LATTICE DYNAMICS
AND PHASE TRANSITIONS

Optical and X-ray Diffraction Investigations of the Symmetry of Distorted Phases of the $(NH_4)_2KGaF_6$ Crystal

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

** Kirensky 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: msv@iph.krasn.ru
Received December 14, 2001

Abstract—Powders and single-crystal plates of different sections of an $(NH_4)_2KGaF_6$ crystal are investigated using polarized light microscopy and x-ray diffraction over a wide temperature range, including the phase transition temperatures. It is established that the sequence of symmetry changes in the crystal under investigation is as follows: O_h^5–$Fm3m$ ($Z = 4$) $\longleftrightarrow$ C_{4h}^5–$I114/m$ ($Z = 2$) $\longleftrightarrow$ C_{2h}^5–$P112_1/n$ ($Z = 2$). © *2002 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Fluoride crystals of the general formula $A_2BMe^{3+}F_6$ with a perovskite-like structure are characterized by a great diversity of phase transitions with a decrease in temperature. Among these compounds, ammonium crystals have attracted particular attention, because the ammonium ions occupy cation positions: A and B (cryolite) and A or B (elpasolite). In elpasolite and cryolite crystal cells, these ions can occupy two nonequivalent positions, namely, the position A inside a halide octahedron and the position B in a hole between octahedra.

Ammonium crystals of the formula $(NH_4)_3Me^{3+}F_6$ (Me^{3+} = Al, Cr, Ga, V, Fe, Sc, or In) with a cryolite structure (space group $Fm3m$, $Z = 4$) that belong to the family of ammonium perovskite-like compounds have been investigated in sufficient detail. The three-dimensional crystal framework of these compounds is formed by $(NH_4)F_6$ and $Me^{3+}F_6$ octahedra connected by their vertices, and the polyhedra arranged between these octahedra are occupied by ammonium ions. Sasaki *et al.* [1] showed that, in the majority of ammonium cryolites, the transitions from the cubic phase are associated with changes in the orientational motion of two structural groups, namely, $(NH_4)^+$ and $(Me^{3+}F_6)$. Kobayashi *et al.* [2] and Tressaud *et al.* [3] proved that the radius of the Me^{3+} ion affects the number of phase transitions, the sequence of changes in the symmetry upon phase transitions, and the temperature at which the cubic phase loses its stability. The ammonium compounds with a small radius of the trivalent ion ($R_{Me}^{3+} \leq R_{Fe}^{3+}$) are characterized by only one phase transition, whereas the compounds with larger sized cations (In or Sc) undergo two or three phase transitions [3–5]. Our recent x-ray diffraction studies on powders and single crystals [6]

revealed the following sequence of symmetry changes in the $(NH_4)_3ScF_6$ cryolite: 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–$I\bar{1}$ ($Z = 16$). For the $(NH_4)_3GaF_6$ cryolite with a small-sized trivalent cation Ga^{3+} [7], the sequence of symmetry changes proved to be as follows: O_h^5–$Fm3m$ ($Z = 4$) $\longleftrightarrow$ C_i^1–$I\bar{1}$ ($Z = 16$). These investigations demonstrated that ammonium cryolites have identical symmetry of the initial and lowest temperature phases; however, the transitions between these phases can occur in a number of ways.

The difference between the ammonium elpasolite $(NH_4)_2KGaF_6$ and the gallium cryolite $(NH_4)_3GaF_6$ lies in the fact that holes between octahedra in the crystal structure of the former compound are occupied by atomic potassium cations rather than by ammonium molecular ions. According to Flerov *et al.* [8], the $(NH_4)_2KGaF_6$ elpasolite exhibits three anomalies in the heat capacity in the temperature range from 80 to 350 K, specifically at $T_{01} = 288.5$, $T_{02} = 250$, and $T_{03} = 244.5$ K. Moreover, reasoning from the thermodynamic characteristics obtained for the $(NH_4)_2KGaF_6$ elpasolite, Flerov *et al.* [8] proposed a different sequence of symmetry changes in this crystal as compared to that in the cryolites studied in [6, 7].

