
LATTICE DYNAMICS AND PHASE TRANSITIONS

Entropy and the Mechanism of Phase Transitions in Elpasolites

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Abstract—The phase transitions in series of crystals with the general formulas $A_2BB'X_6$ ($X = F, Cl, Br, \text{ or } CN$) and $Pb_2BB'O_6$ that belong to the elpasolite family (space group $Fm\bar{3}m$) are analyzed. The influence of the size and the shape of cations and anions on the entropy and the mechanism of structural distortions is discussed.
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1. INTRODUCTION

Among perovskite-like compounds, the elpasolite family is the 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], more than 350 compounds with a similar structure were known until recently, and, as follows from crystal chemical analysis, more than 1500 new elpasolites can be obtained based on halides alone. In the initial phase, crystals of this family have a cubic symmetry with the space group $Fm\bar{3}m-O_h^5$ ($z = 4$). Unlike the simple perovskites ABX_3 in which all octahedra are equivalent, elpasolites (also referred to as ordered perovskites) contain two types of ionic groups (BX_6 and $B'X_6$) alternating along three fourfold axes. Therefore, an elpasolite cubic cell can be treated as a perovskite cell with twice 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.

As was noted in [2], the most pronounced feature of the perovskite structure is that its topology (i.e., an ideal atomic arrangement) is thermodynamically extremely stable, whereas a real crystal structure (i.e., an actual atomic arrangement) appears very unstable. This statement is likely true for all perovskite-like crystals or, at least, for those with a three-dimensional crystal framework. It is because of the instability of real crystal structures that these crystals can undergo structural phase transitions.

Crystal lattice distortions caused by structural phase transitions are often considered in the framework of two limiting mechanisms, namely, the displacive-type and order–disorder mechanisms. These mechanisms can be most adequately defined as follows. In the case of displacements, the instability arises from long-range cooperative interactions and brings about local distortions, and, in the case of order–disorder, the local distortions stem from local instabilities [3]. As a rule, the

features characteristic of both mechanisms can manifest themselves in one form or another in the behavior of different physical properties of the same crystal. In this respect, the question as to which mechanism plays a leading part in each special case is of particular importance.

Before proceeding to phase transitions in elpasolites (cryolites), we discuss the results obtained for ferroelectrics [3] and ferroelastics [4, 5] with a perovskite structure ($Pm\bar{3}m$). The interpretation of phase transitions in these groups of crystals as the displacive-type transitions was supported by the following experimental results. Compounds of the first group were characterized by the soft modes in the initial and distorted phases and large Curie constants. Compounds of the second group, apart from the soft modes, exhibited insignificant changes in the entropy. At the same time, the experimental data obtained for many compounds of both groups were interpreted as the evidence for the existence of local structural distortions above the phase transition temperature: diffuse x-ray scattering, the central peak in the light scattering spectra, the birefringence, and the excess heat capacity. These findings gave impetus to the development of different theoretical models. For example, according to [6], the cooperative motion of ions in the structure is associated with the possible transition (“crossover”) from the displacive-type mechanism to the order–disorder mechanism at a certain temperature above the phase transition point T_0 . This is caused by a critical increase in the correlation length as the T_0 temperature is approached, resulting in the formation and growth of dynamic clusters—small groups of bound atoms, which are displaced from high-symmetry equilibrium positions in the same direction.

The results of structure refinement within the cluster and (or) anharmonic phonon models were compared for a number of ferroelastic perovskites $SrTiO_3$, $KMnF_3$, $RbCaF_3$, $CsPbCl_3$, and $CsPbBr_3$. Hutton *et al.*

[4, 5] analyzed the precision structural data in the framework of different models and made the following conclusions.

(1) A simple model with a multiple-well potential for X atoms inadequately describes the initial structure: the R factor (15%) is very large even as compared to the harmonic model ($R = 7\%$).

(2) Allowance made for the anharmonicity of atomic vibrations leads to a substantial decrease in the R factor (4%).

(3) It is difficult to decide between two models, namely, the cluster and anharmonic phonon models, when the predicted cluster distribution function does not exhibit a pronounced behavior inherent in the order-disorder systems.

Armstrong [7] analyzed the NMR and NQR data obtained for certain of the aforementioned perovskites and arrived at rather contradictory results. On the one hand, the author believed that these data confirm the crossover above T_0 from the behavior that corresponds to the displacive-type mechanism to the behavior associated with the formation of dynamic clusters in the structure. On the other hand, it was noted that the experimental response of the system is very complex due to the presence of defects in the crystals, so that the experimental data cannot provide a sufficiently reliable corroboration of the crossover phenomenon theory.

Unfortunately, the data on changes in the entropy upon phase transitions were not used in analyzing the results obtained in [4, 5, 7]. It should be mentioned that this change in the entropy is rather small for many perovskite-like crystals studied in these works.

In the present work, we analyzed the data on the structure, phonon spectra, and physical properties of elpasolites (cryolites) and discussed the possible mechanisms of structural phase transitions. Consideration was given to several series of compounds whose composition involves different X atoms (F, Cl, Br, O, and CN). The change in the entropy upon phase transition was used as a major characteristic. Since the entropy is a fundamental quantity and can be determined experimentally, the study of the interrelation between the entropy and specific disordering phenomena is of crucial importance.

