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LATTICE DYNAMICS  
AND PHASE TRANSITIONS

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## A Study of the Phase Diagrams of $(\text{NH}_4)_3\text{Ga}_{1-x}\text{Sc}_x\text{F}_6$ Ammonium Cryolites

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**Abstract**—This paper reports on the results of analyzing  $p$ - $T$  and  $x$ - $T$  phase diagrams and calorimetric properties of solid solutions in  $(\text{NH}_4)_3\text{Ga}_{1-x}\text{Sc}_x\text{F}_6$  cryolites with scandium concentrations  $x = 0.0, 0.1, 0.35, 0.4, 0.6, 0.8,$  and  $1.0$ . The thermodynamic parameters of the phase transitions observed in the studied compounds are determined. The generalized phase diagram and successive structural transformations in a series of  $(\text{NH}_4)_3\text{Me}^{3+}\text{F}_6$  ammonium cryolites are discussed. © 2002 MAIK “Nauka/Interperiodica”.

### 1. INTRODUCTION

Crystals of  $(\text{NH}_4)_3\text{Me}^{3+}\text{F}_6$  ammonium cryolites in the initial high-temperature phase have a cubic lattice ( $Fm\bar{3}m$ ,  $Z = 4$ ) in which  $\text{Me}^{3+}\text{F}_6$  and  $(\text{NH}_4)^+\text{F}_6$  fluorine octahedra alternate along the cubic cell edges and holes between octahedra occupied by ammonium ions. As the temperature decreases, all the known ammonium cryolites undergo either single phase transitions or successive phase transitions. Recent extensive studies of ammonium cryolites with the use of different techniques have revealed a number of specific features in these transitions.

It is found that the phase transition temperatures and sequences of distorted phases formed upon phase transitions in ammonium cryolites substantially depend on the size of the trivalent cation  $\text{Me}^{3+}$ . For example, the ammonium cryolites with large-sized ions  $\text{Me}^{3+}$  ( $\text{Me}^{3+} = \text{Sc}$  or  $\text{In}$ ) are characterized by a sequence of three phase transitions [1–3]. The cryolite crystals with small-sized ions  $\text{Me}^{3+}$  ( $\text{Me}^{3+} = \text{Ga}, \text{V}, \text{Cr},$  or  $\text{Fe}$ ) undergo only a first-order transition from the cubic phase to the triclinic phase [1, 2, 4]. Moriya *et al.* [5] studied the  $(\text{NH}_4)_3\text{AlF}_6$  crystal with the smallest sized cation  $\text{Me}^{3+}$  ( $\text{Me}^{3+} = \text{Al}$ ) and revealed two successive phase transitions in this compound.

The thermodynamic parameters of the phase transitions in ammonium cryolites have been determined from analyzing the results of heat capacity investigations [1–3, 5–8]. The large entropy change observed upon phase transitions is associated with the significant role played by ordering in structural transformations. According to the model considered in [1, 5, 6], the phase transitions in ammonium cryolites are accompanied by orientational ordering of both fluorine octahedral and ammonium tetrahedral ionic groups.

In the model of rigid fluorine regular octahedra, the fluorine ions in the cubic phase can be located either in the  $24e$  positions at the cubic cell edges or in the  $192l$  positions. In the latter case, each octahedron has eight equally probable orientations. The ammonium ions in the cubic cell occupy two different crystallographic positions, namely, the  $8c$  and  $4b$  positions. In the former case, the ammonium ions reside in holes between the octahedra and have only one orientation. In the latter case, the ammonium ions are located inside the octahedra, are disordered in accordance with the symmetry of the occupied site, and have two possible orientations. Therefore, the change in the entropy upon complete orientational ordering of octahedral and tetrahedral ionic groups can be determined as  $\Delta S = R(\ln 2 + \ln 8) = R \ln 16$ . This is in good agreement with the experimental results obtained for cryolites in [1, 2, 5–7].

The above model of a phase transition associated with simultaneous ordering of octahedra and tetrahedra was confirmed by nuclear magnetic resonance (NMR) investigations of gallium cryolite [9]. It was demonstrated that the spin-lattice relaxation times of both protons and fluorine ions exhibit jumps at the phase transition temperature.

