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The Influence of Deuteration on the Phase Transitions in $(NH_4)_3Me^{3+}F_6$ Cryolites (Me^{3+} = Sc and Ga)

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Abstract—The heat capacity of partially deuterated crystals with a cryolite structure, namely, $(NH_4)_3ScF_6$ and $(NH_4)_3GaF_6$, is measured in the temperature range from 80 to 370 K. The p–T phase diagrams of these compounds are investigated at pressures up to p = 0.6 GPa. It is revealed that the deuteration does not affect the sequences of phase transitions observed in the proton-containing ammonium cryolites studied earlier. The isotope effect most clearly manifests itself in significant changes in the thermodynamic parameters of the $I12/m1$–$P\bar{1}$ low-temperature transformation in scandium cryolite. *© 2002 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Ammonium fluoride cryolites of the general formula $(NH_4)_3Me^{3+}F_6$ with a high-temperature cubic phase ($Fm\bar{3}m$, $z = 4$) have been studied using different physical methods in sufficient detail [1–6]. The cryolite structure represents a three-dimensional framework consisting of vortex-shared octahedra whose centers are occupied by one of the three $(NH_4)^+$ ions and one Me^{3+} ion in an alternating manner. These ions are located in the crystallographic positions 4*b* and 4*a*, respectively. The other two ammonium ions occupy the 8*c* positions in polyhedral holes formed by faces of the surrounding octahedra. It is established that the size of the Me^{3+} ion substantially affects the sequence and temperature of the phase transitions. For example, the $(NH_4)_3GaF_6$ crystal undergoes one ferroelastic phase transition $Fm\bar{3}m$–$P\bar{1}$ [1, 2, 6], whereas the $(NH_4)_3ScF_6$ crystal can undergo three successive phase transitions $Fm\bar{3}m$–$P12_1/n1$–$I12/m1$–$P\bar{1}$ [2, 5]. It is found that the entropy change associated with the triclinic distortion remains constant irrespective of the sequence of phase transitions. According to the model considered in [1, 2, 4], the octahedral $(Me^{3+}F_6)^-$ and tetrahedral $(NH_4)^+$ ionic groups are disordered in the cubic phase over eight and two equivalent positions, respectively. It should be noted that only the $(NH_4)^+$ tetrahedra located in the 4*b* position at the centers of the $(NH_4)F_6^-$ octahedra are disordered.

As follows from analyzing the results of calorimetric [2] and nuclear magnetic resonance (NMR) [3] measurements, the lowering of symmetry to monoclinic in the $(NH_4)_3ScF_6$ cryolite due to a phase transition at the temperature T_1 can be caused by partial ordering of the octahedra and ordering of the tetrahedra, whereas the phase transition between two monoclinic phases at the temperature T_2 is most likely associated with complete ordering of the octahedra involved. However, the phase transition between the monoclinic and triclinic phases at the temperature T_3 in scandium cryolite cannot be considered to be a transformation of the order–disorder type because of the very small change in the entropy [2]. The question as to the nature of this transition remains open.

One way to verify the assumption regarding the mechanism of phase transitions in ammonium-containing compounds is to examine their deuterated analogs. It is known that hydrogen bonding plays a decisive role in structural transformations, whereas the substitution of deuterons for protons, as a rule, most clearly manifests itself in the behavior of thermodynamic parameters such as the temperature and entropy of the phase transition and sensitivity to external pressures [7].

