

LATTICE DYNAMICS AND PHASE TRANSITIONS

Dedicated to the 80th Birthday of L.A. Shuvalov

Ferroelastic Phase Transitions in Fluorides with Cryolite and Elpasolite Structures

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Abstract—The ferroelastic phase transitions are investigated in several series of fluoride crystals belonging to the elpasolite and cryolite families (space group $Fm\bar{3}m$) with the general formula $A_2BB'F_6$. The influence of the size and shape of cations and anions on the entropy and the mechanism of structural distortions is discussed.
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INTRODUCTION

Perovskite-like compounds have attracted the particular attention of researchers due to a large variety of physical properties and their possible use in different technical devices. The perovskite structure is characterized by a relatively simple crystal lattice, on the one hand, and the striking flexibility that makes it possible to change the composition of ions forming the lattice over a wide range and, thus, to achieve the desirable properties of the material, on the other hand. In this respect, perovskite compounds play an important role in solid-state physics and materials science. All unique (and practically useful) properties predominantly manifest themselves in compounds whose structure differs from an ideal cubic structure of the ABX_3 perovskite due to different-type distortions, such as polar and antipolar displacements of A and (or) B ions from their positions at the centers of octahedra and cubooctahedra, octahedron rotations, Jahn–Teller distortions, or magnetic ordering.

Investigations into the mechanisms responsible for phase transformations and changes in the sequences of structural distortions occurring in perovskite-like compounds as a result of variations in external (temperature, pressure) and internal (doping, composition) parameters are of considerable interest both from the point of view of elucidation of the composition–structure–property relations and from the practical standpoint of searching for the criteria for syntheses of crystals with controlled properties.

Among perovskite-like compounds, the elpasolite and cryolite families are most representative owing to the great diversity of possible substitutions for atoms in

crystals of the general formula $A_2BB'X_6$. According to [1, 2], more than 350 compounds with a similar structure were known until recently and, as follows from the crystal chemical analysis, more than 1500 new elpasolites can be obtained only based on halides. In the initial phase, crystals of this family have cubic symmetry (space group $Fm\bar{3}m - O_h^6$, $Z = 4$). Unlike the simple perovskites ABX_3 , in which all the octahedra are equivalent, the elpasolites (also referred to as ordered perovskites) contain two types of ionic groups (BX_6 , $B'X_6$) alternating along the three fourfold axes. Therefore, the elpasolite cubic cell can be treated as a perovskite cell with double the unit cell parameter. The crystal structure of the cryolite $A_3B'X_6$, in which the A and B atoms are chemically equivalent, is a special case of the elpasolite structure.

For compounds of these families, the group-theoretic analysis of the possible phase transitions from the initial phase was performed in [3, 4], the symmetry analysis of the lattice vibrations was carried out in [5, 6], and the phase transitions were phenomenologically described in [5]. In the majority of cases, the phase transformations were treated as displacive transitions. However, there are a large number of experimental facts indicating a crossover from the displacive-type mechanism to the order–disorder mechanism of phase transitions with a change in the type of A , B , and B' ions. The problem of possible disordering in perovskites, which was formulated by Comes *et al.* [7], is still debated in the literature [8, 9]. The order–disorder phase transitions most clearly manifest themselves in compounds with nonspherical cations A and B (for example, with tetrahedral ammonium ions). It seems

likely that ordering upon these phase transitions involves not only ammonium ions but also octahedral ions, which, upon other phase transitions, execute small rotations due to softening of the lattice rotational vibration modes. The role played by the ordering processes in the mechanisms of phase transformations in these compounds is still not clearly understood.

In this work, we analyzed the thermal and structural data obtained for several series of fluorides with elpasolite-like and cryolite-like structures in order to elucidate how the sizes and shape of cations affect the position and motion of fluorine ions and the entropy of phase transitions. It should be noted that, according to the results of investigations performed in polarized light, all the studied crystals undergoing displacive and (or) order–disorder phase transitions are ferroelastic materials.