Among the three successive phase transitions  $G_0 \rightarrow G_1 \rightarrow G_2 \rightarrow G_3$  observed in scandium cryolites, only the  $G_0 \rightarrow G_1$  phase transition at the temperature  $T_1$  and the  $G_1 \rightarrow G_2$  transition at the temperature  $T_2$  can be associated with orientational ordering, because it is these phase transitions that are accompanied by considerable entropy changes that are close in magnitude to  $R \ln 8$  and  $R \ln 2$ , respectively. Sasaki *et al.* [10] performed an NMR investigation of  $(\text{NH}_4)_3\text{InF}_6$  indium crystals, which can also undergo three successive phase transitions [1], and revealed that the spin-lattice relaxation times show anomalous behavior only

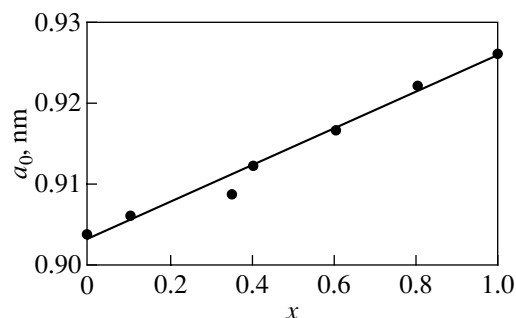
at temperatures  $T_1$  and  $T_2$ . It was found that the motion of fluorine ions changes significantly at both temperatures  $T_1$  and  $T_2$ . Therefore, the change in the entropy upon phase transition from the cubic phase is due to ordering of ammonium tetrahedra ( $R \ln 2$ ) and partial ordering of octahedra ( $R \ln 4$ ) [2, 4, 8]. The complete ordering of the octahedra occurs upon the second phase transition ( $\Delta S_2 = R \ln 2$ ). The third phase transition is a clearly defined first-order transition with an extremely large hysteresis and a small change in entropy [2, 8]. It can be assumed that the  $G_2$  and  $G_3$  phases represent two completely ordered variants of the initial phase and differ from each other only in the orientation of tetrahedra in the  $4b$  position.

The effect of hydrostatic pressure and a decrease in the size of the  $Me^{3+}$  ion bring about a decrease in the unit cell volume of the studied crystal and a change in the interactions in the crystal lattice and, hence, should affect the temperature and sequences of structural transformations. The  $p$ - $T$  phase diagrams of  $(NH_4)_3ScF_6$  and  $(NH_4)_3GaF_6$  ammonium cryolites were analyzed in our earlier works [3, 8]. For both compounds studied under pressure, we revealed triple points and changes in the sequence of structural distortions. At high pressures, the scandium cryolite undergoes a direct phase transition  $G_0 \rightarrow G_3$ , whereas the gallium cryolite is characterized by a sequence of pressure-induced phase transformations  $G_0 \rightarrow G_4 \rightarrow G_5 \rightarrow G_3$ . It was assumed that the phase diagram of the gallium cryolite is a continuation of the phase diagram of the scandium cryolite toward the high-pressure range.

The aim of the present work was to reveal the interrelation between different successive structural distortions in ammonium cryolites and to construct a generalized phase diagram, including all the phase transitions observed under atmospheric and higher pressures in  $(NH_4)_3Me^{3+}F_6$  crystals. For this purpose, we investigated the heat capacity of  $(NH_4)_3Ga_xSc_{1-x}F_6$  solid solutions and analyzed the influence of hydrostatic pressure on the temperature of phase transitions in these compounds.

## 2. SAMPLE PREPARATION

Solid solutions of  $(NH_4)_3Ga_{1-x}Sc_xF_6$  cryolites with scandium concentrations  $x = 0.0, 0.1, 0.35, 0.4, 0.6, 0.8,$  and  $1.0$  were prepared in the form of a finely dispersed powder through solid-phase synthesis at a temperature of  $600$  K. The initial reactants  $(NH_4)_3GaF_6$  and  $(NH_4)_3ScF_6$  were taken in appropriate molar proportions and placed in platinum tubes, which were then sealed in an argon atmosphere. The compounds synthesized were identified using an x-ray diffractometer. It was established that the samples prepared were crystalline compounds with a cryolite structure. No indications of the presence of the initial compounds (more



**Fig. 1.** Dependence of the unit cell parameter  $a_0$  of the cubic phase in  $(NH_4)_3Ga_{1-x}Sc_xF_6$  solid solutions on the scandium concentration  $x$ .