In particular, the isotope effect proved to be rather significant in cryolite-related compounds of the general formula $(NH_4)_2Me^{4+}Cl_6$ with an antifluorite structure ($Fm\bar{3}m$, $z = 4$). In the crystal structure of these compounds, the ammonium ions occupy only the 8*c* positions, whereas the second octahedron remains unoccupied. Muraoka and Matsuo [8] revealed that the deuteration of $(NH_4)_2PtCl_6$ crystals undergoing one phase transition at T_1 = 78 K leads to a slight increase in the temperature of this transition (T_1 = 81 K), on the one hand, and induces another phase transition in the vicinity of 38 K, on the other hand. Kume *et al.* [9] observed an even more interesting phenomenon upon deuteration of the $(NH_4)_2TeCl_6$ antifluorite, which undergoes a transition from the cubic phase to the rhombohedral phase at T = 88 K. For the deuterated compound, the temperature of this transition remains virtually unchanged;

however, at temperatures of 47 and 38 K, there occur additional structural transformations into the monoclinic and tetragonal phases, respectively.

According to the model considered in [1, 4], the cryolite structure is characterized by ordered tetrahedra in crystallographic positions with the coordination number CN = 12. However, Parsonage and Stavely [7] demonstrated that the N–H···F hydrogen bond in antifluorites is disordered with respect to the three nearest fluorine atoms forming the octahedron face. One of the possible reasons for the different degrees of ordering of ammonium groups located at the same crystallographic positions (8*c*) in related structures can be the presence or absence of an ammonium ion in the 4*b* position at the center of one of the octahedra.

The purpose of the present work was to elucidate how the substitution of deuterium for hydrogen affects the sequences of phase transitions occurring in $(NH_4)_3ScF_6$ and $(NH_4)_3GaF_6$ cryolites. The results obtained can provide better insight into the role played by ammonium tetrahedra and (or) hydrogen atoms in the mechanism of distortion of the cryolite structure. To the best of our knowledge, similar investigations have never been performed. In the nearest future, the deuterated cryolites will be examined using neutron diffraction with the aim of refining the coordinates of hydrogen atoms in the initial cubic phase and investigating the structures of distorted phases, specifically of those induced by high pressure [2].

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

The deuterated ammonium cryolites were prepared according to the following procedure. First, we synthesized the hydrogen-containing compounds through the dissolution of Sc_2O_3 and Ga_2O_3 oxides and NH_4HF in hydrofluoric acid (50 vol %) at a temperature of 100°C. After the evaporation of the resultant solution, the precipitate was recrystallized from distilled water with the formation of $(NH_4)_3ScF_6$ and $(NH_4)_3GaF_6$ crystalline powders. Then, these powders were subjected to fourfold recrystallization from D_2O.

The degree of deuteration of the samples prepared was determined by comparing the integral intensities of the ^1H NMR signals taken from $(NH_4)_3ScF_6$ and $(NH_4)_3GaF_6$ and the synthesized analogs $(ND_4)_3ScF_6$ and $(ND_4)_3GaF_6$. It turned out that the substitution of deuterium for hydrogen in scandium cryolite is more efficient than that in gallium cryolite. In the former compound, the degree of deuteration was equal to 78%. In the latter compound, the degree of deuteration proved to be appreciably less (only 20%). In our opinion, this can be associated in particular with the fact that gallium cryolite is less soluble in heavy water.

Since the deuteration in the studied compounds is not complete, the question arises as to which crystallographic positions are occupied by ND_4^+ and NH_4^+ ions, whose ionic radii considerably differ from each other. According to the stability criterion of the $Fm\bar{3}m$ structure [10], the larger sized cation should occupy the 8*c* position in a hole between octahedra. Apparently, it is these positions that are occupied by the ND_4^+ groups in the deuterated $(ND_4)_3GaF_6$ cryolite. In the $(ND_4)_3ScF_6$ compound, the ND_4^+ ions most likely occupy the larger part of 8*c* positions and a certain part of 4*b* positions at the centers of the octahedra.

X-ray diffraction analysis of the studied samples revealed that the deuteration of the $(NH_4)_3ScF_6$ cryolite leads to an increase in the volume of the unit cell of the monoclinic phase at room temperature by approximately 0.5%.

Preliminary calorimetric investigations were carried out using a DSM-2M differential scanning calorimeter. These experiments demonstrated that no radical changes occur in the sequences and temperatures of the phase transitions observed in the deuterated compounds.