ELPASOLITES WITH ATOMIC CATIONS

In $\text{Rb}_2\text{KB}^{3+}\text{F}_6$ crystals, a decrease in the size of the B^{3+} cation (Fig. 1) leads to the change in the sequence of structural distortions from $Fm\bar{3}m \rightarrow P12_1/n1$ ($B^{3+} = \text{Er, Ho, Dy, Y, Tb}$) to $Fm\bar{3}m \rightarrow I4/m \rightarrow P12_1/n1$ ($B^{3+} = \text{Lu, In, Sc}$), a decrease in the stability temperature of the cubic phase, and an increase in the temperature range of the stability of the intermediate tetragonal phase from 3 ($B^{3+} = \text{Lu}$) to 30 K ($B^{3+} = \text{Sc}$) [10]. The triple point with the coordinates $R_{B^{3+}} \sim 0.88 \text{ \AA}$ and $T_0 \sim 370 \text{ K}$ is observed in the $R_{B^{3+}}-T$ phase diagram. The transition to the tetragonal phase is characterized by the small entropy ΔS , which is of the order of $0.2R$ [10]. This value of ΔS indicates that the above transformations can be attributed to displacive phase transitions. The structural distortions in the compounds under consideration are associated with the crystal lattice instability with respect to small rotations of fluorine octahedra (the rotational modes Γ_4^+, X_2^+) [5]. The tetragonal symmetry is caused by the (00ϕ) rotations of octahedra about one of the fourfold axes of the cubic cell [5] due to the condensation of the Γ_4^+ rotational mode at the center of the Brillouin zone. The monoclinic distortion $P12_1/n1$ is associated with the condensation of the X_2^+ rotational mode and can be treated as a superposition of the $(\psi\phi\phi)$ rotations of octahedra about three principal cubic axes at once. The total entropy change upon transition from the cubic phase to the monoclinic phase depends on the size of the trivalent ion and decreases from $1.3R$ (Ho) to $0.7R$ (Sc) [10]. The maximum value ($1.3R$) is rather large for purely displacive transitions but does not allow us to assign these transformations to order–disorder transitions. In this case, an increase in the entropy with an increase in the size of the trivalent cation is associated with the

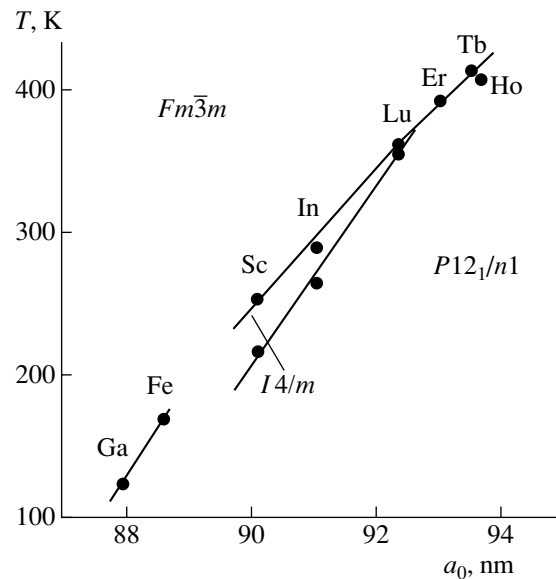


Fig. 1. Dependence of the phase transition temperature T_i on the parameter a_0 of the cubic unit cell for $\text{Rb}_2\text{KB}^{3+}\text{F}_6$ elpasolites.

increase in the anharmonicity and anisotropy of vibrations of fluorine ions, which is confirmed by the results of structural investigations [10, 11].

A further decrease in the parameter of the cubic unit cell of $\text{Rb}_2\text{KB}^{3+}\text{F}_6$ crystals ($B^{3+} = \text{Fe, Cr, Ga}$) leads to only one ferroelastic first-order transition, which is accompanied by a considerable volume jump and, consequently, results in the failure of single-crystal samples [10, 12]. Symmetry of the distorted phase in these crystals is not established uniquely [13–15]. The experimental data cannot be described in the framework of the models successfully used for rotational phase transitions and suggest that the phase transitions in crystals with small-sized trivalent cations proceed through a mechanism different from the purely rotational mechanism. The $R_{B^{3+}}-T$ phase diagram should be complex in the range between the sizes of the Sc^{3+} and Fe^{3+} ions. In this range, the competition between different mechanisms of phase transitions can be responsible for the appearance of new distorted phases and triple points (Table 1).

In order to elucidate the changes in the sequence and mechanism of structural distortions, $\text{Rb}_2\text{KGa}_x\text{Sc}_{1-x}\text{F}_6$ solid solutions were studied in [13, 16–20]. Figure 2 depicts the composition–temperature phase diagram of these solid solutions. The temperature dependences of the heat capacity $C_p(T)$ and the interplanar distance d_{440} for compounds with $x \leq 0.6$ exhibit two anomalies associated with the phase transitions from the cubic phase to the tetragonal phase $I4/m$ and then to the monoclinic phase $P12_1/n1$. The entropy change $\Delta S_2/R \sim 0.51$ upon second phase transition agrees well with that obtained for the $I4/m \rightarrow P12_1/n1$ transition in pure

