

LATTICE DYNAMICS AND PHASE TRANSITIONS

Thermodynamic Properties of $(\text{NH}_4)_2\text{KGaF}_6$ Elpasolite

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Abstract—The heat capacity of $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite is measured in the temperature range from 80 to 350 K. A sequence of three phase transitions at $T_1 = 288.5$ K, $T_2 = 250$ K, and $T_3 = 244.5$ K is revealed, and the thermodynamic characteristics of these transitions are determined. The influence of hydrostatic pressure on the phase transition temperature is investigated. The results obtained are discussed within the model of orientational ordering of NH_4^+ and GaF_6^{3-} ionic groups. © 2001 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Crystals of the elpasolite and cryolite family of the general formula $A_2^+B^+M^3+F_6$ (in a cryolite structure, $A^+ \equiv B^+$) have a high-temperature cubic phase and belong to a wide class of ordered perovskites with the space group $Fm\bar{3}m$ ($Z = 4$). Compounds of this family with atomic cations A^+ and $B^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{or Cs}^+$ ($R_{A^+} > R_{B^+}$) can undergo structural phase transitions upon cooling due to lattice instability with respect to rotational distortions of the crystal framework which consists of vortex-shared octahedra B^+F_6 and M^3+F_6 [1–3]. The phase transitions occur through the condensation of soft librational modes of octahedral ionic groups.

The presence of NH_4^+ ammonium ions in the structure substantially affects the mechanism of the phase transitions. In elpasolite and cryolite crystal cells, these ions can occupy two nonequivalent positions, namely, $4b$ (inside a halide octahedron) and $8c$ (in a hole between octahedra) positions with coordination numbers of 6 and 12, respectively. In the $(\text{NH}_4)_3M^3+F_6$ cryolite structure, ammonium ions occupy both positions. For an elpasolite structure, there are two variants: (1) ammonium tetrahedra can be located only in holes between octahedra in the $(\text{NH}_4)_2B^+M^3+F_6$ compounds and (2) ammonium tetrahedra can occupy only halide octahedra in the $A_2^+\text{NH}_4M^3+F_6$ compounds.

Among ammonium compounds, the $(\text{NH}_4)_3M^3+F_6$ cryolites are the best understood. For these compounds, the heat capacity has been carefully measured and the thermodynamic parameters of phase transitions have been reliably determined in a number of works [4–10]. Moreover, the effect of hydrostatic pressure was analyzed in our recent works [9, 10]. The character of the

reorientational motion of hydrogen and fluorine was investigated earlier by NMR spectroscopy [4, 11].

In the $(\text{NH}_4)_3M^3+F_6$ cryolites, as in compounds with atomic cations [2], the phase transition temperature and the sequence of formation of distorted phases essentially depend on the size of the trivalent cation. Earlier, two successive phase transitions were revealed in an ammonium-containing cryolite with $M^{3+} = \text{Al}^{3+}$ [4, 12] and one transition from a cubic phase to a triclinic phase was observed in compounds with $M^{3+} = \text{Cr}^{3+}, \text{Ga}^{3+}, \text{V}^{3+}, \text{and Fe}^{3+}$ [6–8, 13, 14]. It was found that, for compounds with larger-sized trivalent ions ($M^{3+} = \text{Sc}^{3+}$ and In^{3+}), the low-temperature triclinic phase is formed upon three phase transitions [8–11, 15].

For the aforementioned cryolites, the total entropy change due to the transition from the cubic to the triclinic phase varies in a narrow range (2.33–2.99) R from crystal to crystal and does not depend on the sequence of phase transitions. The large entropy clearly indicates that ordering processes proceed in the structure. In [7, 8], it was assumed that the phase transitions are associated with orientational ordering of both tetrahedral ammonium and octahedral fluorine ionic groups. Of the above two types of ammonium ions that occupy different crystallographic positions ($8c$ and $4b$), only in the latter case, tetrahedral ions in the cubic phase are disordered over two equivalent orientations according to the symmetry of the occupied position. Fluorine octahedra remain rigid and regular when fluorine atoms in the cubic phase are distributed over the $24e$ or $192l$ positions. In the former case, they occupy a special position on the cell edge. In the latter case, they are distributed over eight positions; i.e., each octahedron is characterized by eight equivalent orientations. Consequently, the entropy change that corresponds to complete ordering of the ionic groups is equal to $R\ln 2 + R\ln 8 = R\ln 16 = 2.77R$. This value is in reasonable agreement with the experimental data for ammonium-containing cryolites.

