LATTICE DYNAMICS
AND PHASE TRANSITIONS

Polarization-Optical and X-ray Diffraction Investigations on the Symmetry of Distorted Phases of Ammonium Cryolite $(NH_4)_3ScF_6$

S. V. Mel'nikova*, S. V. Misyul'**, A. F. Bovina*, and M. L. Afanas'ev*

* Kirenskiĭ Institute of Physics, Siberian Division, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia
** Krasnoyarsk State Agricultural University, pr. Mira 88, Krasnoyarsk, 660049 Russia
e-mail: flerov@iph.krasnoyarsk.su

Abstract—Single-crystal plates of different sections of the $(NH_4)_3ScF_6$ crystal have been investigated by polarization-optical microscopy and X-ray diffraction over a wide temperature range, including the temperatures of two known phase transitions and the third transition found recently. It is established that the symmetry of phases changes in the following sequence: $O_h^5 - Fm3m$ $(Z = 4)$ $\longleftrightarrow$ $C_{2h}^5 - P12_1/n1$ $(Z = 2)$ $\longleftrightarrow$ $C_{2h}^3 - I12/m1$ $(Z = 16)$ $\longleftrightarrow$ $C_i^1 - I\bar{1}$ $(Z = 16)$. © 2000 MAIK "Nauka/Interperiodica".

The crystals $A_3M^{3+}X_6$ with the cryolite structure (space group $Fm3m$, $Z = 4$) belong to one of the related families of perovskite-like compounds. The three-dimensional crystal framework of these compounds is formed by the AX_6 and $M^{3+}X_6$ octahedra shared by their vertices, and the polyhedra arranged between these octahedra are occupied by the A^+ cations. As a rule, fluoride crystals with the atomic cations A^+ undergo structural phase transitions at sufficiently high temperatures, which makes their detailed exploration difficult. In this respect, the ammonium compounds (in which phase transitions have been found rather recently) are more attractive objects of investigations. In many cases, the presence of ammonium in the structure considerably decreases the temperature at which the cubic phase remains stable in these compounds [1–8].

By now, it has been established that, in the majority of ammonium cryolites, the transitions from the cubic phase are associated with the change in the orientational motion of two structural groups: $(NH_4)^+$ and $(MF_6)^{3+}$. The temperature at which the cubic phase loses its stability depends on the size of the M^{3+} ion. This factor also determines the sequence of changes in the symmetry upon phase transitions observed in crystals. The compounds with a small radius of trivalent ion ($R_M^{3+} \leq R_{Fe}^{3+}$) undergo only one phase transformation into the triclinic phase with the hypothetical symmetry $P\bar{1}$ [6, 8]. The compounds with larger-sized cations (Sc or In) are characterized by two phase transitions [8]. More recent research on the heat capacity of the

$(NH_4)_3ScF_6$ polycrystalline samples by the adiabatic calorimetry revealed three anomalies at temperatures $T_1 = 330$ K, $T_2 = 293$ K, and $T_3 = 243$ K [9].

In [8], the symmetry of this crystal was found to be cubic ($Fm3m$, $Z = 4$) at temperatures above T_1 and monoclinic ($P2_1/n$, $Z = 2$) at 290 K. The X-ray diffraction analysis of the powders at temperatures corresponding to the G_0, G_1, and G_2 phases showed a substantial splitting of reflections in the diffraction patterns upon transition from the cubic phase, even though no abrupt change were observed in the volume. However, the transition from the G_1 phase at T_2 ($T_{exp} = 290$ K) was not accompanied by changes in the number of reflections and their intensities.

It should be noted that the X-ray diffraction investigations of small-scale structural distortions and changes in the symmetry in perovskite-like crystals are more efficient with single-crystal samples rather than with powders, because the single-crystal experiments provide more detailed information. Actually, a complex sequence of the symmetry changes was revealed in elpasolites upon twinning of their structure when studying the X-ray reflections of oriented single-crystal plates [10, 11]. In this respect, the purpose of the present work was to confirm the existence of three phase transitions found in [9] and to determine the symmetry of distorted phases of the $(NH_4)_3ScF_6$ cryolite.

