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LATTICE DYNAMICS AND PHASE TRANSITIONS

Optical Studies of Phase Transitions in Oxyfluoride $(NH_4)_2NbOF_5$

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Abstract—Polarization-optical studies and measurements of the birefringence Δn and the angle of rotation of the optical indicatrix for the $(NH_4)_2NbOF_5$ crystal have been carried out in the temperature range 100–350 K. Two anomalies of the birefringence have been revealed at the temperatures T_{01} = 258 K and $T_{02} \approx$ 219 K. According to the twinning pattern, the crystal undergoes successive changes in symmetry: orthorhombic $\longleftrightarrow$ monoclinic 1 $\longleftrightarrow$ monoclinic 2. The twofold axis of the monoclinic phases (or the normal to the plane) is directed along $[001]_{or}$. The effect of the uniaxial compression along $[011]_{or}$ and the electric field $E \approx 25$ kV/cm along $[100]_{or}$ on the twin structure has been studied. The ferroelastic phase transition at T_{01} is due to the appearance of the shear deformation $x_4(T)$ and is accompanied by significant anomalies of the birefringence. Strong pretransition phenomena mask the jumps in the birefringence $\Delta n(T)$ and in the angle of rotation of the indicatrix $\varphi(T)$ at T_{01}.

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1. INTRODUCTION

The interest expressed in oxyfluoride $A_2MO_xF_{6-x}$ crystals is explained by a possibility to obtain new functional materials with a wide transparency range and acentric symmetry, since the structure of the compounds contains isolated polar complexes MO_xF_{6-x}. These pseudooctahedral polyhedra have usually complete or partial disordering of F(O) atoms. As the temperature decreases, a gradual ordering of these elements occurs relatively often upon phase transitions $G_0 \longleftrightarrow G_1 \longleftrightarrow G_2$ [1–3]. In the crystals of this family studied earlier [1–3], the dipole moments of the polar complexes are compensated in the unit cell, and the crystal symmetry is nonpolar. However, according to recent structural investigations [4], the $(NH_4)_2NbOF_5$ crystal contains polar symmetry groups in three different temperature ranges: $Cmc2_1$ (293 K), $C2$ (233 K), and Ia (198 K). This result was achieved by introduction of certain laws of twinning of the crystal in all three cases, among them, at room temperature. According to the symmetry groups, the spontaneous polarization in $(NH_4)_2NbOF_5$ changes its direction in different temperature ranges. Thus, we can reasonably expect an anomalous behavior of the permittivity during the phase transitions. The absence of generation of the optical second harmonic in the material is explained in [4] by the influence of the aforementioned twins. According to the investigations of the heat capacity and the permittivity [5], the $(NH_4)_2NbOF_5$ crystal actually has a sequence of three phases $G_0 \longleftrightarrow G_1 \longleftrightarrow G_2$ separated by the first-order phase transitions at temperatures T_{01} = 258 K and T_{02} = 218.9 K. The phase transformations are accompanied by large changes in the entropy: $\Delta S_1 = 21.6 \pm 2.1$ J/(mol K) and $\Delta S_2 = 16.6 \pm 1.6$ J/(mol K). However, the permittivity is slightly stepwise changed at T_{01} and demonstrates complete absence of any anomalies at T_{02} [5], which is indicative of the nonferroelectric nature of the transitions.

In this work, the polarization-optical studies and measurements of the birefringence of the $(NH_4)_2NbOF_5$ crystal were performed in the temperature range 90–350 K in order to investigate the nature of the phase transitions in it. We attempted to reveal twins in all the phases. We also investigated the effect of the mechanical compression X_4 and the electric field E on the twinning structure.

2. EXPERIMENTAL RESULTS

The temperature dependence of the birefringence $\Delta n(T)$ of the $(NH_4)_2NbOF_5$ crystal was investigated on the plates of cuts (100) (Δn_a), (010) (Δn_b), and (001) (Δn_c) using Berek compensators (Leica) at an accu-

† Deceased.

