

LATTICE DYNAMICS  
AND PHASE TRANSITIONS

Optical and X-ray Studies of the Structural Phase Transition  
in Cryolite  $(\text{NH}_4)_3\text{GaF}_6$

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Received December 15, 2000

**Abstract**—Optical polarization and x-ray diffraction studies of powders and single-crystal plates of different cuts of an  $(\text{NH}_4)_3\text{GaF}_6$  crystal are carried out in a broad temperature range, including the phase transition point.

The following sequence of symmetry changes is found to occur:  $O_h^5 - Fm3m (Z = 4) \longleftrightarrow C_i^1 - I\bar{1} (Z = 16)$ .

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$(\text{NH}_4)_3M^{3+}\text{F}_6$  ( $M^{3+}$ : Al, Cr, Ga, V, Fe, Sc, In) crystals with cryolite structure (the space symmetry group  $Fm3m$ ,  $Z = 4$ ) belong to a family of perovskite-like compounds. The three-dimensional crystalline framework of these compounds is formed by the octahedra  $(\text{NH}_4)\text{F}_6$  and  $M^{3+}\text{F}_6$ , which are connected through their vertices, and the polyhedra between the octahedra are occupied by ammonium ions.

For most ammonium cryolites, transitions from the cubic phase are accompanied by a change in the orientation of two structural groups:  $(\text{NH}_4)^+$  and  $(M^{3+}\text{F}_6)$  [1]. It has been shown [2, 3] that the temperature at which the cubic phase becomes unstable depends on the  $M^{3+}$  ion size. The number of the observed phase transitions (PTs) and the sequence of symmetry changes also depend on this factor. In substances with a trivalent ion of small radius ( $R_M^{3+} \leq R_{\text{Fe}}^{3+}$ ), only one PT takes place, while in compounds with larger cations (In), two PTs are observed [3]; in  $(\text{NH}_4)_3\text{ScF}_6$ , three PTs occur [4, 5]. Recent studies of powders and single crystals [6] revealed the following series of symmetry changes in cryolite containing scandium:  $O_h^5 - Fm3m (Z = 4) \longleftrightarrow C_{2h}^5 - P12_1/n1 (Z = 2) \longleftrightarrow C_{2h}^3 - I12/m1 (Z = 16) \longleftrightarrow C_i^1 - I\bar{1} (Z = 16)$ .

The lowest symmetry phase is triclinic. Its Bravais cell is chosen to be body-centered and is four times larger in volume compared to the initial face-centered cubic cell.

For the  $(\text{NH}_4)_3\text{GaF}_6$  compound containing a small trivalent cation  $\text{Ga}^{3+}$  [3], x-ray diffraction studies of powders in a temperature range including the PT have shown that the crystals have cubic symmetry  $Fm3m$  ( $Z = 4$ ) above  $T_0 = 250$  K, while line splitting is

observed on diffractograms below the phase transition. Superstructure reflections, which possibly indicate a change in the translation symmetry, were not detected. The diffractogram line identification was carried out for a tetragonal pseudocell with parameters  $a_t \approx a_0/\sqrt{2}$  and  $c_t \approx a_0$ . The symmetry of the low-temperature phase was determined in [3] to be possibly triclinic  $P\bar{1}$ .

According to [5], all ammonium cryolites have the same symmetry of the lowest temperature phase. This conclusion was made on the basis of the similar values of the total entropy changes in the phase transitions in  $(\text{NH}_4)_3\text{GaF}_6$  and  $(\text{NH}_4)_3\text{ScF}_6$  and from their ( $P$ - $T$ ) diagrams.

It is well known that x-ray diffraction studies of small structure distortions should be carried out on single-crystal samples, not on powders. In [6], a complex series of changes in the symmetry of  $(\text{NH}_4)_3\text{ScF}_6$  was determined by studying crystal twinning and by observing x-ray reflections from oriented single-crystal plates. In that paper, in contrast to [3], a superstructure was observed and a change in the translation symmetry was detected. The present investigation is carried out with the aim of obtaining detailed information on the symmetry of the  $(\text{NH}_4)_3\text{GaF}_6$  low-temperature phase.

