

## Calorimetric investigations of phase transitions in the cryolites (NH<sub>4</sub>)<sub>3</sub>Ga<sub>1-x</sub>Sc<sub>x</sub>F<sub>6</sub> (x = 1.0, 0.1, 0)

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The specific heat of the cryolites (NH<sub>4</sub>)<sub>3</sub>Ga<sub>1-x</sub>Sc<sub>x</sub>F<sub>6</sub> with  $x = 1.0, 0.1$ , and 0 was measured. The thermodynamic parameters of the phase transitions were determined. A previously unknown phase transition was found in the scandium compound at  $T = 243$  K. © 1999 American Institute of Physics. [S1063-7834(99)03003-8]

A<sub>3</sub>M<sup>3+</sup>X<sub>6</sub> crystals having the cryolite structure (space group  $Fm\bar{3}m$ ,  $z = 4$ ) are one of the related families in a series of perovskite-like compounds having a three-dimensional crystal framework formed by AX<sub>6</sub> and M<sup>3+</sup>X<sub>6</sub> octahedra joined to one another at the vertices. In this framework the interoctahedral polyhedra are occupied by a A<sup>+</sup> cation. Fluoride crystals with A<sup>+</sup> atomic cations, as a rule, undergo structural phase transitions (PTs) at quite high temperatures, which makes it somewhat difficult to study them in detail. In this respect, the ammonium compounds in which PTs have been discovered comparatively recently<sup>1,2</sup> are more attractive objects of investigation. In many cases, the presence of ammonium in the structure greatly decreases the temperature at which the cubic phase of the cryolites is stable.<sup>1-6</sup>

Quite extensive experimental data have now been accumulated on the ammonium cryolites (NH<sub>4</sub>)<sub>3</sub>M<sup>3+</sup>F<sub>6</sub>. Specifically, it has been found that in the series of compounds with trivalent ions M<sup>3+</sup> = Al, Ga, Cr, V, Fe, Sc, and In the temperature at which the cubic phase becomes unstable increases with the unit cell parameter  $a_0$ .<sup>6</sup> The size of the ion M<sup>3+</sup> likewise influences the sequence of PTs in the crystals. In compounds with the M<sup>3+</sup> ionic radius  $R_M^{3+} \leq R_{Fe}^{3+}$  one PT occurs and the symmetry of the distorted phase is assumed to be triclinic with space group  $P\bar{1}$ .<sup>6,7</sup> Further increase of the size of the M<sup>3+</sup> ion leads to two successive structural transformations in compounds with scandium and indium. These transformations were discovered by calorimetric investigations.<sup>6</sup> At the same time, large differences in the x-ray diffraction patterns of the intermediate and low-temperature phases obtained from powder samples were not observed in structural investigations of these cryolites: neither according to the appearance of new lines nor according to a change in the intensities of the reflections.<sup>6</sup> The symmetry of the low-temperature phase at room temperature has been determined for both compounds, first as tetragonal  $P4/mnc$ ,  $z = 2^4$  and then as monoclinic  $P2_1/n$ ,  $z = 2$ .<sup>6,8</sup>

The entropy changes  $\Delta S$  associated with structural transformations have been determined from specific-heat measurements of all ammonium cryolites named above.<sup>2,5,6,9</sup> For compounds with  $R_M^{3+} \leq R_{Fe}^{3+}$ ,  $\Delta S$  ranges from 19.4 to 24.9

J·mol<sup>-1</sup>·K<sup>-1</sup> and is almost two times larger than the total entropy change  $\Delta S \approx 12.8$  J·mol<sup>-1</sup>·K<sup>-1</sup> due to two successive PTs in cryolites with the ions M<sup>3+</sup> = Sc, In.<sup>6</sup> Thus it has turned out that ammonium cryolites (NH<sub>4</sub>)<sub>3</sub>M<sup>3+</sup>F<sub>6</sub> can be divided into two groups differing both in the symmetry of the distorted phases and the thermodynamic parameters. It should be noted, however, that both groups of compounds were investigated by different calorimetric methods: the first group using an adiabatic calorimeter and the second group by the differential scanning calorimetry (DSC). The latter method makes it possible to determine reliably the integrated characteristics (enthalpy and entropy) only for sharp first-order PTs and can lead to a large error in investigations of transformations close to a tricritical point.<sup>10</sup>