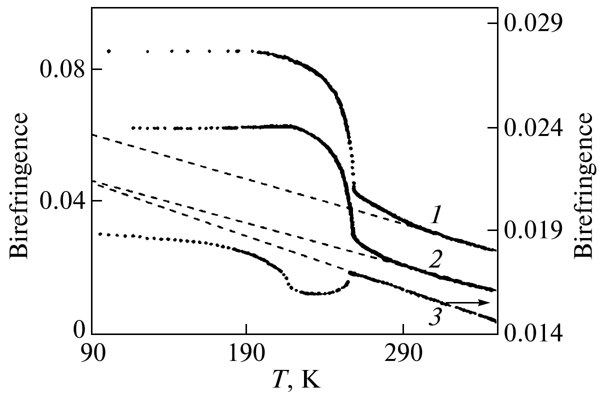

Fig. 1. Temperature dependences of the birefringences (1) Δn_a, (2) Δn_c, and (3) Δn_b for the $(NH_4)_2NbOF_5$ crystal.

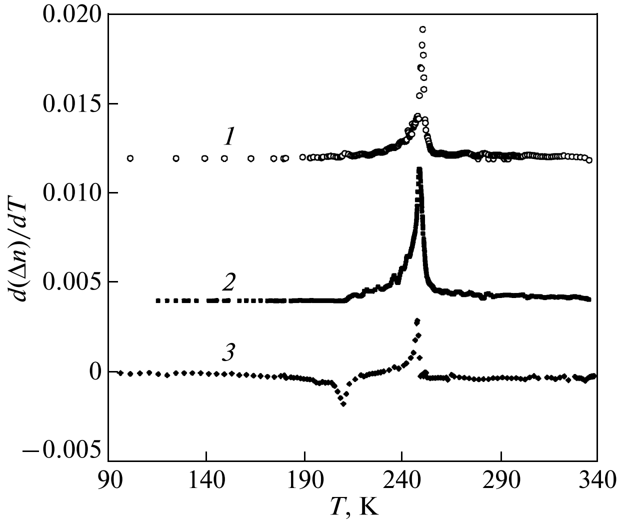

Fig. 2. Temperature dependences of the temperature coefficient of the birefringence $d(\Delta n)/dT$ for the $(NH_4)_2NbOF_5$ crystal: (1) Δn_a, (2) Δn_c, and (3) Δn_b.

racy of $\cong 10^{-5}$ and Senarmont compensators with a sensitivity of no less than $\cong 10^{-7}$ at a wavelength of 6328 Å in the temperature range 100–350 K. The former method was used to determine the magnitude of the measured quantity, and the latter method allowed one to investigate its temperature dependence with a high accuracy. The crystallooptical observations were carried out using an Axioskop 40 polarization microscope. The electric field was applied along [100] using transparent electrodes; the uniaxial mechanical compression was performed along [011] (here and in what follows, the crystallographic setting of the orthorhombic phase was used).

Figure 1 depicts the measured temperature dependences of the birefringence Δn_a, Δn_b, and Δn_c of the $(NH_4)_2NbOF_5$ crystal. It is seen that the crystal exhibits a large anisotropy of the optical constants, and it can be classified with strongly birefringence materials. At room temperature, the highest birefringence ($\Delta n_a = 0.035$) is in the [100] direction, and the least birefringence ($\Delta n_b = 0.016$) is observed along [010]. As the light propagates along [001], the crystal birefringence is $\Delta n_c = 0.019$. During cooling in the range 350–290 K, the $\Delta n(T)$ dependence is linear; below 290 K, there are substantial deviations from the linearity in the (100) and (001) cuts, and, at $T_{01} = 258$ K, the optical anisotropy increases strongly and smoothly. At temperatures below 200 K, the difference of the refractive indices is: $\Delta n_a = 0.085$ and $\Delta n_c = 0.062$. The phase transition at $T_{02} \approx 219$ K is practically invisible in the $\Delta n_a(T)$ and $\Delta n_c(T)$ dependences. In this temperature range, there is a bend in the $\Delta n_b(T)$ curve. Both the phase transitions are most pronounced in the anomalies of the temperature coefficient of the birefringence $d(\Delta n)/dT$ (Fig. 2).