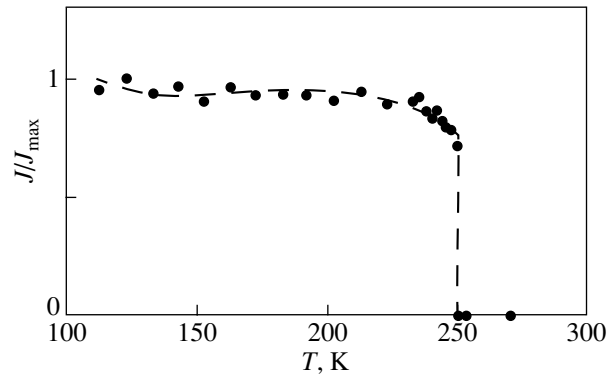
The  $(\text{NH}_4)_3\text{GaF}_6$  compound was synthesized by means of interaction of equivalent amounts of a  $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$  solution in 40 vol % hydrofluoric acid (evaporated until the onset of crystallization) and of an  $\text{NH}_4\text{F}$  saturated solution. Small (2–3 mm<sup>3</sup>) well-faceted single crystals were grown by means of slow controlled evaporation of a solution of the synthesized substance in 10 vol % HF acid by gradually lowering (over 7 days) the crystallization temperature from 333 to 293 K.

Investigations with the help of a polarizing microscope were carried out on thin crystalline platelets cut along different crystallographic directions. On cooling, a PT from the cubic phase was observed at the temperature  $T_0 = 250$  K. This PT was accompanied by the formation of twins and by cracking. An extremely complicated mixed twinning structure with a nonuniform, temperature-dependent, extinction position is observed in polarized light in a very thin ( $<0.05$  mm) sample. The domain walls are oriented along the  $[100]$  and  $[110]$  directions. In general, the twinning structure is analogous to that observed in the triclinic phase of  $(\text{NH}_4)_3\text{ScF}_6$ . However, in our case, the domains are smaller. Unfortunately, we were not able to obtain sufficiently large monodomain areas; for such areas, it would have been possible (as was done in [6]) to measure the temperature dependence of the orientation of the optical indicatrix precisely. However, the results obtained are sufficiently accurate for us to draw the conclusion that the following symmetry change takes place in an  $(\text{NH}_4)_3\text{GaF}_6$  crystal: cubic ( $G_0$ )  $\longleftrightarrow$  triclinic ( $G_1$ ).

X-ray diffraction studies of  $(\text{NH}_4)_3\text{GaF}_6$  crystals were carried out in a broad temperature range 100–300 K on a Dron-2.0 diffractometer equipped with a low-temperature URNT-180 attachment ( $\text{CuK}_\alpha$  radiation, graphite monochromator). Single-crystal platelets of the  $(110)_0$  and  $(111)_0$  cuts, as well as powders obtained from  $(\text{NH}_4)_3\text{GaF}_6$  single crystals, were used as experimental samples. Here and further on, subscripts on the symbols of planes and directions designate the crystal phase.

The set of x-ray reflections in the initial  $G_0$  phase corresponds to cubic symmetry with a face-centered cell  $F$  [7]. The parameters of this cell at 353 K are shown in the table. Below the PT temperature  $T_0 = 250$  K, changes in the profiles of the x-ray reflections from single-crystal plates arise and splitting of reflections on the powder diffractograms are observed (see table).

Moreover, below the phase transition temperature (the  $G_1$  phase), a system of superstructure reflections of the  $(hk0)$ ,  $(hkl)$ , and  $(h + 1/2, h + 1/2, h + 1/2)$  types is formed. Here,  $h$  is an arbitrary integer. The reflection splitting in the  $G_1$  phase corresponds to triclinic symmetry. The formation of superstructure reflections characterized by noninteger values of index  $h$  indicates a change in the Bravais cell volume due to the PT. Figure 1 shows the temperature dependence of the integral intensity of the  $(5/2, 5/2, 5/2)$  superstructure reflection. It is evident from Fig. 1 that, in the course of the transition from the  $G_0$  to the  $G_1$  phase, the above-mentioned reflection arises suddenly and almost immediately reaches saturation. Since the superstructure reflection intensity characterizes shifts in the atom in the elementary cell with respect to their initial positions, we draw the conclusion that the main structural distortions in the



