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STRUCTURAL DISTORTIONS IN FAMILIES OF PEROVSKITE-LIKE CRYSTALS

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The crystallographic and group theoretical analysis of the structural phase transitions in perovskite and perovskite-like crystals is reviewed. We include ABX_3 perovskites and their relative crystals of ReO_3 type ($G_0 = O_h^1$), elpasolites, cryolites and their relatives ($G_0 = O_h^5$), layered crystals of $TlAlF_4$ series ($G_0 = D_{4h}^1$), Aurivillius and Ruddlesden-Popper series ($G_0 = D_{4h}^{17}$). The structures in their initial phase G_0 often contain n layers ($n = 1, 2, 3$) of vertex linked octahedra. The distorted phases produced by one kind of tilt and by superposition of tilts in the slabs are enumerated. Most of the tilts correspond to symmetry changes, which can be associated to definite librational lattice modes irreducible representations of the G_0 group. The softening of modes associated to the PT has been found experimentally in many perovskites, elpasolites and layered crystals with $n = 1$. In contrast, no such soft modes have been found yet for even-layered ($n = 2$) crystals. Examples of successive phase transitions due to the superposition of tilts in these types of crystals have been collected.

Keywords: Structural phase transitions; Perovskites; Perovskite-like crystals; Group theoretical Classification

1. INTRODUCTION

There exist many broad families among perovskite-like crystals, which have similar structures. Often their initial phase belongs to the same

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space group (aristophase) and undergoes one or more phase transitions when the temperature or external pressure is varied. All these structures have in common the presence of constituent octahedra of anions with a cation inside.

In these families of crystals many authors have studied structural distortions both theoretical and experimentally. One of the lines of these studies was the crystallographic analysis of the possible symmetry changes due to different types of distortions, such as polar or antipolar displacements of ions located in octahedra, Jahn-Teller distortions of the octahedra and tilting of the octahedral constructions. There exist also many examples in which the low symmetry structure is determined by a combination of two or more types of these distortions.

The results of the crystallographic analysis of these phase transitions are scattered in many journals. As far as we know, these results have never been collected except in the book by Aleksandrov and Beznosikov (1997) which was published in Russian with a very restricted number of copies and, therefore, it is of scarce visibility for the general scientific community. The renewed scientific interest on these families of compounds, because of the recent discovery of Giant Magnetoresistance in some of them, has deemed us useful to present a review of these publications. Besides, the content of the present work has been extended to cover new types of distortions in perovskite-like crystals and to solve some contradictions in published data and interpretations.

Perovskites themselves form a broad family of compounds which have the structure named after the mineral Perovskite, $CaTiO_3$. This family of compounds, in many cases with a slightly distorted structure just as $CaTiO_3$ itself (Sasaki, Prewitt, Bass *et al.*, 1987), contains a large variety of compounds of general formula ABX_3. Most metal ions can be incorporated into the structure in different combinations at the A and B sites. Perovskites have been studied among oxides and fluorides, other halides (Brynestad, Yakel and Smith, 1966; Aleksandrov, Anistratov, Beznosikov and Fedoseeva, 1981), hydrides (Messer, Eastman, Mers and Maeland, 1963; Goodenough and Longo, 1970; Thomas, 1996a, b), sulphides (Clearfeld, 1963; Aslanov and Kovba 1964a; Brochu, Padion *et al.*, 1970) and selenides (Aslanov, 1964b), oxinitrides (Bacher, Antoine, Marchand *et al.*,

1988) and cianides (Goodenough and Longo, 1970). If one takes into account rather complex disordered compositions such as $(A'A''A''')$ $(B'B''B''')(X'X''\cdots)_3$ it is probably impossible to say, at present, how many substances belong to the perovskite family.

The ABX_3 stoichiometry with cubic perovskite structure belongs to the $G_0 = Pm3m$ Space Group (Sp.Gr. hereafter). The A-cation is located in the cuboctahedron ($Z = 12$) cavity formed by the X-anions of eight BX_6-octahedra, and the B-cation sits on the center of each octahedron. The X-anion has two B- and four A-ions as nearest neighbors. The structure of the ideal perovskite is most commonly described as a three dimensional network of corner sharing octahedra (Fig. 1a). In short, a rather large A-cation is located on the center of the cubic unit cell with the centers of the octahedra (B-ions) at its vertices.

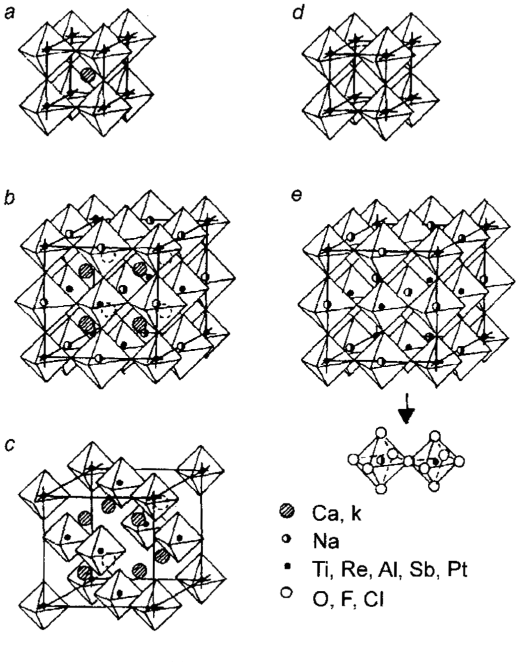

FIGURE 1 Structures of perovskite and perovskite-like crystals with three-dimensional octahedral framework; A-cations are not shown. (a) ABX_3-perovskite; (b) $A_2BB'X_6$-elpasolite; (c) A_2BX_6-antifluorite; (d) BX_3 of ReO_3-type; (e) $BB'X_6$-ordered crystal of ReO_3-type.