Precision measurements of the heat capacity were performed on an adiabatic calorimeter over a wide range of temperatures in the course of discrete and continuous heating by analogy with our earlier measurements of the heat capacity of proton-containing ammonium cryolites [11]. The weighed portions of the scandium and gallium cryolites were equal to 1.069 and 0.985 g, respectively.

The pressure–temperature phase diagrams were constructed from the results of investigations into the effect of hydrostatic pressure on the phase transition temperatures measured using differential thermal analysis [2].

3. RESULTS AND DISCUSSION

Figure 1 presents the results of our measurements of the heat capacity $C_p(T)$ for $(ND_4)_3ScF_6$ and $(ND_4)_3GaF_6$ deuterated cryolites over a wide range of temperatures. It can be seen from Fig. 1 that the heat capacity of $(ND_4)_3ScF_6$ and $(ND_4)_3GaF_6$ exhibits three and one anomalies, respectively, due to phase transitions observed earlier in the proton-containing analogs $(NH_4)_3ScF_6$ and $(NH_4)_3GaF_6$ [2, 11]. The phase transition temperatures and the behavior of the heat capacity in the vicinity of these temperatures were refined using continuous heating (cooling) at a low rate of temperature change: $|dT/dt| \approx 2 \times 10^{-2}$ K/min. The quasi-static thermograms depicted in Fig. 2 for both deuterated cryolites upon transition from the cubic phase at the temperature T_1 are typical of first-order transformations. As follows from the table, the deuteration of both cryolites brings about an insignificant increase in the temperature T_1 and temperature hysteresis δT_1. At the same time, the latent heat δH_1 of the phase transition remains

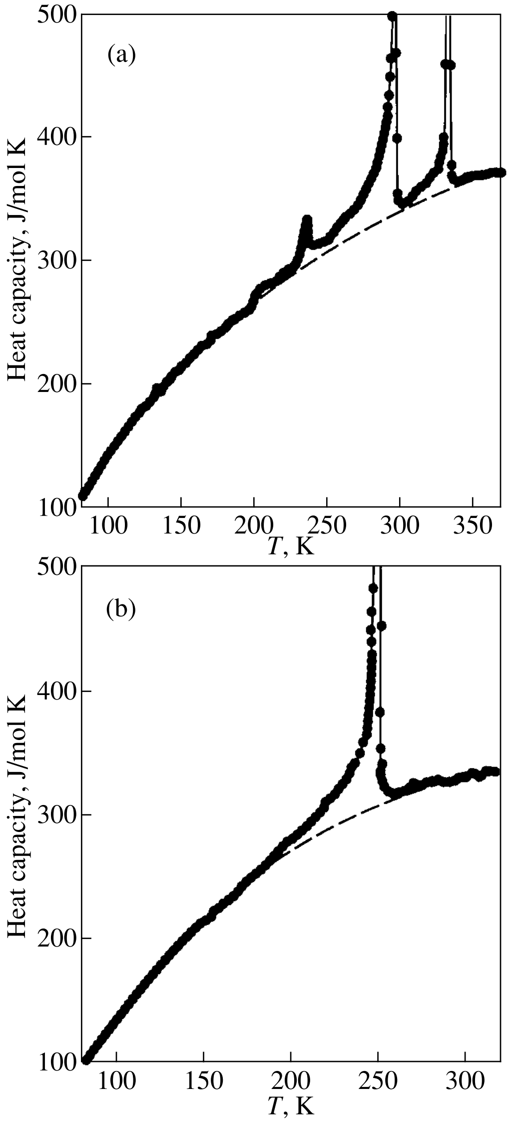

Fig. 1. Temperature dependences of the heat capacity for (a) $(ND_4)_3ScF_6$ and (b) $(ND_4)_3GaF_6$ deuterated cryolites. The dashed line shows the lattice heat capacity.