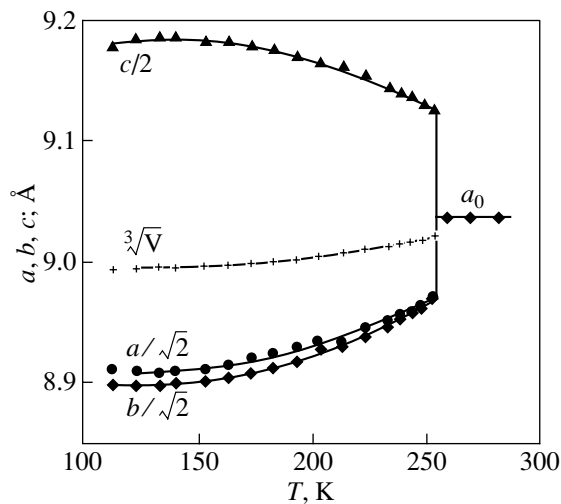
**Fig. 1.** Temperature dependence of the integral intensity for the  $(5/2, 5/2, 5/2)$  superstructure reflection. The reflection indices are in accordance with the parameters of the cell of the initial  $G_0$  phase.

crystal studied take place in a narrow temperature range below the PT.

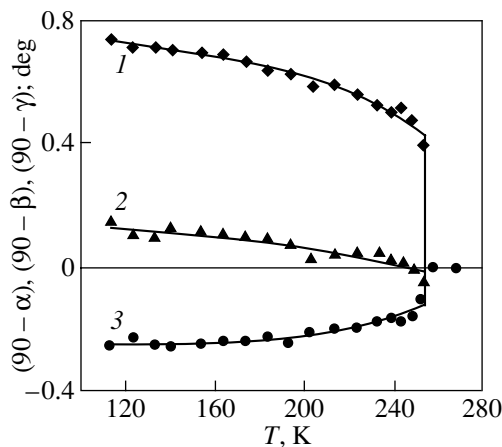
The temperature dependences of the linear and angular parameters of the crystal cell in the  $G_0$  and the  $G_1$  phases were determined from the positions of the components of the  $(8, 8, 0)$  reflection. The results of these investigations are represented in Figs. 2 and 3. It is clear from Fig. 2 that the elementary-cell parameters

Crystallographic data for  $(\text{NH}_4)_3\text{GaF}_6$

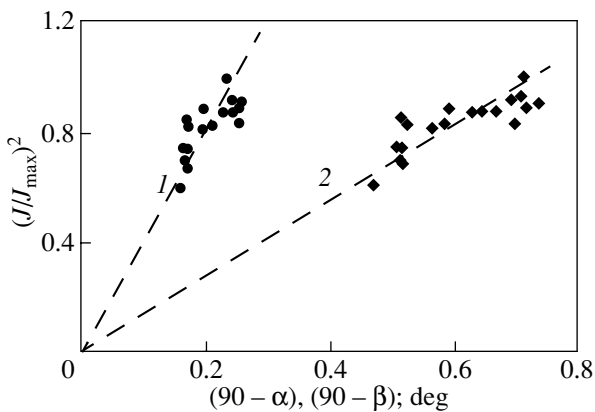
	$G_1$	$G_0$
Space group	$C_i^1 - I\bar{1}$	$O_h^5 - Fm\bar{3}m$
$Z$	16	4
$T_{\text{exp}}, \text{K}$	170	300
Bravais cell parameters		
$\mathbf{a}, \text{\AA}$	$-\mathbf{b}_0 + \mathbf{c}_0$ 12.605	$\mathbf{a}_0$ 9.039
$\mathbf{b}, \text{\AA}$	$\mathbf{b}_0 + \mathbf{c}_0$ 12.590	$\mathbf{b}_0$ 9.039
$\mathbf{c}, \text{\AA}$	$2\mathbf{a}_0$ 18.363	$\mathbf{c}_0$ 9.039
$\alpha, \text{deg}$	90.24	90
$\beta, \text{deg}$	89.31	90
$\gamma, \text{deg}$	89.89	90
$V, \text{\AA}^3$	2914.118	738.514
Reflection splitting scheme		
$(hk0)$		
$(hhh)$		
The presence of superstructure reflections	+	-



**Fig. 2.** Temperature dependence of the linear dimensions and volume of the Bravais cell for an  $(\text{NH}_4)_3\text{GaF}_6$  crystal. The elementary-cell volume  $V$  is four times smaller in the  $G_1$  phase.