The polarization-optical measurements show that, at room temperature, the plates of straight crystallographic cuts of $(NH_4)_2NbOF_5$ demonstrate an even and forward extinction characteristic of the orthorhombic symmetry. We performed special investigations in order to detect the twin structure assumed in [4] by etching and introducing compensators. However, the results were negative: at room temperature, any twin structure was not detected using an optical microscope. During cooling of the (010) and (001) cut plates, a good extinction remains over entire temperature range investigated. In the (100) cut sample, the extinction becomes smooth at temperatures $(T - T_{01}) \le 1$–2 K, and, then, at $T_{01} = 258$ K, a stripe domain structure is formed along the [010] and [001] directions with intersecting boundaries. The twin regions formed are 10–100 μm wide and differ in the extinction positions by an angle of 2φ. During further cooling, the twins are enlarged with predominance of one component volume (Figs. 3a and 3b). Owing to this phenomenon, the birefringence $\Delta n(T)$ and the angle $\varphi(T)$ can be measured in the same domain. There are no additional changes in the twinning pattern or in the extinction state at the latter phase transition $T_{02} \approx 219$ K. As aforementioned, at temperatures below T_{01}, the clear extinction is retained in the (010) and (001) cut plates. Twins are invisible. However, they can be visualized, e.g., by introduction of the Berek compensator (Fig. 3c). The photography shows that, in the left part of the sample, there are kinks of the interference fringes of the compensator at the twin boundaries along [100]. Thus, the crystal twin structure occurred below $T_{01} = 258$ K is a system of intersecting regions with the domain walls along (010) and (001). In the (100) cut, the twins are discernible in polarized light due to rotation of the optical indicatrix because of occurrence of the shear deformation x_4. The temperature dependence of the angle of rotation of the optical

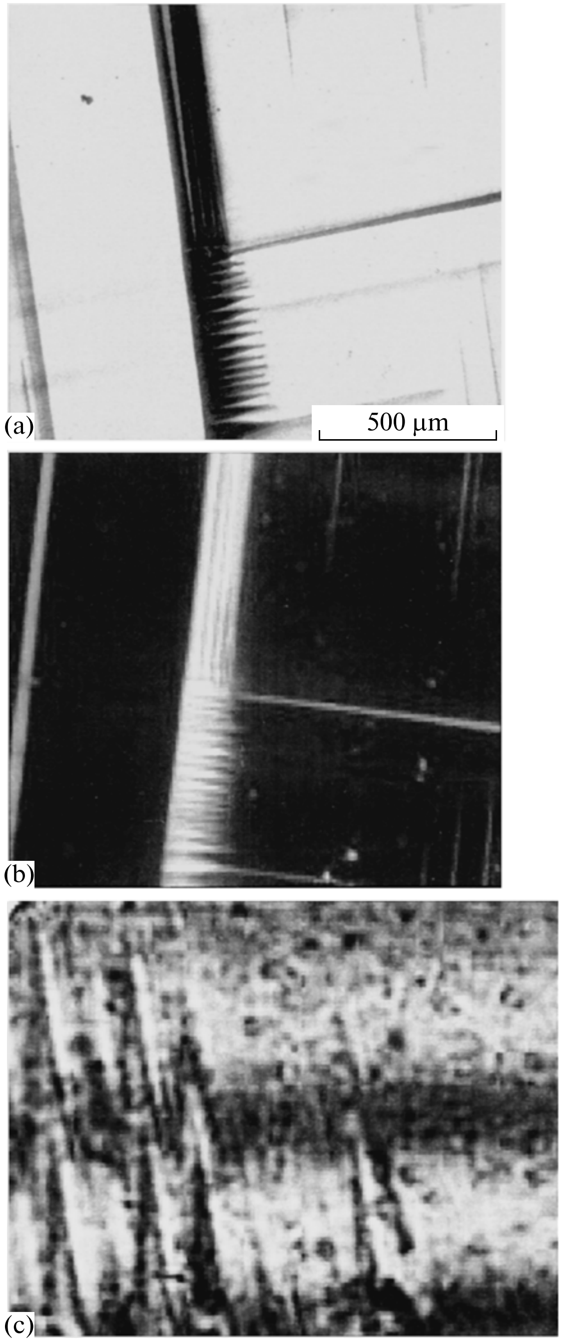

Fig. 3. Observation of twinning in samples of different cuts of the $(NH_4)_2NbOF_5$ crystal in the phases G_1 and G_2. (a, b) Difference in the positions of the extinction of the components of the twin structure in the (100) cut. (c) Visualization of the twin structure in the (010) and (001) cut plates using a Berek compensator.