2. HALOID ELPASOLITES WITH ATOMIC IONS

According to crystal chemical analysis [1], the elpasolite structure can be realized in halides containing fluorine, chlorine, and bromine.

As a rule, the refinement of the initial cubic structure of halogen-containing crystals is performed within one or, in the best case, two approximations without consideration of alternative models and, rather frequently, under the assumption that halogen atoms occupy the $24e$ position (on the edge of a cubic cell). As can be seen from Table 1, the thermal parameters substantially differ for different elpasolites and the same

crystal studied by different authors. Of special interest are the results obtained in the theoretical treatment of structural models that account for the anisotropy and the anharmonicity of vibrations of halogen atoms and their possible arrangement in other crystallographic positions. The inclusion of anisotropic thermal vibrations led to a decrease in the R factor in K_2NaCrF_6 and K_2NaFeF_6 crystals [12]. The anisotropy parameter B_{33}/B_{11} for the Rb_2KFeF_6 crystal, which undergoes a phase transition at $T_0 \approx 170$ K, appears to be two or three times larger than that for the Rb_2NaFeF_6 crystal [10, 11], in which, according to the analysis of interatomic bond strengths [8], no phase transition occurs down to 0 K.

Makarova *et al.* [9] thoroughly examined the temperature dependence of the thermal vibration amplitudes for the $Cs_2NaNdCl_6$ elpasolite. It was shown that the thermal ellipsoids for Cs, Na, and Nd atoms are spherical, and only the vibrations of chlorine atoms are characterized by an appreciable anisotropy and anharmonicity. Note that both the anisotropy and the anharmonicity for elpasolite structures turned out to be more pronounced than those for perovskites [8]. These results indicate that only halogen ions are crucial; i.e., they are responsible for the lattice instability which leads to the phase transition.

Attempts were made to refine the structure of the Rb_2KScF_6 elpasolite in the isotropic approximation when fluorine atoms occupy one of the crystallographic positions $24e$, $96j$, and $192l$ [8]. It follows from Table 1 that the disordering of fluorine atoms over four ($96j$) or eight ($192l$) positions results in a substantial decrease in the thermal parameter B_{iso} compared to that for the $24e$ position. Since the thermal parameters and the reliability factors are very close for both variants of disordering, it is rather difficult to choose a particular variant. In our opinion, these findings suggest that a considerable anharmonicity of vibrations is more likely to be characteristic of fluorine atoms than the disordering over several positions.

A substantial number of haloid elpasolites either undergo structural phase transitions (whose nature is usually ferroelastic) or exist in a distorted phase up to the melting temperature. According to the group-theoretic analysis [14], diverse distortions of the $Fm\bar{3}m$ structure become possible due to octahedron rotations and (or) polar displacements of atoms.

Among chlorides and bromides, series of crystals with the general formula $Cs_2NaM^{3+}Cl(Br)_6$ that undergo one phase transition to the tetragonal phase $I4/m$ have been studied most extensively [8]. In terms of the model proposed in [14], the corresponding structural distortions can be attributed to the (00ϕ) rotations of octahedra about one of the fourfold axes of the cubic cell.

Fluoro-elpasolites exhibit a greater diversity of the A_2B combinations of atoms. As a result, these com-

Table 1. Thermal parameters for halogen atoms in different crystallographic positions of the cubic phase in the isotropic (B_{iso}) and anisotropic (B_{11}/B_{33}) approximations

Compound	24e			96j	192l	T_1 , K	Reference
	$B_{\text{iso}}, \text{\AA}^2$	$(B_{11}/B_{33})_{\text{h}}$	$(B_{11}/B_{33})_{\text{anh}}$	$B_{\text{iso}}, \text{\AA}^2$	$B_{\text{iso}}, \text{\AA}^2$		
$\text{Cs}_2\text{NaPrCl}_6$	2.2 ($R = 4.4\%$)					153	[8]
$\text{Cs}_2\text{NaNdCl}_6$		4.3 (2.9%)	6.5 (2.8%)			132	[9]
$\text{Rb}_2\text{NaHoF}_6$	1.2 (5.8%)					172	[8]
$\text{Rb}_2\text{NaFeF}_6$		2.6 (4%)				<0	[10]
		1.3 (1.3%)				<0	[11]
Rb_2KFeF_6		5.3 (4%)				170	[10]
		4.4 (1.9%)				170	[11]
K_2NaCrF_6		3.2 (2.1%)				?	[11]
	1.95 (13%)	5.6 (12.5%)				?	[12]
K_2NaFeF_6	1.84 (5.9%)	16 (4.6%)				?	[12]
Rb_2KScF_6	6.2 (6.4%)			1.8 (5.0%)	1.8 (5.5%)	252	[8]
$(\text{Nb}_4)_3\text{GaF}_6$					1.8 (12%)	250	[13]

Note: The reliability factors R are given in parentheses. T_1 is the temperature of the phase transition from the cubic phase. The subscripts "h" and "anh" refer to the harmonic and anharmonic models, respectively.

pounds can undergo the single $Fm\bar{3}m-I4/m$ (Rb_2Na and Cs_2K), successive $Fm\bar{3}m-I4/m-P2_1/n$ (Rb_2K) and $Fm\bar{3}m-I4/m-C2/m-P2_1/n$ (Cs_2Rb), and flip-flop $Fm\bar{3}m-P2_1/n$ (Rb_2K) phase transitions [8].