The purpose of the present work was to determine the sequence of symmetry changes $(G_0) \longleftrightarrow (G_1) \longleftrightarrow (G_2) \longleftrightarrow (G_3)$ in the $(NH_4)_2KGaF_6$ crystal. This study was performed by analogy with our previous works [6, 7]. We investigated the twin laws and analyzed the changes observed in the x-ray reflections from powders
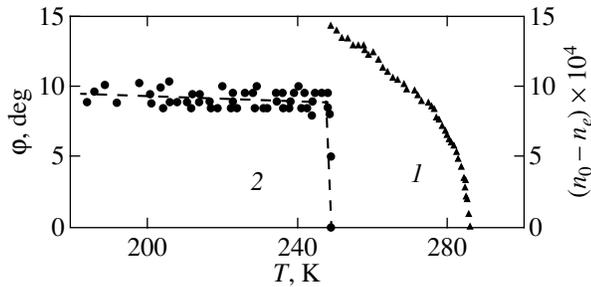
Fig. 1. Temperature dependences of (*1*) the birefringence and (*2*) the rotation angle of the optical indicatrix with respect to the $[110]_0$ direction in the $(NH_4)_2KGaF_6$ crystal.

and oriented single-crystal plates over a wide range of temperatures.

2. SAMPLE PREPARATION

The $(NH_4)_2KGaF_6$ compound was synthesized according to the following procedure. Gallium hydrate $Ga(OH)_3$ was dissolved in hydrofluoric acid HF and was then evaporated almost to dryness. A saturated aqueous solution of $(NH_4)HF_2$ and KHF_2 taken in equivalent amounts was added to the gallium fluoride GaF_3 formed by the above reaction. The resultant polycrystalline compound and a mother solution were placed in a high-pressure bomb. The hermetically sealed bomb was heated to 500 K, allowed to stand for 48 h at this temperature, and was then slowly cooled over ten days to room temperature. The hydrothermal synthesis in the high-pressure bomb resulted in the formation of small-sized ($\approx$30 mm^2), well-faceted crystals of the $(NH_4)_2KGaF_6$ compound. Single-crystal plates of three crystallographic orientations, namely, the $(100)_0$, $(110)_0$, and $(111)_0$ sections cut from these crystals, served as samples in x-ray diffraction and optical investigations (hereafter, the subscript in the designations of the crystallographic planes and directions indicates the type of crystal phase).

3. RESULTS AND DISCUSSION

Thin crystal plates ($\approx$0.05 mm) of different crystallographic sections were examined using a polarizing microscope. It was revealed that, during cooling of the studied samples in the vicinity of the temperature $T_{01} = 288$ K, the crystal exhibits optical anisotropy and small-sized, poorly defined crystal twins manifest themselves in the form of dark spots. The twin boundaries observed in the $(100)_0$ section are aligned parallel to the $[110]_0$ direction. Extended single-domain regions with pronounced temperature-independent extinctions of reflections along the $[100]_0$ direction are arranged between the spots. In these regions, the birefringence was measured using the Berec compensator technique with an accuracy of ~10^{-4}. Figure 1 illustrates the temperature

behavior of the main birefringence $\Delta n = (n_0 - n_e)$ in the $(NH_4)_2KGaF_6$ crystal. It can be seen that the birefringence arises below $T_{01} = 288$ K, gradually increases with a decrease in the temperature, and reaches $\Delta n = 14 \times 10^{-4}$ in the vicinity of 250 K.

At $T_{02} = 250$ K, the $(NH_4)_2KGaF_6$ crystal undergoes a first-order phase transition. It is seen that the twin pattern changes drastically. In particular, there arise regions of a new phase with a complex twin structure. In the $(100)_0$ section, this structure is predominantly composed of twins with a preferred orientation of their boundaries along the $[100]_0$ direction, in which the optical indicatrices are rotated through an angle $\pm\varphi$ with respect to the $[110]_0$ direction. Crystal twins with extinctions of the reflections along the $[100]_0$ direction are observed more rarely. The new phase regions are not formed simultaneously throughout the bulk of the sample. Upon cooling, their formation is observed to a temperature of 245 K. At 250 K, the angle φ abruptly increases from zero to 10° and remains nearly constant in the course of cooling (Fig. 1). No additional changes are revealed in the twin pattern in the vicinity of the third anomaly in the heat capacity ($T_{03} = 244.5$ K).