indicatrix $\varphi(T)$ around the [100] axis in a single twin is shown in Fig. 4. The rotation angle appears smoothly at 258 K, then it increases to $\varphi \approx 7.5°$, and is not longer changed below ~200 K. At $T_{02} \approx 219$ K, the $\varphi(T)$ dependence has no additional anomaly.

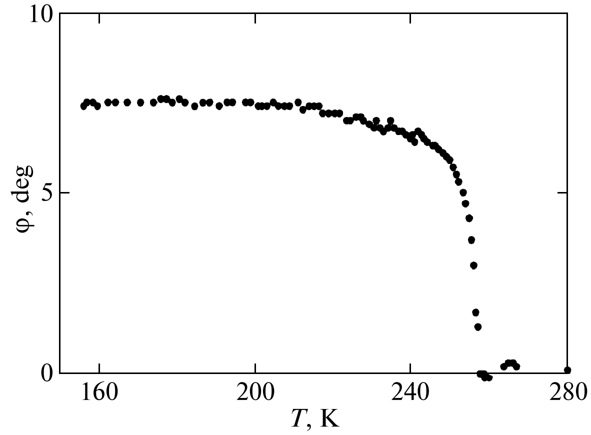

Fig. 4. Temperature dependence of the angle of rotation of the optical indicatrix $\varphi(T)$.

In order to elucidate the nature of the twinning, we investigated the effect of the mechanical compression X_4 and the electric field E on the twin structure of the $(NH_4)_2NbOF_5$ crystal which is visualized in the (100) plate at temperatures $T \le T_{01}$. It was established that, as the compressing stress is applied along [011], the twin boundaries are displaced and the single-domain state is formed only in the nearest vicinity of the transition ($T_{01} - T \le 2$ K). At lower temperatures, the uniaxial compression does not influence the twin pattern up to the crystal fracture. However, a dc electric field up to $E = 25$ kV/cm applied along [100] does not switch the twin regions. No generation of the optical second harmonic was found in aforementioned temperature range.

3. DISCUSSION OF THE RESULTS

Our investigations confirm information [5] that the $(NH_4)_2NbOF_5$ crystal actually has a sequence of three phase $G_0 \longleftrightarrow G_1 \longleftrightarrow G_2$ separated by the phase transitions ($T_{01} = 258$ K and $T_{02} \approx 219$ K). The observations performed in a polarized light show that the symmetry of the high-temperature phase G_0 is really orthorhombic. In the low-temperature G_1 and G_2 phases, we detected the twin structure with boundaries along (010) and (001) (Fig. 3) and the indicatrix rotation in the (100) cut. This fact shows that, as a result of the phase transition at T_{01}, the component of shear spontaneous deformation $x_4(T) \sim \varphi(T)$ occurs, and the transition can be called ferroelastic transition. The careful investigation of thin (~100 μm) samples of the (100) cut in the temperature range $(T - T_{01}) \le 1$–2 K shows that the extinction smoothness is due to formation, in the pretransition region, of very fine pseudodomain structure on the sample defects: scratches, growth stresses, etc. These phenomena decrease during annealing. Thus, in the $(NH_4)_2NbOF_5$crystal,

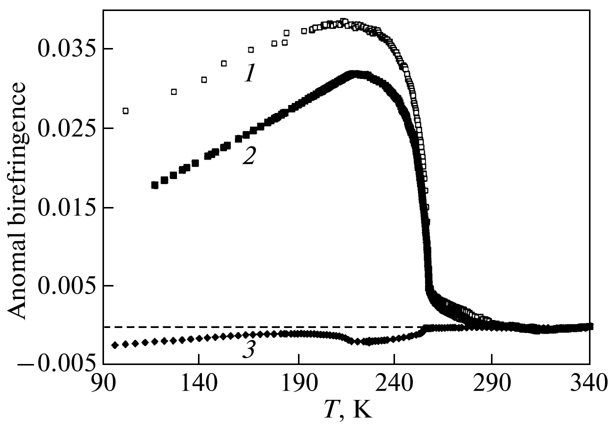

Fig. 5. Temperature dependences of the anomalous part of the birefringence (*1*) δn_a, (*2*) δn_c, and (*3*) δn_b for the $(NH_4)_2NbOF_5$ crystal.