A similar dependence of the crystallographic and thermodynamic characteristics on the size of the M<sup>3+</sup> ion has been observed in the series of crystals Rb<sub>2</sub>KM<sup>3+</sup>F<sub>6</sub> having the related elpasolite structure ( $Fm\bar{3}m$ ,  $z = 4$ ).<sup>11,12</sup> Compounds with M<sup>3+</sup> ions from Ga to Fe undergo one PT with  $\Delta S \approx 15.6$  J·mol<sup>-1</sup>·K<sup>-1</sup> to a phase whose symmetry has still not been determined unequivocally, but among others including the triclinic symmetry  $P\bar{1}$ . For crystals with the ions M<sup>3+</sup> = Sc, In, Lu a sequence of PTs  $Fm\bar{3}m - I4/m - P2_1/n$  with a much smaller total entropy  $\Delta S \approx 6$  J·mol<sup>-1</sup>·K<sup>-1</sup> is characteristic. The part of the phase diagram for intermediate ionic radius  $R_{Fe}^{3+} \leq R_M^{3+} \leq R_{Sc}^{3+}$  has been found to be quite complicated.<sup>13</sup> In the solid solutions Rb<sub>2</sub>KGa<sub>1-x</sub>Sc<sub>x</sub>F<sub>6</sub> a sharp decrease of temperature and entropy of the PT has been observed with a low degree of substitution of scandium for gallium ( $x = 0.05 - 0.1$ ).

To determine more accurately the thermodynamic parameters of PTs in ammonium cryolites undergoing successive structural transformations and to determine the details (hysteresis of the PT temperature, latent heat of the transformation, the degree of closeness to the tricritical point) of the structural transformation  $Fm\bar{3}m - P\bar{1}$ , which were not reported in Refs. 2, 5, 6, and 9, as well as the effect on them of a partial substitution of the M<sup>3+</sup> ion, we investigated the compounds (NH<sub>4</sub>)<sub>3</sub>Ga<sub>1-x</sub>Sc<sub>x</sub>F<sub>6</sub> with  $x = 1.0, 0.1$ , and 0 using an adiabatic calorimeter.