In the case when ammonium cryolites undergo successive phase transitions, the structural ordering processes occur in two stages [9]. The phase transition from the cubic phase to the monoclinic phase is associated with a partial ordering of octahedra ($\Delta S = R \ln 4$), which results in a forced ordering of ammonium tetrahedra ($\Delta S = R \ln 2$). The octahedra are completely ordered upon the second phase transition between two monoclinic modifications ($\Delta S = R \ln 2$). The third phase transition (to the triclinic phase) is accompanied by an insignificant change in the entropy and is, most likely, a first-order transition between two completely ordered, distorted modifications [9, 16]. The model under consideration is consistent with the NMR data obtained by Sasaki *et al.* [11] for the $(\text{NH}_4)_3\text{InF}_6$ cryolite. For cryolites with successive phase transitions, the spin-lattice relaxation times of protons (T_{1H}) and fluorine nuclei (T_{1F}) exhibit an anomalous behavior upon phase transition from the cubic phase. However, upon the second phase transition, only the T_{1F} time changes considerably.

It should be noted that, in ammonium elpasolites, an NH_4^+ ion occupies only one of the two possible crystallographic positions ($4b$ or $8c$). This slightly simplifies the problem of elucidating the role of ammonium ions in structural phase transitions and their influence on the motion of fluorine octahedra.

If the model proposed in [8, 9, 16] provides an adequate description of the ordering of structural units upon phase transitions, the $A_2^+ \text{NH}_4 M^{3+} F_6$ elpasolites, like $(\text{NH}_4)_3 M^{3+} F_6$ cryolites, can undergo phase transitions with ordering of the ammonium tetrahedra and fluorine octahedra. As regards the $(\text{NH}_4)_2 B^+ M^{3+} F_6$ elpasolites, only the fluorine octahedra can be disordered in their cubic structure. In these two cases, the maximum entropy change can be equal to $R \ln 16$ and $R \ln 8$, respectively.

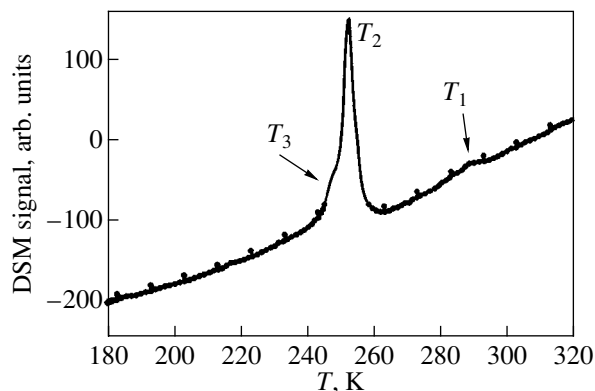


Fig. 1. DSC curve for the $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite (DSM-2M instrument).

In the present work, we carefully investigated the heat capacity and the p - T phase diagram for the $(\text{NH}_4)_2\text{KGaF}_6$ compound over a wide range of temperatures and pressures. The aim of this work was to determine the thermodynamic parameters of phase transitions and to elucidate how the substitution of an atomic cation for ammonium in the crystallographic position $4b$ in the $(\text{NH}_4)_2\text{NH}_4\text{GaF}_6$ cryolite structure affects the thermodynamic properties.

2. SAMPLE PREPARATION AND PRELIMINARY INVESTIGATIONS

The $(\text{NH}_4)_2\text{KGaF}_6$ compound was prepared using two methods. In the first method, we synthesized this compound from a solution. A solution of $\text{Ga}(\text{OH})_3$ in concentrated hydrofluoric acid was evaporated to the onset of crystallization. Then, a saturated solution of an equimolar mixture in hydrofluoric acid on a $2\text{NH}_4\text{HF}_2 + \text{KHF}_2 + \text{Ga}(\text{OH})_3$ basis was added to the $\text{Ga}(\text{OH})_3$ solution. The resultant solution was allowed to stand in a crystallizer at a temperature of 70°C until fine crystals were formed and was then cooled to room temperature at a rate of 0.5 K/h. As a result, we obtained crystals approximately 0.5 mm³ in volume.