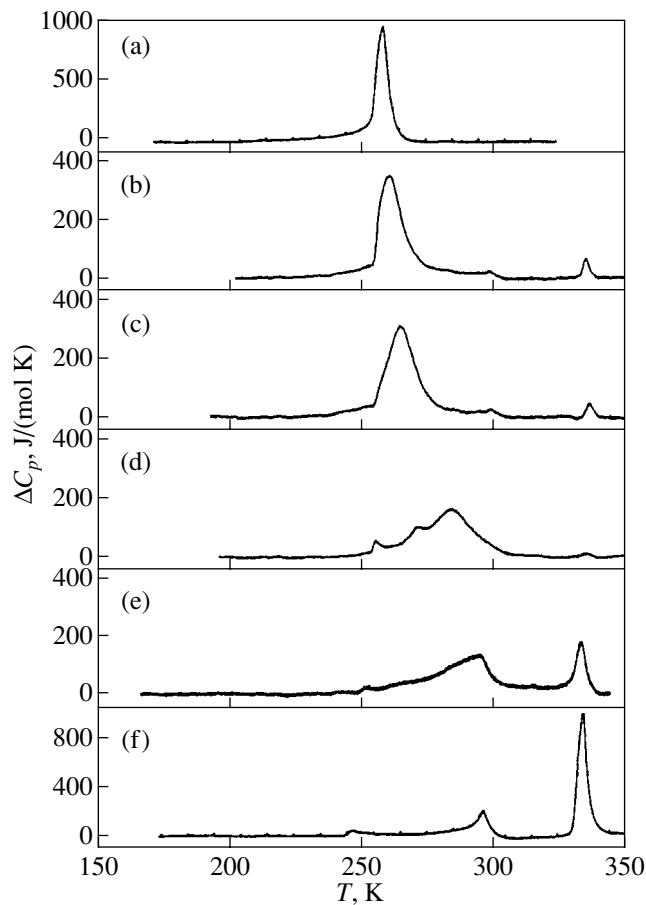
than 5%) in the resultant solid solutions were revealed. At room temperature, the ammonium compounds with scandium concentrations  $x = 0.6, 0.4, 0.35,$  and  $0.1$  had a cubic structure, whereas the solid solution with  $x = 0.8$  exhibited monoclinic symmetry, which corresponded to one of the distorted phases of the scandium cryolite. In the last-mentioned sample, the cubic phase was observed at temperatures above  $\sim 330$  K.

## 3. RESULTS AND DISCUSSION

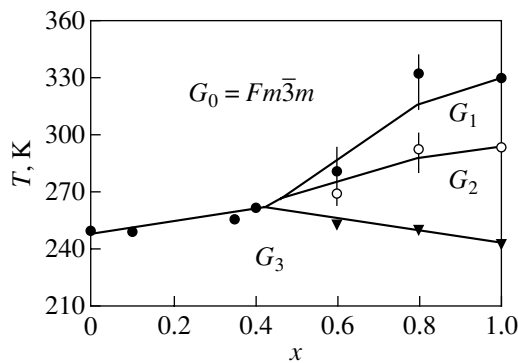
The unit cell parameters  $a_0$  in the cubic phase were calculated from the x-ray diffraction data. According to the Vegard rule [9], a continuous series of solid solutions of two compounds is characterized by a linear relationship between the unit cell parameter  $a_0$  and the concentration  $x$  of the solid solution. As can be seen from Fig. 1, the unit cell parameters  $a_0$  of all the studied compounds are well approximated by a straight line. The only exception is the solid solution with  $x = 0.35$ , for which the deviations from the approximating line are equal to  $\sim 0.1$  for the concentration  $x$  and  $0.002$  nm for the unit cell parameter. The accuracy in the x-ray diffraction determination of the unit cell parameter  $a_0$  is  $\sim 0.001$  nm. The problem of accuracy in the determination of the concentration  $x$  will be considered below when analyzing the results of the calorimetric measurements.