Table 1. Thermodynamic characteristics of the phase transitions in haloid elpasolites with atomic cations

| $A_2B^+B^{3+}X_6$ | Type of distorted structure | System of octahedron rotations | T_i , K | $T^{-1}dT/dp$, GPa $^{-1}$ | $\Delta S/R$ |
|---|-----------------------------|--------------------------------|-----------|-----------------------------|--------------|
| Rb ₂ KFeF ₆ | ? | ? | 170 | 0.78 | 1.88 |
| Rb ₂ KGaF ₆ | ? | ? | 123 | 0.90 | 1.73 |
| Rb ₂ KGa _{0.95} Sc _{0.05} F ₆ | <i>I4/m</i> ? | 00 ϕ | 130 | | |
| | ? | ? | 123.5 | | |
| Rb ₂ KGa _{0.9} Sc _{0.1} F ₆ | ? | ? | 117 | | |
| Rb ₂ KGa _{0.6} Sc _{0.4} F ₆ | <i>I4/m</i> | 00 ϕ | ? | | |
| | <i>P2₁/n</i> | $\psi\phi\phi$ | 102.5 | | |
| Rb ₂ KGa _{0.2} Sc _{0.8} F ₆ | <i>I4/m</i> | 00 ϕ | 218 | | |
| | <i>P2₁/n</i> | $\psi\phi\phi$ | 189 | | |
| Rb ₂ KScF ₆ | <i>I4/m</i> | 00 ϕ | 252 | 0.07 | 0.20 |
| | <i>P2₁/n</i> | $\psi\phi\phi$ | 223 | 0.01 | 0.51 |
| Rb ₂ KInF ₆ | <i>I4/m</i> | 00 ϕ | 283 | 0.07 | 0.18 |
| | <i>P2₁/n</i> | $\psi\phi\phi$ | 264 | 0.03 | 0.59 |
| Rb ₂ KLuF ₆ | <i>I4/m</i> | 00 ϕ | 370 | 0.06 | |
| | <i>P2₁/n</i> | $\psi\phi\phi$ | 366 | 0.05 | 1.05 |
| Rb ₂ KErF ₆ | <i>P2₁/n</i> | $\psi\phi\phi$ | 395 | 0.06 | 0.95 |
| Rb ₂ KHoF ₆ | <i>P2₁/n</i> | $\psi\phi\phi$ | 400 | 0.05 | 1.13 |
| Rb ₂ KTbF ₆ | <i>P2₁/n</i> | $\psi\phi\phi$ | 412 | 0.06 | |

Note: R is the gas constant.

Rb₂KScF₆. The phase transition from the cubic phase to the tetragonal phase in compounds with $x > 0.4$ was not observed by the calorimetric methods due to the small entropy of this transition and a possible smearing of

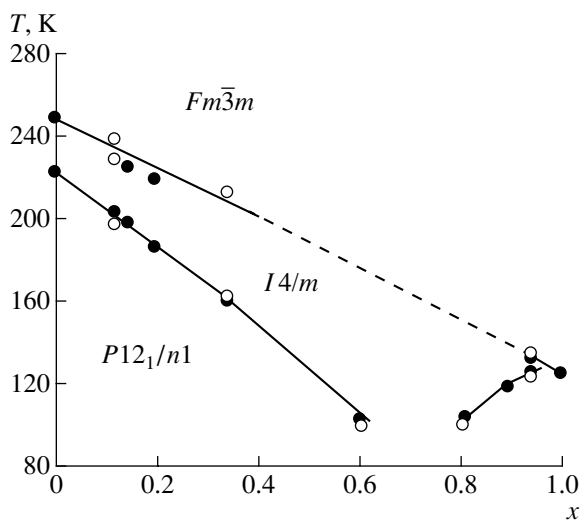


Fig. 2. x - T phase diagram of Rb₂KGa _{x} Sc_{1- x} F₆ elpasolites according to the calorimetric (closed circles) and X-ray diffraction (open circles) data.

anomalies in the heat capacity. Therefore, in the solid solutions (at least, in the range $x = 0$ – 0.6), the sequence of the phase transitions $Fm\bar{3}m \rightarrow I4/m \rightarrow P12_1/n1$ remains unchanged and corresponds to a sequential increase in the rotational distortions induced by the lattice vibrational and X_2^+ modes.

For compounds with $x \geq 0.8$, the temperatures of two phase transitions become close to each other and the intermediate phase disappears at a gallium content close to $x = 1$. The entropy and the quantity dT/dp considerably exceed the values characteristic of rotational transitions and are in good agreement with the results obtained for the Rb₂KFeF₆ compound [12]. The difference in the sequences of structural transformations in compounds with $x < 0.6$ and $x > 0.8$ is confirmed by the X-ray diffraction and elastic neutron scattering data [18, 20].

An analysis of the structural and Raman scattering data for compounds with $x = 0.8$ – 1.0 [15, 21] demonstrates that, among all possible space groups, the groups $I4/m$, $P2_1/m$, and $P112_1/n$ are most probable and consistent with the experimental data. The arising instability of the cubic cell in these compounds can be associated not only with the two purely rotational

modes X_2^+ and Γ_4^+ but also with the low-lying X_2^+ mode [15, 21], which is due to the octahedron rotations and the displacements of Rb ions in holes between octahedra. The interaction of these modes can result in the triggered $Fm\bar{3}m \rightarrow P112_1/n$ and successive $Fm\bar{3}m \rightarrow I4/m \rightarrow P112_1/n$ and $Fm\bar{3}m \rightarrow I4/m \rightarrow P2/m \rightarrow P112_1/n$ phase transitions. These sequences involve the intermediate tetragonal phase $I4/m$, which is observed in other compounds of the solid solutions under consideration.