In the second method, the $(\text{NH}_4)_2\text{KGaF}_6$ compound was prepared by hydrothermal synthesis. A 35% aqueous solution of HF (in an amount of 20% of the total weight of the initial components) was added to a $2\text{NH}_4\text{HF}_2 + \text{KHF}_2 + \text{GaF}_3 \cdot 3\text{H}_2\text{O}$ mixture in a Teflon vessel. The vessel with the prepared mixture was placed in a high-pressure nickel bomb. The hermetically sealed bomb was held for 48 h at 230°C and then was slowly cooled for 72 h to room temperature. In this manner, we obtained octahedral crystals 30 – 50 mm³ in volume.

Analysis of the x-ray diffraction patterns showed that impurities of the initial components and foreign phases are absent in the samples. At room temperature, the $(\text{NH}_4)_2\text{KGaF}_6$ compound has a cubic symmetry ($Fm\bar{3}m$, $Z = 4$) with the unit cell parameter $a_0 = 8.866$ Å. According to the chemical formula, ammonium ions occupy the $8c$ positions in the unit cell. No indications of composition disordering of ammonium and potassium ions over the $8c$ and $4a$ positions were found.

Two $(\text{NH}_4)_2\text{KGaF}_6$ samples prepared using different methods were studied by differential scanning calorimetry (DSC) on a DSM-2M instrument in the temperature range 150 – 320 K. The experimental data obtained for the sample grown by hydrothermal synthesis are shown in Fig. 1. It can be seen that the heat capacity exhibits two anomalies proportional to the DSM signals at temperatures $T_1 \approx 290$ K and $T_2 \approx 250$ K. Moreover, a small deviation from a smooth decrease in the DSM signal is observed below T_2 in the range of $T_3 \approx 245$ K. In order to make certain that the third anomaly is not

accidental and does not depend on the sample preparation procedure, we performed calorimetric measurements with the same instrument for the sample synthesized from the solution. The results of both experiments turned out to be identical: the temperatures of each of the three anomalies in the heat capacity coincided to within 1–2 K, i.e., within the accuracy ensured by the DSM-2M instrument. The enthalpy change upon the phase transition at the T_1 temperature was found to be $\Delta H_1 = 150 \pm 25$ J/mol. Since the difference between the temperatures T_2 and T_3 was small, we succeeded only in determining the total enthalpy change upon two successive transitions: $\Delta H_2 + \Delta H_3 = 3500 \pm 550$ J/mol.

The preliminary polarization-optical investigation of the $(\text{NH}_4)_2\text{KGaF}_6$ samples prepared by hydrothermal synthesis revealed that twins with a structure typical of tetragonal distortion are formed at temperatures below T_1 . Below the T_2 temperature, the pattern of twinning changes and the symmetry becomes lower (most probably, monoclinic). Unfortunately, reliable data on the phase transition at the T_3 temperature are unavailable. Detailed results of optical and structural investigations will be published in a separate paper.

3. HEAT CAPACITY MEASUREMENTS

In order to refine the thermodynamic parameters of the phase transitions under investigation and to reveal possible phase transitions with a small enthalpy (i.e., transitions that cannot be recorded using the DSC method because of its relatively low sensitivity to thermal effects), the temperature dependence of the heat capacity was carefully measured using an adiabatic calorimeter in the temperature range 80–350 K.

For this purpose, a sample (1.46 g) was placed in an indium cell, which was then hermetically sealed in a helium atmosphere. The heat capacity of the cell was determined in a separate experiment. The measurements were carried out upon discrete and continuous heating. In their immediate vicinity, the phase transitions were investigated by the quasi-static thermogram method during heating and cooling at mean rates $|dT/dt| \approx 2.5 \times 10^{-2}$ K/min.

The temperature dependences of the heat capacity of the $(\text{NH}_4)_2\text{KGaF}_6$ compound over the entire temperature range studied and, in greater detail, at temperatures near 250 K are displayed in Figs. 2a and 2b, respectively.