Judging from the above findings, we can state that the $(NH_4)_2KGaF_6$ crystal is characterized by the following changes in symmetry: cubic (G_0) ⟷ tetragonal (G_1) ⟷ monoclinic (G_3). Analysis of the extinctions of the reflections in different twins of the monoclinic phase indicates that the twofold axis of the unit cell of the monoclinic phase coincides with one of the pseudocubic axes, whereas the other two axes are aligned along the face diagonals. It turned out that both the twin pattern and the sequence of symmetry changes in the $(NH_4)_2KGaF_6$ crystal are closely similar to those observed in the Rb_2KScF_6 elpasolite [9].

X-ray diffraction analysis of the $(NH_4)_2KGaF_6$ crystal was carried out on a DRON-2.0 diffractometer equipped with a URNT-180 low-temperature attachment (CuK_α radiation, graphite monochromator). The measurements were performed over a wide range of temperatures (100–300 K). The samples used in x-ray diffraction investigations were prepared in the form of single-crystal plates of the $(100)_0$, $(110)_0$, and $(111)_0$ sections and powders produced from $(NH_4)_2KGaF_6$ single crystals.

The x-ray reflections taken from the initial phase G_0 correspond to cubic symmetry with a face-centered unit cell F [10]. The unit cell parameters at 293 K are listed in the table. Upon cooling in the temperature range from 288 to 250 K, we observed a very slight broadening of x-ray reflections from single-crystal plates. Unfortunately, in this range of temperatures, we failed to reveal noticeable splittings of reflections that would suffice to determine the symmetry of the G_1 phase from the x-ray diffraction experiment. However, the observed twin pattern indicates that the unit cell of the

Crystallographic characteristics of distorted phases of the $(NH_4)_2KGaF_6$ crystal

Characteristics	G_3	G_1	G_0
Space group	$C_{2h}^5 - P112_1/n$	$C_{4h}^5 - I114/m$	$O_h^5 - Fm3m$
Z	2	2	4
T_{exp}, K	198 K	273 K	293 K
		Unit cell parameters	
	$1/2(\mathbf{a}_0 + \mathbf{b}_0)$	$1/2(\mathbf{a}_0 + \mathbf{b}_0)$	$\mathbf{a}_0$
$\mathbf{a}_i$, Å	6.203	6.256	8.850
	$1/2(\mathbf{a}_0 - \mathbf{b}_0)$	$1/2(\mathbf{a}_0 - \mathbf{b}_0)$	$\mathbf{b}_0$
$\mathbf{b}_i$, Å	6.252	6.256	8.850
	$\mathbf{c}_0$	$\mathbf{c}_0$	$\mathbf{c}_0$
$\mathbf{c}_i$, Å	8.928	8.847	8.850
α, deg	90	90	90
β, deg	90	90	90
γ, deg	89.72	90	90
V, Å^3	346.23	346.22	693.13
$(h\,0\,0)$			
$(h\,h\,0)$			
$(h\,h\,h)$			
Presence of superstructure reflections	+	−	−

G_1 phase is characterized by a tetragonal distortion. Moreover, the lack of superstructure reflections in the G_1 phase suggests that the phase transition occurs without a multiple change in the unit cell volume. The parameters and the scheme of crystallographic axis of the Bravais cell in the tetragonal phase of the $(NH_4)_2KGaF_6$ crystal are given in the table.

