



Thermal properties and phase transitions in $(\text{NH}_4)_3\text{ZrF}_7$

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ARTICLE INFO

Article history:

Received 13 May 2013

Received in revised form 8 July 2013

Accepted 8 July 2013

Available online 16 July 2013

Keywords:

Cubic fluorides

Phase transitions

Entropy

Thermal dilatation

Permittivity

Pressure effect

ABSTRACT

The heat capacity, thermal dilatation, permittivity, and T - p phase diagram of $(\text{NH}_4)_3\text{ZrF}_7$ have been studied in wide temperature and pressure ranges. Two phase transitions were found in addition to previously known structural transformations. The stability of crystal phases to temperature and pressure has been examined and a possibility of transition between two cubic phases has been discussed. The total excess entropy change $\sum \Delta S_i = R \ln 6$ is characteristic for the order–disorder processes, but its stepwise increase is not consistent with the structural model associated with the strong disorder assumed in the initial cubic phase.

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1. Introduction

Among fluorides and oxyfluorides, there exist a lot of compounds with structures containing six-, hepta- and even eight-coordinated anionic polyhedra formed by ligands of the same or different types [1–5]. Rather often the room temperature structure of such species is not stable to temperature or pressure and can be transformed to lower symmetry due to structural phase transitions. Crystals with zirconium as a central atom also belong to this series of compounds.

In spite of a long-standing interest of researches to the fluoride $(\text{NH}_4)_3\text{ZrF}_7$, some experimental results were in contradiction to each other. The first structural study performed by X-ray powder diffractometry did not reveal the space group of the cubic unit cell [6]. It was assumed that the crystal structure consisted of NH_4^+ , ZrF_6^{2-} and F^- ions. Subsequently, the relation between the structures of ammonium heptafluorozirconate and cryolite (Fm-3m, $Z = 4$) was suggested and the coordination number 7 was postulated for the Zr atom [7]. On the other hand, a reliable

evidence for the heptacoordinated polyhedra ZrF_7^{3-} was not found in NMR studies [8].

Detailed X-ray and neutron structural studies on single crystal samples of $(\text{NH}_4)_3\text{ZrF}_7$ were performed in [9,10]. The authors have assumed that, first, zirconium atom was surrounded by seven fluorine ligands and, second, the symmetry of cubic structure was Fm-3m. However the refining of structure in such a way yielded rather short distances between some fluorine atoms.

The latter was the reason why later the structural model of $(\text{NH}_4)_3\text{ZrF}_7$ was reconsidered in the X-ray single crystal experiments [2]. It was found that the subscribing of the room temperature cubic structure to the space group F23 ($Z = 4$) yielded an adequate value of all F–F distances at a low value of R-factor.

Nevertheless, the results of optic and X-ray studies on oriented single crystal plates and analysis in the framework of space group theory allowed the authors of [11] to suppose the centrosymmetric sp. gr. Fm-3m.

There is also no consensus on what is the shape of the heptacoordinated polyhedron $[\text{ZrF}_7]$. In line with [6,12], it is a monocapped trigonal prism, and in [2,9,10] polyhedron was characterized as a slightly distorted pentagonal bipyramid. The configuration of the heptacoordinated anion strongly affects the degree of its disordering in a cubic phase.

Starting from the first structural and NMR studies performed at room temperature, the researches postulated the orientational (dynamical) disorder of both anions and ammonium cations

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[2,9,10,12,13]. According to these experimental facts, one can suppose the presence of structural phase transitions in $(\text{NH}_4)_3\text{ZrF}_7$ associated with the ordering of structural elements on cooling.

The first information about possible symmetry change in $(\text{NH}_4)_3\text{ZrF}_7$ was mentioned in [12]. The endothermic effect in thermographic experiments was detected at about 253 K. The powder X-ray examination showed the symmetry lowering from cubic to orthorhombic one in the range 213–235 K [13].

Polarizing-optic observations and X-ray studies on cooling have revealed four successive transformations between the following phases: cubic ($\text{Fm}\bar{3}\text{m} \equiv \text{G1}$; $T_1 = 280 \text{ K}$) \leftrightarrow orthorhombic $\text{Immm} \equiv \text{G2}$; $T_2 = 269\text{--}270 \text{ K}$) \leftrightarrow monoclinic 1 ($\text{I2/m} \equiv \text{G3}$; $T_3 = 246 \text{ K}$) \leftrightarrow triclinic ($\text{P}\bar{1} \equiv \text{G4}$; $T_4 = 235 \text{ K}$) \leftrightarrow monoclinic 2 (G5) [11]. Measurements on heating have shown a significant hysteresis for some phase transitions found at following temperatures $T_1 = 280 \text{ K}$, $T_2 = 279.6 \text{ K}$, $T_3 = 260\text{--}265 \text{ K}$, $T_4 = 238 \text{ K}$.