It can be seen from Fig. 2 that the heat capacity exhibits three anomalies, as is the case in the experiments performed with the DSM-2M instrument. The refined temperatures of the phase transitions are as follows: $T_1 = 288.5 \pm 0.5$ K, $T_2 = 249.3 \pm 0.1$ K, and $T_3 = 244.6 \pm 0.5$ K. The behavior of the heat capacity in the vicinity of the T_1 temperature is characteristic of second-order phase transitions. Thermographic investigations (quasi-static thermogram method) demonstrated

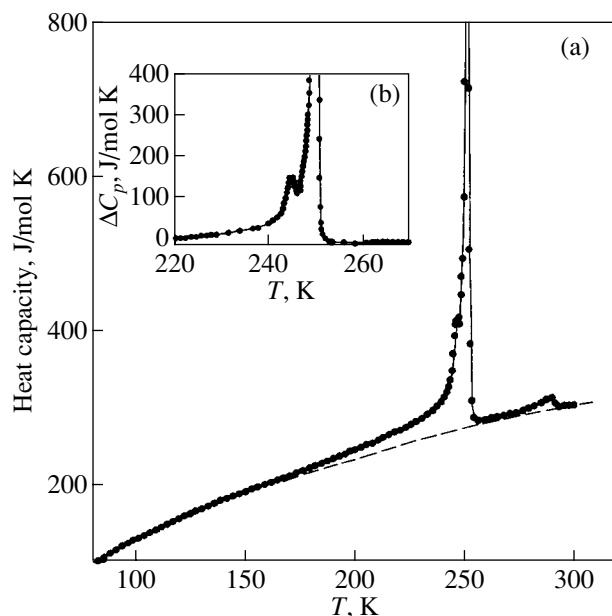


Fig. 2. Temperature dependences of the heat capacity for the $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite (a) over a wide range of temperatures and (b) in the temperature range of phase transitions at T_2 and T_3 . The dashed line shows the lattice heat capacity.

that the anomalies observed in the heat capacity at T_2 and T_3 are associated with the first-order phase transformations, which are characterized by the temperature hystereses $\delta T_2 = 1.24 \pm 0.05$ K and $\delta T_3 = 2.06 \pm 0.2$ K.

The integrated thermodynamic characteristics of the phase transitions were obtained in the processing of the anomalous component of the heat capacity $\Delta C_p(T) = C_p(T) - C_{\text{lat}}(T)$. The lattice component of the heat capacity $C_{\text{lat}}(T)$ was determined by approximating the experimental data outside the phase transition range ($T < 150$ K and $T > 300$ K) with the use of the Debye and Einstein functions. The temperature dependence of the lattice heat capacity is shown by the dashed line in Fig. 2a. The spread of experimental points about the smoothed dependence in these temperature ranges did not exceed 0.7%. The change in the entropy with temperature was calculated by integrating of the $\Delta C_p(T)/T$ function. The temperature dependence of the excess entropy is depicted in Fig. 3.

The total entropy change for the three phase transitions is equal to 16.0 ± 1.5 J/mol K. The entropy change due to the first phase transition is rather small: $\Delta S_1 = (0.12 \pm 0.01)R$; this value is characteristic of displacive-type transitions. Since the temperatures of the two other transitions are very close to each other, the entropy change attributed to each of these transitions cannot be distinguished. The total entropy change for these transitions is $\Delta S_2 + \Delta S_3 = 1.8R$. This value slightly exceeds the entropy change ($1.68R$) determined by the DSM method.

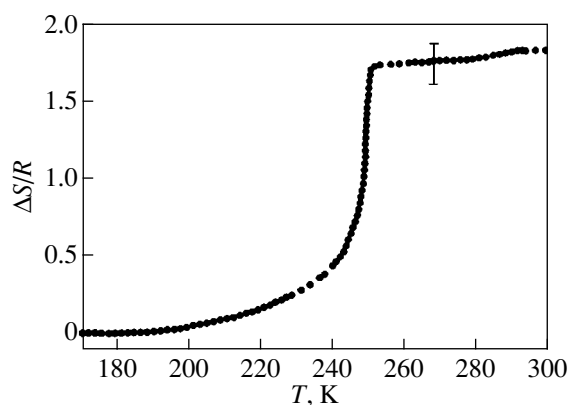


Fig. 3. Temperature dependence of the excess entropy.