The results of differential scanning microcalorimetric (DSM) analysis of the solid solutions in the temperature range  $150$ – $350$  K are displayed in Fig. 2. In this range of temperatures, the initial cryolites undergo phase transitions and mixed cryolites can form distorted phases.

It can be seen from Fig. 2 that the heat capacity of the pure scandium cryolite and mixed compounds with scandium concentrations  $x = 0.8$  and  $0.6$  exhibits three peaks attributed to three phase transitions. As the scandium concentration decreases, the temperature ranges of existence of the intermediate distorted phases  $G_1$  and  $G_2$  become narrower and vanish at concentrations  $x$  in the range from  $0.6$  to  $0.4$  (Fig. 3). Reasoning from the



**Fig. 2.** DSM curves for  $(\text{NH}_4)_3\text{Ga}_{1-x}\text{Sc}_x\text{F}_6$  solid solutions at different scandium concentrations  $x$ : (a) 0, (b) 0.35, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.0.



**Fig. 3.** Dependence of the temperature of phase transitions in  $(\text{NH}_4)_3\text{Ga}_{1-x}\text{Sc}_x\text{F}_6$  solid solutions on the scandium concentration  $x$ .

anomalies observed in the heat capacity (Fig. 2), we can draw the conclusion that the solid solutions with concentrations  $x = 0.4$  and  $0.35$  undergo only one phase transition. However, the DSM curve of the solid solution with  $x = 0.4$  has inflection points in the temperature

ranges approximately 10 K above and below the temperature of the main maximum in the heat capacity  $\Delta C_p$  (at  $\sim 262$  K), which can also be attributed to phase transitions with close temperatures.

It should also be noted that all the studied compounds are characterized by small anomalies in the heat capacity whose temperatures remain constant with a change in the composition of the solid solution. These temperatures are in satisfactory agreement with the phase transition temperatures  $T_1 = 330$  K and  $T_2 = 291$  K for the scandium cryolite. The latter circumstance indicates that a certain part of  $(\text{NH}_4)_3\text{ScF}_6$  did not react in the course of the solid-phase synthesis. However, as was noted above, the x-ray diffraction analysis did not reveal the initial compounds in the solid solutions to within the accuracy of the analysis. The amount of  $(\text{NH}_4)_3\text{ScF}_6$  which did not enter into the solid-phase reaction according to the results of calorimetric measurements was determined by comparing the enthalpy of the phase transition in the scandium cryolite and the thermal effect observed in the solid solutions at a temperature of 330 K. It was found that, in different samples, the calculated content of unreacted  $(\text{NH}_4)_3\text{ScF}_6$  varies from 1 to 4%; i.e., it is within the sensitivity of the x-ray diffraction method used in our measurements.

The accuracy in the determination of the phase transition temperatures of the solid solutions under investigation (Fig. 3) is not very high because of the considerable smearing and overlapping of the heat capacity anomalies. For this reason, we determined only the total entropy change for the solid solution with  $x = 0.6$ . In this case, the total entropy change was found to be equal to  $2.02R$ . The thermodynamic parameters of the phase transitions in solid solutions were determined with due regard for the content of unreacted initial components.

The choice of samples for further comprehensive investigations into the thermodynamic properties was made for the following reasons. In our earlier work [2], we performed a detailed calorimetric analysis of the solid solution with  $x = 0.1$  and revealed that this compound undergoes one phase transition similar to the phase transformation in gallium cryolite under atmospheric pressure. Consequently, in the present work, we examined only the effect of hydrostatic pressure on the temperature of the phase transformation in this compound. According to the  $x$ - $T$  phase diagram (Fig. 3), the solid solutions with scandium concentrations  $x = 0.4$  and  $0.6$  are close in composition to the points at which the temperature ranges of existence of the intermediate phases  $G_1$  and  $G_2$  vanish. In this respect, the samples with concentrations  $x = 0.4$  and  $0.6$  proved to be the most convenient objects for the investigation of the disappearance of the intermediate phases with a decrease in the volume of the unit cell under pressure. Moreover, the heat capacity of the solid solution with  $x = 0.4$  was measured using an adiabatic calorimeter in order to refine the DSM data on the number of phase transitions.