Analysis of Raman spectra obtained on cooling did not exclude the existence of six structural transformations in $(\text{NH}_4)_3\text{ZrF}_7$ at 291 K, 275 K, 266 K, 247 K, 238 K, 225 K [14]. The most pronounced changes were found in the region of spectra associated with vibrations of the pentagonal bipyramid $[\text{ZrF}_7]$. In addition, the slowing of the ammonium ion's motion was observed with the temperature decrease. One can see that there is no strong agreement between temperatures of anomalies observed in optic [11] and Raman [14] studies.

Thus, the question about the quantity and temperature of phase transitions in $(\text{NH}_4)_3\text{ZrF}_7$ is still open up. Also, no information is available about energetic characteristics of structural distortions as well as stability of crystal phases to external pressure. The calorimetric and dilatometric methods are the most sensitive and reliable ones to elucidate such a complicated situation because of their high sensitivity to phase transitions of different mechanisms and physical nature.

For detailed studies of phase transitions in ammonium heptafluorozirconate, in the present paper we have performed measurements of heat capacity, thermal dilatation, permittivity and susceptibility to hydrostatic pressure. Single crystals $(\text{NH}_4)_3\text{ZrF}_7$ with the largest size of about 3 mm were grown by

the method described in [2]. The X-ray study has shown high quality of the samples.

2. Calorimetric measurements

Taking into account a large difference between temperatures of transition from initial cubic phase detected in optic (280 K) [11] and Raman (291 K) [14] studies, we performed calorimetric measurements in a wide temperature range 120–330 K. In the first stage, the temperature stability of cubic and distorted structures of $(\text{NH}_4)_3\text{ZrF}_7$ was examined with a DSM-2M differential scanning microcalorimeter (DSM) at the heating and cooling rates fixed at 8 K/min. Measurements were carried out in a helium atmosphere on powdered samples of mass 0.10–0.12 g set in an aluminium sample holder. A good agreement between the results for several samples was found. Fig. 1a depicts the temperature dependence of the excess heat capacity ΔC_p obtained as a difference between the total heat capacity C_p and nonanomalous lattice contribution C_{lat} . On heating, a series of peculiarities in the $\Delta C_p(T)$ behaviour was found associated with at least five phase transitions at $287 \pm 2 \text{ K}$, $279 \pm 1 \text{ K}$, $265 \pm 1 \text{ K}$, $260 \pm 2 \text{ K}$, $238 \pm 1 \text{ K}$. Close positions of ΔC_p peaks (Fig. 1a) prevents correcting the determination of integral thermodynamic characteristics. The total enthalpy change between 225 and 300 K associated with the series of phase transitions observed was determined as $\Sigma \Delta H_i = \int \Delta C_p(T) dT = 3000 \pm 400 \text{ J/mol}$. On cooling, large thermal hysteresis was found for all phase transformations.

Detailed heat capacity studies in the same temperature range were performed using a homemade adiabatic calorimeter with three screens described in [15]. More equilibrium conditions compared to experiments with DSM were provided by slow continuous ($dT/dt = 0.16 \text{ K/min}$) and stepwise ($\Delta T = 1.3 \text{ K}$) temperature changes. The $(\text{NH}_4)_3\text{ZrF}_7$ sample involving several single crystal pieces with total mass of 1.28 g was put into an indium container sealed under helium atmosphere, which, in turn, was placed in accessories with a heater. Information about the heat capacity of the sample $C_s(T)$ was obtained using the heat capacity of the accessories and indium cell $C_{\text{ac}}(T)$ determined in separate measurements.