There is a different way to present the same structure, namely, as the close packing of AX_3 layers (in cubic sequence), where the A-ions do not touch each other, and the octahedral holes formed by X-anions are filled by B-ions. This description leads to many possible polytypes depending on the sequence of the AX_3 layers. The best known structures, found mainly in oxides and halides, are the so called h-, hhc- and hcc-polytypes which in their unit cell have two, nine and six layers respectively. They have the same general formula ABX_3 and belong to the hexagonal or rhombohedral Sp.Gr's (Goodenough and Longo, 1970; Brandwijk, 1972; Schippers, Brandwijk and Gorter, 1973). These structures are related to the ideal perovskite, since the latter can be considered as a particular case in which the layers follow a c-sequence. Polytypes ABX_3 and their deficient varieties undergo some structural phase transitions (PT's hereafter), but this branch of the perovskite "family tree" needs special attention and we shall not consider it below since it has been reviewed elsewhere (Darriet and Subramanian, 1995; Aleksandrov and Beznosikov, 1997).

Our main attention will be paid to the distortions of the perovskite and related structures. In crystal chemistry language, the stability of the structure is ruled by certain relations between the ionic radii R_A, R_B, R_X (Shannon, 1976), particularly in many ionic compounds. The best known relation is the Goldschmidt's tolerance factor t:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_X + R_B)}$$

(Goldschmidt, 1926), which, however, leads to a rather crude estimation of stability. In fact, in a real substance the stability is determined by more delicate factors (Woodward, 1997b).

Compounds with perovskite structure attract much interest due to the wonderful diversity of their physical properties and to the technologically relevant applications of many of these substances. Magnetic, dielectric, optical, electrical and catalytic properties of perovskites have been widely studied. Such phenomena as ferro- and antiferroelectricity, piezoelectricity and electrostriction, non-linear optical and acousto-optical and specific magnetic properties have led to a variety of devices widely used in capacitor industry, audio- and ultrasonic acoustics, radio-electronics both in the low and very high frequency bands, opto-electronics, informatics and chemical synthesis, *etc.* In the last years paramount attention has been paid to new phenomena which have appeared in doped perovskites, such as superconductivity and colossal magnetoresistivity. Such versatility leads the perovskite structure to be one of the most important in material science.

All these properties appear mostly in compounds whose structure deviates from the cubic ideal one due to several types of distortions, such as polar or antipolar shifts of B- and/or A-ions from their exact position in the center of the octahedra or cuboctahedra, different types of octahedral tilts, Jahn-Teller distortions, or magnetic ordering. The first two types of distortions are driven by the lattice instability with respect to some lattice modes (soft modes), which belong to the center or to some boundary points of the Brillouin zone of the cubic structure. The last two types are determined either by electronic instability of some ions in a definite surrounding or by ordering of spins. Distortions due to magnetic ordering will not be discussed in this review. Far less cubic perovskites than distorted ones are known; most crystals in normal conditions belong to lower groups of symmetry, from tetragonal down to triclinic symmetry. As a rule, when the temperature or the pressure varies, the structural PT's takes place and the distortions of G_0 appear. Moreover, successive PT's are also frequent in perovskites as several distortions, of the same or different nature, take place. In some cases the distortions lead to great changes in their physical properties, especially the electric and magnetic ones.

In some substances, with a distorted structure at normal conditions, the increase of temperature or pressure does not lead to the cubic structure or a change of distortion, but to a different structural type, thus destroying the three dimensional framework of the linked octahedra. Transitions from perovskite to other polytypes, and from perovskite to $CsCdCl_3$ structural type are examples of these transformations (Goodenough and Longo, 1970; Aleksandrov, Anistratov, Beznosikov *et al.*, 1981). These first-order reconstructive PT's are out of the scope of this review.

In most examples of PT's under consideration the three dimensional octahedral frame of the cubic perovskite is conserved. This is the main feature not only for the perovskite itself, but also for other perovskite-related structures such as elpasolites, $A_2BB'X_6$, cryolites, A_3BX_6, substances of ReO_3- and $BB'X_6$-type structures. These structures (Fig. 1) are the nearest relatives to the perovskite. Less close to the perovskite is the antifluorite structure, A_2BX_6, Figure 1c, where the sequence of B-B′-B octahedra, present in elpasolite, Figure 1b, is changed to B-#-B separated octahedra (# is vacancy). In spite of this difference, the structural PT's in antifluorites are determined by the same rules as for the other structural types just mentioned above.

Perovskite-like compounds are not restricted to the nearest relatives. It is well known that many types of layered structures belong to the same "family tree". It is easy to imagine that an octahedral frame can be cut in three simple ways: by the planes $(001)_c$ $(110)_c$ and $(111)_c$. In the first case it leads to tetragonal (undistorted) structures which have one or several perovskite-like square layers (slabs), with intermediate layers (blocks) in between. The second way leads to slabs with even layers of vertex-linked octahedra with A-cations between the slabs. Compounds with general formula $A_nB_nX_{3n+2}$ are formed in this case with $n \geq 2$, and $BaMnF_4$ ($n=2$) and $Sr_2Ta_2O_7$ ($n=4$) are examples of these structures (Wells, 1975). Slabs formed when the octahedral frame has been cut by (111)-planes are known in polytypes and other more complex intergrowth structures (Darriet and Subramanian, 1995; Aleksandrov and Beznosikov, 1997).

The distortions in tetragonal layered structures, which are present mainly in crystals of the Ruddlesden-Popper and Aurivillius families, and in some other structures will be discussed below.