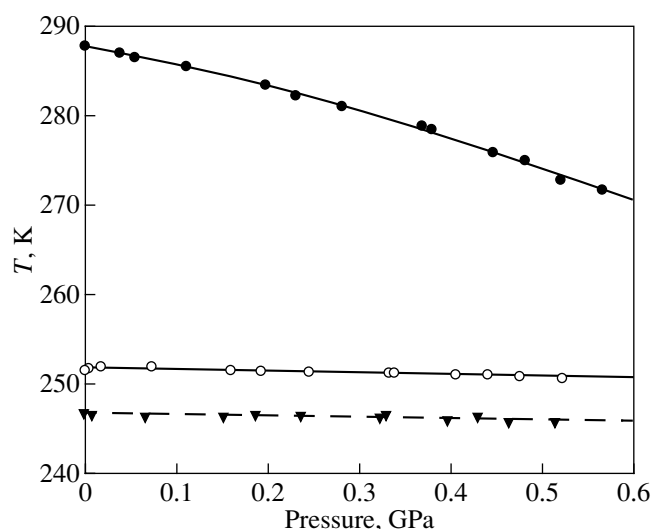


Fig. 4. The p - T phase diagram for the $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite.

4. PHASE DIAGRAM

The effect of hydrostatic pressure on the phase transition temperatures was studied with the same sample as was used in the heat capacity measurements. The phase transition temperature and its change with a variation in pressure were determined from a differential thermal analysis (DTA). A copper–germanium thermocouple served as the sensitive element. A quartz reference sample was placed on one junction of the thermocouple, and a small copper cell with the studied compound was placed on the other junction of the thermocouple. The high sensitivity of the thermocouple made it possible to measure reliably even the phase transition at T_1 with a small anomaly in the heat capacity ($\Delta C_p/C_{\text{lat}} \approx 6\%$). A pressure as high as 0.6 GPa was produced in a cylinder–piston-type chamber connected to a booster. A mixture of silicone oil and pentane was used as the pressure transferring medium. The pressure

in the chamber was measured on a manganin resistance pressure gauge, and the temperature was measured using a copper–constantan thermocouple. The errors of measurements were equal to $\pm 10^{-3}$ GPa and ± 0.3 K, respectively. The reliability of the results was checked by measuring the shift in the phase transition temperatures with an increase and a decrease in the hydrostatic pressure.

Figure 4 shows the p - T phase diagram of the $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite. It is seen that the stability loss temperature of the cubic phase decreases with an increase in the pressure. It is worth noting that the dependence $T_1(p)$ is obviously nonlinear. The shift in the phase transition temperature dT_1/dp is equal to -18.5 K/GPa at $p = 0$ and reaches a value of -30 K/GPa at $p = 0.5$ GPa. The temperatures of the two other structural transformations also decrease but considerably more slowly: $dT_2/dp = -(2.3 \pm 0.3)$ K/GPa and $dT_3/dp = -(1.4 \pm 0.4)$ K/GPa. It is evident that a further increase in the pressure can lead to the disappearance of the first distorted phase. According to the estimates, this can occur at $p = 1.0$ – 1.2 GPa.

5. DISCUSSION

The substitution of the K^+ cation for the ammonium ion in the $4b$ position leads to quite a different pattern of phase transitions as compared to that observed in the $(\text{NH}_4)_2\text{NH}_4\text{GaF}_6$ cryolite. Let us consider the $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite structure in the framework of the model proposed for cryolites in [7–9]. Within this model, fluorine octahedra alone, most probably, fulfill the function of “critical” ions; i.e., they play an active part in the phase transitions. Now, we attempt to either validate or disprove this assumption. In the $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite, the entropy change upon the phase transition from the cubic phase is small ($\Delta S_1 = 0.1R$) and comparable to the quantity $\Delta S \approx 0.2R$. This entropy change is characteristic of a large number of halide elpasolites (including fluoro-elpasolites) with atomic cations, which undergo phase transitions to the tetragonal phase [2]. According to [2], the entropy change of $0.2R$ is attributed to the rotation of fluorine octahedra through a small angle about one of the four-fold axes of the cubic cell. As was noted above, the preliminary optical investigations also demonstrated that the first distorted phase in the $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite has a tetragonal symmetry. Therefore, if the transformation at T_1 in the $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite is also associated with rotations of the octahedra, we can state with assurance that disordering of the fluorine atoms (or fluorine octahedra) is absent in the cubic phase. To put it differently, the change in the character of octahedron motion upon phase transitions at T_2 and T_3 can contribute to the mechanism of structural transformations only through further octahedron rotations with small entropy changes ΔS . On the other hand, close examination of

the structure shows that, under the assumption of octahedron disordering in the $Fm\bar{3}m$ phase, the rotation of orientationally disordered octahedra through a small angle cannot provide for the formation of a tetragonal structure with rigid octahedra. Consequently, the considerable entropy change ($\Delta S_2 + \Delta S_3$) most likely corresponds to the ordering of other structural units.