Therefore, investigations of a number of $Rb_2KB^{3+}F_6$ crystals made it possible to refine the phase diagram and elucidate the influence of the size of the trivalent ion on the sequences and mechanisms of phase transitions.

AMMONIUM CRYOLITES $(NH_4)_3B^{3+}F_6$

In structural investigations of halide compounds, authors often noted that the thermal parameter of halogen atoms in the cubic phase is rather large and, in this respect, proposed different variants of possible orientational disordering of octahedra [11, 22, 23]. However, the refinement of the structural data in the framework of these models did not lead to a substantial decrease in the R factor [11, 23]. Moreover, the thermodynamic data unambiguously indicate that the phase transformations in halide compounds with atomic cations are displacive phase transitions associated with the condensation of lattice modes. This allows us to assume that a considerable anharmonicity of vibrations rather than disordering over several positions is characteristic of fluorine atoms.

A different situation occurs in the case when atomic cations in the elpasolite structure are replaced by tetrahedral ammonium cations. These compounds with small-sized trivalent cations (Ga, Cr, Fe, V) undergo phase transitions from the cubic phase $Fm\bar{3}m$ to the triclinic phase $P\bar{1}$ with a large entropy change, which suggests that the transformations are associated with the ordering processes [24–27]. On the other hand, compounds with large-sized trivalent cations (Sc, In) are characterized by the successive $Fm\bar{3}m \rightarrow P112_1/n \rightarrow I12/m1 \rightarrow P\bar{1}$ phase transitions [28]. The deuteration of ammonium cryolites does not lead to noticeable changes in the thermodynamic parameters, which indicates that hydrogen bonds do not play a significant role in the mechanism of phase transitions [29]. It is worth noting that the total entropy changes for all compounds are close to $R\ln(16)$ irrespective of whether a compound undergoes one phase transition or a sequence of transitions (Table 2). Consequently, these transformations proceed through the order–disorder mechanism.

In the structure under investigation, ionic groups of two types, namely, NH_4 tetrahedra and fluorine octahedra, are involved in ordering. The ammonium tetrahedra located in the holes between octahedra in the cubic phase (position $8c$, CN = 12) are ordered, because their symmetry corresponds to symmetry of the occupied site. The tetrahedra situated at the center of the fluorine octahedra (position $4b$, CN = 6) in the cubic phase can have two possible orientations. The fluorine ions in the cubic lattice with symmetry $Fm\bar{3}m$ in the general case can be distributed over twelve different crystallographic positions. Among them, only two positions, $24e$ and $192l$, satisfy the conditions of a rigid regular octahedron [26]. If the fluorine ions are located at the cubic cell edges (positions $24e$), the octahedra are ordered. When the fluorine ions are distributed over the $192l$ positions, each fluorine octahedron in the cubic phase can have eight equally probable orientations [26]. Complete ordering of the octahedra and tetrahedra should result in an entropy change of $R\ln(16)$, which is in good agreement with the experimental results.

In the case of single phase transitions, for example, in the gallium compound, the octahedra and tetrahedra are ordered simultaneously. This is confirmed by the nuclear magnetic resonance (NMR) data [33]. It was found that the spin–lattice relaxation times of both protons and fluorine ions exhibit jumps upon phase transition, which indicates a change in the character of their motion.

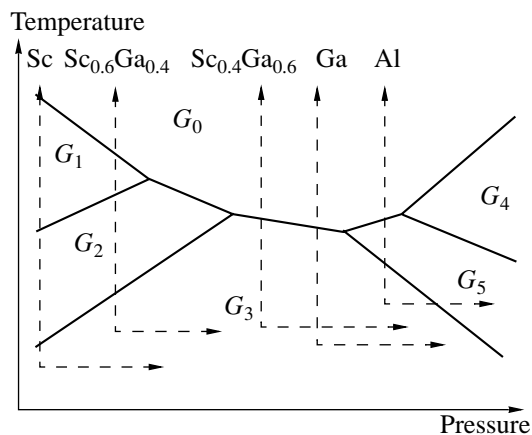
For successive phase transitions, for example, in the scandium cryolite, the first two transitions according to the calorimetric data [$\Delta S_1 = R\ln 8$, $\Delta S_2 = R\ln 2$] can be associated with the order–disorder processes. The third phase transition with a small change in the entropy is the transformation between two completely ordered distorted phases. We could assume that the first and second transitions are due to complete ordering of octahedra and tetrahedra, respectively. However, ordering of the octahedra should necessarily be accompanied by the change in symmetry of the position occupied by the tetrahedra and their forced ordering. Moreover, according to the NMR data [33], the spin–lattice relaxation time of fluorine ions exhibit jumps upon the first and second transitions. On the other hand, the spin–lattice relaxation time of protons considerably changes only upon the first phase transition. It was assumed that the phase transition from the cubic phase is due to complete ordering of the tetrahedra and partial ordering of the octahedra. In the distorted phase, the octahedra can have two equally probable orientations. The second phase transition results in complete ordering of the octahedra.