So, our main aim is to review the previously published crystallographic data on perovskites and other perovskite-like crystals with the necessary corrections, and the presentation of some new experimental data on crystals that display successive PT's as the temperature changes. We intend to check the earlier assumption that, in most cases, symmetry changes at successive PT's correspond to the increase of the tilt- and/or displacement components when the temperature is lowered (Aleksandrov, 1976).

The structure of the review is as follows: in Section 2 the distortions in ABX_3 perovskites and ReO_3-type crystals, due to polar and antipolar displacements, and due to octahedral tilts and their combinations, will be considered; Jahn-Teller type of distortions will be shortly revised in those cases they appear in combination with tilts; Section 3 is devoted to distortions in $(AA')(BB')X_6$ elpasolite type crystals and their relatives A_3BX_6, A_2BX_6 and $BB'X_6$, which in their initial phase belong to $G_0 = O_h^5 = Fm3m$ Sp.Gr.; distortions in ABX_4 and other crystals, which in their initial phase belong to P4/mmm and have either odd or even octahedral layers in their structure, will be discussed in Section 4; distortions in Ruddlesden-Popper, Aurivullius crystal series and other layered crystals which belong in their initial phase to $G_0 = D_{4h}^{17} = I4/mmm$ are presented in Section 5. In the Conclusion section the main results of the review are summarized and discussed.

Because different designations of the space groups and irreducible representations (irrep's) are used in the current literature, we shall denominate the Sp.Gr's both by the Hermann-Mauguin and International symbols and shall use for irrep's the Kovalev's (1965, 1986) and Zak, Casher *et al.*, 1969 symbols.

2. STRUCTURAL DISTORTIONS IN PEROVSKITES

Phase transitions in perovskites and their change of structures have attracted attention for the last 50 years, since the ferroelectric properties of barium titanate were discovered (Vul and Goldman, 1945). The first effort to describe the symmetry changes at the ferroelectric PT's was made for all point groups by Zheludev and Shuvalov, 1956. For group O_h^1 it is easy to show that the appearance of spontaneous polarization (P_s) along $[001]_c$, $[110]_c$ and $[111]_c$ lead to tetragonal, orthorhombic and rhombohedral groups C_{4v}, C_{2v} and C_{3v}, respectively. The space groups for the mentioned polar distortions and for other P_s directions are shown in the first line of Table II (see below).

But the most widespread distortions in perovskites are the symmetry changes due to tilts of the octahedra. The changes of the tilt system lead to successive PT's and in some cases the tilting and polar (or antipolar) distortions appear at a definite temperature range in the same sample.

2.1. Distortions Due to Octahedral Tilts

Megaw, 1973 was the first who considered the various components of the structure distortions, on the basis of her previous reports at Meetings on Ferroelectricity (Prague, 1966; Saarbrucken, 1969; Dijon, 1972), paying paramount attention to octahedral tilts. Ahtee, Glazer and Megaw (1972) and Megaw (1974) proved experimentally that in

$NaNbO_3$ the symmetry changes at some PT's could be described using the proposed model of tilts. Glazer (1972) proposed the well known classification of possible tilt systems in the octahedral framework of the perovskite. He later described some corrections to the first paper and proposed a simple method to determine the tilt system in a distorted perovskite crystal, by the analysis of the types of superstructure reflections observed by a diffraction method (Glazer, 1975). It was also mentioned that the nature of a particular tilt system is related to the condensation below the PT of one or more soft modes of the lattice group G_0.

Some assumptions were made in the cited papers. First, the octahedra were considered as rigid units; *i.e.*, small deviations from their cubic symmetry in the distorted phase were not taken into account as a secondary effect (see below). Second, instead of considering the tilt of each octahedron around one of its symmetry axes, it was assumed that tilts around $[110]_c$ and $[111]_c$ axes could be considered as the superposition of two or three equal tilt components, respectively, around the 4-fold axes. Third, in those cases that the tilt angles are small, less than 15° (Megaw, 1973), the components of the different types of tilts were considered to be independent.

It is known that two types of tilts are possible in the three dimensional octahedral framework. The tilt of an octahedron around $[001]_c$, for example, by an angle ω results in the distortion of the whole (001)-plane of octahedra, with $-\omega$ tilts of the nearest neighboring octahedra. In addition, the adjacent octahedra in the next $(001)_c$-layer may be tilted by either the same or opposite angle with respect to the first octahedron. Glazer (1972, 1975) used the following symbols for these two types of tilts: The tilt system is described by three letters which refer to the cubic axes $[100]_c$, $[010]_c$ and $[001]_c$ (unequal in the general case of distorted phase G_i). Each letter has an upper index $+$ or $-$ for the two types of tilts and 0 for no tilt, respectively (see Fig. 2). For example, the symbol $a^- b^0 c^+$ means that successive octahedra along $[100]_c$ axis have opposite signs of the tilts, the same signs along $[001]_c$ and that there is no tilt along $[010]_c$.

Aleksandrov (1976) considered the same assumptions as Glazer's, but used other much less known symbols to increase the information given. Again, the system of tilts is indicated by three letters which correspond to the cubic axes, but the Greek letters ψ instead of $+$ and