Upon cooling below the phase transition temperature $T_{02} = 250$ K, the x-ray diffraction profiles of single-crystal plates and the splittings of reflections in the x-ray powder diffraction patterns change drastically (see table). The cooling of the studied sample leads to the appearance of a set of $(h\,k\,0)$ and $(h\,k\,l)$ superstructure reflections for which the sums $(h + k)$, $(h + l)$, and $(k + l)$ are odd numbers and the $(h\,0\,0)$ and $(h\,h\,0)$ reflections are characterized only by even indices h. The temperature dependence of the $(1\,0\,5)$ superstructure reflection (Fig. 2) clearly demonstrates that a change in the translational symmetry occurs upon the $G_1 \longrightarrow G_3$ phase transition. The splittings of reflections in the G_3 phase correspond to the monoclinic symmetry (see table).

The temperature dependences of the linear and angular parameters of the unit cell in different phases of

the $(NH_4)_2KGaF_6$ crystal were determined from the location of the components of the $(6\,6\,0)$ reflection. The results obtained are presented in Figs. 3 and 4, respectively. It can be seen from Fig. 3 that, as the temperature decreases, the unit cell parameters remain constant upon the $(G_0) \longleftrightarrow (G_1)$ phase transition but exhibit abrupt jumps at temperatures below $T_{02} = 250$ K. The
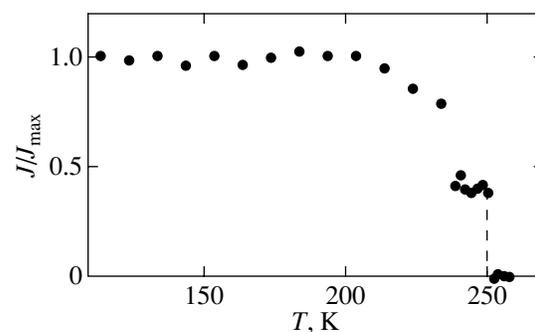

Fig. 2. Temperature behavior of the integral intensity of the $(1\,0\,5)$ superstructure reflection. The reflection indices are given in the setting and crystallographic axes of the unit cell of the initial cubic phase G_0.
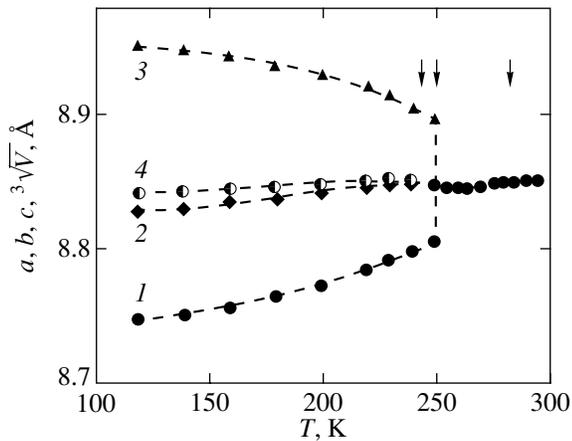
Fig. 3. Temperature dependences of the linear dimensions and the volume of the Bravais cell in the $(NH_4)_2KGaF_6$ crystal: (1) $a\sqrt{2}$, (2) $b\sqrt{2}$, (3) c, and (4) $3\sqrt{V}$. The volume of the Bravais cell in the monoclinic and tetragonal phases is doubled.
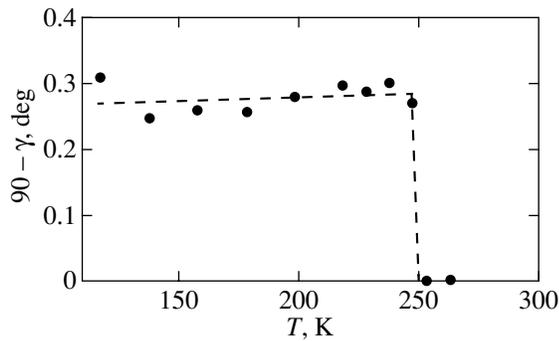
Fig. 4. Temperature dependence of the angular parameter $(90° - \gamma)$ of the Bravais cell in the $(NH_4)_2KGaF_6$ crystal.
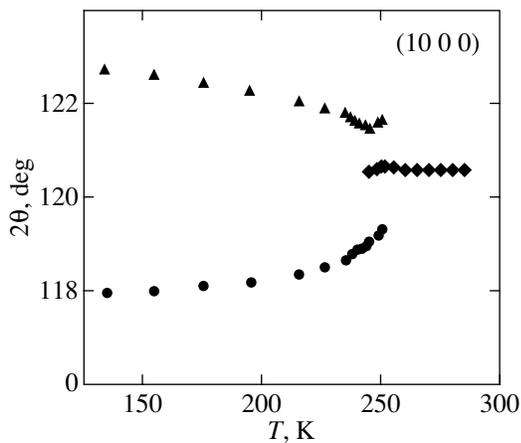
Fig. 5. Positions of the components of the $(10\,0\,0)$ reflection in the x-ray diffraction pattern at different temperatures (CuK_α radiation).