Samples in the form of powders were prepared by solid-

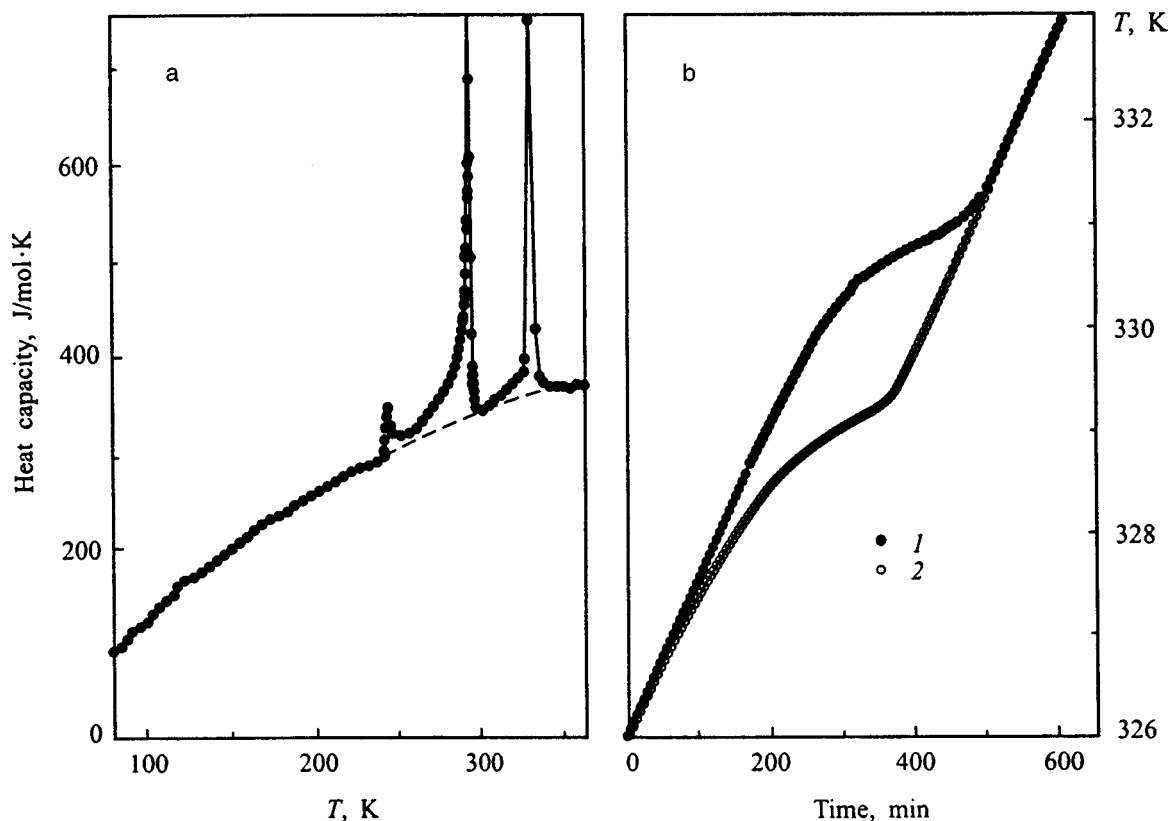


FIG. 1. Temperature dependence of the specific heat of  $(\text{NH}_4)_3\text{ScF}_6$  (a) and thermograms (b) measured in heating (1) and cooling (2) regimes near the phase transition at  $T_1$ . Dashed line — lattice specific heat.

state synthesis at the Institute of the Chemistry of Condensed Materials (Bordeaux, France).

The methods of discrete and continuous heatings were used to measure the specific heat in the temperature interval from 80 to 370 K. Regions close to the PT temperatures were investigated by the method of quasistatic thermograms in the heating and cooling regimes with rates of temperature variation  $|dT/dt| \approx (0.9-1.5) \times 10^{-2}$  K/min.

Figure 1a shows the results of measuring the specific heat  $C_p(T)$  of cryolite  $(\text{NH}_4)_3\text{ScF}_6$ . Three anomalies of the specific heat were found. Two high-temperature peaks have maxima at temperatures 330 and 293 K, differing little from the PT temperatures reported in Ref. 7. The third specific-heat anomaly was recorded at 243 K. Repeated measurements showed that this PT is reproducible.

In all specific-heat measurements a large increase in the time required to establish thermal equilibrium in the sample was observed near the temperatures of all PTs: from 5–10 to 60–90 min. This is a characteristic indication of a first-order PT, as is confirmed by the results of thermographic investigations.

The more accurate value of the temperature of the phase transition from the cubic phase  $T_1 = 330.8 \pm 0.2$  K is characterized by a comparatively large hysteresis  $\delta T_1 = 1.8 \pm 0.2$  K (Fig. 1b). The latent heat of this transformation was  $\delta H_1 = 3820 \pm 370$  J·mol $^{-1}$ .

The enthalpies corresponding to the latent heat for the two other PTs were significantly smaller, and for greater clarity the results of the investigations near the transforma-

tion temperatures  $T_2 = 293.4$  K and  $T_3 = 243.1$  K are presented in Figs. 2a and b in the form of the temperature dependences of the specific heat which were calculated from thermograms measured in heating and cooling regimes. The corresponding values of the hysteresis and latent heat for these transitions are  $\delta T_2 = 0.52 \pm 0.15$  K,  $\delta H_2 = 160 \pm 20$  J·mol $^{-1}$  and  $\delta T_3 = 7.1 \pm 0.3$  K,  $\delta H_3 = 170 \pm 25$  J·mol $^{-1}$ .

To determine the total changes in the enthalpy and entropy which are associated with PTs, the lattice specific heat was separated out by interpolating the low- and high-temperature specific heats far from  $T_i$  into the anomalous region. The corresponding values of  $\Delta H_i$  and  $\Delta S_i$  were obtained by integrating the functions  $\Delta C_p(T)$  and  $(\Delta C_p/T) \times (T)$ :

$$\Delta H_1 = 4420 \pm 310 \text{ J} \cdot \text{mol}^{-1},$$

$$\Delta S_1 = 13.36 \pm 0.95 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1},$$

$$\Delta H_2 = 1970 \pm 140 \text{ J} \cdot \text{mol}^{-1},$$

$$\Delta S_2 = 6.73 \pm 0.48 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1},$$

$$\Delta H_3 = 170 \pm 25 \text{ J} \cdot \text{mol}^{-1},$$

$$\Delta S_3 = 0.70 \pm 0.10 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