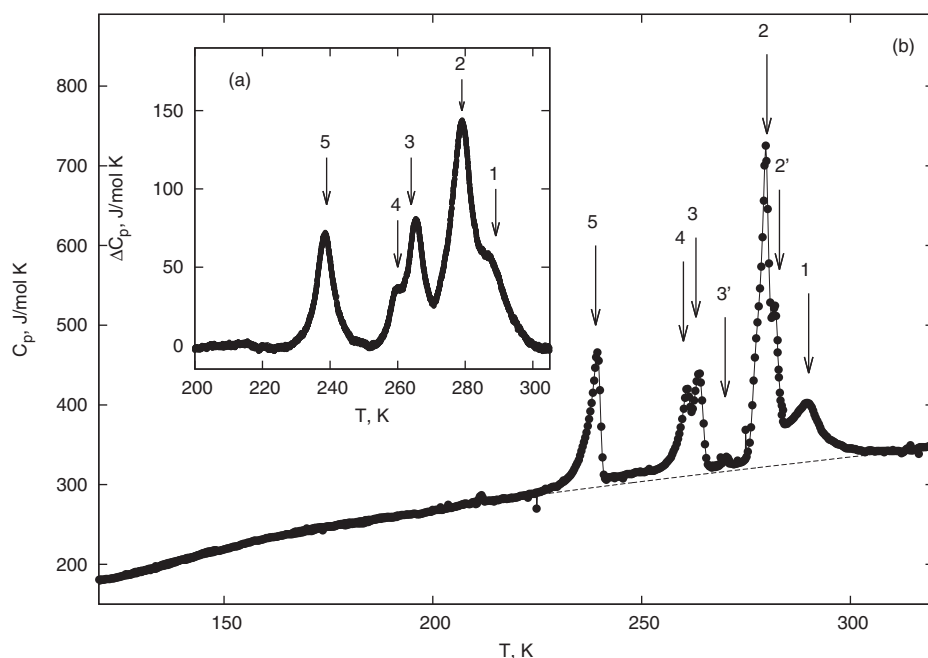


Fig. 1. Temperature dependences of the heat capacity of $(\text{NH}_4)_3\text{ZrF}_7$ measured on heating with DSM (a) and adiabatic calorimeter (b). Dashed line indicates the lattice heat capacity.

The results of investigations with adiabatic calorimeter on heating are presented in Fig. 1b as the temperature dependence of the molar heat capacity. Seven peaks of C_p were observed. The temperatures of five anomalies at 289.5 ± 0.5 K, 278.9 ± 0.2 K, 263.9 ± 0.3 K, 260.7 ± 0.3 K, and 239.4 ± 0.2 K are in a good agreement with those found in measurements with DSM. Besides, two anomalies were detected at 281.0 ± 0.2 K and 270.3 ± 0.5 K.

Lattice contribution to the heat capacity of $(\text{NH}_4)_3\text{ZrF}_7$ was determined by the polynomial approximation of the experimental data excluding the temperature interval of anomalous contribution between 220 and 305 K. In Fig. 1b C_{lat} is presented as a dashed line. Due to equilibrium conditions of measurements in adiabatic calorimeter, the integral characteristics of phase transitions can be determined more correctly. Later, we will return to this question, just after the correlation between the phase transition temperatures found by us and the succession of phases suggested in [11]. Here we only note that the total enthalpy change $\sum \Delta H_i = 3900 \pm 400$ J/mol is higher than that determined by the DSM data analysis.

3. Thermal dilatation

The thermal expansion of $(\text{NH}_4)_3\text{ZrF}_7$ was measured in the temperature range 100–350 K with a heating rate of 2–5 K/min using a NETZSCH model DIL-402C pushrod dilatometer. Two samples were studied: single crystal of a size of 2.8 mm along the direction of measurements ($[111]_c$ direction of the cubic cell) and the ceramic sample prepared from powdered single crystals in the form of a cylinder (8 mm in diameter and 6.35 mm in length). The investigation was made under a helium atmosphere flowing at 40 ml/min. To eliminate the effect of system thermal expansion, the results were calibrated using SiO_2 and Al_2O_3 as standard references.

Fig. 2 depicts the temperature dependences of the linear deformation $(\Delta L/L)_{[111]_c}$ and the coefficient of thermal linear expansion α . One can see that both properties also show the anomalous behaviour in the temperature range of about 230–300 K. The pronounced changes in the thermal expansion of $(\text{NH}_4)_3\text{ZrF}_7$ can be most clearly appreciated from the $\alpha(T)$ dependence. Here we use the same notation to label the specific temperature points related to the structural transformations, as it was done for the $C_p(T)$ dependence. Six anomalies are seen in Fig. 2b on first heating (curve A) at 290 ± 2 K, 285 ± 1 K, 280 ± 1 K,

271 ± 2 K, 267 ± 1 K, 242 ± 1 K. The second series of measurements (curve B in Fig. 2a and b) showed some peculiarities compared to the first heating. The α anomalies at the points 1, 2' and 2 decreased. The strongest change was observed in the behaviour of both $(\Delta L/L)_{[111]_c}(T)$ and $\alpha(T)$ at the point 5. Such a peculiarity means that heating-cooling cycling leads to the decrease of the sample volume instead of the increase according to the first heating. The reason of such a peculiar behaviour can be related, first, to the strong complicated twinning of $(\text{NH}_4)_3\text{ZrF}_7$ crystal on cooling [11] and, second, to the cracking of the sample observed during thermal cycling.