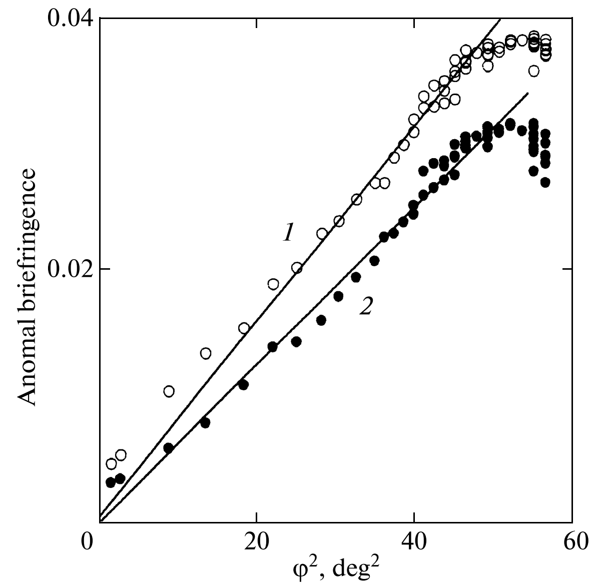

Fig. 6. Linear interrelation between the anomalous part of the birefringence and the square of the angle of rotation of the optical indicatrix in the G_1 phase of the $(NH_4)_2NbOF_5$ crystal: (*1*) δn_a and (*2*) δn_c.

inhomogeneous stresses can induce a ferroelastic phase in the pretransition region of the initial phase. Below the latter phase transition (T_{02}), the twinning pattern and the crystal system are not changed. Thus, the former phase transition is ferroelastic, and the latter phase transition is not such a transition.

It follows from the data obtained that, in the crystal, there is a sequence of changes in the symmetry: orthorhombic ⟷ monoclinic 1 ⟷ monoclinic 2. In this case, the twofold axis of the monoclinic phases (or a normal to the plane) is directed along [100]. This conclusion quite agrees with the structural data from [4]. However, the geometry of the twin structure under observation is indicative of the loss of two planes of symmetry (010) and (001) at T_{01}; the latter of the planes is absent in the polar symmetry group $Cmc2_1$ of the initial phase G_0 [4] but exists in the group *Cmcm* of the initial phase of other crystals of this family such as $(NH_4)_2MoO_2F_4$ and $(NH_4)_2WO_2F_4$ [6]. It should be noted that the twin laws which were chosen in [4] for the $(NH_4)_2NbOF_5$ in the G_1 phase do not coincide with the laws which we observed and described above. We did not find also the experimental proofs of the belongness of this crystal to polar symmetry groups: there is no generation of the optical second harmonic in all the phases; we failed to scan the dielectric hysteresis loop and did not detect any influence of the electric field on the twins detected. Moreover, the temperature dependence of the permittivity of the crystal indicates that the phase transitions are not ferroelectric transitions [5].

Figure 5 depicts the anomalous part of the birefringence $\delta n(T)$ of the $(NH_4)_2NbOF_5$crystal that is the deviation of the measured value from the value extrapolated from the high-temperature segment of the linear $\Delta n(T)$ dependence (Fig. 1). It is seen that in the crystal investigated, over a wide temperature range above the phase transitions, strong pretransition phenomena occur forming the birefringence tails extended by ≈30 K. At T_{01}, the anomalous part $\delta n(T)$ is 10% of the maximum value and, thus, masks the birefringence jump. Because of this the fact that we observe a first-order phase transition is pronounced in our experiments only as a thermal hysteresis $\delta T_{01} \approx$ 1 K. Because of absence any phase front and clear extinction at T_{01}, the jump during measuring the angle of rotation of the indicatrix $\varphi(T)$ is also invisible. The temperature dependence of the birefringence in the G_1 phase is well described by the Landau theory for the first order transitions close to the tricritical point.