The analysis of the thermodynamic parameters and the phase diagrams allows us to construct the generalized pressure–temperature (or cell volume–temperature) phase diagram for the entire series of ammonium cryolites (Fig. 3). This diagram illustrates a gradual evolution of the sequences of phase transitions with a

Table 2. Thermodynamic characteristics of the phase transitions in $(\text{NH}_4)_3\text{B}^{3+}\text{F}_6$ ammonium cryolites

| B^{3+} : | | Al | V | Fe | Ga | $\text{Ga}_{0.6}\text{Sc}_{0.4}$ | $\text{Ga}_{0.4}\text{Sc}_{0.6}$ | Sc |
|-----------------------|---------------------------------|---------------------------------|------|------|----------|----------------------------------|----------------------------------|---------------|
| $G_0 \rightarrow G_1$ | $\Delta S/R$ dT/dp , K/GPa | | | | | | -8.2 | 1.63 -16.4 |
| $G_1 \rightarrow G_2$ | $\Delta S/R$ dT/dp , K/GPa | | | | | | 46.4 | 0.81 57.5 |
| $G_2 \rightarrow G_3$ | $\Delta S/R$ dT/dp , K/GPa | | | | | | 65.2 | 0.08 59.9 |
| $G_0 \rightarrow G_2$ | $\Delta S/R$ dT/dp , K/GPa | | | | | | | |
| $G_0 \rightarrow G_3$ | $\Delta S/R$ dT/dp , K/GPa | | 2.99 | 2.77 | 2.76 | 2.60 | | |
| $G_0 \rightarrow G_4$ | $\Delta S/R$ dT/dp , K/GPa | | | | | | | |
| $G_4 \rightarrow G_5$ | $\Delta S/R$ dT/dp , K/GPa | 50.4 ± 1.2 | | | | | | |
| $G_5 \rightarrow G_3$ | $\Delta S/R$ dT/dp , K/GPa | -670 ± 100 | | | | | | |
| $G_0 \rightarrow G_5$ | $\Delta S/R$ dT/dp , K/GPa | 0.5 ± 0.1 -700 ± 100 | | | | | | |
| | | 2.22 ± 0.08 | | | | | | |
| | | -11.8 ± 4 | | | | | | |
| References | | [27, 30] | [25] | [26] | [31, 32] | [32] | [32] | [31, 32] |

variation in the parameters. The scandium and gallium compounds have the following distorted phases with symmetries determined in [28, 34]: $G_1(P12_1/n1, Z=2)$, $G_2(I12/m1, Z=16)$, and $G_3(I\bar{1}, Z=16)$. Symmetries of the high-pressure phases G_4 and G_5 in the gallium cryolite still remain unknown.

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

AMMONIUM ELPASOLITES

In order to elucidate the role played by the ammonium ions occupying different crystallographic positions, two types of ammonium elpasolites were examined in our earlier works [35, 36]. In $\text{Cs}_2\text{NH}_4\text{GaF}_6$, the NH_4 ions are located at the cubic cell edges at the centers of fluorine octahedra. In the $(\text{NH}_4)_2\text{KGaF}_6$ compound, the ammonium ions occupy the holes between octahedra.

The $\text{Cs}_2\text{NH}_4\text{GaF}_6$ elpasolite undergoes one phase transition with the large entropy change $R\ln(8)$ [36]. No high-pressure phases or triple points were found in the p - T phase diagram [36]. We believe that, like the transitions in ammonium cryolites, this transition is accompanied by complete ordering of the NH_4 tetrahedra and partial ordering of the octahedra. The complete ordering of the octahedra can occur at temperatures below the liquid-nitrogen temperature. Thus, a comparison with the $(\text{NH}_4)_2\text{NH}_4\text{GaF}_6$ compound shows that the presence of the Cs^+ spherical cation in the hole between octahedra renders the crystal structure more rigid and stable. This can be judged from the lower temperature of the transition from the cubic phase (162 K) in $\text{Cs}_2\text{NH}_4\text{GaF}_6$ and the absence of splitting of the phase boundary under pressure.