1. EXPERIMENTAL

The $(NH_4)_3ScF_6$ compound was synthesized from equivalent amounts of NH_4F and Sc_2O_3 in HF (10%).
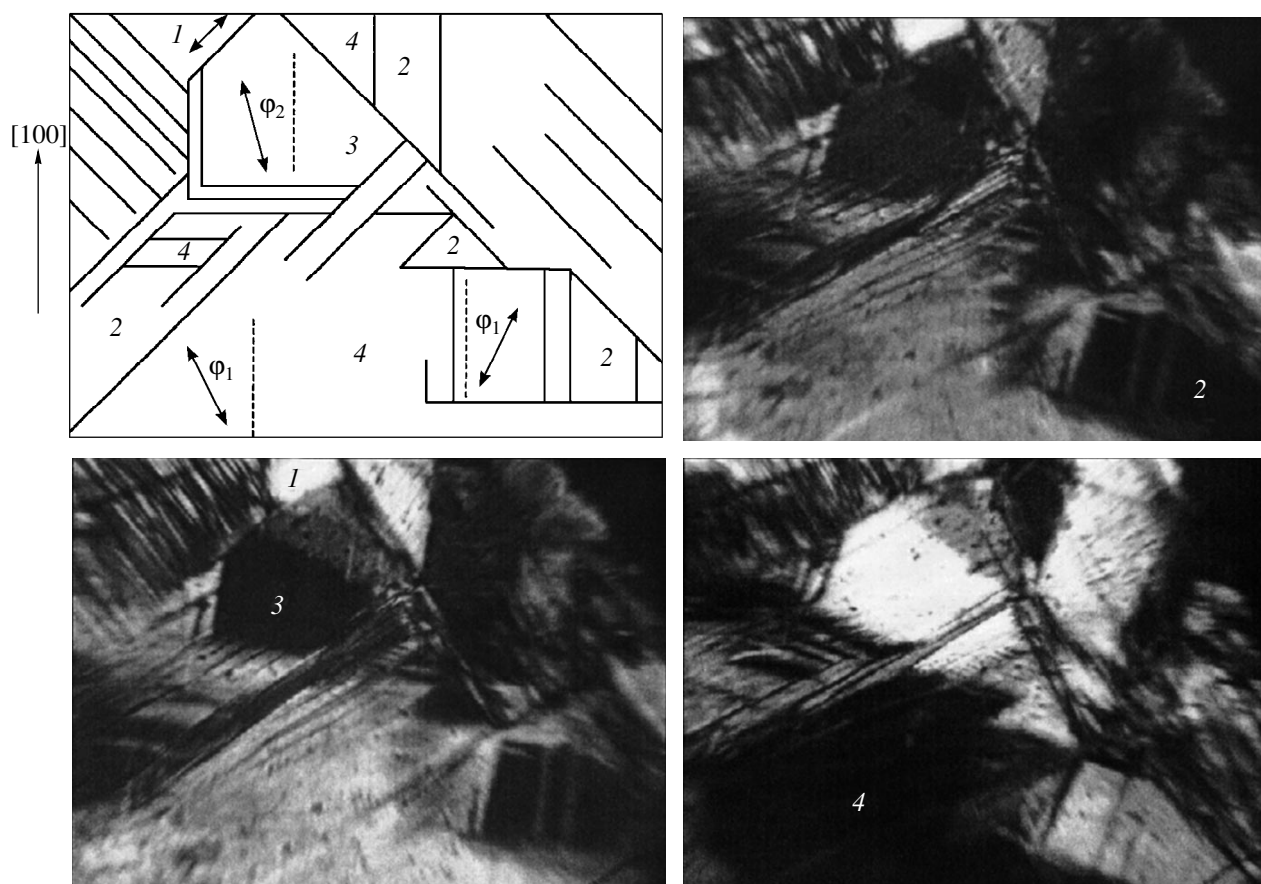
Fig. 1. Photographs of the twinned structure and a scheme of twinning in the $(100)_0$ section of the $(NH_4)_3ScF_6$ crystal at room temperature.

Large-sized faceted single crystals were grown by the slow controlled evaporation of a neutral saturated aqueous solution at a temperature of 305 K for 8 months.

X-ray diffraction analysis of the $(NH_4)_3ScF_6$ crystal was carried out on a DRON-2.0 diffractometer equipped with URNT-180 low-temperature and GPVT-2000 high-temperature attachments (CuK_α radiation, graphite monochromator) over a wide range of temperatures (120–360 K). Single-crystal plates of the $(100)_0$, $(110)_0$, and $(111)_0$ sections and the powders prepared from the $(NH_4)_3ScF_6$ single crystals were used as samples (hereafter, the subscript in the designation of planes and directions indicates the type of the crystal phase).