The heat capacity was measured in the course of discrete and continuous heating in the temperature range 80–320 K. A 1.05-g sample was placed in an indium tube, which was then hermetically sealed in a helium atmosphere. The heat capacity of the tube was measured in a separate experiment. The spread of experimental points about the smoothed curve did not exceed 0.5%. As can be seen from Fig. 4, the temperature dependence of the heat capacity, like the DSM curves (Fig. 2c), exhibits a small anomaly at a temperature of  $\sim 295$  K due to the presence of a minor amount of scandium cryolite in the studied sample. The principal peak of the heat capacity at  $T \sim 262$  K also has inflections, which, most likely, can be associated with composition inhomogeneities of the sample, because  $(\text{NH}_4)_3\text{GaF}_6$  and  $(\text{NH}_4)_3\text{ScF}_6$  cryolites in this range of temperatures are characterized by heat capacity anomalies due to phase transitions. However, we cannot rule out the possibility that the second phase transition occurs below the temperature of the main anomaly in the heat capacity. The total entropy change upon the phase transition in the solid solution with  $x = 0.4$  is estimated as  $\Delta S = (2.6 \pm 0.2)R$  (Fig. 4b). This result is in good agreement with the total changes in the entropy of other cryolites [1–3, 5–8] and the solid solutions studied in the present work (see table).

The influence of hydrostatic pressure on the phase transition temperatures was examined with samples weighing approximately 0.2 g. The phase transition temperatures and their changes under pressure were measured using differential thermal analysis [8, 11]. A pressure as high as 0.6 GPa was produced in a chamber of the cylinder–piston type. A mixture of silicone oil and pentane was used as a pressure transmitting medium. In the chamber, the pressure was measured by a manganin resistance pressure gauge and the temperature was measured using a copper–constantan thermocouple. The errors in measurements were equal to  $\pm 10^{-3}$  GPa and  $\pm 0.3$  K, respectively. The reliability of the results obtained was checked by measuring the shifts in the phase transition temperatures with both an increase and a decrease in the hydrostatic pressure. Figure 5 shows the phase diagrams of solid solutions with scandium concentrations  $x = 0.4$  and 0.6 and the phase diagrams obtained for  $(\text{NH}_4)_3\text{GaF}_6$  and  $(\text{NH}_4)_3\text{ScF}_6$  cryolites in our earlier work [8]. Since the addition of 10% Sc does not substantially affect the parameters of the phase diagram of the gallium cryolite, it is not shown in the figure.

It is found that the  $(\text{NH}_4)_3\text{Ga}_{0.4}\text{Sc}_{0.6}\text{F}_6$  cryolite undergoes three phase transitions at  $p = 0$ ; however, the disappearance of the distorted phase  $G_1$  occurs at a lower pressure (0.22 GPa) compared to that in the scandium cryolite (0.52 GPa). The second triple point, at which the  $G_2$  phase disappears, is observed in the experiments under a pressure of 0.38 GPa. For  $(\text{NH}_4)_3\text{ScF}_6$ , we succeeded in determining the parameters of this point (1.2 GPa) only through the extrapola-

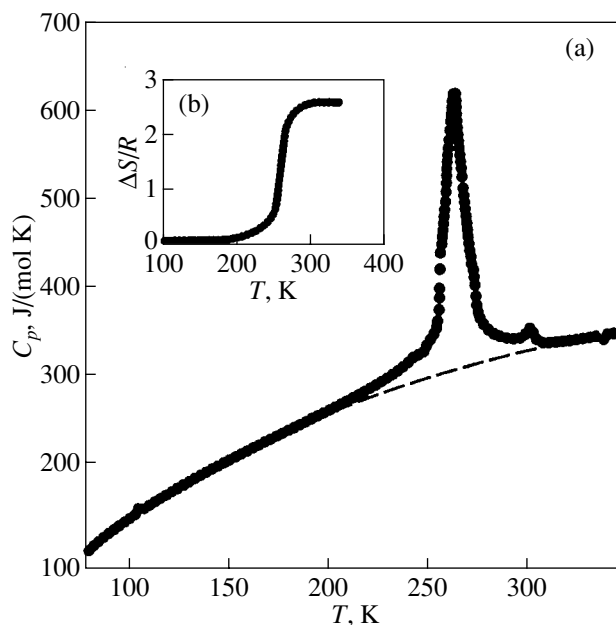


Fig. 4. Temperature dependences of (a) the heat capacity and (b) the entropy change in the  $(\text{NH}_4)_3\text{Ga}_{0.6}\text{Sc}_{0.4}\text{F}_6$  solid solution. The dashed line shows the lattice heat capacity.

tion of the phase boundaries  $G_0 \rightarrow G_3$  and  $G_2 \rightarrow G_3$  [8].