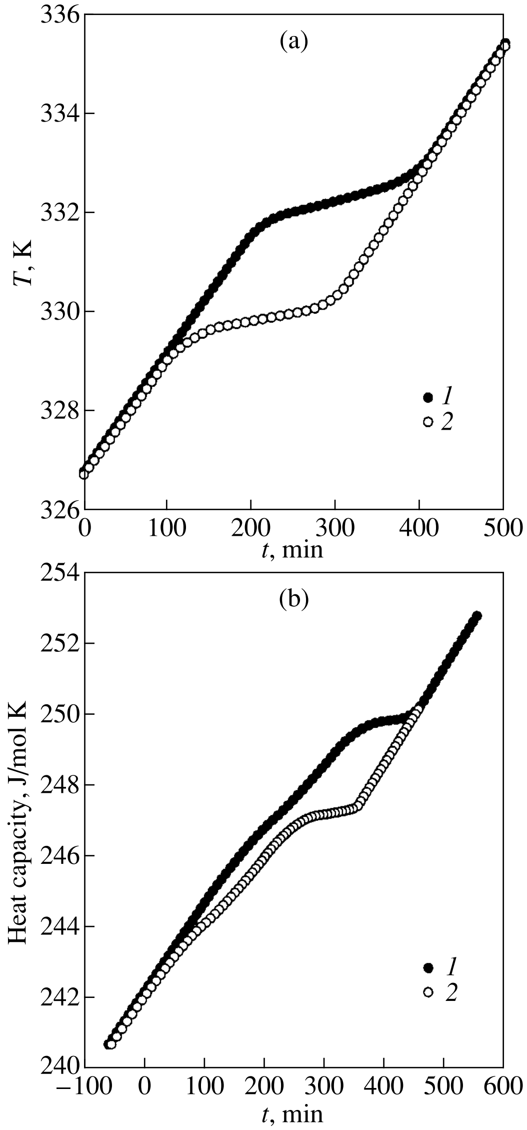

Fig. 2. Thermograms measured in the course of (*1*) heating and (*2*) cooling in the vicinity of the phase transition from the cubic phase in (a) $(ND_4)_3ScF_6$ and (b) $(ND_4)_3GaF_6$ deuterated cryolites.

unchanged within the accuracy in the determination of its magnitude. It is worth noting that the time dependence of the temperature for the deuterated $(ND_4)_3GaF_6$ cryolite exhibits another slight inflection at a temperature of approximately 3 K below T_1. Most likely, this phenomenon can be associated with the inhomogeneity of the studied sample, because no splitting of the heat capacity peak is observed for the considerably smaller volume of the $(ND_4)_3GaF_6$ cryolite studied under pressure (see below).

Since the latent heats of structural transformations in the deuterated $(ND_4)_3ScF_6$ cryolite at temperatures T_2 and T_3 appeared to be rather small, the results of the thermographic measurements were expressed in terms of heat capacity for the benefit of clarity (Fig. 3). It can be seen from the table that, compared to the $(NH_4)_3ScF_6$ compound, the phase transition in the deuterated $(ND_4)_3ScF_6$ cryolite at the temperature T_2 is characterized by an insignificant increase in thermodynamic parameters such as the temperature T_2, its hysteresis δT_2, and the latent heat δH_2 of the phase transition.

The isotopic substitution H $\longrightarrow$ D most strongly affects the thermodynamic parameters of the phase transition at T_3 (see table). This effect more clearly manifests itself in a substantial decrease in the phase transition temperature T_3 and an increase in the temperature hysteresis δT_3.