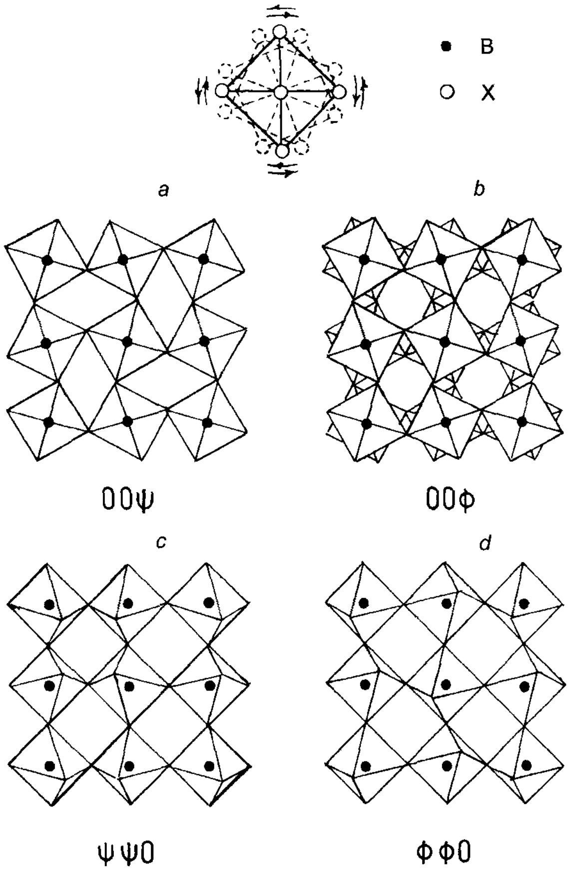

FIGURE 2 Two types of octahedral tilts in perovskites. (a) $(a^0a^0a^+)$ or (00ψ)-tilt around vertical [001] axis; (b) $(a^0a^0a^-)$ or (00ϕ)-tilt around vertical [001]; (c) $(a^+a^+a^0)$ or $(\psi\psi0)$-tilt around both [100] and [010] axes; (d) $(a^-a^-a^0)$ or $(\phi\phi0)$- tilt around both [100] and [010] axes.

ϕ instead of $-$ are used. So, in the above-considered example, the tilt system is described as $\phi0\psi$. However, when the tilts of the same type have different values around the different axes a lower index is used, $\phi_1\phi_20$ for example ($a^-b^-c^0$ in Glazer's notation).

Two more assumptions were considered by Aleksandrov (1976). *First; it is possible that both types of tilts can exist around the same cubic axis, i.e.,* $\Delta = \phi \pm \psi$. It can lead to unequal, either ϕ_1 and ϕ_2 or ψ_1 and ψ_2, tilts of neighboring octahedra along the tilt axis, depending on the relative values of $|\phi|$ and $|\psi|$. *Second; in the course of successive PT's the number of tilt components increases when the temperature is lowered.* It leads (as a rule) to symmetry lowering in successive phases $G_0-G_1-G_2\cdots$ and to Sp.Gr's of the low temperature phases that are usually subgroups of G_0. The assumption is fulfilled in most substances studied experimentally, as will be shown below, but some exceptions exist.

Group-subgroup relations for $G_0 = O_h^1$ have been considered several times (Aleksandrov, Zinenko, Michelson and Sirotin, 1969; Vinberg, Gufan, Sachnenko and Sirotin, 1974). It has been shown that among active irrep's of the vibrational representation of the group, there exist two irrep's that characterize the modes of pure octahedral librations in the cubic phase, that belong to M and R boundary points of the Brillouin zone (see Fig. 3a), namely M_3 and R_{25} modes. Cowley (1964, 1980) showed that two more modes, Γ_{15} and M_3', responsible for polar and antipolar distortions, respectively, are the low frequency modes of the lattice. The librational M_3 and R_{25} modes are usually the soft modes in the majority of perovskites, and due to their

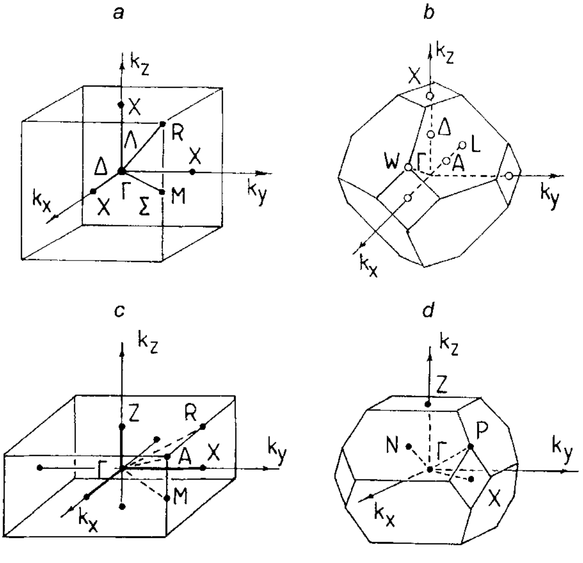

FIGURE 3 First Brillouin zones of perovskite-like crystals which in the initial phase belong to G_0 Sp.Gr.: (a) $O_h^1 = Pm\bar{3}m$; (b) $O_h^5 = Fm\bar{3}m$; (c) $D_{4h}^1 = P4/mmm$; (d) $D_{4h}^{17} = I4/mmm$.

condensation the $\psi(a^+)$- and $\phi(a^-)$- tilts appear in the crystals (Aleksandrov, 1976). The condensation of both tilt and polar modes will be considered in Section 2.2.

In the last few years a renewed interest on the symmetry of possible distorted phases has arisen. Thomas (1989, 1996a, b, 1998) has evaluated the relation between the volumes of A-cuboctahedra and B-octahedra (V_A/V_B) in perovskites and has shown for some ferroelectrics, where both cation displacements and tilts coexist, that the ratio is equal to 5 (Thomas, 1989).

Later, distorted perovskites with different tilt systems have been investigated on the same basis and some systems which preferentially appear in real crystals have been selected (Thomas, 1996a, b). Woodward (1997a) has worked out a special computer program to analyze symmetry and additional octahedral distortions for many tilt systems in perovskites and related structures. He has found that in some systems published by Glazer (1972, 1975) and Aleksandrov (1976) it is impossible to retain a three dimensional network of perfectly rigid octahedra and, consequently, further distortions must occur (see also Thomas and Beitollahi, 1994; Darlington, 1996; Thomas, 1996a, b, 1998).