The identification of the phase boundaries presents no special problems in any of the studied compounds, except for  $(\text{NH}_4)_3\text{Ga}_{0.6}\text{Sc}_{0.4}\text{F}_6$ . In this compound, as was already noted in analyzing the DSM data, the low-temperature anomaly can be associated with both the second phase transition  $G_2 \rightarrow G_3$  and the presence of small amounts of initial cryolites in the studied sample. This anomaly is small compared to the anomaly observed upon the  $G_0 \rightarrow G_3$  transition from the cubic phase, it is substantially smeared, and it is not observed at pressures above 0.05 GPa. Moreover, this anomaly cannot be assigned with confidence to a phase transformation similar to the  $G_2 \rightarrow G_3$  transition in the scandium cryolite, judging from its temperature behavior with a change in pressure. At a pressure of 0.3 GPa, the boundary between the  $G_0$  and  $G_3$  phases has a clearly defined kink, which, most likely, can be associated with the presence of the triple point characterized by the phase transitions  $G_0 \rightarrow G_3 \rightarrow G_5$ . This assumption is confirmed by the pressure ratio (0.05 GPa) at the triple points for  $(\text{NH}_4)_3\text{Ga}_{0.6}\text{Sc}_{0.4}\text{F}_6$  and gallium cryolite [8]. The  $G_5 \rightarrow G_3$  phase transition was not observed in our experiments. This can be explained by the insignificant thermal effect and smearing of the heat capacity anomaly at high pressures.

The table presents the quantities  $dT/dp$  for all the phase transitions observed in the experiments under pressure.

Thermodynamic parameters of the phase transitions in  $(\text{NH}_4)_3\text{Ga}_{1-x}\text{Sc}_x\text{F}_6$  cryolites

Phase transition	Thermodynamic parameters	$x$						
		0	0.1	0.35	0.4	0.6	0.8	1
$G_0 \rightarrow G_1$	$\Delta S/R$						~1	1.63
	$dT/dp, \text{K/GPa}$					-8.2		-16.4
$G_1 \rightarrow G_2$	$\Delta S/R$						~1	0.81
	$dT/dp, \text{K/GPa}$					46.4		57.5
$G_2 \rightarrow G_3$	$\Delta S/R$						~0.05	0.08
	$dT/dp, \text{K/GPa}$					65.2		59.9
$G_0 \rightarrow G_2$	$\Delta S/R$							
	$dT/dp, \text{K/GPa}$							
$G_0 \rightarrow G_3$	$\Delta S/R$	2.76	2.56	2.16	2.60			
	$dT/dp, \text{K/GPa}$	-12.1	-6.5		-15.3	-8.1		
$G_0 \rightarrow G_4$	$\Delta S/R$							
	$dT/dp, \text{K/GPa}$	101.3	100.8					
$G_4 \rightarrow G_5$	$\Delta S/R$							
	$dT/dp, \text{K/GPa}$	~0	-8.8					
$G_5 \rightarrow G_3$	$\Delta S/R$							
	$dT/dp, \text{K/GPa}$	-22.5	-26.3					
$G_0 \rightarrow G_5$	$\Delta S/R$							
	$dT/dp, \text{K/GPa}$	73.1	82.3		60.1			
References		[2.8]	[2]					[2, 8]

Reasoning from the analysis of the entropy changes upon phase transitions and  $p$ - $T$  phase diagrams of the studied compounds, we constructed a generalized phase diagram (Fig. 6) including all structural transformations observed in the ammonium cryolites. The

dashed lines in Fig. 6 indicate regions corresponding to the experimentally observed phase diagrams of the studied compounds.