2. RESULTS

Thin crystal plates of different crystallographic sections were examined under a polarizing microscope. At a sample thickness of 0.1 mm and more, only one phase transition from the cubic phase can be observed at $T_1 \downarrow = 326$ K ($T_1 \uparrow = 328$ K) upon cooling. This transition is attended by the appearance of crystal twins and cracking. In the polarized light, the studied sample at room temperature has a complex interlacing twinned structure. A further cooling below T_2 and T_3 does not bring about additional changes in the twinning picture; and only when the sample thickness is chosen to be less than 0.5 mm, there appear extended single-domain regions characterized by a clear-cut extinction, in which all three phase transitions take place. Simple observations in polarized light clearly demonstrate only two phase transitions. The twinned structure arises at T_1 and becomes more complex at temperatures below T_3. No changes are observed at temperature $T \approx T_2$.

At room temperature, the thin sample of the $(100)_0$ section is characterized by twin boundaries along the $[100]_0$ and $[110]_0$ directions (Fig. 1). The twins observed can be classified into three types: (1) the extinction direction along $[110]_0$ in the G_1 and G_2 phases (twin 1), (2) the extinction direction differs from $[100]_0$ by the angle $\pm\varphi_1$ and depends on the temperature (twins 2 and 4), and (3) the extinction direction along $[100]_0$ in the G_1 phase and along $[100]_0 \pm \varphi_2$ in the G_2 phase (twin 3). Figure 2 depicts the temperature dependences of the angles of rotation of the optical indicatri-

ces $\varphi_1(T)$ and $\varphi_2(T)$ for different twins in the $(100)_0$ plane. The cooling below $T_1 = 326$ K results in a small disorientation of the optical indicatrices $2\varphi_1$ in twins 2 and 4 ($\varphi_1 \approx 4° \pm 1°$). Somewhat below room temperature ($T_2 = 290$ K), the φ_1 angle sharply increases and becomes equal to $20° \pm 1°$ at temperatures about 230 K. No changes in the twinning picture are observed in this case. A further cooling below T_3 leads to the appearance of additional twins. The clear-cut extinction observed along $[110]_0$ in region 1 is disturbed. The first-order phase transition occurs with a large temperature hysteresis. Note that, upon cooling, the temperature $T_3 \downarrow$ of this phase transition is not constant and depends on many factors such as the cooling rate, the choice of the twin under observation, etc. As a result, the temperature hysteresis varies in the range $\Delta T_3 = 30$–13 K. Upon heating, the phase transition is always observed at $T_3 \uparrow = 230$ K.

The optical observations in the polarized light indicate that the $(NH_4)_3ScF_6$ crystal undergoes phase transitions in the following order: $Fm3m$ (G_0) $\longleftrightarrow$ monoclinic (G_1) $\longleftrightarrow$ monoclinic (G_2) $\longleftrightarrow$ triclinic (G_3). As follows from the extinctions in twins, the twofold axis in the G_1 and G_2 monoclinic phases lies along the $[110]_0$ direction.

The changes observed in the X-ray diffraction profiles of single-crystal plates and the splittings of reflections in the powder diffraction patterns at different temperatures (see table) suggest at least two phase transitions at $T_1 \uparrow = 328$ K and $T_3 \uparrow = 230$ K. The initial phase G_0 is the cubic modification with the face-centered unit cell F. The unit cell parameters at 353 K are listed in the table. According to the splittings of the main reflections, the monoclinic symmetry is assigned to the G_1 and G_2 distorted phases, and the triclinic symmetry, to the G_3 phase.

The cooling below T_1 (G_1 phase) gives rise to a set of the $(hk0)$ and (hkl) superstructure reflections, for which the sums $(h + k)$, $(h + l)$, and $(k + l)$ are odd numbers. Among the $(h00)$ and $(hh0)$ reflections, only the reflections with the even indices h are observed (the h, k, and l indices of reflections are chosen with respect to the axes in the unit cell of the G_0 cubic phase). Although the splittings of reflections in the temperature ranges T_1–T_2 and T_2–T_3 virtually coincide and do not indicate phase transitions, apart from the already observed reflections, one can see the superstructure reflections $(h + 1/2, h + 1/2, h + 1/2)$, $(h00)$, and $(hh0)$ (where h is any integer number) at temperatures below T_2. The superstructure reflections found in the G_1 and G_2 phases are also observed in the low-symmetry phase G_3. The splitting of reflections and the appearance of superstructure reflections clearly demonstrate the existence of three phase transitions.