As follows from the group-theoretic analysis of possible distortions of the elpasolite structure [14], the $Fm\bar{3}m-I4/m$ phase transition is associated with the soft mode at the center of the Brillouin zone. Actually, the soft mode belonging to the Γ point was found in studies of inelastic neutron scattering in the cubic phase of $\text{Cs}_2\text{NaBiCl}_6$ [15] and $\text{Cs}_2\text{NaTmBr}_6$ [16] crystals. Let us now dwell on the characteristic features of the cubic phase in the aforementioned elpasolites. First, we note the quasi-two-dimensional motion of octahedra, which

can be explained by the fact that a rotation of one octahedron about a particular cubic axis results in the distortion of the whole octahedron layer orthogonal to this axis. Second, a substantial damping of phonons was revealed at temperatures 10–20 K below the T_0 temperature, which made unambiguous determination of the soft mode frequency impossible in this temperature range. The temperature determined by the extrapolation of the linear dependence $\omega^2(T)$ to $\omega^2 = 0$ turned out to be considerably below the phase transition temperature obtained in other experiments. According to Bührer and Güdel [16], this discrepancy is caused by the deviation of the $\omega^2(T)$ function from the linear behavior in the vicinity of T_0 due to the interaction between acoustic and optical modes with the same symmetry. However, it should be noted that the afore-

Table 2. Thermodynamic characteristics of phase transitions in haloid elpasolites with atomic cations [8]

$A_2B^+B^{3+}X_6$	Type of distorted structure	SR	T_i , K	$T^{-1}dT/dp$, GPa^{-1}	$\Delta S/R$
$\text{Cs}_2\text{NaBiCl}_6$	$I4/m$	00 ϕ	100	0.28	0.20
$\text{Cs}_2\text{NaNdCl}_6$	$I4/m$	00 ϕ	132	0.33	0.23
$\text{Cs}_2\text{NaPrCl}_6$	$I4/m$	00 ϕ	153	0.32	0.21
$\text{Cs}_2\text{NaLaCl}_6$	$I4/m$	00 ϕ	210	0.26	0.26
$\text{Cs}_2\text{NaTmBr}_6$	$I4/m$	00 ϕ	102	0.32	0.21
$\text{Cs}_2\text{NaYBr}_6$	$I4/m$	00 ϕ	139	0.31	0.18
$\text{Rb}_2\text{NaDyF}_6$	$I4/m$	00 ϕ	166		0.20
Cs_2KDyF_6	$I4/m$	00 ϕ	160		0.20
$\text{Cs}_2\text{RbDyF}_6$	$I4/m$	00 ϕ	251	0.06	0.20
	$C2/m$	0 $\phi\phi$	205	-0.05	} 0.47
	$P2_1/n$	$\psi\phi\phi$	196	-0.09	
Rb_2KFeF_6	?	?	170	0.78	
Rb_2KGaF_6	?	?	123	0.90	1.73
Rb_2KScF_6	$I4/m$	00 ϕ	252	0.07	0.20
	$P2_1/n$	$\psi\phi\phi$	223	0.01	0.51
Rb_2KInF_6	$I4/m$	00 ϕ	283	0.07	0.18
	$P2_1/n$	$\psi\phi\phi$	264	0.03	0.59
Rb_2KLuF_6	$I4/m$	00 ϕ	370	0.06	} 1.05
	$P2_1/n$	$\psi\phi\phi$	366	0.05	
Rb_2KErF_6	$P2_1/n$	$\psi\phi\phi$	395	0.06	0.95
Rb_2KHoF_6	$P2_1/n$	$\psi\phi\phi$	400	0.05	1.13
Rb_2KTbF_6	$P2_1/n$	$\psi\phi\phi$	412	0.06	

Note: SR denotes the system of octahedron rotations, and R is the gas constant.

mentioned elpasolites undergo the first-order phase transition, and this is primarily the reason why the T_c temperature (at which $\omega^2(T) = 0$) does not coincide with the phase transition temperature T_0 . At the same time, the $T_0 - T_c$ values determined from the neutron scattering [16] and calorimetric [17, 18] data differ significantly and, hence, the assumption that the $\omega^2(T)$ function deviates from the linearity near the T_0 temperature holds some validity.

The phonon spectra of fluoro-elpasolites were studied in the tetragonal phase of Rb_2KScF_6 by Raman spectroscopy and in the cubic phase of Rb_2KHoF_6 by neutron scattering [8]. However, the soft vibrational modes were found in none of the crystals. Furthermore, a diffuse scattering peak was observed for the cubic phase of Rb_2KHoF_6 . These data, together with the above results of the structural investigations of Rb_2KScF_6 (in which the best results were obtained in the case when fluorine atoms in the cubic phase were disordered over four or eight positions), allowed us to assume that the mechanism of phase transitions in flu-

orine-containing crystals has specific features as compared to chloride and bromide crystals.