4. Hydrostatic pressure effect: dielectric measurements

The study of the hydrostatic pressure effect on the temperatures and succession of phase transitions in $(\text{NH}_4)_3\text{ZrF}_7$ was performed with differential thermal analysis (DTA) allowing to detect the heat capacity anomalies. A single crystal sample with a mass of 0.03 g was placed in a small copper container glued onto one of two junctions of a germanium-copper thermocouple. A quartz sample chosen as a reference substance was cemented to the other junction. The system, mounted in such a manner, was placed inside the piston-and-cylinder type vessel associated with the multiplier. Silicon oil was used as the pressure-transmitting medium. Pressure measurements were carried out on heating up to 0.6 GPa. To ensure the results reliability, both increasing and decreasing pressure cycles were used. The measurements of pressure and temperature were performed with a manganin gauge and a copper-constantan thermocouple with accuracies of about 10^{-3} GPa, and 1 K, respectively.

The results of DTA-measurements are presented in the pressure-temperature phase diagram in Fig. 3. Five DTA-anomalies were detected at ambient pressure. However the anomaly at the point 1 associated with transition from initial cubic phase was not observed even at small pressure (~ 0.03 GPa). It seems plausible that this small heat capacity anomaly (Fig. 1b) is smeared under pressure because of silicon oil thermal conductivity increase.

The measurements of permittivity were carried out using an E7-20 imittance metre at a frequency of 1 kHz on heating and cooling at a rate of about 1.0 K/min in the temperature range 150–310 K. Since the crystals of $(\text{NH}_4)_3\text{ZrF}_7$ were found to be cracked in cooling-heating cycling, the study of its dielectric properties was performed on the “quasi-ceramic” sample in the form of pressed

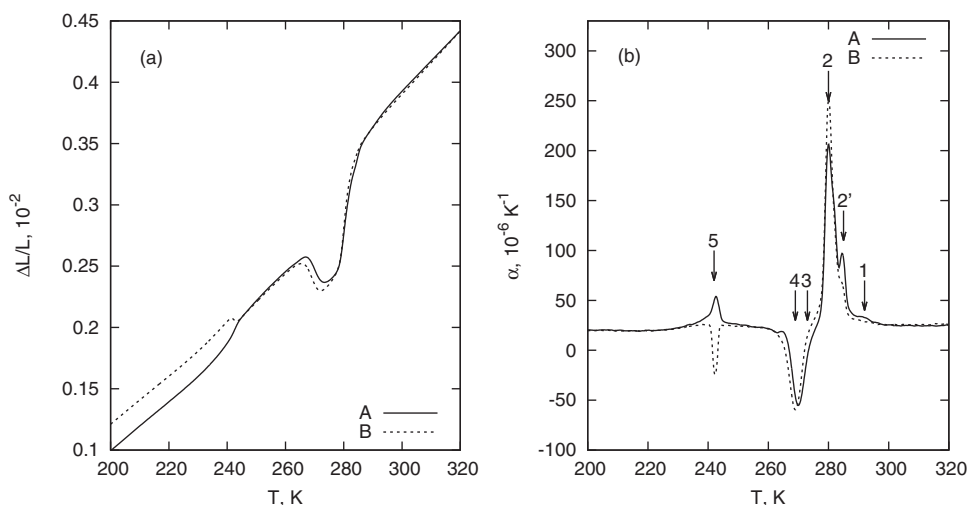


Fig. 2. Temperature dependences of the linear deformation $(\Delta L/L)_{[111]_c}$ (a) and the coefficient of thermal linear expansion α (b) of $(\text{NH}_4)_3\text{ZrF}_7$ measured on heating in two series A and B.

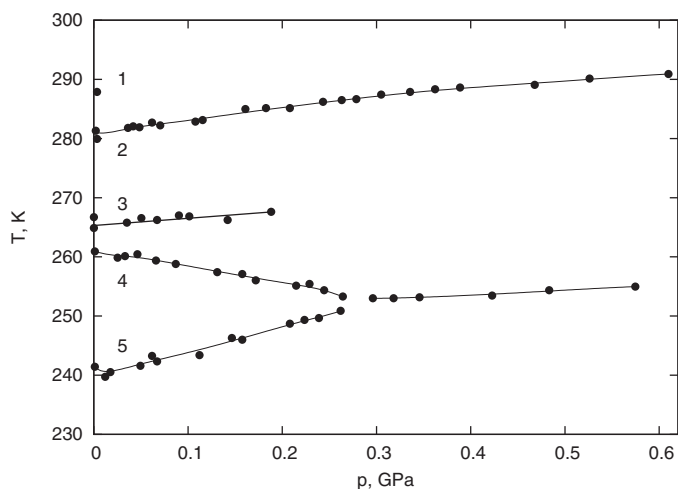


Fig. 3. The T - p phase diagram of $(\text{NH}_4)_3\text{ZrF}_7$.

pellet 8 mm in diameter and 1.75 mm in height prepared without heat treatment. Copper electrodes were deposited on a sample in a vacuum.