The temperature dependences of the specific heats of the gallium compound and the solid solution  $(\text{NH}_4)_3\text{Ga}_{0.9}\text{Sc}_{0.1}\text{F}_6$ , which are presented in Figs. 3a and 3b,

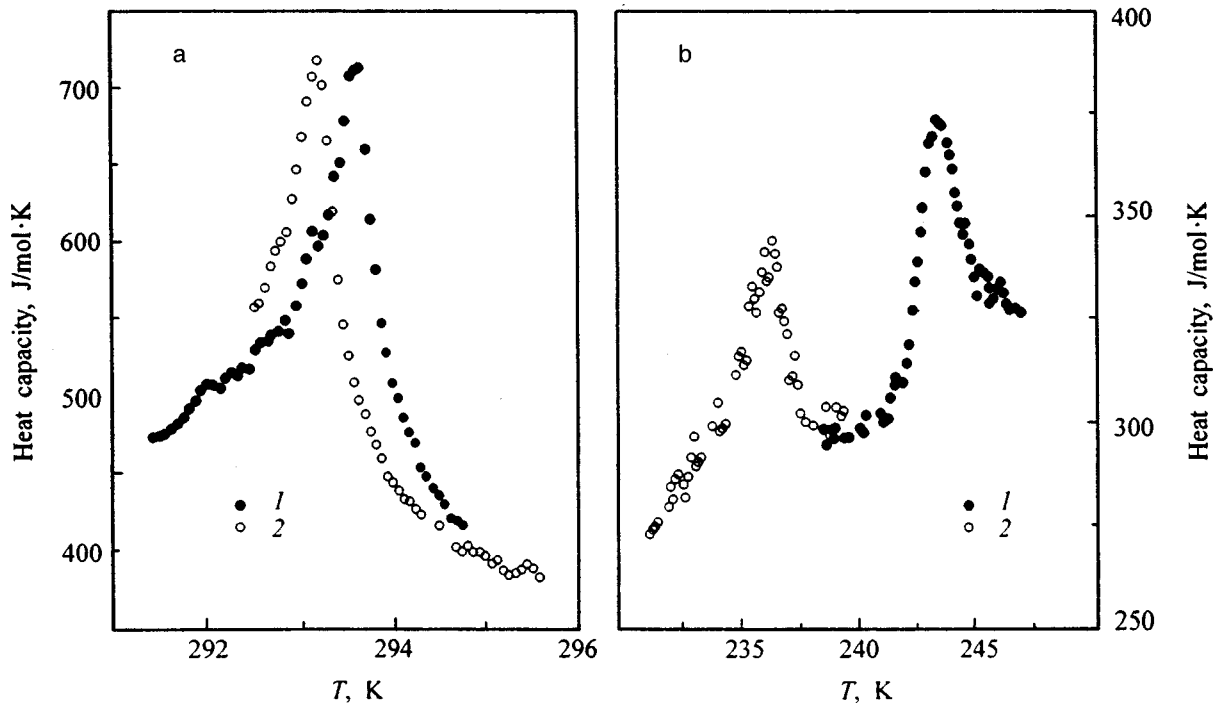


FIG. 2. Temperature dependences of the specific heat near phase transitions at  $T_2$  (a) and  $T_3$  (b) in the compounds  $(\text{NH}_4)_3\text{ScF}_6$ . 1 — Heating regime, 2 — cooling regime.

are essentially identical. The PT temperature in gallium cryolite  $T_0 = 249.8 \pm 0.2$  K was found to be  $\sim 3.5$  K higher than the temperature reported in Ref. 6. A 10% substitution of scandium for gallium did not change the temperature of the PT  $Fm\bar{3}m - P\bar{1}$  within the limits of its uncertainty (for the

solid solution  $T_0 = 249.7 \pm 0.2$  K), but it did result in a broadening of the temperature interval of the latent heat, as is clearly demonstrated in Figs. 4a and b. The hysteresis of the PT temperature and the latent heat were, respectively,  $\delta T_0 = 0.84 \pm 0.20$  K and  $\delta H_0 = 2690 \pm 190$  J·mol $^{-1}$  for gal-