Now, we consider how the phase transitions in haloid elpasolites can be characterized according to the calorimetric data. As follows from the heat capacity measurements in bromides ($M^{3+} = \text{Y}$ and Tm) [18] and chlorides ($M^{3+} = \text{Bi}$, Nd , Pr , and La) [17], the $Fm\bar{3}m-I4/m$ transition is the first-order phase transformation close to the tricritical point. An increase in the size of the M^{3+} ion from crystal to crystal leads to an increase in the temperature of the phase transition and the degree of its closeness to the tricritical point. It was also found that the entropy change upon the phase transition does not depend on the size of M^{3+} and X^- ions and has a relatively small value: $\Delta S = (0.18-0.26)R$ (Table 2).

Unlike chlorides and bromides, the $Fm\bar{3}m-I4/m$ transition in all the fluorides studied is the second-order phase transformation close to the tricritical point. One of the possible reasons for the difference in the type of phase transitions in these groups of elpasolites is the

different scale of effects caused by the coupling between the order parameter and the deformation, which is determined by the reduced shift in the phase transition temperature under the hydrostatic pressure $(dT_0/dp)T_0^{-1}$ [8]. This quantity in crystals with $X = \text{Cl}$ and Br is almost five times larger than that in fluoride crystals (Table 2). It should be mentioned that the reduced shift in the temperature of the $I4/m-P2_1/n$ phase transition increases with an increase in the size of the M^{3+} ion and, for the compound with $M^{3+} = \text{Lu}^{3+}$, becomes as large as the shift typical of the $Fm\bar{3}m-P2_1/n$ flip-flop transition. At the same time, the entropy changes upon the $Fm\bar{3}m-I4m$ phase transition in fluorides fall in the range of entropy changes that are characteristic of chlorides and bromides (Table 2). Consequently, the entropy $\Delta S = (0.22 \pm 0.04)R$ (which can more likely be treated as typical of the displacive phase transition) could be considered as corresponding to one vibrational degree of freedom due to rotations of octahedral ionic groups in the elpasolite structure. Indeed, even in the case when three phase transitions associated with the successive rotations of octahedra about three axes of the cubic phase occur in $\text{Cs}_2\text{RbDyF}_6$ (Table 2), the total entropy change is equal to the sum of the entropies corresponding to the simple rotations $\Sigma\Delta S_i \approx 0.67R \approx 3 \times 0.22R$ [8].

However, the “universality” of the entropy change is not necessarily observed in haloid elpasolites. Examples are provided by a number of $\text{Rb}_2\text{KM}^{3+}\text{F}_6$ crystals (Table 2) [8]. Unfortunately, the space group of the distorted phase is unknown, and, hence, it is difficult to assign the considerable entropy change $\Delta S = R\ln 6 = 1.79R$ to particular critical ions in compounds with $M^{3+} = \text{Ga}$ and Fe (Table 2). It can only be stated that this value with a high probability corresponds to ordering processes in the structure. This assumption is supported by the data obtained by Massa *et al.* [11], who did not rule out that fluorine ions in the $Fm\bar{3}m$ phase can occupy four positions. An increase in the size of M^{3+} ions (and, correspondingly, the unit cell parameter a_0) leads to the successive $(000)-(00\phi)-(\psi\phi\phi)$ ($M^{3+} = \text{Sc}$, In , and Lu) and, then, flip-flop $(000)-(\psi\phi\phi)$ ($M^{3+} = \text{Er}$, Ho , and Tb) phase transitions with the resulting monoclinic distortion owing to a superposition of octahedra rotations. An increase in the a_0 parameter in a series of $\text{Rb}_2\text{KM}^{3+}\text{F}_6$ crystals is accompanied by a change in the bond strength which causes an increase in the anisotropy (and anharmonicity) of atomic vibrations of fluorine [8]. In turn, this should bring about an increase in the entropy of the corresponding phase transitions [19]. Actually, the quantity $\Sigma\Delta S = \Delta S_1 + \Delta S_2$ increases from crystal to crystal according to the increase in the anharmonicity parameter $\langle x \rangle^2/a_0^2$ of atomic vibrations of fluorine, where $\langle x \rangle$ is the mean displacement of critical atoms [8]. However, even the maximum experimental

value $\Sigma\Delta S = 1.13R$ (for Rb_2KHoF_6) appeared to be less than the entropy $\Sigma\Delta S = 1.39R = R\ln 4$ which would be observed for the phase transition associated with a partial ordering of fluorine ions occupying eight and two positions in the $Fm\bar{3}m$ and $P12_1/n1$ phases, respectively [8]. At the same time, it is not improbable that the last phase transition can take place in $\text{Rb}_2\text{KM}^{3+}\text{F}_6$ elpasolites with a further increase in the size of M^{3+} ions and, correspondingly, in the anharmonicity parameter (for example, at $M^{3+} = \text{La}^{3+}$). Thus, the series of crystals under consideration can likely provide an example of the possible change in the mechanism of the phase transition from the displacive type to the order-disorder type due to an increase in the anharmonicity of the vibrations of critical ions.