Recently Howard and Stokes (1998) have repeated the theoretical analysis of G_0-groups and paid special attention to the combined result of M_3 and R_{25} mode condensation. They introduced a six-dimensional reducible representation, as direct sum of both irrep's corresponding to these modes, and restricted themselves to "simple" tilt systems where only one type of tilt could appear around any cubic axis. The main result of the analysis is the conclusion that, from the group theory point of view, instead of 23 tilt systems proposed earlier (Glazer 1972, 1975; Aleksandrov, 1976) only 15 systems are non-equivalent. Among some systems such as $a^0a^+a^+$, $a^0b^+c^+$, $a^0b^+b^+$, $a^+a^+a^-$, $a^+b^+c^-$, $a^+b^+b^-$, $a^+a^+c^-$ and other groups, only the last systems of each group, *i.e.*, $a^0b^+b^+$ *and* $a^+a^+c^-$ are compatible with the requirements of group theory. However, it is necessary to remember that in the tables given by Glazer (1975) and Aleksandrov (1976) there were only 16 systems of different symmetry. Howard and Stokes have stated that one of these, namely $a^+b^+c^-$ $(\psi_1\psi_2\phi)$ is not 'simple'; it inevitably contains Δ-tilts around the c-axis and should be marked as $a^+b^+\Delta$ $(\psi_1\psi_2\Delta)$ (see Tab. I).

TABLE I Possible distortions in ABX_3 perovskites and crystals of ReO_3-type, which belong to $G_0 = O_h^1$ in their initial phase, due to superposition of octahedral tilts

Symbols	*Symbols*		*Unit cell parameters*			*Formula*
Aleksandrov	*Glazer*	*Space groups*	*a*	*b*	*c*	*units Z*
000	$a^0a^0a^0$	$O_h^1 = Pm\bar{3}m$	1	1	1	1
00ψ	$a^0a^0a^+$	$D_{4h}^5 = P4/mbm$	$\sqrt{2}$	$\sqrt{2}$	1	2
$\psi\psi0$	$a^+a^+a^0$	$D_{4h}^{17} = I4/mmm$	2	2	2	8
$\psi\psi\psi$	$a^+a^+a^+$	$T_h^5 = Im\bar{3}$	2	2	2	8
$0\psi_1\psi_2$	$a^0b^+c^+$	$D_{2h}^{25} = Immm$	2	2	2	8
$\psi_1\psi_2\psi_3$	$a^+a^+c^+$	$D_{2h}^{25} = Immm$	2	2	2	8
$\psi_1\psi_2\psi_3$	$a^+b^+c^+$	$D_{2h}^{25} = Immm$	2	2	2	8
00ϕ	$a^0a^0c^-$	$D_{4h}^{18} = I4/mcm$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\phi\phi0$	$a^-a^-c^0$	$D_{2h}^{28} = Imam$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\phi\phi\phi$	$a^-a^-a^-$	$D_{3d}^6 = R\bar{3}c$	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$	2
$\phi_10\phi_2$	$a^-b^0c^-$	$C_{2h}^3 = I2/m$	$\sqrt{2}$	2	$\sqrt{2}$	4
$\phi_1\phi_1\phi_2$	$a^-a^-c^-$	$C_{2h}^6 = I2/c$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\phi_1\phi_2\phi_3$	$a^-b^-c^-$	$C_i^1 = P\bar{1}$	$\sqrt{2}$	2	$\sqrt{2}$	4
$0\phi\psi$	$a^0b^-c^+$	$D_{2h}^{17} = Cmcm$	2	2	2	8
$00\Delta^*$	–	$D_{4h}^5 = P4/mbm$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\phi\phi\psi$	$a^-a^-c^+$	$D_{2h}^{16} = Pbnm$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\psi\psi\phi$	$a^+a^+c^-$	$P4_2/nmc$	2	2	2	8
$\psi_1\psi_2\Delta$	–	$D_{2h}^{13} = Pmmn$	2	2	2	8
$\phi_1\psi\phi_2$	$a^-b^+c^-$	$C_{2h}^2 = P2_1/m$	$\sqrt{2}$	2	$\sqrt{2}$	4
$\psi0\Delta$	–	$C_{2h}^3 = C2/m$	2	2	2	8
$\phi\psi\Delta$	–	$C_{2h}^2 = P2_1/m$	2	2	2	8
$\phi\phi\Delta$	–	$C_{2h}^5 = \mathrm{P}2_1/a$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\phi_1\phi_2\Delta$	–	$C_i^1 = P\bar{1}$	$\sqrt{2}$	$\sqrt{2}$	2	4

$\Delta = \phi \pm \psi$.

Woodward (1997a) has reproduced all 23 systems from Glazer's works and has analyzed (Woodward, 1997b) the different V_A/V_B ratios and interatomic A–X distances in the most symmetrical systems. Based on a great number of experimental data it was shown "*that those tilt systems in which all A-cation sites remain crystallographically equivalent are strongly favored if all A-sites are occupied by the same ion type*".

Now it is possible to compile the different tables of tilt systems published by Glazer (1972, 1975); Aleksandrov (1976); Aleksandrov and Beznosikov (1997); Woodward (1997a) and Howard and Stokes (1998). The compilation is made in Table I, where all 23 systems have been retained and systems with unequal $\Delta=\psi+\phi$ tilts around the same axis, given in the paper by Aleksandrov (1976) have been added. We essentially agree with the arguments given by Howard and Stokes, 1998, but we have taken into consideration that in some crystals the tilt angles could change with temperature or pressure in a particular way. For example, among the three unequal tilts required by the group theory in such a tilt system as $a^+b^+c^+$ (D_{2h}^{25} = Immm), two tilts are identical ($a^+a^+c^+$). This particular condition may modify some properties of the crystal, – for example, the form of the optical ellipsoid from biaxial to uniaxial as an example, *without any change of the symmetry*. Therefore, the data in Table I, and in any other crystallography and group-subgroup Tables, contain information in excess but they are especially useful when experimentally a new example appears.