The  $(\text{NH}_4)_3\text{ScF}_6$  cryolite is characterized by the largest unit cell volume and, under atmospheric pres-

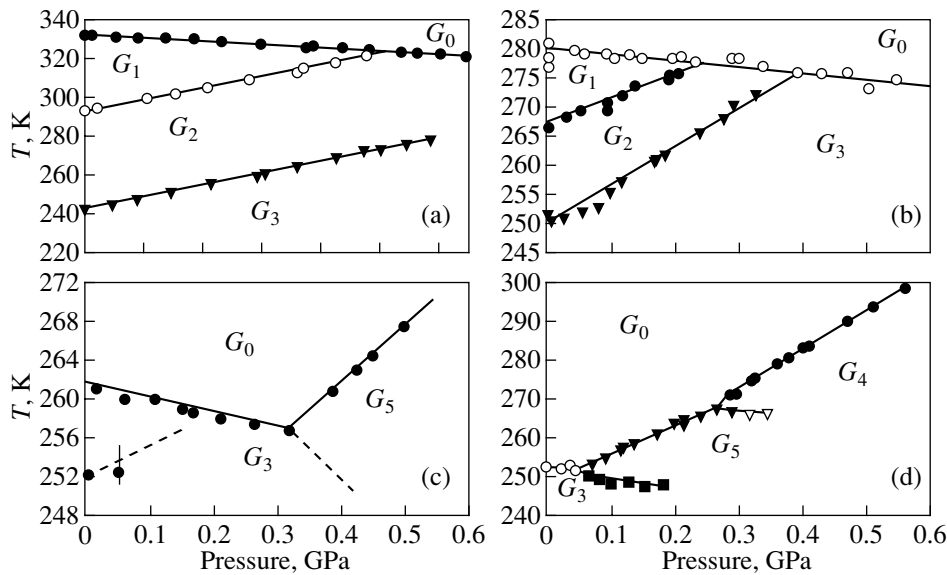


Fig. 5. Phase  $p$ - $T$  diagrams for (a)  $(\text{NH}_4)_3\text{ScF}_6$  [8], (b)  $(\text{NH}_4)_3\text{Ga}_{0.4}\text{Sc}_{0.6}\text{F}_6$ , (c)  $(\text{NH}_4)_3\text{Ga}_{0.6}\text{Sc}_{0.4}\text{F}_6$ , and (d)  $(\text{NH}_4)_3\text{GaF}_6$  compounds [8].

sure, undergoes three successive phase transitions  $G_0 \rightarrow G_1 \rightarrow G_2 \rightarrow G_3$ . The first phase transition is accompanied by the partial ordering of fluorine octahedra ( $\Delta S = R \ln 8/2 = 1.4R$ ). The change in symmetry of the crystallographic positions occupied by ammonium ions inevitably results in complete ordering of ammonium tetrahedra arranged inside the octahedra ( $\Delta S = R \ln 2 = 0.7R$ ). The second phase transition leads to complete ordering of fluorine octahedra ( $\Delta S = R \ln 2$ ). The third phase transition  $G_2 \rightarrow G_3$  is attended by a small entropy change and is unrelated to ordering processes. It seems likely that the third phase transition is a transition between completely ordered phases with different types of ordering of ammonium groups. Preliminary results of investigations into the properties of deuterated cryolites have demonstrated that the deuteration of the initial cryolites substantially affects the temperature of only the third phase transition.

As the pressure increases or, what is the same, the unit cell volume decreases with a decrease in the scandium concentration in the solid solutions, the temperature of the phase transition  $G_0 \rightarrow G_1$  decreases, whereas the temperatures of the other two transitions  $G_1 \rightarrow G_2$  and  $G_2 \rightarrow G_3$  increase. The  $G_1$  and  $G_2$  phases sequentially disappear at two triple points, which are experimentally observed in the scandium cryolite (Fig. 5a) and in the  $(\text{NH}_4)_3\text{Ga}_{0.4}\text{Sc}_{0.6}\text{F}_6$  solid solution (Fig. 5b). With a further increase in the pressure, the phase transition  $G_0 \rightarrow G_3$  is split at triple points, first, into two phase transitions  $G_0 \rightarrow G_5 \rightarrow G_3$  and, then, into three phase transitions  $G_0 \rightarrow G_4 \rightarrow G_5 \rightarrow G_3$ . These sequences of phase transitions and the triple points are observed in the  $(\text{NH}_4)_3\text{Ga}_{0.6}\text{Sc}_{0.4}\text{F}_6$  solid solution (Fig. 5c) and gallium cryolite (Fig. 5d) in the experiments under pressure.