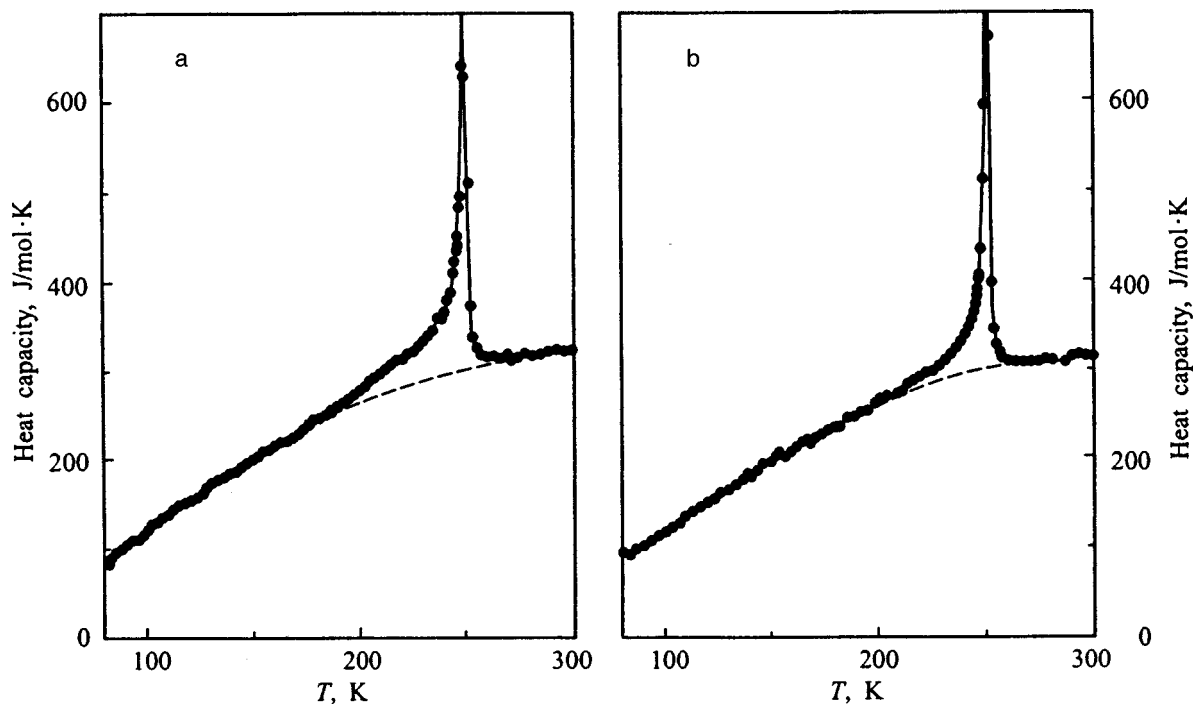


FIG. 3. Temperature dependences of the specific heat of the compounds  $(\text{NH}_4)_3\text{GaF}_6$  (a) and  $(\text{NH}_4)_3\text{Ga}_{0.9}\text{Sc}_{0.1}\text{F}_6$  (b). Dashed line — lattice specific heat.