In Fig. 4a and b, one can see small anomalies on the temperature dependence of the permittivity. The more reliable results one can

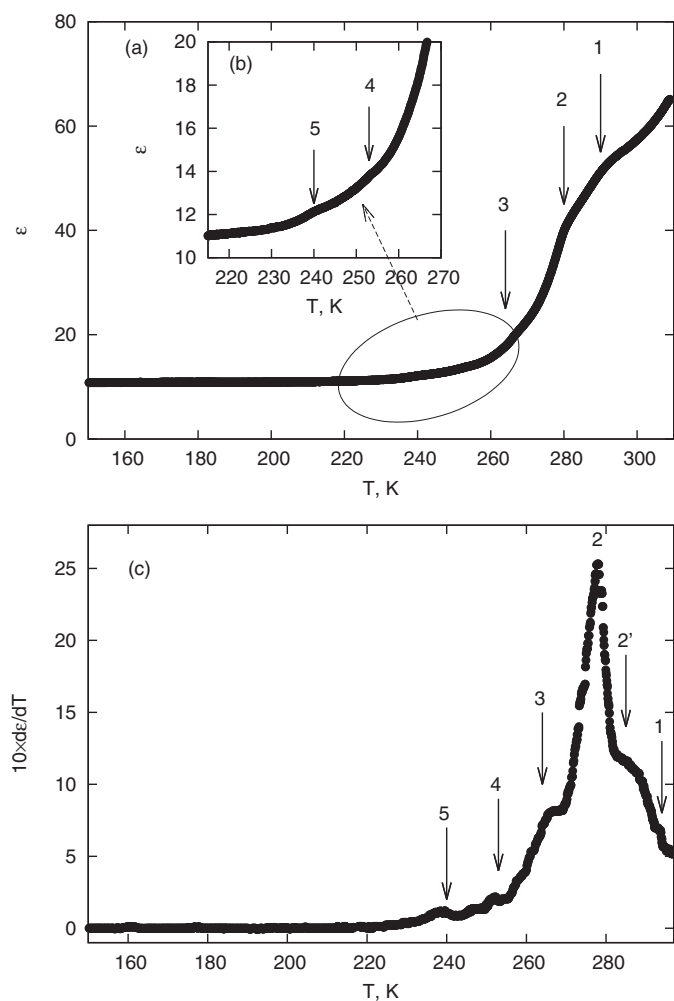


Fig. 4. Temperature dependences of the permittivity ϵ over a wide temperature range (a) and in the region of points 4 and 5 (b), and the $d\epsilon/dT$ derivative (c) for $(\text{NH}_4)_3\text{ZrF}_7$.

obtain considering the $d\epsilon/dT$ derivative against temperature (Fig. 4c). Peculiar behaviour was observed at six temperatures (293 ± 1 K, 283 ± 2 K, 278 ± 1 K, 267 ± 1 K, 252 ± 1 K, 240 ± 2 K) which are in agreement with some phase transition temperatures found in experiments with adiabatic calorimeter. The behaviour of the permittivity proves the ferroelastic nature of transformations observed in polarizing-optic experiments [11].

A rather strong ϵ increase above 270 K is, most likely, connected with dielectric losses in the “quasi-ceramic” sample prepared without heat treatment.

5. Discussion

First of all it is necessary to compare the phase transition temperatures found in the present study with those detected in the previous investigations of $(\text{NH}_4)_3\text{ZrF}_7$. As was mentioned above, contrary to succession of four transformations $G1 \leftrightarrow G2 \leftrightarrow G3 \leftrightarrow G4 \leftrightarrow G5$ suggested in [11], we observed minimum five and maximum seven temperature points associated with an anomalous behaviour of different properties: $C_p(T)$, $\alpha(T)$, $\epsilon(T)$, $T(p)$. All peculiar temperatures are summarized in Table 1 together with the data obtained in optic [11] and Raman [14] experiments. We will keep notation of T_i suggested in [12] and mark by T_i the temperatures of additionally found transformations. The heat capacity peak at the point 3' in Fig. 1b was not taken into account because of a negligible value of the respective enthalpy change ($<0.01 \sum \Delta H_i$) and the absence of peculiarities at this point in other properties. One can see that in all cases, including Raman data [14], the top peculiar temperature exceeds significantly the temperature T_1 determined in the polarizing-optic observations [11]. We believe that this large difference is not resulted from any mistake of measurements in many experiments. Therefore, it was decided that the highest peculiar temperature was not associated with the optical isotropy appearance on heating [11], and the T_0 notation was chosen for point 1 in Figs. 1–4.