We return now to the successive PT's due to tilts. The different ways of successive PT's were proposed by Aleksandrov (1976) and more recently were reproduced partially by Thomas (1998) and Howard and Stokes (1998). Comparison of the data allows us now to present a modern version of previous figures in which some changes have been introduced (see Fig. 4). Here it is proposed again (see above) that the natural tendency is towards an increase in the number of tilt components at successive PT's, when the temperature is lowered.

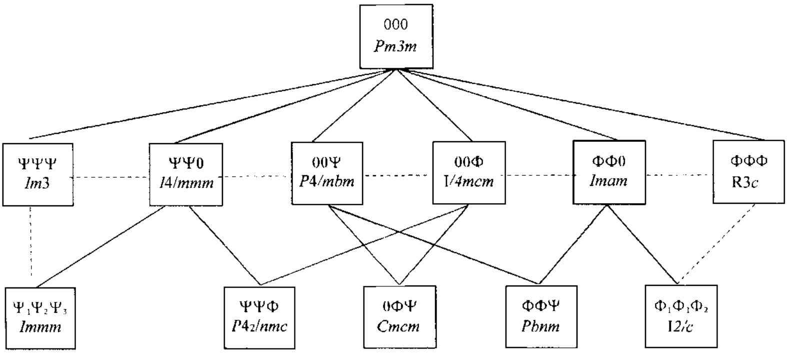

FIGURE 4 Possible paths of successive phase transitions due to tilts in perovskites. Full lines correspond to possible PTs of the second-order; broken lines to PTs of the first-order.

2.2. Superposition of Tilts and Ionic Displacements

The superposition of tilts and polar/antipolar displacements has been considered by Aleksandrov (1978). The diagram presented in Figure 5 illustrates the task. A pyramid is shown there with the G_0 phase located on its top and successive PT's due to R_{25} (OR-line), M_3 (OM), Γ_{15} (OΓ) and M'_3(OM$'$) on its edges. The space groups formed by the superposition of ψ and ϕ tilts are located on the ORM plane. The resulting systems formed by the combined action of polar (p) displacements and ϕ-tilts are located on the ORΓ plane, *etc.*

The simplest case corresponds to the superposition of tilts and polar displacement, because the latter does not change the translational symmetry of a phase already distorted by tilts. It is necessary to find the polar subgroups, for different directions of the polar vector, of the groups shown in Table I. This task was done by Aleksandrov (1978) and was published later in the book by Aleksandrov, Anistratov, Beznosikov and Fedoseeva (1981). The results are reproduced in

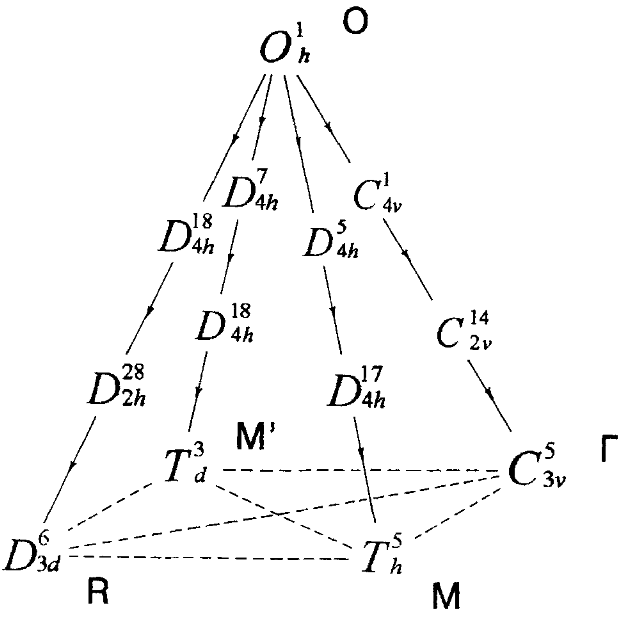

FIGURE 5 Schematic representation of possible phase transitions in perovskites due to the superposition of different distortions (see text).

Table II for the main Sp.Gr's in Table I, except group ($\phi_1\phi_2\phi_3$) tilts, where the appearance of any p-component leads to the triclinic polar group P1. As an example, the superposition of ($\psi\psi$0) and (pp0) distortions gives the Fmm2 Sp.Gr., which does not allow the tilts and polar components to be equal; thus the real distortion in the Fmm2-phase should be ($\psi_1\psi_2$0)($p_1p_2$0).

The Sp.Gr's of the distorted phases originated by the superposition of tilts and antipolar (a) displacements have been systematized by Misyul and published in the book by Aleksandrov, Anistratov, Beznosikov and Fedoseeva (1981). However, in this case the superposition of the displacement yields to the multiplication of the unit cell which results after the distortion by the tilts, and, consequently we have collected in Table III the possible changes of unit cells. Thereafter, the symmetry of those phases where tilts and antipolar displacements are superposed and the changes of primitive unit cell vectors, have been determined (Tab. IV). From this table it is clearly seen that the same Sp.Gr. can result from many different complex distortions (for example, groups $P4_32_1$ or $P2_1/c$). Hence, in certain cases it is difficult to determine the definite type of distortion just by the symmetry of the distorted phase. It is interesting to mention here that, in spite of the fact that both tilts and antipolar components are centrosymmetric, the resulting distortion may belong in many cases to a non-centrosymmetrical Sp.Gr. This unusual result can be explained in terms of the Curie principle, namely, only common symmetry elements are maintained at the superposition of different elementary distortions. A similar situation will be met in the course of our review on layered crystals (see Sections 4 and 5).