linear dimension of the monoclinic cell of the $(NH_4)_2KGaF_6$ crystal decreases along the **a** direction and increases along the **c** direction with a decrease in the temperature, whereas the linear parameter along the **b** direction remains virtually unchanged. Upon cooling, the volume of the chosen cell only slightly changes when passing through the temperature T_{02}.

Figure 4 shows the temperature dependence of the angular parameter of the Bravais cell. At $T_{02} = 250$ K, the deviation of the angular unit-cell parameter from the right angle $(90° - \gamma)$ abruptly increases from zero to saturation. A similar temperature dependence is observed for the rotation angle φ of the optical indicatrix (Fig. 1).

At temperatures below $T_{01} = 288$ K, the extinctions of the reflections observed correspond to two tetragonal space groups, namely, $I4/mmm$ and $I4/m$. According to the results of measurements of the birefringence and heat capacity [8], the transformation from the cubic phase into the tetragonal phase is a second-order phase transition. On this basis, we chose the space group $I114/m$ for the G_1 phase of the $(NH_4)_2KGaF_6$ crystal in the same manner as was done by Flerov *et al.* [9] for the Rb_2KScF_6 crystal. Reasoning from the aforementioned experimental data, for the low-temperature phase G_3, we chose the space group $P112_1/n$, in which the screw axis 2_1 coincides with the $[001]_0$ direction of the unit cell of the initial phase G_0. The parameters of the chosen Bravais cell for the monoclinic phase are listed in the table.

Now, it remains to be seen whether the $(NH_4)_2KGaF_6$ crystal undergoes any transformation in the temperature range from 250 to 245 K (the G_2 phase). In this respect, noteworthy is the temperature dependence of the integral intensity of the $(1\,0\,5)$ superstructure reflection (Fig. 2). Upon transition from the G_1 phase to the G_2 phase with a decrease in the temperature, the integral intensity of the $(1\,0\,5)$ superstructure reflection abruptly increases from zero to a certain value, remains nearly constant within a range of approximately 10 K, and increases to saturation only below 240 K. On the one hand, since the intensity of the superstructure reflection accounts for the displacement of atoms in the unit cell with respect to their initial positions, we can assume that an additional transformation of the crystal structure occurs in this range of temperatures ($T < T_{03}$). On the other hand, the intensity of the superstructure reflection depends on the amount of the material involved in the phase transition. In the case when observations in polarized light demonstrate that the phase transition in different parts of the sample occurs at different temperatures just below T_{02}, this circumstance should be reflected in the temperature dependence of the intensity of the reflection under investigation.

Figure 5 depicts the temperature dependence of the components of the $(10\,0\,0)$ reflection in the x-ray dif-

fraction pattern of the $(100)_0$ section of an oriented plate. At temperatures below 250 K, the (10 0 0) reflection is split into three components. It should be noted that, after the splitting, the intensity of the component observed at the initial position ($2\theta \approx 120.5°$) in the temperature range from 250 to 245 K decreases to zero, whereas the intensities of the other two components increase. In the low-temperature range, this reflection has only two components. Most likely, this finding suggests the coexistence of the G_1 and G_3 phases at these temperatures.

