Structural Changes during Phase Transitions and the Critical
and Noncritical Order Parameters
in the (NH₄)₃Nb(O₂)₂F₄ Crystal
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Abstract—The structures of two phases of the (NH₄)₃Nb(O₂)₂F₄ crystal, namely, the parent cubic phase and the most distorted low-temperature phase, have been determined from data of an X-ray diffraction experiment performed for a powder sample. The profile and structural parameters have been refined according to the procedure implemented in the DDM program. The results obtained have been discussed with invoking the group-theoretical analysis of the complete order parameter condensate, which takes into account the critical and noncritical atomic displacements and allows the interpretation of the obtained experimental data. It has been found that the most probable sequence of structural transformations occurring in the crystal can be schematically represented in the following form:

\[ \Gamma_5^{(11-7)} \otimes \Sigma_2^{4-2} \otimes \Sigma_3^{4-3} \]

PHASE TRANSITIONS

1. INTRODUCTION

The specific features of the structure of compounds with the general formula \( A_2BM_{O_x}F_{6-x} \) (where \( A = K, Rb, Cs; B = Ti, Mo, W; x = 1, 2, 3 \)) have been repeatedly reported in the literature [1, 2] and, in particular, in our previous papers [3–5]. It is especially important that the main structural elements in these compounds are noncentrosymmetric oxyfluoride anions \( MO_{x}F_{6-x} \), which, under specific conditions, allow the formation of polar structures with ferroelectric properties [3]. However, the majority of fluoride–oxygen compounds crystallize in the nonpolar phase of the cubic elpasolite-like structure with a face-centered lattice (space group \( Fm\overline{3}m \), \( Z = 4 \)).

An attempt to determine the structures of the compounds \( (NH_4)_3Nb(O_2)_2F_4 \) and \( (NH_4)_3Ta(O_2)_2F_4 \) with the cubic symmetry \( Fm\overline{3}m (Z = 4) \) at room temperature was made by Ružić-Toroš et al. [6]. According to the data obtained by those authors, in the parent cubic phase of these compounds, the fluorine atoms are located in the position \( 24e \) and disordered over six positions, whereas the oxygen atoms are located in the position \( 96j \) and distributed over 24 positions. However, in such compounds, the oxygen atoms form dumbbell-like groups \( (O_2)^2– \). Therefore, it is more expedient to speak about the \( (O_2) \) group rather than about a single oxygen atom. Then, the center of mass of the \( (O_2) \) dumbbell is located in the position \( 24e \) and distributed over 12 positions.

Unfortunately, in [6], a number of questions remained open. In particular, the coordinates of the hydrogen atoms of the ammonium groups were not determined and the geometry of the \( Nb(O_2)_2F_4 \) polyhedron was not elucidated. Furthermore, in the aforementioned paper, the authors presented a figure with the cis location of peroxide groups in the \( Nb(O_2)_2F_4 \) polyhedron, which is in contradiction with the vibrational spectra obtained by Von Schmidt et al. [7] for the \( (NH_4)_3Ta(O_2)_2F_4 \) compound. Reasoning only from the information on the structures of the cubic phases of the \( (NH_4)_3Nb(O_2)_2F_4 \) and \( (NH_4)_3Ta(O_2)_2F_4 \) compounds, which were determined in [6], one can construct several variants of the location of the \( (O_2) \)...
features: first-order structural transformations at close temperatures, revealed the occurrence of three adjacent anomalies observed in the heat capacity during cooling of the (NH₄)₃Nb(O₂)₂F₄ compound and, from the changes investigated of the phase transitions in the (NH₄)₃Nb(O₂)₂F₄ crystal.

It can be seen from Figs. 2 and 3 that, as the temperature decreases after the first phase transition at the temperature $T_1 = 193.0$ K, the shape of the X-ray diffraction pattern taken from the powdered sample of the (NH₄)₃Nb(O₂)₂F₄ compound remains almost unchanged. In these X-ray diffraction patterns, there are no superstructure reflections or a noticeable split-

more accurate temperature X-ray powder diffraction investigations of the structural characteristics of the crystal and their changes during the phase transitions observed in this crystal.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Niobium oxyfluoride (NH₄)₃Nb(O₂)₂F₄ was synthesized in the form of a white crystalline powder by the solution crystallization method.

The X-ray diffraction patterns from polycrystalline samples of the (NH₄)₃Nb(O₂)₂F₄ compound were recorded using an Anton Paar TTK450 temperature chamber installed on a D8-ADVANCE X-ray powder diffractometer (CuKα radiation, θ–2θ scan mode, VANTEC linear position-sensitive detector). Liquid nitrogen was used as a coolant. The scan step in the angle 2θ was equal to 0.016°, and exposure per frame was 0.3 s. The experiments were carried out at temperatures in the range from 155 to 253 K with a step of 2 K. This made it possible to reveal regularities in the variations of the structural characteristics of the crystal during the phase transition. In order to more reliably refine the structures of the parent phase $G_0$ and the distorted phase $G_3$ at two temperatures (298 and 133 K), each being fairly different from the phase transition temperatures, the exposure at each experimental step was increased to 0.6 s. The temperatures of the chosen experiments excluded the influence of transient phenomena.

3. EXPERIMENTAL RESULTS

It can be seen from Figs. 2 and 3 that, as the temperature decreases after the first phase transition at the temperature $T_1 = 193.0$ K, the shape of the X-ray diffraction pattern taken from the powdered sample of the (NH₄)₃Nb(O₂)₂F₄ compound remains almost unchanged. In these X-ray diffraction patterns, there are no superstructure reflections or a noticeable split-

![Fig. 1. (a–e) Variants of the arrangement of the molecular groups (O₂) in the Nb(O₂)₂F₄ polyhedron of the cubic phase of the (NH₄)₃Nb(O₂)₂F₄ crystal.](image)

![Fig. 2. Fragments of the X-ray diffraction patterns of the (NH₄)₃Nb(O₂)₂F₄ compound measured at temperatures varying from 155 to 253 K in steps of 2 K. The arrows indicate the superstructure reflections, and the asterisks denote the reflections obtained from the ice phase.](image)