Thermodynamic parameters of the phase transitions in cryolites

Parameters	$(NH_4)_3ScFe_6$ [2]	$(ND_4)_3ScF_6$	$(NH_4)_3GaF_6$ [2]	$(ND_4)_3GaF_6$
T_1, K	330.8 ± 0.2	332.3 ± 0.2	249.02 ± 0.2	249.9 ± 0.2
δT_1, K	1.8 ± 0.2	2.3 ± 0.1	0.84 ± 0.20	1.0 ± 0.2
δH_1, J/mol	3820 ± 370	3615 ± 350	2690 ± 190	2740 ± 200
$\Delta S_1 R$	1.68 ± 0.13	1.5 ± 0.1	2.77 ± 0.19	2.72 ± 0.20
$\delta S_1/\Delta S_1$	0.83	0.87	0.47	0.49
dT_1/dp, K/GPa	–(16.4 ± 1.3)	–(17.9 ± 0.8)	–(12 ± 20)	~0
T_2, K	293.4 ± 0.2	294.5 ± 0.2		
δT_2, K	0.52 ± 0.15	1.35 ± 0.15		
δH_2, J/mol	160 ± 20	368 ± 90		
$\Delta S_2/R$	0.84 ± 0.06	1.03 ± 0.07		
$\delta S_2/\Delta S_2$	0.08	0.15		
dT_2/dp, K/GPa	57.5 ± 1.7	55.7 ± 0.9		
T_3, K	243.1 ± 0.3	234.5 ± 0.2		
δT_3, K	7.1 ± 0.3	9.9 ± 0.2		
δH_3, J/mol	179 ± 25	250 ± 40		
$\Delta S_3/R$	0.11 ± 0.02	0.14 ± 0.02		
$\delta S_3/\Delta S_3$	0.80	0.92		
dT_3/dp, K/GPa	59.9 ± 1.2	50.1 ± 0.9		

The total entropy change upon successive phase transitions was determined by integrating the function $(\Delta C_p/T)(T)$. In order to calculate the anomalous contribution ΔC_p, we determined the lattice component of the heat capacity $C_{lat}(T)$. For this purpose, the low-temperature and high-temperature portions of the dependence $C_p(T)$ outside the range of phase transition temperatures were approximated using a combination of Debye and Einstein functions. In the temperature range under investigation, the heat capacity is not very sensitive to details of the phonon spectrum due to a relatively low Debye temperature; therefore, the chosen approximation, in our opinion, is entirely justified.

For both deuterated cryolites, the changes in the entropy $\Delta S_i/R$ due to phase transitions are close in magnitude to those for the proton-containing compounds, within the accuracy of the entropy determination (see table). The temperature dependences of the excess entropy are displayed in Fig. 4. It is clearly seen from this figure that a rapid increase in the entropy of the deuterated gallium cryolite $(ND_4)_3GaF_6$ in the temperature range of phase transitions occurs in two steps. At present, the reason for this behavior remains unclear. However, it is quite probable that an examination of $(ND_4)_3GaF_6$ gallium cryolites with a higher degree of deuteration would provide an answer to this problem.

As is known, the degree of closeness of the phase transition to the tricritical point is characterized by a quantity defined as the ratio of the entropy jump at a temperature T_i to the total entropy change $\delta S_i/\Delta S_i$. It follows from the table that, upon deuteration, this quantity increases appreciably only due to phase transitions in the deuterated $(ND_4)_3ScF_6$ cryolite at temperatures T_2 and T_3. This result is in good agreement with the aforementioned substantial increase in the temperature hysteresis of these transformations and indicates that the deuteration of the studied compound leads to a decrease in the degree of closeness of two first-order phase transitions to the tricritical point.

Figure 5 shows the p–T phase diagrams of the deuterated and proton-containing cryolites studied under pressure. It can be seen from the table that, for $(NH_4)_3ScF_6$ and $(ND_4)_3ScF_6$ scandium cryolites, the slopes of the phase boundaries dT_1/dp and dT_2/dp and the coordinates of the triple point observed in the phase diagram virtually coincide. However, in the case of the transition to the triclinic phase at the temperature T_3, the slope dT_3/dp decreases significantly (see table). Judging from the increase in the stability region of the monoclinic phase $I12/m1$ of the deuterated $(ND_4)_3ScF_6$ cryolite, the parameters of the second (hypothetical) triple point (note that, to its right in the p–T phase diagram, there exists only a boundary between the cubic and triclinic phases) should be characterized by a higher pressure and a lower temperature as compared to those of the proton-containing $(NH_4)_3ScF_6$ cryolite.