As the measurements are carried out in the coordinates of the initial G_0 phase, the anomalous part of the birefringence δn appeared in the G_1 phase is due to the appearance the transition parameter η and is related to the parameter by a squared dependence: $\delta n \sim \eta^2$. In the case of the proper (pseudoproper) transition, $\varphi(T) \sim x_4(T) \sim \eta(T)$. Figure 6 combines the results of measurements of the birefringence and the angle of rotation of the optical indicatrix of the $(NH_4)_2NbOF_5$ crystal. It is seen that over almost entire region of the G_1 monoclinic phase, the anomalous part of the birefringence of the crystal is changed proportionally to the square of the rotation angle: $\delta n \sim \varphi^2$. This fact favors that this phase transition can be classified with the class of proper ferroelastic transitions.

Comparing the results of investigations of the birefringence for three representatives of the $A_2MO_xF_{6-x}$ family such as $(NH_4)_2WO_2F_4$ [1], $(NH_4)_2MoO_2F_4$ [2], and $(NH_4)_2NbOF_5$, we cannot overlook an external view similarity of the $\Delta n(T)$ dependence in these crystals. The temperature dependence of the birefringence has two singular points: at T_{01}, the optical constants vary strongly, while at T_{02} there is only a weak kink in the $\Delta n(T)$ dependences. At the same time, the crystals are different in the sequence of the symmetry change during the phase transitions.

In $(NH_4)_2WO_2F_4$, the sequence of the symmetry change is orthorhombic $\longleftrightarrow$ triclinic 1 $\longleftrightarrow$ triclinic 2; in $(NH_4)_2NbOF_5$, the sequence is orthorhombic $\longleftrightarrow$ monoclinic 1 $\longleftrightarrow$ monoclinic 2; and, in $(NH_4)_2MoO_2F_4$, the crystal system sequence is not changed: orthorhombic $\longleftrightarrow$ orthorhombic 1 $\longleftrightarrow$ orthorhombic 2. In the tungsten and niobium compounds, in a wide temperature range above the ferroelastic transitions at T_{01}, there are substantial pretransition tails of the birefringence, while the molybdenum compound demonstrates a rigorous linear $\Delta n(T)$ dependence in the initial phase up to the temperature transition.

4. CONCLUSIONS

Our investigations of the $(NH_4)_2NbOF_5$ crystal performed in this work allowed the detection of two temperatures at which the $\Delta n(T)$ dependences undergo anomalies $T_{01} = 258$ K and $T_{02} \approx 219$ K. The phase transition at $T_{01} = 258$ K is accompanied by twinning in the (100)-cut plates, significant anomalies of the birefringence, and characteristic thermal hysteresis $\delta T \approx 1$ K. The strong pretransition phenomena mask the $\Delta n(T)$ jump. At $T_{02} \approx 219$ K, the anomaly of the birefringence is slightly pronounced, and the phase transition is in no way be manifested in the twinning pattern appeared below T_{01}. According to the observations in polarized light, the crystal undergoes the sequence of changes in the symmetry as follows: orthorhombic (G_0) $\longleftrightarrow$ monoclinic 1 (G_1) $\longleftrightarrow$ monoclinic 2 (G_2) (the monoclinic axis is directed along [100]). The phase transition at T_{01} is due to the occurrence of the shear deformation $x_4(T) \sim \varphi(T)$. In the region of the G_1 phase, the anomalous part of the birefringence δn is proportional to φ^2. The experiments showed that the electric field up to $E \approx 25$ kV/cm directed along [100] does not influence the arrangement of the twin boundaries; because of this the twins observed are not ferroelectric domains. At the same time, as a compressing stress is applied along [011], we detected the displacement of the twin boundaries and the formation of the single-domain state in very narrow temperature range near the transition ($T_{01} - T \sim 2$ K). The set of experiments performed suggests that the phase transition at T_{01} is a proper (pseudoproper) ferroelastic transition provided by the appearance of the transition parameter: $\eta(T) \sim x_4(T) \sim \varphi(T) \sim \sqrt{\delta n}(T)$.

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