Because of close values of T_1 and T_2 on heating [11] to the temperatures of the C_p anomalies at points 2' and 2 in Fig. 1b, we have supposed that they were associated with the same succession of two phase transitions. A strong evidence that this is the case was obtained in measurements with the adiabatic calorimeter by quasistatic thermograms ($dT/dt = |8 \times 10^{-2}|$ K/min) in heating-cooling cycle in the range of 268–282 K (Fig. 5). One can see that the C_p anomaly at point 2 is characterized by a very large value of the thermal hysteresis ~ 9 K close to that observed for δT_2 in [11] (Table 1). The transformation at the point 2' was also found as the first order one with hysteresis $\delta T_1 \approx 1.5$ K lower compared to δT_2 .

Let us consider the nature of an anomalous behaviour of different physical properties at T_0 taking into account the ambiguity of the space group determination at room temperature

Table 1

Temperature of anomalies detected in [11,14] and the present studies on heating (without brackets) and on cooling (in brackets). DSM – differential scanning microcalorimeter; AC – adiabatic calorimeter; TCLE – thermal coefficient of linear expansion.

T_i (K)	Optics [11]	DSM	AC	ϵ (T)	$T(p)$	TCLE	Raman [14]
T_0		287 (280)	289.5	293	288	290	(291)
T_1	280 (280)		281 (279.5)	283		285	(275)
T_2	279.5 (269)	279 (271)	278.9 (270)	278	280	280	
T_3	260–265	265 (236)	263.9	267	267	271	(247)
$T_{3'}$		260 (236)	260.7	253	261	267	
T_4	238 (235)	239 (220)	239.4	240	240	242	(225)

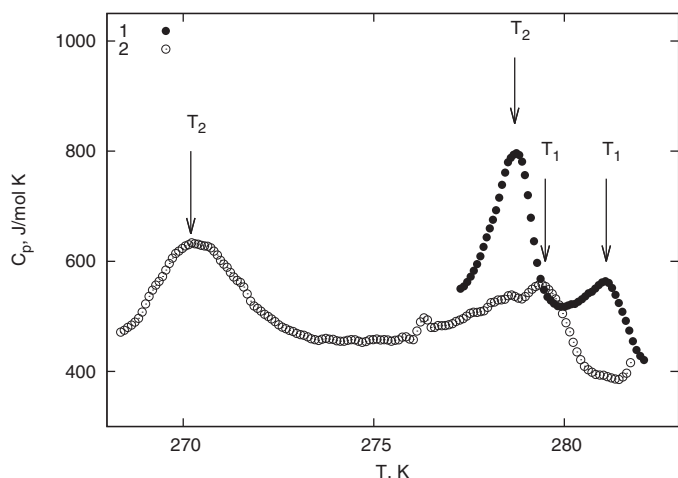


Fig. 5. Temperature dependences of the heat capacity obtained in the thermographic measurements around T_1 and T_2 on heating (1) and on cooling (2).

(Fm-3m [9,10] and F23 [2]). The analysis of the phase transitions sequence in the framework of the group theory [11] has shown that both cubic phases can be transformed into an orthorhombic one Immm at T_1 . But in the case of F23, the transformation should be of the first order. The existence of such a situation in $(\text{NH}_4)_3\text{ZrF}_7$ was proved by observation of a significant hysteresis δT_1 (Table 1). On the one hand, the phase transition Fm-3m \leftrightarrow F23 without singony change cannot be detected with polarizing-optic experiments. On the other hand, all properties studied in the present paper and [14] are sensitive to such a transformation. Thus, one can suppose that both cubic phases can exist in $(\text{NH}_4)_3\text{ZrF}_7$, and the transition between them takes place at T_0 .

The phase transition at T_3 was characterized in optic experiments [11] as smeared on heating in the range of 260–265 K and sharp on cooling at 246 K. In the experiments performed in this paper, we have observed two anomalies of properties on heating at the points 3 (T_3) and 4 (T_3') (Table 1). The results of DSM and Raman experiments proved the existence of one anomaly on cooling. So we suppose that $(\text{NH}_4)_3\text{ZrF}_7$ undergoes two first order phase transitions on heating at T_3 and T_3' . Because of rather different hysteresis ($\delta T_3 > \delta T_3'$) the intermediate phase G_3' between T_3 and T_3' disappears on cooling.

A rather good agreement between the T_4 values determined in different studies was found (Table 1).