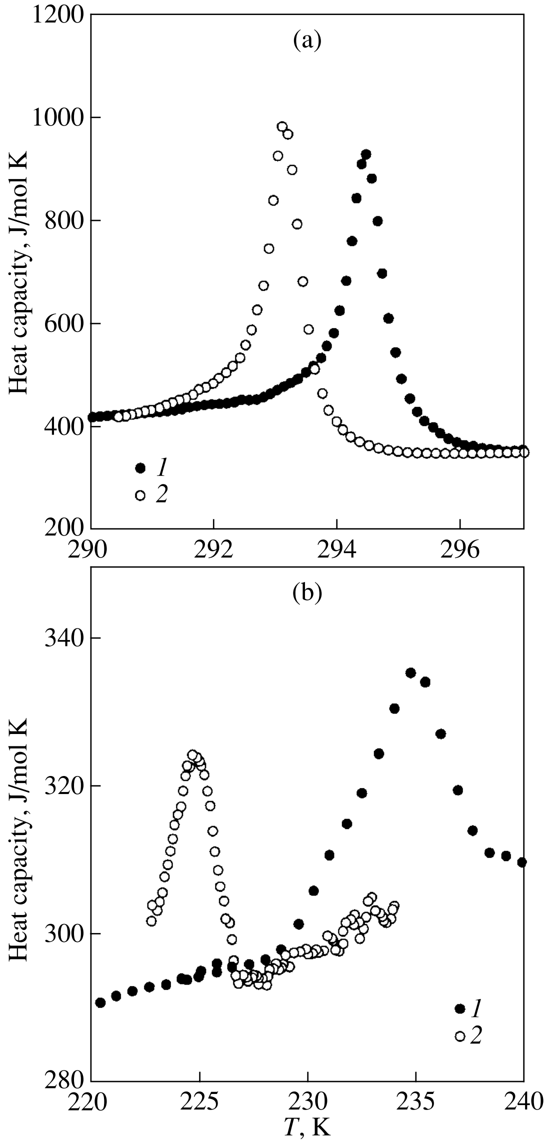

Fig. 3. Temperature dependences of the heat capacity in the vicinity of the phase transitions at temperatures (a) T_2 and (b) T_3 for the $(ND_4)_3ScF_6$ deuterated cryolite upon (*1*) heating and (*2*) cooling.

Upon partial deuteration of the gallium cryolite, no appreciable changes are observed either in the phase transition temperatures under pressure dT_i/dp or in the parameters of the triple points. Unfortunately, for both gallium cryolites, $(NH_4)_3GaF_6$ and $(ND_4)_3GaF_6$, the boundaries between the high-pressure phases were determined reliably only in phase diagram regions of small extent. This circumstance makes the unambiguous interpretation of the constancy of the quantities dT_i/dp with a change in the pressure more difficult. Moreover, the experiments performed under pressure did not reveal anomalies attributed to the aforementioned inflection points in the curves $C_p(T)$ and $T(t)$.

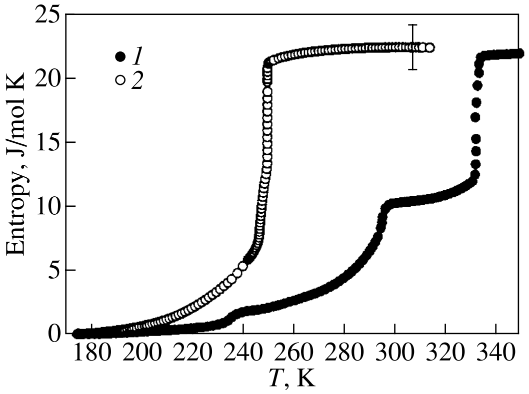

Fig. 4. Temperature dependences of the entropy associated with the phase transitions in (*1*) $(ND_4)_3ScF_6$ and (*2*) $(ND_4)_3GaF_6$ deuterated cryolites.