3. HALOID ELPASOLITES AND CRYOLITES WITH MOLECULAR CATIONS

There is another way to affect the vibrations of critical fluorine ions and (or) their position in the structure of the initial cubic phase and, hence, the phase transition mechanism. The elpasolite (cryolite) structure is retained when the spherical atomic cations of potassium and (or) rubidium in $\text{Rb}_2\text{KM}^{3+}\text{F}_6$ crystals are replaced by the tetrahedral ammonium ions [8]. A number of substituted compounds, such as $(\text{NH}_4)_3\text{M}^{3+}\text{F}_6$ ($M^{3+} = \text{Al}$, Ga , Cr , V , Fe , Sc , and In), $(\text{NH}_4)_3\text{KM}^{3+}\text{F}_6$ ($M^{3+} = \text{Al}$ and Fe), and $\text{Cs}_2(\text{NH}_4)\text{FeF}_6$, undergo phase transitions (Table 3) [20–22]. Unfortunately, the data on ammonium elpasolites are insufficient for detailed

Table 3. Thermodynamic characteristics of phase transitions in fluorine-containing cryolites and elpasolites with ammonium cations [8, 20–23]

Compound	Type of distorted structure	T_i , K	$\Delta S/R$
$(\text{NH}_4)_2\text{KAlF}_6$?	250	
	?	186	
$(\text{NH}_4)_2\text{KFeF}_6$?	290	
$\text{Cs}_2(\text{NH}_4)\text{FeF}_6$?	190	
$(\text{NH}_4)_3\text{AlF}_6$?	220	2.23
	?	190	0.51
$(\text{NH}_4)_3\text{CrF}_6$	<i>Tr</i>	270	2.33
$(\text{NH}_4)_3\text{GaF}_6$	<i>Tr</i>	250	2.77
$(\text{NH}_4)_3\text{VF}_6$	<i>Tr</i>	280	2.99
$(\text{NH}_4)_3\text{FeF}_6$	<i>Tr</i>	267	2.98
$(\text{NH}_4)_3\text{ScF}_6$	$P2_1/n1$	330	1.61
	$I12/m1$	290	0.81
	$P\bar{1}$	243	0.08

Note: *Tr* denotes the triclinic symmetry, and *R* is the gas constant.

consideration. In the $(\text{NH}_4)_3\text{M}^{3+}\text{F}_6$ cryolites, as in fluoro-elpasolites with atomic cations, an increase in the M^{3+} ion size (the a_0 parameter) leads to an increase in the temperature of the stable initial cubic phase. However, there are considerable differences in the properties of these compounds. First, the triclinic symmetry of the low-temperature phase and the absence of the intermediate tetragonal phase $I4/m$ upon successive phase transitions are characteristic of ammonium cryolites [23]. Second, the total entropy change upon transition from the cubic phase to the triclinic phase varies in the narrow range $\Sigma\Delta S = (2.33\text{--}2.99)R$ from crystal to crystal and does not depend on the sequence of phase transitions (Table 3). A large entropy clearly indicates that certain processes of structural ordering proceed in ammonium cryolites as a result of successive ($\text{M}^{3+} = \text{Al}$, Sc , and In) or single ($\text{M}^{3+} = \text{Cr}$, Ga , V , and Fe) phase transitions. The model proposed by Tressaud *et al.* [21] for the possible ordering of ions upon the $Fm\bar{3}m\text{--}P\bar{1}$ phase transition was also successfully applied to the description of the successive phase transitions [22]. The orientational disordering of $(\text{M}^{3+}\text{F}_6)^{3-}$ octahedra in the cubic phase is due to the distribution of fluorine atoms over eight positions ($192l$) [13] [see the data for $(\text{NH}_4)_3\text{GaF}_6$ in Table 1]. In the triclinic low-temperature phase, the octahedra (fluorine atoms) are completely ordered and occupy one position. To put it differently, the contribution of octahedron ordering to the entropy change is equal to $R\ln 8 = 2.08R$. Out of two ammonium ions that occupy different crystallographic positions ($8c$ and $4b$), only the latter ion in the cubic phase is disordered over two orientations according to the symmetry of its position. Consequently, the entropy change that corresponds to the ordering of ammonium ions is equal to $R\ln 2 = 0.69R$. Thus, the ordering processes in ammonium cryolites cannot be attended by an entropy change of larger than $\Sigma\Delta S = R(\ln 8 + \ln 2) = 2.77R$. This value is in reasonable agreement with the experimental data (Table 3). In the crystals characterized by successive phase transitions, the ordering processes occur in two steps [22]. The phase transition from the cubic 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 transition between two monoclinic modifications ($\Delta S_2 \approx R\ln 2$). The third phase transition ($\Delta S_3 = 0.08R$) is unrelated to the order-disorder processes. The model under consideration is consistent with the NMR data obtained by Sasaki *et al.* [24]. For cryolites with successive phase transitions, an anomalous behavior is observed at the temperature T_1 for the spin-lattice relaxation times of protons (T_{1H}) and fluorine nuclei (T_{1F}). At the temperature T_2 , considerable changes are observed only for T_{1F} .