2.3. Some Experimental Data

Many summaries on distorted phases in perovskites, especially for oxides, fluorides and some hydrides, have been published earlier (Galasso, 1959, 1990; Salje, 1990; Glazer, 1972, 1975; Aleksandrov, 1976; Thomas, 1996a, b; Woodward, 1997b, *etc.*). Since it is inane to repeat here all these data, below we shall collect only some examples from these publications, mainly for crystals where successive PT's have been observed and the symmetry of the phases has been determined by direct diffraction methods. Some attention will be paid to halides,

TABLE II Symmetry of structures distorted by tilts and polar displacements

Unit cell volume	*Space*		*Polar displacements*								
in units a_0	*group*	*Symbol*	$00p$	$0p0$	$p00$	$pp0$	p_1p_20	$p0p$	$0pp$	$p_1p_1p_2$	ppp
$1 \times 1 \times 1$	$O_h^1 = Pm\bar{3}m$	000	$P4mm$	$P4mm$	$P4mm$	Amm	Pm	Amm	Amm	$P1$	$R3m$
$\sqrt{2} \times \sqrt{2} \times 1$	$D_{4h}^5 = P4/mbm$	00ψ	$P4bm$	$Pmc2_1$	$Pmc2_1$	Amm	Pm	Pc	Pc	Cm	$P1$
$2 \times 2 \times 2$	$D_{4h}^{17} = I4/mmm$	$\psi\psi0$	$I4mm$	$Imm2$	$Imm2$	$Fmm2$	Cm	Cm	Cm	Cm	$P1$
$2 \times 2 \times 2$	$T_h^5 = Im\bar{3}$	$\psi\psi\psi$	$Imm2$	$Imm2$	$Imm2$	Cm	Cm	Cm	Cm	$P1$	$R3$
$2 \times 2 \times 2$	$D_{2h}^{25} = Immm$	$\psi_1\psi_2\psi_3$	$Imm2$	$Imm2$	$Imm2$	Cm	Cm	Cm	Cm	$P1$	$P1$
$\sqrt{2} \times \sqrt{2} \times 2$	$D_{4h}^{18} = I4/mcm$	00ϕ	$I4cm$	Ima	$Imm2$	$Fmm2$	Cm	Cc	Cc	Cm	$P1$
$\sqrt{2} \times \sqrt{2} \times 2$	$D_{2h}^{28} = Imam$	$\phi\phi0$	$Imm2$	$Imm2$	$Imm2$	Cm	Cm	Cc	Cm	$P1$	$P1$
$\sqrt{2} \times \sqrt{2} \times \sqrt{2}$	$D_{3d}^6 = R\bar{3}c$	$\phi\phi\phi$	$C2$	$C2$	$C2$	$P1$	$P1$	$P1$	$P1$	Cc	$R3c$
$2 \times 2 \times 2$	$C_{2h}^3 = C2/m$	$\phi_10\phi_2$	Cm	$C2$	Cm	$P1$	$P1$	Cm	$P1$	$P1$	$P1$
$2 \times 2 \times 2$	$D_{2h}^{17} = Cmcm$	$0\phi\psi$	$Cmc2_1$	$Amm2$	$Ama2$	Pm	Pm	Cc	Cm	$P1$	$P1$
$\sqrt{2} \times \sqrt{2} \times 2$	$C_{2h}^6 = C2/c$	$\phi_1\phi_2\phi_2$	Pm	$P2$	Pm	$P1$	$P1$	Pm	$P1$	$P1$	$P1$
$\sqrt{2} \times \sqrt{2} \times 2$	$D_{2h}^{16} = Pnma$	$\phi\phi\psi$	$Pmn2_1$	$Pna2_1$	$Pmc2_1$	Pc	Pc	Pm	Pc	$P1$	$P1$
$2 \times 2 \times 2$	$D_{2h}^{15} = P4_2/nmc$	$\psi\psi\phi$	$P4_2mc$	Pm	Pm	Pc	$P1$	$P1$	$P1$	$P1$	$P1$
$2 \times 2 \times 2$	$C_{2h}^2 = P2_1/m$	$\phi_1\psi\phi_2$	Pm	$P2_1$	Pm	$P1$	$P1$	Pm	$P1$	$P1$	$P1$
$2 \times 2 \times 2$	$D_{2h}^{13} = Pmmn$	$\psi_1\psi_2\phi$	$Pmm2$	$Pmn2_1$	$Pmn2_1$	Pc	$P1$	$P1$	$P1$	$P1$	$P1$

TABLE III Vectors of star and basic vectors of the unit cells distorted by tilts

Lattice type	*Vectors of star*	*Primitive unit cell basic vectors* a	b	c	V_i/V_0
1	$K^{(1)}=0$	a_1	a_2	a_2	1
2	$K^{(2)}=(b_1+b_2+b_3)\cdot 1/2$	a_2+a_3	a_3+a_1	a_1+a_2	2
3a	$K_j^{(3)}=b_j\cdot 1/2$	$2a_1$	$2a_2$	$2a_3$	8
3b	$K_j^{(3)}=b_j\cdot 1/2$	$2a_1$	$2a_2$	a_3	4
3c	$K_j^{(3)}=b_j\cdot 1/2$	a_1	a_2	$2a_3$	2
4a	$K_j^{(4)}=(b_e+b_m)\cdot 1/2$	$-a_1+a_2+a_3$	$a_1-a_2+a_3$	$a_1+a_2-a_3$	4
4b	$K_j^{(4)}=(b_e+b_m)\cdot 1/2$	a_1-a_2	a_1+a_2	a_3	2

omitted in the cited papers, though we have used only the most modern review papers on previous experiments.