The temperature behavior of the components of the (6 6 6) reflection is also of considerable interest. As the temperature decreases, the number of components of this reflection progressively changes from one component above 250 K to two components in the range 250–245 K and three components below 240 K. Judging from the number of components of the (6 6 6) reflection, we can make the inference that the symmetry of the G_2 phase differs from that of the G_3 phase; furthermore, we can assume that the G_2 phase has the symmetry $P12_1/n1$. In this case, the screw axis 2_1 should be directed along the face diagonal of the cubic cell. However, polarized light microscopy does not confirm this symmetry (Fig. 1). For the proposed variant of symmetry, the rotation angle of the optical indicatrix with respect to the [110] direction must be equal to zero. We believe that the disappearance of one of the components of the (6 6 6) reflection in the temperature range from 250 to 245 K most likely can be associated with the changes in the intensity and width of the other two, stronger components of this reflection in the x-ray diffraction pattern. As a result, the third (weak) component of the reflection is buried in the total profile (see table). One of the possible reasons for the observed changes in the profiles of x-ray reflections is the nucleation and intergrowth of one phase into the other phase, i.e., the intergrowth of the tetragonal phase into the monoclinic phase and vice versa (heating and cooling).

4. CONCLUSION

Thus, the results of the above investigations allowed us to propose the following sequence of symmetry changes in the $(NH_4)_2KGaF_6$ elpasolite: O_h^5–$Fm3m$ ($Z = 4$) $\longleftrightarrow$ C_{4h}^5–$I114/m$ ($Z = 2$) $\longleftrightarrow$ C_{2h}^5–$P112_1/n$ ($Z = 2$). Unfortunately, our investigation did not answer

the question regarding additional symmetry changes in the temperature range of existence of the G_2 phase. We made the assumption that two phases coexist at these temperatures. This assumption is supported by the results obtained by Flerov *et al.* [8], who studied the (p–T) phase diagram of the $(NH_4)_2KGaF_6$ elpasolite. These authors demonstrated that, under pressure, the phase transition temperatures T_{02} and T_{03} decrease almost identically [8]: $dT_{02}/dp = -(2.3 \pm 0.3)$ K/GPa and $dT_{03}/dp = -(1.4 \pm 0.4)$ K/GPa. The stability loss temperature of the cubic phase decreases more rapidly with an increase in the pressure: $dT_{01}/dp = -30$ K/GPa.

REFERENCES

1. A. Sasaki, Y. Furukawa, and D. Nakamura, Ber. Bunsen-Ges. Phys. Chem. **93**, 1142 (1989).
2. K. Kobayashi, T. Matsuo, H. Suga, *et al.*, Solid State Commun. **53** (8), 719 (1985).
3. A. Tressaud, S. Khairoun, L. Rabardel, *et al.*, Phys. Status Solidi A **98** (2), 407 (1986).
4. I. N. Flerov, M. V. Gorev, and T. V. Ushakova, Fiz. Tverd. Tela (St. Petersburg) **41** (3), 523 (1999) [Phys. Solid State **41**, 468 (1999)].
5. M. V. Gorev, I. N. Flerov, and A. Tressaud, J. Phys.: Condens. Matter **11**, 7493 (1999).
6. S. V. Mel'nikova, S. V. Misyul', A. F. Bovina, and M. L. Afanas'ev, Fiz. Tverd. Tela (St. Petersburg) **42** (2), 336 (2000) [Phys. Solid State **42**, 345 (2000)].
7. S. V. Mel'nikova, S. V. Misyul', A. F. Bovina, and M. L. Afanas'ev, Fiz. Tverd. Tela (St. Petersburg) **43** (8), 1533 (2001) [Phys. Solid State **43**, 1594 (2001)].
8. I. N. Flerov, M. V. Gorev, M. L. Afanas'ev, and T. V. Ushakova, Fiz. Tverd. Tela (St. Petersburg) **43** (12), 2209 (2001) [Phys. Solid State **43**, 2301 (2001)].
9. I. N. Flerov, M. V. Gorev, S. V. Mel'nikova, *et al.*, Fiz. Tverd. Tela (Leningrad) **34** (7), 2185 (1992) [Sov. Phys. Solid State **34**, 1168 (1992)].
10. *International Tables for X-ray Crystallography* (Kynoch, Birmingham, 1952), Vol. 1.

Translated by O. Borovik-Romanova