It was found that the structure of ammonium cryolites strongly depends on the external pressure [22]. The investigation of the pressure-temperature phase

diagram for a cryolite with $\text{M}^{3+} = \text{Sc}$ that underwent three phase transitions demonstrated that both intermediate monoclinic phases disappear with a decrease in the volume of the unit cell under the pressure. At $p \geq 1.2$ GPa, the direct $Fm\bar{3}m\text{--}P\bar{1}$ phase transition is observed, as is the case in compounds with a smaller size of the M^{3+} ion (Cr , Ga , V , and Fe) at atmospheric pressure. This is the reason why the total entropy change upon successive phase transitions in $(\text{NH}_4)_3\text{ScF}_6$ corresponds to the entropy of the phase transition in $(\text{NH}_4)_3\text{GaF}_6$. In turn, at relatively low pressures $p \geq 0.045$ GPa, the $(\text{NH}_4)_3\text{GaF}_6$ cryolite undergoes two phase transitions, as is the case in $(\text{NH}_4)_3\text{AlF}_6$ which has the least volume of the $Fm\bar{3}m$ unit cell among ammonium cryolites. Three phase transitions are observed in the gallium compound at $p \geq 0.25$ GPa. Therefore, it is not improbable that the third transition can occur in aluminum cryolite under the pressure.

In order to elucidate in greater detail the role played by particular ionic groups in the phase transition within the above model, it is desirable to perform the following investigations.

(i) It is expedient to refine the positions of atoms and their thermal parameters in the cubic and distorted phases not only for cryolites, but also for elpasolites with ammonium ions, because spherical and tetrahedral cations can occupy different crystallographic positions in the latter compounds. In this case, several alternative structural models should be taken into consideration.

(ii) Reliable information on the entropy of phase transitions in ammonium elpasolites should be obtained by calorimetric techniques.

(iii) The effect of the pressure on the phase transitions in $(\text{NH}_4)_3\text{AlF}_6$ and ammonium elpasolites should be studied with the aim of constructing the generalized $p\text{--}T$ phase diagram.

4. ELPASOLITES WITH MOLECULAR ANIONS

Let us analyze how the elpasolite structure in crystals with atomic cations is affected by replacing spherical halogen ions with molecular ions $(\text{CN})^-$. The space group $Fm\bar{3}m$ is retained in $\text{Cs}_2\text{LiM}^{3+}(\text{CN})_6$ compounds. The structure of these compounds was investigated by Swanson and Lucas [25]. In their work, the authors considered a model in which Cs , Li , and M atoms occupy special positions (with the coordinates $1/4, 1/4, 1/4; 1/2, 1/2, 1/2$; and $0, 0, 0$, respectively), and the C and N atoms are located on the cell edge ($24e$). A pronounced anisotropy of vibrations is characteristic of the $(\text{CN})^-$ molecular anion. The vibration amplitudes of the C and N atoms along the z axis (cell edge) are virtually identical. The displacements in the direction perpendicular to the cell edge are substantially larger, especially for the nitrogen atom. The motion of the Cs atom is also characterized by an anomalously large

root-mean-square amplitude of vibrations. For all the studied $\text{Cs}_2\text{LiM}^{3+}(\text{CN})_6$ compounds, the Cs–N interatomic distances are appreciably larger than the sum of their ionic radii. On the other hand, the Li–N bond length is comparable to this sum. According to [25], these are the reasons for the weak interaction between Cs^+ and $(\text{CN})^-$ ions and the considerable thermal displacements of cesium and nitrogen atoms.

A large volume of holes occupied by cesium atoms between octahedra plays a decisive role in the instability of the cubic phase: as the unit cell parameter increases, the cubic lattice becomes increasingly unstable with respect to the displacements of Cs atoms and the rotations of $\text{M}^{3+}(\text{CN})_6^{3-}$ octahedra. In this respect, it is interesting to note the correlation between a monotonic increase in the vibration amplitudes of Cs, N, and C atoms and an increase in the cell size. Since the bond lengths remain unchanged to within the error of their determination in all the $\text{Cs}_2\text{LiM}^{3+}(\text{CN})_6$ compounds, the changes in the unit cell parameter a_0 and the size of the hole occupied by cesium atoms between octahedra are determined by the change in the M^{3+} –C bond length. Some characteristics of the phase transitions in $\text{Cs}_2\text{LiM}^{3+}(\text{CN})_6$ elpasolites are listed in Table 4. It is seen that the stability loss temperature of the cubic phase increases with an increase in the unit cell parameter a_0 . The sole exception is provided by the elpasolite with $\text{M}^{3+} = \text{Ir}$. As was shown in [25], the phase transition to the tetragonal phase $P4/nmc$ belongs to the first-order transformations and is associated with the condensation of the X_2^+ soft mode at a point of the Brillouin zone boundary. The structural distortions can be explained by the antiferrodistorsion rotations of $\text{M}^{3+}(\text{CN})_6$ octahedra. Note that this type of tetragonal distortion of the elpasolite structure differs from that observed in the haloid crystals (see Section 2). The next phase transition (to the monoclinic phase $P2_1/n$) is the second-order transformation associated with the condensation of the X_5^+ mode that corresponds to the octahedron rotations and the displacements of Cs atoms. It is worth noting that investigations of the monoclinic phase structure and the Raman spectra did not reveal noticeable distortion of the octahedra in $\text{Cs}_2\text{LiCr}(\text{CN})_6$ [25] and $\text{Cs}_2\text{KFe}(\text{CN})_6$ [26] crystals.