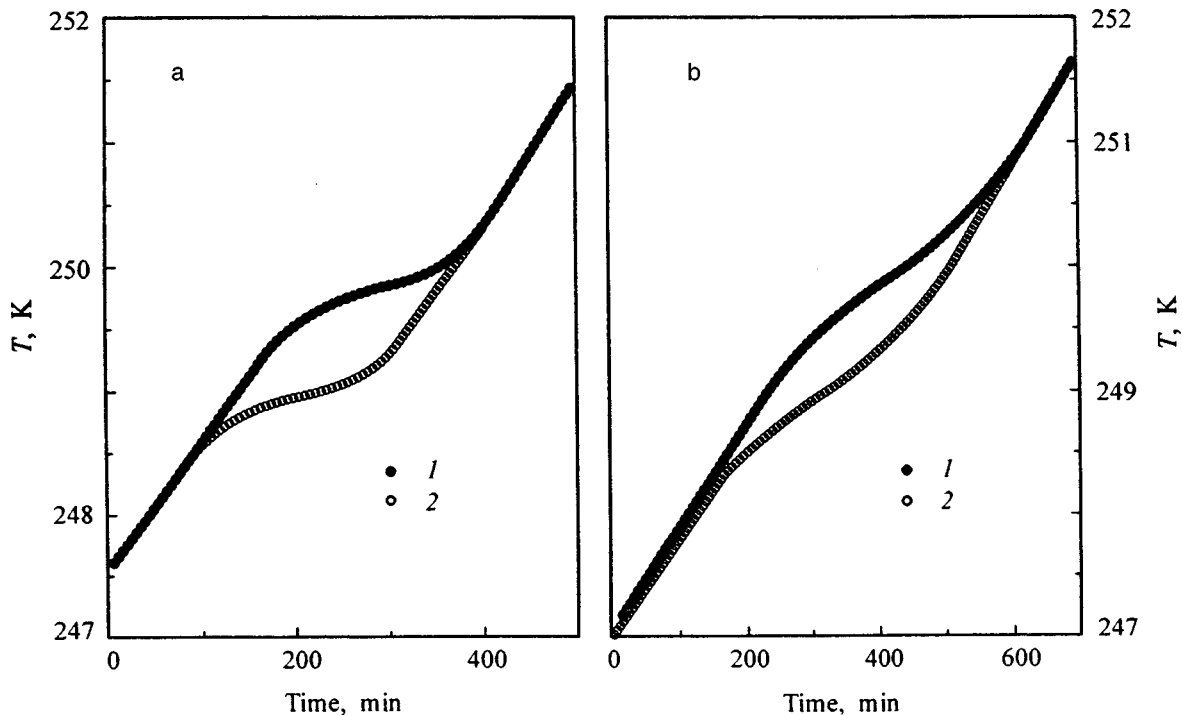


FIG. 4. Thermograms measured in heating (1) and cooling (2) regimes near phase transitions in  $(\text{NH}_4)_3\text{GaF}_6$  (a) and  $(\text{NH}_4)_3\text{Ga}_{0.9}\text{Sc}_{0.1}\text{F}_6$  (b).

lium cryolite and  $\delta T_0 = 0.80 \pm 0.20$  K and  $\delta H_0 = 2550 \pm 200$   $\text{J} \cdot \text{mol}^{-1}$  for the solid solution. The integrated characteristics of the two samples likewise differ little:

$$(\text{NH}_4)_3\text{GaF}_6: \quad \Delta H_0 = 5600 \pm 390 \text{ J} \cdot \text{mol}^{-1},$$

$$\Delta S_0 = 23.0 \pm 1.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1},$$

$$(\text{NH}_4)_3\text{Ga}_{0.9}\text{Sc}_{0.1}\text{F}_6: \quad \Delta H_0 = 5040 \pm 350 \text{ J} \cdot \text{mol}^{-1},$$

$$\Delta S_0 = 21.3 \pm 1.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

The absence of appreciable changes in the thermodynamic parameters of the PT in the solid solution with  $x=0.1$  as compared with the gallium compound indicates that it would be useful to continue studying the mixed compounds with composition close to scandium cryolite.

It can be concluded on the basis of the results of our work and of Ref. 6 that scandium ammonium cryolite undergoes three structural transformations with the following sequence of phases:  $Fm\bar{3}m - ? - P2_1/n - ?$ . It should be noted that the observation of a specific-heat anomaly in the compound  $(\text{NH}_4)_3\text{InF}_6$  at temperature  $\sim 230$  K has been reported in a previous work.<sup>14</sup> Together with the data of Ref. 6, this suggests that there exists a third PT in this cryolite also.

The total change in entropy for the indicated sequence of PTs in  $(\text{NH}_4)_3\text{ScF}_6$ ,  $\Sigma \Delta S_i = 20.83 \pm 1.45$   $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , is much larger than the value  $\Sigma \Delta S_i = 12.8$   $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  determined by DSC,<sup>6</sup> and it falls in the range of values  $\Delta S_0 = 19.4 - 24.9$   $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  which are characteristic for ammonium cryolites undergoing the PT  $Fm\bar{3}m - P\bar{1}$  (Fig. 5).