The assumption regarding the occurrence of the second phase transition is supported by the data obtained for the $\text{Cs}_2\text{NH}_4\text{ScF}_6$ elpasolite. An increase in the size of the B^{3+} ion leads not only to an increase in the stability temperature of the cubic phase ($T_1 = 285$ K) but also to the second phase transition ($T_2 = 195$ K).

A quite different situation is observed for the $(\text{NH}_4)_2\text{KGaF}_6$ compound characterized by the sequence of two transformations [35]. The entropy change ($\Delta S = 0.12R$) upon phase transition from the cubic phase uniquely indicates that this is the displacive phase transition associated with the condensation of lattice modes. According to the structural data, the first distorted phase has symmetry $I4/m$. This symmetry is identical to symmetry of the distorted phase in compounds with atomic cations (see $\text{Rb}_2\text{KB}^{3+}\text{F}_6$). In this case, the fluorine octahedra are ordered in the cubic phase and the phase transition is due to the condensation of the Γ_4^+ mode.

The large entropy change ($\Delta S = 1.8R$) upon the second phase transition suggests that this transformation proceeds through the order–disorder mechanism. When considering the ammonium cryolites, we assumed that the NH_4 ions in the holes between octahedra are ordered completely. However, symmetry $Fm\bar{3}m$ is also retained if the hydrogen ion is shifted from the three-fold axis and the nitrogen–hydrogen bonds are directed toward fluorine ions. In this situation, the tetrahedron in the cubic phase has three equally probable orientations. This disordering is most pronounced in the ammonium antiferroite with a similar structure [37]. For completely ordered tetrahedra, the entropy change should be equal to $2R\ln(3)$. This value agrees well with the experimentally determined entropy change ΔS . The above model of structural distortions is confirmed by the NMR data [38]. The spin–lattice relaxation time of fluorine ions remains unchanged upon both the first and second transitions. The spin–lattice relaxation time of protons substantially changes only upon the second phase transition.

The $(\text{NH}_4)_2\text{KScF}_6$ elpasolite is characterized by appreciably higher temperatures of the phase transitions and a considerably narrower temperature range of the stability of the tetragonal phase ($T_1 = 367$ K, $T_2 = 361$ K). However, as follows from the data on the entropy change, the structural transformations occur through the same mechanism.

Therefore, the analysis of the ammonium compounds allows us to make the inference that the replacement of the atomic cations at the center of the fluorine octahedra by the NH_4 tetrahedra results in orientational disordering of the octahedra and pronounced order–disorder phase transitions. The presence of the ammonium ions in the holes between octahedra does not affect the character of octahedron motion, and the phase transformations are the displacive transitions associated with

Table 3. Strengths μ_A and μ_B of interatomic bonds and the temperatures T_1 of transitions from the cubic phase of fluoride compounds

| | $B^{3+} = \text{Ga}^{3+}$ | | | $B^{3+} = \text{Sc}^{3+}$ | | |
|--|---------------------------|-------------|-----------|---------------------------|-------------|-----------|
| | μ_A , % | μ_B , % | T_1 , K | μ_A , % | μ_B , % | T_1 , K |
| $\text{Cs}_2\text{NH}_4B^{3+}\text{F}_6$ | 4.7 | 10.3 | 162 | 2.4 | 10.4 | 285 |
| $(\text{NH}_4)_2\text{NH}_4B^{3+}\text{F}_6$ | 0.4 | 11.5 | 250 | –2.0 | 11.5 | 330 |
| $(\text{NH}_4)_2\text{KB}^{3+}\text{F}_6$ | 2.0 | 12.4 | 280 | –0.1 | 13.9 | 367 |
| $\text{Rb}_2\text{KB}^{3+}\text{F}_6$ | 4.3 | 13 | 126 | 1.9 | 13.0 | 280 |
| $\text{Cs}_2\text{KB}^{3+}\text{F}_6$ | 7.0 | 11.7 | <77 ? | 4.4 | 11.3 | <77 ? |

the condensation of soft lattice modes. The ammonium tetrahedra are disordered and undergo ordering at lower temperatures.

ON THE INTERATOMIC BOND STRENGTH

We studied four series of compounds with the elpasolite and cryolite structures and revealed that different sequences and mechanisms of phase transitions can be observed in these compounds depending on the unit cell volume and the cation shape. However, the “closed” elpasolite series $(\text{NH}_4)_2\text{NH}_4\text{—Cs}_2\text{NH}_4\text{—Cs}_2\text{K—Rb}_2\text{K—}(\text{NH}_4)_2\text{K—}(\text{NH}_4)_2\text{NH}_4$, which is formed by sequential replacements of cations at a constant size of the $B^{3+}\text{F}_6$ octahedron, involves compounds with a Cs_2K combination of cations that are absent among the objects under consideration. In the studied Cs_2KGaF_6 and Cs_2KScF_6 crystals, no phase transitions were found at temperatures down to 77 K. This circumstance and the stability of the cubic phase can be explained in terms of the hypothesis of interatomic bond strength [39].