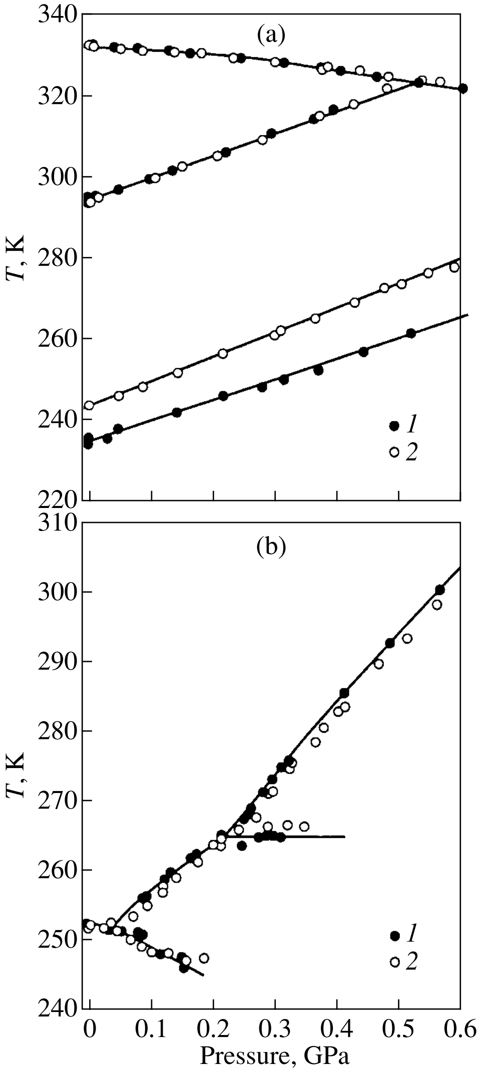

Fig. 5. Phase *p*–*T* diagrams for (a) (*1*) $(ND_4)_3ScF_6$ and (*2*) $(NH_4)_3ScF_6$ scandium cryolites and (b) (*1*) $(ND_4)_3GaF_6$ and (*2*) $(NH_4)_3GaF_6$ gallium cryolites.

4. CONCLUSIONS

The main results obtained in the above investigation can be summarized as follows.

(1) The total entropy change $\Sigma\Delta S_i/R$ observed upon a triclinic distortion of the low-temperature phase in $(NH_4)_3ScF_6$ and $(NH_4)_3GaF_6$ cryolites remains unchanged in $(ND_4)_3ScF_6$ and $(ND_4)_3GaF_6$ deuterated compounds, within the accuracy of the measurements, even though the degrees of deuteration of the latter compounds differ significantly. Therefore, it can be assumed that the protons (deuterons) are of little importance in structural ordering associated with considerable changes in the entropy.

(2) The deuteration does not substantially affect the thermodynamic parameters of the phase transitions at temperatures T_1 and T_2. This result confirms the assumption made earlier in [1, 4] that these transformations are due to ordering of ammonium tetrahedra and fluorine octahedra.

(3) The thermodynamic parameters of the $I12_1/m1$–$P\bar{1}$ phase transition in the deuterated scandium cryolite $(ND_4)_3ScF_6$ change considerably as compared to those of the proton-containing scandium compound $(NH_4)_3ScF_6$. This indicates that the structural distortions observed upon this transition are associated with transformations in the subsystem of tetrahedra. The clearly defined transformation revealed at the temperature T_3 can be considered a first-order transition between two completely ordered phases differing only in the orientation of the tetrahedra in the 4*b* positions [7]. This inference is also supported by the insignificant change in the entropy ΔS_3.

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