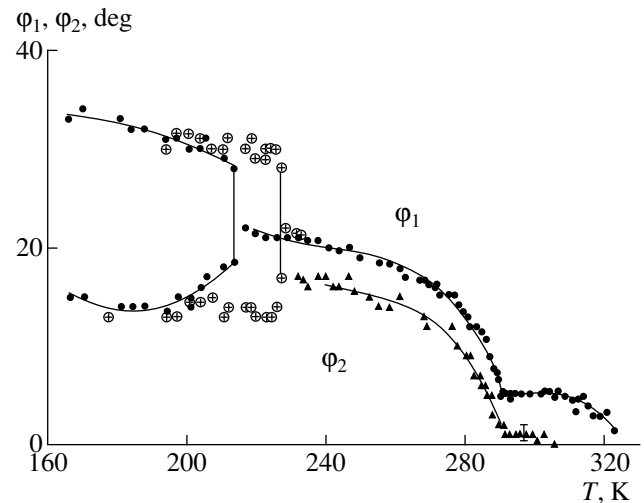The temperature dependences of the linear and angular unit-cell parameters for the G_0, G_1, G_2, and G_3

Fig. 2. Temperature dependences of the angle of rotation of the optical indicatrix for $(NH_4)_3ScF_6$.

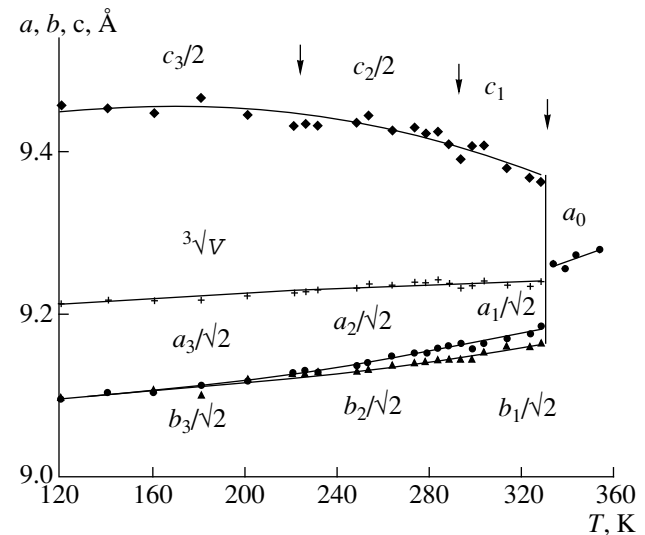**Fig. 3.** Temperature dependences of the linear sizes and the volume of the Bravais cell in the $(NH_4)_3ScF_6$ crystal. The unit cell volume is doubled for the G_1 phases and is reduced by a factor of four for the G_2 and G_3 phases.

phases were determined from the location of components of the (880) reflection (Figs. 3, 4). The scheme of the splitting of this reflection is given in the table. As can be seen from Fig. 3, the linear unit-cell parameters sharply change upon transition from the cubic phase to the G_1 phase. An abrupt change observed in the unit-cell volume at the same temperature is equal to 0.5% V_0. No features in the behavior of the linear unit-cell parameters are observed in the transitions at temperatures T_2 and T_3. The parameters of the monoclinic and triclinic unit cells along the a_i and b_i directions virtually coincide. The temperature dependences of the angular unit-cell parameters (Fig. 4) exhibit three singular

Crystallographic characteristics of four phases $(NH_4)_3ScF_6$

Phase	G_3	G_2	G_1	G_0
Space group	$C_i^1-I\bar{1}$	$C_{2h}^3-I12/m1$	$C_{2h}^5-P12_1/n1$	O_h^5-Fm3m
Z	16	16	2	4
T_{exp}, K	173	273	303	353
Unit-cell parameters				
$\mathbf{a}_i$, Å	12.874($-\mathbf{b}_0 + \mathbf{c}_0$)	12.944($-\mathbf{b}_0 + \mathbf{c}_0$)	6.481(1/2($-\mathbf{b}_0 + \mathbf{c}_0$))	9.281($\mathbf{a}_0$)
$\mathbf{b}_i$	12.875($\mathbf{b}_0 + \mathbf{c}_0$)	12.926($\mathbf{b}_0 + \mathbf{c}_0$)	6.472(1/2($\mathbf{b}_0 + \mathbf{c}_0$))	9.281($\mathbf{b}_0$)
$\mathbf{c}_i$	18.898($2\mathbf{a}_0$)	18.860($\mathbf{a}_0$)	9.408($\mathbf{a}_0$)	9.281($\mathbf{c}_0$)
α, deg	90.19	90	90	90
β, deg	89.60	89.78	89.90	90
γ, deg	90.09	90	90	90
V, Å^3	3132.216	3155.522	394.618	799.308
Scheme of reflection splitting				
(h00)				
(hh0)				
(hhh)				
Presence of superstructure reflections	++	++	+	–

points at temperatures corresponding to the three phase transitions. The temperature behavior of the angle $\beta(T)$ (Fig. 4) is similar in character to that of the rotation angle for the optical indicatrix $\varphi_1(T)$ (Fig. 2).