The closeness of the PT to the tricritical point can be estimated from the ratio  $\delta S/\Delta S$  of the entropy jump at the transition point and the total entropy change. The PT from the cubic phase in the gallium compound is much closer to

the tricritical point ( $\delta S_0/\Delta S_0 = 0.46$ ) than in the scandium compound ( $\delta S_1/\Delta S_1 = 0.86$ ). For the other two PTs, in the latter compound  $\delta S_2/\Delta S_2 = 0.08$  and  $\delta S_3/\Delta S_3 \approx 1$ . Thus the PT at  $T_2$  into the monoclinic phase  $(\text{NH}_4)_3\text{ScF}_6$  is very close to the tricritical point, and this is why the total entropy change  $\Delta S_2$  determined in the present work using an adiabatic calorimeter is three times larger than the values found by DSC.<sup>6</sup>

Thus, the quantities characterizing the total entropy change in crystals which have undergone single and successive PTs are close. How do the PT mechanisms in ammonium cryolites of both types differ? The possibility of attributing the PT  $Fm\bar{3}m - P\bar{1}$  to ordering of ionic groups was considered in Refs. 2, 5, and 6. The ammonium group located at the center of the  $(\text{NH}_4)\text{F}_6$  octahedra and in the interoctahedral polyhedra are structurally nonequivalent. Only tetrahedra of the first type participate in the PT, since the cubic symmetry of their location in the initial phase permits two possible orientations. Thus, as the symmetry is lowered, the contribution of ordering of the ammonium tetrahedra to the entropy of the PT is  $\Delta S = R \ln 2$ . However, to substantiate the large value found experimentally for  $\Delta S$ , it must be conjectured that the  $\text{M}^{3+}\text{F}_6$  octahedra are also disordered in the cubic phase. If the fluorine atoms occupy 192l or 96k positions, the contributions of their ordering (one position in the monoclinic phase) to the entropy of the PT are  $R \ln 8$  and  $R \ln 4$ , respectively. The interval of possible entropy changes, determined in this manner, for the PT  $Fm\bar{3}m - P\bar{1}$  corresponds to the experimentally found values of  $\Delta S$  for the compounds  $(\text{NH}_4)_3\text{M}^{3+}\text{F}_6$  with the ions  $\text{M}^{3+} = \text{Al}, \text{Ga}, \text{Cr}, \text{V}, \text{Fe}$ . The correctness of the choice of model for describing this PT is confirmed by NMR investigations of compounds

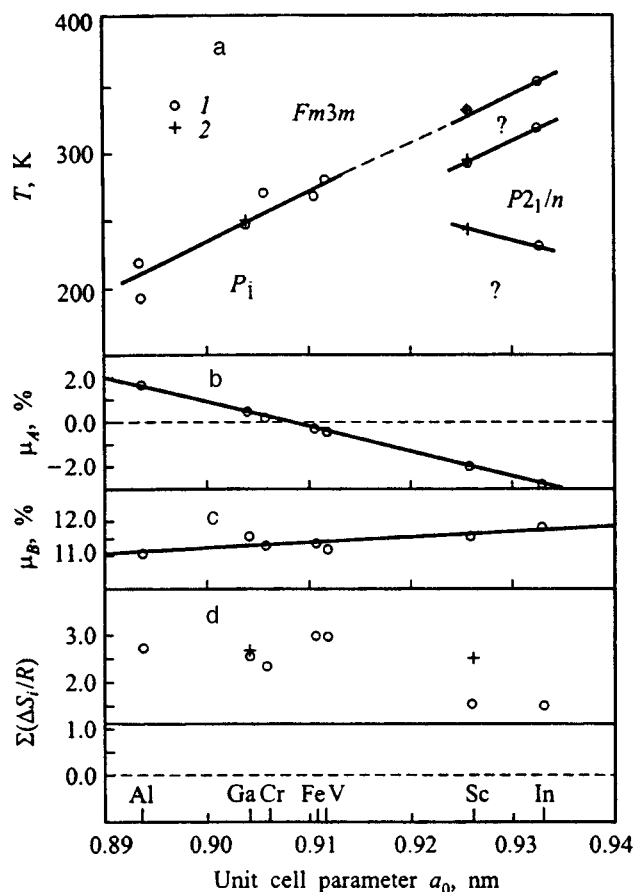


FIG. 5. Effect of the cubic lattice parameter  $a_0$  of ammonium cryolites  $(\text{NH}_4)_3\text{M}^{3+}\text{F}_6$  on the phase-transition temperatures (a), bond strains  $\mu_A$  (b) and  $\mu_B$  (c), and the total excess entropy (d). 1 — Data of Refs. 2, 5, 6, 9, and 14; 2 — data of the present work.

with gallium and aluminum.<sup>5,15</sup> Substantial jumps in the quantities characterizing the spin-lattice relaxation time of hydrogen and fluorine nuclei have been found at temperatures corresponding to the PT temperatures. This attests to a change in the nature of the motion of both the  $\text{NH}_4$  tetrahedral and  $\text{M}^{3+}\text{F}_6$  octahedral ionic groups.