According to this hypothesis, the stability of the initial cubic phase is determined by the ratio between the ion sizes and the lattice parameter a_0 , i.e., by the ion bond strength in the $A^+\text{—F}^-$ and $B^{3+}\text{—F}^- \text{—} B^+\text{—F}^- \text{—} B^{3+}$ chains. The ratios $\mu_A = (a'_p - a_0)/a_p$ and $\mu_B = (a_p - a_0)/a_p$, where $a_p = 2(R_{B^+} + 2R_F + R_{B^{3+}})$ and $a'_p = 2\sqrt{2}(R_{A^+} + R_F)$, can serve as the quantitative measures of the strength. An increase in the μ_B value is equivalent to an increase in the repulsion energy in the crystal potential and leads to an increase in the anisotropy of motion of F atoms and, hence, to a decrease in the stability of the initial phase. An increase in the μ_A value causes a hindrance to the octahedron rotation and results in an increase in the stability of the undistorted lattice.

The validity of this hypothesis for the closed series of crystals can be illustrated using the examples presented in Table 3. An increase in the size of the $B^{3+}F_6$ octahedron upon replacement of Ga by Sc in all the cases primarily leads to a substantial change in the μ_A value and, correspondingly, to an increase in the stability temperature of the cubic phase. From analyzing the structural data and the parameters of the phase transitions in compounds with rare-earth elements as the B^{3+} cation, we established that no phase transitions should occur in Ga and Sc compounds for the Cs_2K combination of cations. It can be seen from Table 3 that the predicted absence of phase transitions is associated with the considerable difference in the μ_A values for these crystals. An increase in the temperature T_1 is also observed in the series of the compounds formed upon replacement of the A cation: $Cs_2K-Rb_2K-(NH_4)_2K$.

Thus, the hypothesis of interatomic bond strength appeared to be fruitful for describing not only the displacive phase transitions but also the order-disorder transitions. In ammonium cryolites, an increase in the unit cell size is attended by a substantial decrease in the μ_A value and an increase in the μ_B value, which results in an increase in the phase transition temperatures [32]. Furthermore, these data demonstrate that, in ammonium cryolites with successive transformations, the transition from the cubic phase is predominantly associated with ordering of octahedral ionic groups. This ordering upon order-disorder phase transition can also be treated as octahedron rotation but through a considerably larger angle. However, when the structural distortions cannot be described by octahedron rotations, the hypothesis is invalid, which was shown earlier for cryolites with atomic cations [40].