The occurrence of two different sequences of phase transitions, namely,  $G_0 \rightarrow G_1 \rightarrow G_2 \rightarrow G_3$ , at low pressures (large parameters  $a_0$  of the cubic unit cell) and  $G_0 \rightarrow G_4 \rightarrow G_5 \rightarrow G_3$  at high pressures (small parameters  $a_0$  of the cubic unit cell), can be associated with the presence of two possible variants of partial ordering of octahedral ionic groups in the  $G_1$  phase, as is the case with the distortions  $(0\ 0\ \psi)$  and  $(0\ \psi\ \psi)$  in elpasolites containing atomic ions  $A^+$  and  $\text{Me}^{3+}$  [12].

The existing model of phase transitions is based primarily on the experimentally found changes in the entropy and symmetry of crystallographic positions occupied by ordered ions in the initial phase. To the best of our knowledge, there is no reliable experimental evidence for this disordering of octahedra and tetrahedra. Massa *et al.* [13] made an attempt to interpret x-ray diffraction data in the framework of the model of orientationally disordered octahedra for some elpasolites with atomic cations. It was shown that the fluorine ions are displaced from the edge of the cubic unit cell and can occupy the crystallographic positions 96k, 96j, or 192l. Unfortunately, these authors could not uniquely

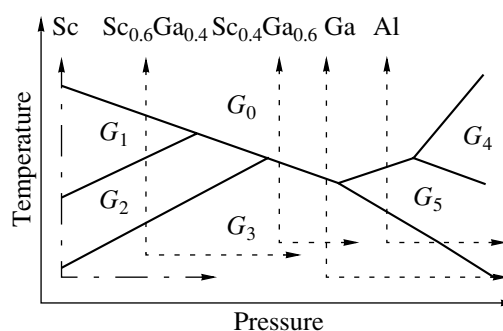


Fig. 6. Generalized phase diagram of  $(\text{NH}_4)_3\text{Me}^{3+}\text{F}_6$  ammonium cryolites.

determine the fluorine-occupied position reasoning only from data on the  $R$  factor, even though they were inclined to choose the variant 96j [13]. However, in this case, the phase transition should result in a distortion of the octahedra, which was not supported by experimental results. In our earlier work [12], we demonstrated that elpasolites with atomic cations undergo displacive phase transitions and that the motion of fluorine ions is characterized by substantial anharmonicity and anisotropy rather than by hopping between local disordered positions.

As follows from preliminary x-ray diffraction investigations of the structure of the  $(\text{NH}_4)_3\text{GaF}_6$  ammonium cryolite, the cubic phase can be well refined under the assumption that the fluorine ions are disordered over the 192l positions.

For  $(\text{NH}_4)_3\text{ScF}_6$  and  $(\text{NH}_4)_3\text{GaF}_6$  cryolites, the symmetry of disordered phases was analyzed earlier in [3, 14]. It was found that scandium cryolite is characterized by the following sequence of phases:  $G_1 = G_{2h}^5 (P12_1/n1, Z = 2)$ ,  $G_2 = G_{2h}^3 (I12/m1, Z = 16)$ , and  $G_3 = G_i^1 (P\bar{1}, Z = 16)$ . The structure of the low-temperature phase in gallium cryolite is identical to that of the  $G_3$  phase in scandium cryolite [14]. We observed the  $G_4$  and  $G_5$  phases in the studied system only under pressure. However, it is quite possible that the  $G_5$  phase corresponds to an intermediate phase in the  $(\text{NH}_4)_3\text{AlF}_6$  cryolite characterized by two phase transitions at  $p = 0$  [5]. Unfortunately, the structure of the  $(\text{NH}_4)_3\text{AlF}_6$  cryolite has not been studied thoroughly; it is only known that, at a temperature of 93 K, the structure of  $(\text{NH}_4)_3\text{AlF}_6$  is not cubic [15]. Detailed investigations into the structure of distorted phases and the  $p$ - $T$  phase diagram of this compound could refine the generalized phase diagram and mechanisms of phase transformations in cryolites.

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