Combining the results of [11] and the data discussed above one can suggest the following sequence of phase transitions in $(\text{NH}_4)_3\text{ZrF}_7$: cubic (Fm-3m \equiv G0; T_0) \leftrightarrow cubic (F23 \equiv G1; T_1) \leftrightarrow orthorhombic (Immm \equiv G2; T_2) \leftrightarrow monoclinic 1 (I2/m \equiv G3; T_3) \leftrightarrow ? (? \equiv G3'; T_3') \leftrightarrow triclinic (P-1 \equiv G4; T_4) \leftrightarrow monoclinic 2 (G5). We believe that there are a few examples of crystals undergoing such a strong complicated succession of structural distortions, as was found in $(\text{NH}_4)_3\text{ZrF}_7$.

Pressure measurements have revealed 5 DTA-anomalies on the T - p phase diagram (Fig. 3) connected with phase transitions at T_0 , T_2 , T_3 , T_3' and T_4 (Table 1). The pressure increase suppresses the anomaly at T_0 . The pressure dependence of the T_2 temperature can be described adequately with the equation of the type $T_2(p) = 280 + 29p - 2p^2$. Three linear phase boundaries are characterized by the following baric coefficients $dT_3/dp = 9$ K/GPa, $dT_3'/dp = -27$ K/GPa, $dT_4/dp = 41$ K/GPa. One can see (Fig. 3) that the triclinic phase G4 having the broadest interval of temperature stability at $p = 0$ wedges out at rather low pressure. The parameters of the triple point are $T_{tr} = 252$ K, $p_{tr} = 0.3$ GPa.

It was very interesting to see, are the phenomena observed in $(\text{NH}_4)_3\text{ZrF}_7$ associated with the order-disorder or/and displacive

mechanism of structural distortions? One can try to find the answer to this question by analyzing the experimental data on the structure and heat capacity.

The strong disorder of both the ZrF_7^{3-} ions and the ammonium cations was assumed in X-ray, neutron, and NMR investigations [2,9,10,12,13]. In the Fm-3m structure, 24 equivalent orientations of pentagonal bipyramid and dynamical disorder of both NH_4^+ ions occupying nonequivalent crystallographic positions 8c and 4b [9,10] were suggested. In accordance with [2], a positional disorder of ligands in the F23 structure gives 6 orientations of the ZrF_7^{3-} ion, and ammonium cations are disordered only in 4b site having 6 orientations. Taking into account the latter assumption, one can conclude that these NH_4^+ cations should be also disordered in the Fm-3m structure. Both structural models do not contradict the space group theory. As was shown in [11,16], the phase transition Fm-3m \rightarrow F23 is related to the ordering and displacement of fluorine and hydrogen atoms. In fact, the comparison of disorder in both cubic structures shows that the F23 phase has partial ordering of ZrF_7^{3-} ion and total ordering of two NH_4^+ ions occupying 8c site, which were dynamically disordered in the Fm-3m phase. The entropy of Fm-3m \rightarrow F23 transformation could be at least about $\Delta S_{T_1} = R \ln(24/6) = R \ln 4 \approx 11.5$ J/mol K. The ordering of the structural elements disordered in F23 phase should also be accompanied by rather large entropy change $\Delta S_{\text{total}}^{\text{F23}} = R(\ln 6 + \ln 6) = R \ln 36$. Thus, the total ordering of the disordered Fm-3m structure leads to very large entropy change $\Delta S_{\text{total}}^{\text{Fm-3m}} \approx 41$ J/mol K.

Let us analyze the results of the experimental study with adiabatic calorimeter to get information about the entropy change ($\Delta S_{\text{total}}^{\text{Fm-3m}}_{\text{EXP}}$) resulted from the successive structural distortions in $(\text{NH}_4)_3\text{ZrF}_7$. This value was determined by integration of the $(\Delta C_p/T)(T)$ function. The temperature dependence of the anomalous entropy change between G0 and G5 phases is shown in Fig. 6. Because of phase transition temperatures closeness to each other the anomalous heat capacities and entropies are overlapped (Figs. 1b and 6). Nevertheless, one can evaluate the entropy changes associated with the phase transition successions of G0 \leftrightarrow G1 \leftrightarrow G2 \leftrightarrow G3 ($\Delta S_{T_0-T_2} = 8.3 \pm 0.8$ J/mol K) and G3 \leftrightarrow G3' \leftrightarrow G4 ($\Delta S_{T_3-T_3'} = 3.2 \pm 0.3$ J/mol K) as well as with the transformation G4 \leftrightarrow G5 ($\Delta S_{T_4} = 3.0 \pm 0.3$ J/mol K). In Fig. 6 one can see also that entropy changes of phase transitions grouped together into two groups are equally rather strong to $R \ln 3$ (G0 \leftrightarrow G1 \leftrightarrow G2 \leftrightarrow G3) and $R \ln 2$ (G3 \leftrightarrow G3' \leftrightarrow G4 \leftrightarrow G5).