In  $(\text{NH}_4)_3\text{InF}_6$  undergoing successive structural transformations the behavior of the relaxation times of fluorine and oxygen is the same only in the intermediate phase: In both cases this quantity increases rapidly on heating from  $T_2$  to  $T_1$ .<sup>15</sup> At the point of the transition to the cubic phase, the spin-lattice relaxation time of fluorine undergoes a substantial jump-like increase, just as in crystals with one PT. For protons, however, this quantity, after reaching a maximum at  $T_1$ , decreases with further heating. Therefore it can be inferred that in ammonium cryolites, which have undergone successive structural transformations  $Fm3m-?-P2_1/n-?$ , at least the PT from the cubic phase is related with ordering of the octahedral ionic groups  $\text{M}^{3+}\text{F}_6$ . The experimentally determined value  $\Delta S_1=1.61R$  for the scandium compound also attests to an order-disorder PT, though it is less than  $\Delta S_0$  for the transformation  $Fm3m-P\bar{1}$ . The PT into the monoclinic phase at  $T_2$  is characterized by an entropy change close to  $R\ln 2$ . It is tempting to infer that it is related with the ordering of the tetrahedra. However, such conclu-

sion, which is based on the temperature dependence of the proton relaxation time, is premature.

According to Ref. 5, the presence of ammonium in the position  $(1/4, 1/4, 1/4)$  energetically stabilizes the cubic structure of cryolite. On the other hand, the question of the stability of the cubic phase can be studied from the standpoint of the hypothesis of the strains of the interatomic bonds.<sup>16</sup> It has been shown in previous work that this hypothesis makes it possible to describe satisfactorily displacement-type PTs associated with small rotations of the octahedral ionic groups,<sup>17,18</sup> and it is not applicable in the case when distortions in the perovskite-like structures cannot be interpreted in terms of the rotations of octahedra.<sup>19</sup> Ordering of octahedral ionic groups accompanying an order-disorder type PT can also be regarded as a rotation of octahedra, but by a larger angle. In this case there is nothing to prevent the applicability of the above-mentioned hypothesis to the PT under study. The stability of the initial cubic phase is determined by the ratio of the sizes of individual ions and the lattice parameter  $a_0$ , i.e. the strains of the bonds of the ions in the chains  $(\text{NH}_4)^+-\text{F}^-$  and  $\text{M}^{3+}-\text{F}^--(\text{NH}_4)^+-\text{F}^--\text{M}^{3+}$ . The following quantities can serve as a quantitative measure of these strengths:

$$\mu_A = (a'_p - a_0)/a'_p, \quad \mu_B = (a_p - a_0)/a_p,$$

where  $a_p = 2(R_{\text{NH}_4} + 2R_{\text{F}} + R_{\text{M}^{3+}})$  and  $a'_p = 2\sqrt{2}(R_{\text{NH}_4} + R_{\text{F}})$ . An increase of  $\mu_B$  is equivalent to an increase in the repulsion energy in the crystal potential and intensifies the anisotropy of the motion of  $F$  ions and therefore decreases the stability of the initial phase. An increase in  $\mu_A$  prevents rotation of the octahedra and tends to stabilize the undistorted lattice.

In ammonium cryolites an increase in the size of the unit cell is accompanied by a substantial decrease in  $\mu_A$  and an increase in  $\mu_B$ , which increases the PT temperature (Fig. 5). Therefore the bond strain hypothesis is also applicable to order-disorder type PTs. On the other hand, the present results show that in ammonium cryolites undergoing successive transformations the PT from the cubic phase is associated mainly with the ordering of octahedral ionic groups.

To further clarify the characteristic features of the PT mechanisms in ammonium cryolites, it is certainly of interest to investigate the effect of hydrostatic pressure. This will be done in the near future.

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