**Fig. 3.** Temperature dependences of the angular parameters of the Bravais cell for an  $(\text{NH}_4)_3\text{GaF}_6$  crystal: (1)  $90 - \beta$ , (2)  $90 - \gamma$ , and (3)  $90 - \alpha$ .



**Fig. 4.** Dependence of the square of the integral intensity of the  $(5/2, 5/2, 5/2)$  superstructure reflection upon distortion of the rectangular Bravais cell in the triclinic phase of the  $(\text{NH}_4)_3\text{GaF}_6$  crystal: (1)  $90 - \alpha$  and (2)  $90 - \beta$ .

are changed abruptly in the course of the transition from the cubic  $G_0$  to the  $G_1$  phase. However, the jump in cell volume is not large and equals approximately 0.4 percent of  $V_0$ . The linear dimensions of the triclinic cell of  $(\text{NH}_4)_3\text{GaF}_6$  along the  $\mathbf{a}$  and  $\mathbf{b}$  directions are decreased and virtually coincide in value, while the cell parameter along the  $\mathbf{c}$  axis is increased. Similar temperature dependences of the cell dimensions have been observed in scandium cryolite, whose parameters are approximately 0.2 Å greater.

The angular parameters of the Bravais cell (Fig. 3) also have many common features in these two crystals. In triclinic phases,  $\beta < 90^\circ$  and  $\alpha > 90^\circ$  and  $\gamma$  does not differ considerably from  $90^\circ$ . At  $T = T_0$ , the deviations of the angular parameters of the Bravais cell from the right angle ( $90 - \alpha$ ) and ( $90 - \beta$ ) appear in a jump and then grow gradually over the whole temperature range studied. This dependence differs considerably from the behavior of the intensity of the superstructure reflections (Fig. 1).

The extinction of the structural and the superstructure reflections, as well as the splittings of the specially chosen x-ray reflections from the single-crystal plates, allowed us to determine the crystal group of the crystal. By standard definition (see [7]), the Bravais cell of the triclinic  $G_1$  phase should be simple. However, for convenience, we took the bulk-centered cell  $I\bar{1}$  ( $Z = 16$ ). It is clear that this Bravais cell of the  $G_1$  phase has a four times greater volume than that of the  $G_0$  phase. However, the primitive cells of the  $G_0$  and  $G_1$  phases contain 1 and 8 formula units, respectively. The data on the  $(\text{NH}_4)_3\text{GaF}_6$  phase symmetry and sizes and orientation of the Bravais cells are listed in the table.

Contrary to the results of [3], where the  $G_3$  phase symmetry was determined to be  $P\bar{1}$  but the Bravais cell was not chosen, our findings allow one to establish the point symmetry group and are indicative of the change in the translation symmetry. Thus, the studies carried out by us allow one to affirm that the high-temperature phases, as well as the low-temperature phases, of the two ammonium cryolites  $(\text{NH}_4)_3\text{GaF}_6$  and  $(\text{NH}_4)_3\text{ScF}_6$  have the same symmetry, namely,  $Oh^5-Fm\bar{3}m$  ( $Z = 4$ ) and  $C_i^1-I\bar{1}$  ( $Z = 16$ ), respectively. The former crystal is immediately converted into the triclinic phase on cooling, while the latter is transformed in three steps. Studies of the heat capacity [5] also revealed that the structural changes due to phase transitions are identical in these two crystals. The total entropy change in  $(\text{NH}_4)_3\text{ScF}_6$  in the course of the three PTs is  $\Delta S \Delta S_i = 20.79 \pm 1.53 \text{ J mol}^{-1} \text{ K}^{-1}$ , while in  $(\text{NH}_4)_3\text{GaF}_6$ , we have  $\Delta S = 23.0 \pm 1.6 \text{ J mol}^{-1} \text{ K}^{-1}$ .

Our investigations allow one to make some conclusions regarding the possible relation between the order parameter of the phase transition and the shear deformation that appears below the phase transition. As

shown above, the changes in elementary-cell angular parameters are not proportional to the changes in superstructure reflection intensity. However, according to Fig. 4, these quantities have a quadratic relation. On this basis, one can conclude that the ferroelastic PT in  $(\text{NH}_4)_3\text{GaF}_6$  is improper and that the dependence shown in Fig. 1 reflects the temperature behavior of its microscopic parameter.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project nos. 00-02-16034 and 00-15-96790.

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*Translated by A. Sonin*