine, and nitrogen atoms. The positions of hydrogen atoms (or orientational positions of ammonium ions) in the high-temperature G_0 phase were not established because of the dominant contribution of scattering from tungsten atoms.

The crystal structure of $(NH_4)_2WO_2F_4$ at room temperature was determined by powder X-ray diffraction. The measurements were performed on a D8 ADVANCE X-ray diffractometer (Bruker AXS) using

Table 2. X-ray diffraction data on the atomic coordinates and isotropic thermal parameters (B_{iso}) of the $(NH_4)_2WO_2F_4$ crystal structure

Atom	x	y	z	B_{iso}
W	0.000000	0.391660	0.750000	3.836446
O1	0.000000	0.513553	0.750000	4.112780
O2	0.230256	0.377678	0.574270	4.527557
F2	0.230256	0.377678	0.574270	4.527557
F3	0.000000	0.253836	0.750000	4.430417
N1	0.000000	0.276167	0.250000	1.534965
N2	0.000000	0.062092	0.750000	3.142882

Cu $K\alpha 1$ radiation (Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences (RAS)). The crystal structure was identified using the DDM software [13]. The atomic positions, except for hydrogen and B_{iso} , are in good coincidence with the single-crystal and powder X-ray diffraction data [2, 4–6]; they are listed in Table 2. Figure 2a shows the measured X-ray profile I_{obs} (symbols), calculated X-ray spectrum I_{cal} (solid line), and the difference profile $I_{obs} - I_{cal}$ (solid line). The positions of Bragg reflections are indicated by vertical lines (\square). The small difference $I_{obs} - I_{cal}$ indicates the high reliability of the structural parameters found.

Powder Neutron-Diffraction Study of $(NH_4)_2WO_2F_4$ Crystal Structure

Preliminary measurements of a powder neutron diffraction pattern from an $(NH_4)_2WO_2F_4$ sample were performed at room temperature on a D7a diffractometer (Institute of Metal Physics, Ural Branch, RAS), located on the IVV-2M reactor in the town of Zarechnyi (near Yekaterinburg). The fitting of the powder neutron diffraction pattern allowed us to determine the orthorhombic lattice parameters, which turned out to be in good agreement with the data in the literature [2, 4–6] and confirmed the single-phase character of the $(NH_4)_2WO_2F_4$ sample.

Then powder neutron diffraction patterns from the $(NH_4)_2WO_2F_4$ sample were measured on the HRPT diffractometer of the reactor at the Paul Scherrer Institute (Switzerland) [14].

The crystal structure of $(NH_4)_2WO_2F_4$ in the G_0 phase was refined using the FullProf package [15]. These programs make it possible to describe profiles of powder neutron diffraction patterns for molecular ionic crystals using the model of rotational molecular structural factor.

The results of studying the $(NH_4)_2WO_2F_4$ high-temperature phase by IINS showed that ammonium ions can be considered within the hindered rotation model. In this case, one can use the structural factor