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REFERENCES

1. B. V. Beznosikov and K. S. Aleksandrov, Preprint No. IFSO-753F, IF SO RAN (Inst. of Physics, Siberian Division, Russian Academy of Sciences, Krasnoyarsk, 1994).
2. K. S. Aleksandrov and B. V. Beznosikov, *Perovskite-Like Crystals* (Nauka, Novosibirsk, 1997).
3. V. I. Zinenko and S. V. Misyul', *Possible Phase Transitions in Crystals with Space Group O_h^3* , Available from VINITI, No. 313-78 (Moscow, 1978).
4. G. P. O'Leary and R. G. Wheeler, *Phys. Rev. B* **1**, 4409 (1970).
5. K. S. Aleksandrov and S. V. Misyul', *Kristallografiya* **26** (5), 1074 (1981) [*Sov. Phys. Crystallogr.* **26**, 612 (1981)].
6. S. V. Misyul', *Kristallografiya* **29** (5), 941 (1984) [*Sov. Phys. Crystallogr.* **29**, 554 (1984)].
7. R. Comes, M. Lambert, and A. Guinier, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **26** (2), 244 (1970).
8. J.-M. Kiat, G. Baldinozzi, M. Dunlop, *et al.*, *J. Phys.: Condens. Matter* **12**, 8411 (2000).
9. Ch. Malibert, B. Dkhil, M. Dunlop, *et al.*, *Ferroelectrics* **235** (1), 97 (1999).
10. I. N. Flerov, M. V. Gorev, K. S. Aleksandrov, *et al.*, *Mater. Sci. Eng. R* **24** (3), 81 (1998).
11. H. Faget, J. Grannec, A. Tressaud, *et al.*, *Eur. J. Solid State Inorg. Chem.* **33** (9), 893 (1996).
12. M. V. Gorev, I. N. Flerov, V. N. Voronov, *et al.*, *Fiz. Tverd. Tela (St. Petersburg)* **36** (4), 1121 (1994) [*Phys. Solid State* **36**, 609 (1994)].
13. J. M. Dance, J. Grannec, A. Tressaud, *et al.*, *Phys. Status Solidi B* **173** (2), 579 (1992).
14. C. Marco de Lucas, F. Rodriguez, J. M. Dance, *et al.*, *J. Lumin.* **48/49** (2), 553 (1991).
15. A. Tressaud, S. Khairoun, J.-P. Chaminade, and M. Couzi, *Phys. Status Solidi A* **98** (2), 417 (1986).
16. M. V. Gorev, A. F. Bovina, G. V. Bondarenko, *et al.*, *Fiz. Tverd. Tela (St. Petersburg)* **37** (3), 819 (1995) [*Phys. Solid State* **37**, 444 (1995)].
17. M. V. Gorev, I. N. Flerov, A. Tressaud, and J. Grannec, *Fiz. Tverd. Tela (St. Petersburg)* **39** (10), 1844 (1997) [*Phys. Solid State* **39**, 1647 (1997)].
18. M. V. Gorev, I. N. Flerov, A. F. Bovina, *et al.*, *Izv. Akad. Nauk, Ser. Fiz.* **62** (4), 1532 (1998).
19. M. V. Gorev, I. N. Flerov, A. Tressaud, *et al.*, *BENSC Experimental Reports 1995* (Hahn-Meitner Inst., Berlin, 1996), p. 180.
20. M. V. Gorev, I. N. Flerov, A. Tressaud, *et al.*, *Ferroelectr. Lett. Sect.* **22** (5-6), 127 (1997).
21. M. Couzi, S. Khairoun, and A. Tressaud, *Phys. Status Solidi B* **98** (1), 423 (1986).
22. R. Haegle, W. Verscharen, and D. Babel, *Z. Naturforsch.* **30** (3), 462 (1975).
23. W. Massa, D. Babel, M. Eppele, and W. Rudorff, *Rev. Chim. Miner.* **23** (4-5), 508 (1986).
24. A. Tressaud, S. Khairoun, L. Rabardel, *et al.*, *Phys. Status Solidi A* **96**, 407 (1986).
25. K. Kobayashi, T. Matsuo, and H. Suga, *Solid State Commun.* **53** (8), 719 (1985).
26. K. Moriya, T. Matsuo, H. Suga, and S. Seki, *Bull. Chem. Soc. Jpn.* **50** (8), 1920 (1977).
27. K. Moriya, T. Matsuo, H. Suga, and S. Seki, *Bull. Chem. Soc. Jpn.* **52** (11), 3152 (1979).
28. M. V. Gorev, I. N. Flerov, S. V. Mel'nikova, *et al.*, *Izv. Akad. Nauk, Ser. Fiz.* **64** (6), 1104 (2000).
29. I. N. Flerov, M. V. Gorev, M. L. Afanas'ev, and T. V. Ushakova, *Fiz. Tverd. Tela (St. Petersburg)* **44** (10), 1870 (2002) [*Phys. Solid State* **44**, 1961 (2002)].
30. M. V. Gorev, I. N. Flerov, A. Tressaud, and E. Durand, *J. Phys.: Condens. Matter* **14** (25), 6447 (2002).
31. M. V. Gorev, I. N. Flerov, and A. Tressaud, *J. Phys.: Condens. Matter* **11**, 7493 (1999).

32. I. N. Flerov, M. V. Gorev, and T. V. Ushakova, *Fiz. Tverd. Tela (St. Petersburg)* **41** (3), 523 (1999) [*Phys. Solid State* **41**, 468 (1999)].
33. A. Sasaki, Y. Furukawa, and D. Nakamura, *Ber. Bunsenges. Phys. Chem.* **93**, 1142 (1989).
34. S. V. Mel'nikova, S. V. Misyul', A. F. Bovina, and M. L. Afanas'ev, *Fiz. Tverd. Tela (St. Petersburg)* **43** (8), 1533 (2001) [*Phys. Solid State* **43**, 1594 (2001)].
35. I. N. Flerov, M. V. Gorev, M. L. Afanas'ev, and T. V. Ushakova, *Fiz. Tverd. Tela (St. Petersburg)* **43** (12), 2209 (2001) [*Phys. Solid State* **43**, 2301 (2001)].
36. M. V. Gorev, I. N. Flerov, A. Tressaud, *et al.*, *Solid State Sci.* **4** (1), 15 (2002).
37. E. O. Schlemper, W. C. Hamilton, and J. J. Rush, *J. Chem. Phys.* **44** (5), 2499 (1966).
38. K. Hirokawa and Y. Furukawa, *J. Phys. Chem. Solids* **49** (9), 1047 (1988).
39. K. S. Aleksandrov, A. T. Anistratov, B. V. Beznosikov, and N. V. Fedoseeva, *Phase Transitions in Crystals of ABX₃ Halide Compounds* (Nauka, Novosibirsk, 1981).
40. I. N. Flerov, M. V. Gorev, V. N. Voronov, and A. F. Bovina, *Fiz. Tverd. Tela (St. Petersburg)* **38**, 2203 (1996) [*Phys. Solid State* **38**, 1213 (1996)].

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