To sum up, the experimentally found value of entropy ($\Delta S_{\text{total}}^{\text{Fm-3m}}_{\text{EXP}} = 14.5 \pm 1.4$ J/mol K, on the one hand, is very close to $R \ln 6 = 14.9$ J/mol K and proves the disorder of initial cubic phase. On the other hand, it is less than the value expected from the model of the Fm-3m structural disorder almost by a factor of 3. One

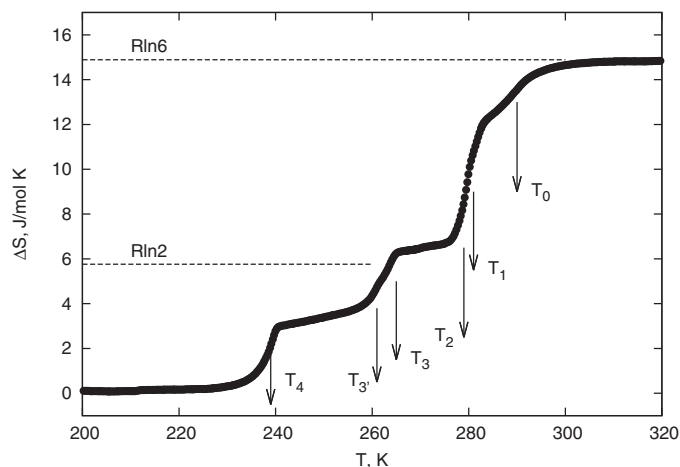


Fig. 6. Temperature dependence of entropy associated with phase transitions in $(\text{NH}_4)_3\text{ZrF}_7$.

can suppose two reasons of such a significant difference. First, in the phase G5 some structural elements remain disordered and $(\text{NH}_4)_3\text{ZrF}_7$ undergoes additional phase transitions below 125 K (the lowest temperature in our experiments). However, the Raman study did not reveal any peculiarities in the spectra below T_4 down to 7 K [14].

Second, there is no such a strong disorder of the Fm-3m and F23 structures as it was supposed in [2,9,10], and cubic symmetry in both cases is preserved owing to strong anharmonicity of critical ions vibrations without their stopping in fixed crystallographic positions, i.e. there is real “dynamic” but not “static” disorder. In that case, the phase transition entropy is characterized by some intermediate value exceeding the value characteristic for the displacive transformations and remains significantly less than the entropy associated with the order–disorder processes [17,18]. Such a hypothesis is proved also by the fact that each of the stepwise symmetry decreases is followed by a small entropy change, namely, at least less than $R\ln 2$. It is also worth mentioning that in [14] Raman spectra were interpreted as associated with slowing of the ammonium ion's motion along with the temperature decrease, but not with their ordering.

It is interesting to consider the relative ambiguous situation concerning the space group (Fm-3m or F23) of cubic phase in oxyfluoride $(\text{NH}_4)_3\text{NbOF}_6$ discussed in [2]. In the case of F23 symmetry, the difference compared to $(\text{NH}_4)_3\text{ZrF}_7$ is that, first, the seven coordinated polyhedron also considered as a pentagonal bipyramid was disordered on 12 equivalent orientations, second, NH_4^+ ions were disordered only in the 4b site having 6 or 12 orientations. The maximum value of entropy associated with the total ordering of structural units should be equal to $R\ln 72$ or $R\ln 144$. The experimentally found entropy change $R(\ln 2.7 + \ln 38.3 + \ln 1.1 + \ln 1.2) \approx R\ln 136$ due to the succession of four structural transformations is rather close to the ΔS value associated with the second model of NH_4^+ cations disorder [19]. From our point of view, this example also supports the hypothesis about rather restricted disorder of structural units in the cubic phase of $(\text{NH}_4)_3\text{ZrF}_7$.

6. Concluding remarks

The study of thermodynamic properties has revealed that $(\text{NH}_4)_3\text{ZrF}_7$ undergoes the succession of six structural phase

transitions of nonferroelectric nature. The transformation between two cubic phases Fm-3m \leftrightarrow F23 is assumed at T_0 . The ranges of all crystal phase stability except G4 are broadened under pressure. The value of the total experimental entropy change $\sum \Delta S_i = R\ln 6$ associated with the sequence of phase transitions, on the one hand, is characteristic for the order–disorder processes, and, on the other hand, allows assuming that the degree of structural disorder of cubic phases should be reconsidered.

Acknowledgements

This work was supported by RFBR, project no. 12-02-00056, and the Council on Grants from the President of the Russian Federation for the Support of Leading Scientific Schools of the Russian Federation (Grant NSh-4828.2012.2).

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