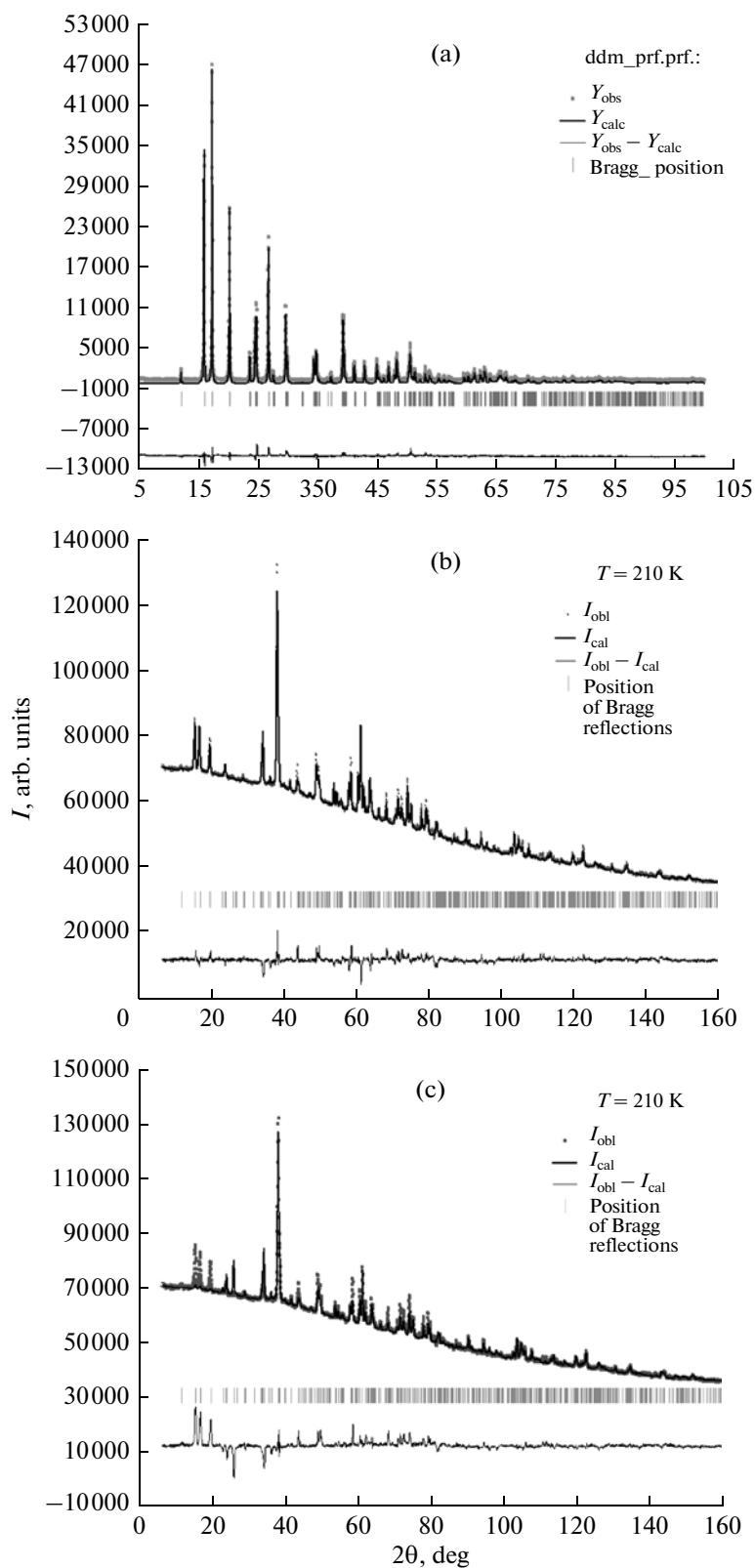


Fig. 2. $(\text{NH}_4)_2\text{WO}_2\text{F}_4$: (a) the powder X-ray diffraction pattern measured at $T = 295$ K; (b) the powder neutron diffraction pattern, $T = 210$ K, I_{calc} is calculated taking into account the rotational structural form factor of the ammonium ion in the spherical approximation; and (c) the calculated neutron diffraction pattern I_{calc} (hydrogen ammonium atoms are disregarded, $T = 210$ K).

for the spherical rotation of an ammonium ion (taking into consideration only the N–H bond length, which is estimated to be 1.0 Å) to describe the rotational molecular structural factor. The results of this approximation are shown in Fig. 2b. I_{obs} and I_{cal} are, respectively, the intensity profiles of the experimental (symbols) and calculated (solid line) neutron diffraction patterns. The positions of Bragg reflections are indicated by vertical lines (|). The difference between profile intensities $I_{obs} - I_{cal}$ indicates the degree of reliability of the proposed model of the orientational disorder of ammonium ions in the G_0 phase of the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ compound in the approximation of free or spherical rotation.

DISCUSSION AND CONCLUSIONS

The results of a structural study of the high-temperature phase G_0 in $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ by neutron scattering showed that the model (based on experimental IINS data) presenting the hindered rotation of ammonium ions in the form of free rotation adequately describes the intensity profiles of experimental neutron diffraction patterns. It is of interest to compare the intensities of X-ray and neutron diffraction scattering from the G_0 -phase crystal structure. The profiles of X-ray and neutron diffraction scattering from the crystal structure of the G_0 phase are shown in Figs. 2a and 2c. It can be seen that the observed Bragg reflections have identical positions on the scale of the $2\theta^\circ$ scattering angle, significantly differ in intensity in some cases, or are absent in the X-ray diffraction profile but present in the neutron diffraction profile. Obviously, this considerable difference in the sets of diffraction reflections in the X-ray and neutron profiles is related to the significant difference in the scattering amplitudes for radiations of different types from atoms and, in particular, the presence of tungsten atoms.

The possibilities of refining the orientational disorder of ammonium ions by powder neutron diffraction were demonstrated using two versions of calculated neutron profile:

(i) the rotational molecular form factor is described within the model of a free rotating ammonium ion (Fig. 2b);

(ii) the neutron profile is calculated taking into account all atoms except for the hydrogen atoms of ammonium ion (Fig. 2c).

A comparison of the results of approximating the profiles of neutron diffraction spectra within the approximation of spherical free rotation using a rotational form factor proved the correctness of the model chosen. The X-ray diffraction profile calculated disregarding hydrogen atoms in the structural factor adequately describes the experimental diffraction profile for the G_0 phase at $T = 295$ K, mainly due to the scattering from tungsten atoms (Fig. 2a). The neutron dif-

fraction profile calculated taking into account the contribution of hydrogen atoms as a structural form factor in the form of free rotating molecular ammonium ions adequately describes the experimental diffraction profile from the G_0 phase at 210 K (Fig. 2b). However, the neutron diffraction profile calculated disregarding the contribution of hydrogen atoms to the structural factor is generally inconsistent with the experimental diffraction profile in the range of scattering angles reaching 30° (Fig. 2b).

Thus, when studying the crystal structure of the $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ high-temperature phase, the complex approach based on the use of X-ray and neutron diffraction played a key role in refining the orientational disorder of anions and cations. The combination of radiations of different types allowed us to determine the orientational disorder of tetrahedral ammonium ions and octahedral WO_2F_4 ions using neutron and X-ray scattering, respectively. Obviously, to more completely describe the orientational disorder of ammonium ions, it will be necessary to calculate the neutron-scattering profile I_{cal} from the G_0 phase with a more rigorous consideration of the possible orientations of ammonium ions for each group. The free-rotation approximation used for ammonium ions in the G_0 phase only proved the necessity for a complex study using X-ray and neutron scattering methods.

The elastic and inelastic neutron scattering data obtained by us confirm that the crystal structure of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ in the high-temperature G_0 phase can be interpreted within the Pauling model [10].

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