Thus, on the one hand, the sequence of phases (cubic–tetragonal–monoclinic), which is realized upon replacement of the atomic cation by the molecular cation in the elpasolite structure, is similar to that observed in fluoro-elpasolites. On the other hand, the phase transition between the cubic and tetragonal phases in cyanides is associated with the soft mode at the point of the Brillouin zone boundary.

Unfortunately, since the data on the entropy of phase transitions in the $\text{Cs}_2\text{LiM}^{3+}(\text{CN})_6$ crystals are unavailable, it is impossible to trace the effect of a con-

Table 4. Characteristics of successive phase transitions in $\text{Cs}_2\text{LiM}^{3+}(\text{CN})_6$ elpasolites [25]

M^{3+}	$a_0, \text{Å}$	T_1, K	Space group	T_2, K	Space group
Co	10.495	183	$P4/nmc$	168	$P2_1/n$
Fe	10.571	221		170	
Mn	10.677	273			
Cr	10.780	348	$P4/nmc$	310	$P2_1/n$
Ir	10.720	418	$P4/nmc$	335	$P2_1/n$

siderable anisotropy of atomic vibrations of nitrogen and cesium on the entropy change.

5. OXYGEN-CONTAINING ELPASOLITES (ORDERED PEROVSKITES)

Many oxides $\text{A}_2\text{B}'\text{B}''\text{O}_6$ crystallize in a perovskite-like structure and can undergo phase transitions of different types. The ratios between the ionic radii of B' and B'' cations and also between their charges affect the character of ordering and, correspondingly, the structural characteristics and physical properties. Partly or completely disordered compounds exhibit diffuse phase transitions and relaxor phenomena. The ordered compounds (elpasolites) undergo “sharp” (non-smearred) transformations whose sequence considerably depends on the cation type. Among these compounds are lead-containing elpasolites such as Pb_2MgWO_6 , Pb_2CoWO_6 , and $\text{Pb}_2\text{MgTeO}_6$.

Baldinozzi *et al.* [27–29] carried out the precision structural investigation of the cubic phase $Fm\bar{3}m$ in these compounds. The composition disorder in the arrangement of the B' and B'' cations was found in none of the elpasolites. At the same time, it turned out that the thermal parameters (or the root-mean-square displacements u^2) and the reliability factors R have the least values for the structural model according to which the oxygen atoms occupy the positions $24e$ and execute pronounced anisotropic vibrations in the plane perpendicular to the B'–O–B'' bond and the lead atoms are disordered over 6, 12, or 4 local positions in accord with the possible displacements along the [100], [110], and [111] directions. As follows from [27, 28], the model in which the lead atoms occupy 12 equivalent positions is most preferential. The u^2 displacements and the R factors for the isotropic and disordering models are presented in Table 5. Thus, the structure of oxide compounds, unlike haloid elpasolites (cryolites), involves two types of critical ions, which, in principle, are responsible for the displacive phase transitions (rotations of oxygen octahedra) and the order–disorder phase transitions (the ordering of lead atoms).

Different sequences of phase transitions are observed in Pb_2MgWO_6 , Pb_2CoWO_6 , and $\text{Pb}_2\text{MgTeO}_6$ elpasolites (Table 6). Incommensurate phases with the

Table 5. Root-mean-square displacements \bar{u}^2 of oxygen and lead atoms for the isotropic model (O and Pb atoms occupy the 24e and 8c positions, respectively) and disordering model

Compound	$\bar{u}^2, \text{\AA}^2$				T_1, K	Reference
	O	Pb	O	Pb		
	24e	8c	Displaced	Model [110]		
Pb_2MgWO_6	0.018	0.036	0.005	0.011	313	[27]
	(5.6%)		(4.5%)			
Pb_2CoWO_6	0.034	0.045	0.005	0.005	303	[28]
	(5.9%)		(5.3%)			
$\text{Pb}_2\text{MgTeO}_6$	0.016	0.020			190	[29]
	4.5%					

Note: T_1 is the stability loss temperature of the cubic phase. The reliability factor R is given in parentheses.

same symmetry were found in the last two compounds. The incommensurate structure in $\text{Pb}_2\text{MgTeO}_6$ is retained, at least, down to 6 K. The existence of the intermediate phase in Pb_2MgWO_6 was not established unambiguously. The structure of the low-temperature phases was refined only for Pb_2MgWO_6 and $\text{Pb}_2\text{MgTeO}_6$ [27, 29]. It was demonstrated that, in the orthorhombic phase of Pb_2MgWO_6 , the lead atoms are displaced along the $[010]_p$ direction of the pseudocubic cell and the octahedra are slightly rotated and distorted. The modulated displacements of oxygen and lead atoms are observed in the rhombohedral phase of $\text{Pb}_2\text{MgTeO}_6$. Moreover, the lead atoms remain disordered. The space group of the orthorhombic phase in Pb_2CoWO_6 was determined ambiguously: $Pm\bar{c}n$ or $P2_1cn$ [28].