3. DISCUSSION

In order to determine the space groups of the distorted crystal phases, we take into consideration the fol-

90 – α, 90 – β, 90 – γ, deg
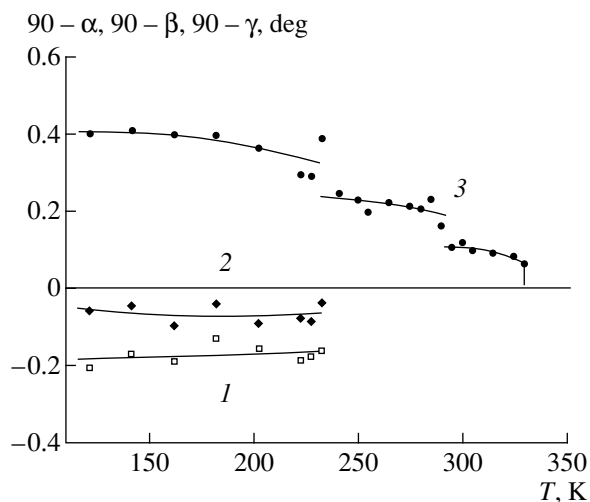
Fig. 4. Temperature dependences of the angular unit-cell parameters of the $(NH_4)_3ScF_6$ crystal: (*1*) $90° - \alpha$, (*2*) $90° - \gamma$, and (*3*) $90° - \beta$.

lowing observations: only the centrosymmetric distorted phases are revealed in the family of the $A_3M^{3+}X_6$ crystals [1–11], and, as follows from the polarization-optical experiments, the twofold axis in the G_1 and G_2 monoclinic phases lies along the $[110]_0$ direction, i.e., along the diagonal of the cubic cell face. These factors substantially reduce the number of possible space groups from C_{2h}^1 to C_{2h}^6 for the low-symmetry monoclinic phases and allow an unambiguous choice of the C_i^1 symmetry for the triclinic phase. Analysis of the absences of structure and superstructure reflections and also the splittings of specially chosen reflections in the X-ray diffraction patterns of single-crystal plates makes it possible to choose particular space groups of the distorted phases. The data on the symmetry of the $(NH_4)_3ScF_6$ phases, sizes, and orientation of the unit cells are summarized in the table. It should be mentioned that, in the conventional setting (see [12]), the Bravais cell should be base-centered in the G_2 monoclinic phase and simple in the G_3 triclinic phases. However, for convenience, we chose the body-centered unit cells for the G_2 and G_3 phases. As is seen, the volume of the Bravais cell is two times smaller in the G_1 phase and it is four times larger in the G_2 and G_3 phases as compared to the unit-cell volume in the G_0 phase. At the same time, the primitive cells in the G_0, G_1, G_2, and G_3 phases contain 1, 2, 8, and 8 formula units, respectively.

Now, let us consider the probable pattern of structural distortions in the $(NH_4)_3ScF_6$ crystal. For this purpose, we invoke the data of recent calorimetric [9] and NMR investigations of cryolites with M^{3+} = Ga, V, Fe, and In [7]. Reasoning from the results obtained in the works [7, 9], it can be concluded that the phase transitions in the scandium cryolite are accompanied by transformations of the order–disorder type. The phase transition at temperature T_1 is associated with a partial ordering of the ScF_6 rigid octahedral groups and the ordering of the NH_4 tetrahedral groups. The complete ordering of the ScF_6 octahedra is observed at T_2. Most likely, the octahedral and tetrahedral groups in the G_2 and G_3 phases are completely ordered, and these phases differ only in the degree of distortions of the unit cells. The change in the entropy upon complete ordering of octahedral and tetrahedral groups is $\Delta S = R(\ln 2 + \ln 8) = 2.77R$, which is in good agreement with the data obtained in [9] for this crystal. According to [9], the overall change in the entropy during all three phase transitions is $\sum \Delta S_i = (2.50 \pm 0.18)R$.

In closing, we briefly dwell on the work [8], in which the $P\bar{1}$ symmetry was assigned to the G_3 phase. The results of the present work complement, rather than contradict, the data reported in [8]. In [8], the symmetry of the $(NH_4)_3ScF_6$ phases was determined from the splitting of reflections in the X-ray diffraction patterns of powder samples. The translational symmetry is difficult to judge from the data obtained in [8]. In the present work, apart from the point symmetry of all the phases, we revealed the change in the translational symmetry, i.e., the Bravais lattices, which was not found in [8].

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