As far as we know, only fragmentary data are available on the properties of crystals belonging to the $(\text{NH}_4)_2\text{B}^+\text{M}^{3+}\text{F}_6$ elpasolite family, namely, $(\text{NH}_4)_2\text{KAlF}_6$ [17], $(\text{NH}_4)_2\text{NaFeF}_6$ [18], and $(\text{NH}_4)_2\text{NaInF}_6$ [19].

Hirokawa and Furukawa [17] investigated the $(\text{NH}_4)_2\text{KAlF}_6$ elpasolite by the DTA technique and revealed two phase transitions at $T_1 = 250$ K and $T_2 = 186$ K. Unfortunately, they did not determine the relevant entropy changes. However, the ratio of areas under the DTA signal anomalies (proportional to the entropy change) indicates that $[\Delta S_2 = \Delta H_2/T_2] \gg [\Delta S_1 = \Delta H_1/T_1]$. In other words, the entropy ratio for the $(\text{NH}_4)_2\text{KAlF}_6$ elpasolite is identical to that for the $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite. The inference made in [17] coincides with our opinion that the phase transition at T_1 is a displacive-type transformation and is most likely associated with rotations of fluorine octahedra through a small angle. Reasoning from the NMR data, Hirokawa and Furukawa [17] argued that the second phase transition, which is accompanied by a substantial entropy change, is most probably due to the ordering of ammonium ions. Unlike the $(\text{NH}_4)_3\text{M}^{3+}\text{F}_6$ ($M^{3+} = \text{Al}$ and Ga) cryolites, in which the spin-lattice relaxation times of fluorine ions and protons change significantly upon phase transitions [4, 8, 11], the $(\text{NH}_4)_2\text{KAlF}_6$ elpasolite is characterized by a considerable change only in the T_{1H} time at the T_2 temperature [17].

In the high-temperature cubic phase, the N–H bonds are dynamically disordered and equiprobably directed to three fluorine ions of the same face of an $(\text{AlF}_6)^{3-}$ octahedron. In an intermediate phase, ammonium tetrahedra remain disordered but three orientations of each N–H bond become nonequivalent due to the lowering of the symmetry. The correlation time of anion reorientation is very long. This suggests a low probability of dynamic disordering of fluorine octahedra in the intermediate phase. In the low-temperature phase, hydrogen atoms are predominantly bonded to one of three fluorine ions. All the aforementioned features are confirmed by the data on the relaxation times of hydrogen and aluminum and the temperature dependence of the second moment of the H and F NMR spectra [17].

The assumption that the ammonium ions in the 8c positions can be orientationally disordered is confirmed by the unusually large temperature parameter of hydrogen atoms in the cubic phase of $(\text{NH}_4)_2\text{NaInF}_6$ [19], which is appreciably larger than the temperature parameters of the other atoms.

If this disordering of ammonium ions actually occurs in the cubic phase, their complete ordering in the low-temperature phase should be attended by the entropy change $\Delta S = 2R\ln 3 = R\ln 9 = 18.3$ J/mol K. This value exceeds the entropy change observed in the experiment for the $(\text{NH}_4)_2\text{KGaF}_6$ elpasolite: $\Sigma\Delta S_i = 16$ J/mol K.

6. CONCLUSION

It was demonstrated that the phase transition from the cubic phase in the $(\text{NH}_4)_2\text{KGaF}_6$ and $(\text{NH}_4)_2\text{KAlF}_6$ elpasolites is accompanied by a small entropy change. This disagrees with the existing elegant model of structural transformations, which is based only on the orientational ordering of the NH_4^+ (in the 4b position) and $M^{3+}\text{F}_6^-$ ionic groups [7, 8]. The determination of the actual positions of fluorine and hydrogen atoms calls for further structural investigations. Moreover, when constructing a model of phase transitions in ammonium compounds, the possible softening of rotational vibrational modes of fluorine octahedra should be taken into account.

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