Analysis of the Raman spectra of the low-temperature phases in Pb_2MgWO_6 [31] and $\text{Pb}_2\text{MgTeO}_6$ [32]

Table 6. Characteristics of phase transitions in oxygen-containing elpasolites

Compound	Type of distorted structure	T_i, K	$\Delta S/R$	Reference
Pb_2MgWO_6	$Pm\bar{c}n$	313	1.7	[27, 30]
Pb_2CoWO_6	IM	303	1.15	[28, 30]
	$Pm\bar{c}n$ $P2_1cn$ } ?	256	0.18	
$\text{Pb}_2\text{MgTeO}_6$	$R\bar{3}m$	188		[29]
	$(\delta\delta\delta)$			
	$R\bar{3}$ $(\delta\delta\delta)$	142		

Note: IM denotes the incommensurate monoclinic phase, and R is the gas constant.

revealed soft modes in the low-frequency range. It was assumed that the phase transition in Pb_2MgWO_6 is associated with the condensation of two modes X_{10} and Σ_3 at the boundary and within the Brillouin zone, respectively. In $\text{Pb}_2\text{MgTeO}_6$, the soft mode is condensed at an incommensurate point of the Brillouin zone.

The study of inelastic neutron scattering in the cubic phase of Pb_2CoWO_6 also revealed the soft mode that belongs to the X point of the Brillouin zone and corresponds to rotations of the oxygen octahedra [33]. The condensation of this mode leads to a lowering in the crystal symmetry to tetragonal [14]. However, the low-temperature phase in Pb_2CoWO_6 has a lower symmetry. This seeming contradiction can be explained by the fact that the phase transitions in this compound, as in other oxygen-containing elpasolites, are governed by two mechanisms and two order parameters. Apparently, the primary parameter corresponds to displacements of oxygen atoms (octahedron rotations) that lead to a distortion of holes between octahedra and a lowering of their symmetry, which gives rise to the secondary order parameter associated with the ordering of lead atoms.

Therefore, in oxygen-containing elpasolites, the structural distortions upon phase transitions can be caused by the simultaneously occurring processes of ordering and displacement of different ions (Pb_2MgWO_6 and Pb_2CoWO_6) and only by the displacement processes ($\text{Pb}_2\text{MgTeO}_6$).

The question arises: How do these models of structural distortions correlate with the data of calorimetric measurements?

Although ordered oxygen-containing perovskites have been thoroughly investigated for many years, the data on the heat capacity of Pb_2MgWO_6 and Pb_2CoWO_6 have been obtained by adiabatic calorimetry only recently. This made it possible to determine

reliably the entropy changes upon phase transitions (Table 6) [30]. In order to separate the contributions from the displacement and ordering processes to the entropy, it would be expedient to obtain the data on the excess entropy of $\text{Pb}_2\text{MgTeO}_6$ in which the phase transitions result only in the displacement of oxygen ions. Unfortunately, at present, detailed information on the heat capacity of $\text{Pb}_2\text{MgTeO}_6$ is unavailable. We intend to perform these investigations in the immediate future. However, it is known (see Section 2) that, in haloid elpasolites, the displacive phase transitions associated with small rotations of octahedra are usually accompanied by relatively small entropy changes $\Delta S/R \approx 0.2$. By assuming that this quantity for oxide compounds differs insignificantly, the main contribution to the entropy of structural transformations in Pb_2MgWO_6 and Pb_2CoWO_6 should be determined by the secondary order parameter of phase transitions, i.e., by the ordering of lead atoms. On the other hand, the experimental entropies for these elpasolites fall in the range $R\ln 4$ – $R\ln 6$. In the framework of the model considered above, this means that lead atoms in the orthorhombic phase are incompletely ordered, because, otherwise, the entropy change should be equal to $R\ln 12$. This assumption is in good agreement with the structural data, according to which lead atoms that occupy 12 local disordered positions in the cubic phase are displaced along the $[010]_p$ direction of the pseudocubic cell in the orthorhombic phase [27]. This implies that lead atoms in the partly ordered low-temperature phase occupy two or four disordered positions, which results in the entropy changes $R\ln 12/2 = R\ln 6$ and $R\ln 12/4 = R\ln 3$, respectively.

6. CONCLUSION

The main results obtained in the above analysis of the phase transitions in the crystals with an elpasolite (cryolite) structure can be summarized as follows.

(1) For the most part, the structural and calorimetric data are in agreement, provided that they are considered within the model concepts of phase transitions.

(2) The mechanism of structural transformations essentially depends on the size and the shape of cations and anions. Changes in the size and the shape of ions can lead to substantial changes in the anharmonicity of vibrations of atomic ions and (or) the appearance of an orientational ordering of nonspherical (molecular) ions. In turn, this affects the magnitude and the behavior of the excess entropy.

(3) In haloid crystals, the entropy of the cubic-to-tetragonal phase transition is constant.

(4) In oxygen-containing compounds, there occur phase transitions associated with two order parameters which arise from the displacement of atoms of one type and the ordering of atoms of another type in the structure. In order to separate the contributions from different mechanisms of transformations to the entropy, it is advisable to carry out the calorimetric investigations of

crystals in which the phase transitions are associated only with displacements of oxygen atoms (for example, $\text{Pb}_2\text{MgTeO}_6$).

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