2.3.1. Successive Phase Transitions in Perovskites

In Table V selected experimental data on compounds with symmetry changes due to the successive condensation of M_3 and R_{25} soft modes and their combination with polar displacements are presented. Here, as well as in following Tables with experimental data, the transition temperatures $T_1, T_2, T_3\ldots$ and distorted phases $G_1, G_2, G_3\ldots$ are ordered in the trend of decreasing temperature, and the G_0 phases above T_1 are excluded.

It is necessary to mention that there exist some favored types of distortions in perovskites. Many $A^{3+}B^{3+}O_3$ oxides, as well as fluorides $B^{3+}F_3$ of ReO_3-type, prefer the $a^-a^-a^-$ $(\phi\phi\phi)$ tilt and their PT's are usually far above RT (Daniel, Bulou, Rousseau *et al.*, 1990; Axe, Fujii, Batlogg *et al.*, 1985; Thomas, 1996b; Magus-Milakcovic, Ravez, Chaminade *et al.* (1995). In $BaCeO_3$, and $PrAlO_3$ the first distortion is also of $(\phi\phi\phi)$-type, with a decrease of the number of tilt components when the temperature is lowered (see Tab. V) (Knight, 1995; Darlington, 1996).

The crystal ScF_3 is cubic at RT. An inelastic scattering study of the crystal has been made (Aleksandrov, Voronov, Bulou *et al.*, 1998) where it was found that it remains cubic down to 4K, but its phonon spectrum contains a soft librational mode which would condense below 0K. The crystal was considered as incipient ferroelastic.

TABLE IV Symmetry of distorted phases due to superposition of tilts and antipolar displacements

Octahedral tilts		*Antipolar displacements*													
Space group	*Symbol*	00*a*	*LT*	0*a*0	*LT*	*a*00	*LT*	*aa*0	*LT*	*a*0*a*	*LT*	0*aa*	*LT*	*aaa*	*LT*
$P4/mbm$	00ψ	$\mathrm{P}42_1$	4*b*	$Ibam$	4*a*	$Ibam$	4*a*	$Ibam$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*
$I4/mmm$	$\psi\psi0$	$\mathrm{I\bar{4}2m}$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*
$Im\bar{3}$	$\psi\psi\psi$	$\mathrm{P}4_32_1$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*	$P4_32_1$	4*a*	$I23$	4*a*
$I4/mcm$	00ϕ	$Cmca$	2	$Cmca$	2	$P4/ncm$	2	$Pbcm$	3*a*	$Pbcm$	3*a*	$P4/ncc$	3*a*	$P\bar{4}2_1c$	3*a*
$Imam$	$\phi\phi0$	$C2/m$	2	$C2/m$	2	$Pnma$	2	$P2_1/c$	3*a*	$P2_1/c$	3*a*	$Cmca$	3*a*	Cmc	3*a*
$R\bar{3}c$	$\phi\phi\phi$	$P2_1/c$	2	$P2_1/c$	2	$P2_1/c$	2	$C2/c$	3*a*	$C2/c$	3*a*	$C2/c$	3*a*	$R\bar{3}$	3*a*
$Cmcm$	$\psi0\phi$	$Pccm$	3*a*	$Pccm$	3*a*	$C222_1$	2	$Pbcm$	3*a*	$Pbcm$	3*a*	$Pccm$	3*a*	$P2_12_12$	3*a*
$P4/mbm$	00Δ	$C222_1$	2	$Pccn$	3*a*	$Pccn$	3*a*	$Pccn$	3*a*	$P2_12_12$	3*a*	$P2_12_12$	3*a*	$P2_12_12$	3*a*
$Pnma$	$\phi\phi\psi$	$P2_12_12$	3*a*	$P2_12_12$	3*a*	$P2_12_12$	3*a*	$P2_12_12$	3*a*	$P2_12_12$	3*a*	$P2_12_12$	3*a*	$P2_12_12$	3*a*

LT – lattice type from Table III.

TABLE V Successive phase transitions, due to superposition of tilts, and tilts and ionic displacements

Crystal	T_1, K	G_1	T_2, K	G_2	T_3, K	G_3	*References*
$CsPbCl_3$	320	P4/mbm	314	Cmcm	310	P2$_1$/m	Fujii, Hoshino, Yamada *et al.*, 1974
$CsPbBr_3$	403	P4/mbm	361	Pnma	–	–	Hirotsu, Harada, Iizumi *et al.*, 1974
$RbCaF_3$	193	I4/mcm	41	Pmmn	–	–	Hidaka, Maeda and Storey, 1985
$KCaF_3$	545	Cmcm	538	Pnma	–	–	Hidaka, Yamashita *et al.*, 1984
$KCdF_3$	485	Cmcm	471	Pmna	–	–	Darlington, 1984
$KMnF_3$	186	I4/mcm	95.5	Cmcm	81	P4/mbm	Minckiewitz, 1975; Hidaka, 1975a.
$NaNbO_3$	914	P4/mbm	848	Cmcm	793	Pmmn?	Darlington and Knight, 1999.
$NaTaO_3$	903	P4/mbm	838	Cmcm	758	Pnma?	Darlington and Knight, 1999.
$PrAlO_3$	1320	R$\bar{3}$c	205	Imam	151	C2/m	Burbank, 1970; Woodward, 1997b.
$SmAlO_3$	2100	R$\bar{3}$c	1100	Pnma	–	–	Woodward, 1997b.
$BaPbO_3$	RT	I2/m	at 4,2 K	Immm	–	–	Ritter, Ihringer *et al.*, 1989.
$BaCeO_3$	1173	Im$\bar{3}$	673	Imcm	563	Pnma	Knight, 1995; Darlington, 1996.
$SrZrO_3$		I4/mcm	1103	Cmcm	973	Pnma	Ahtee, Glazer, Hewat, 1978.
WO_3	993	I4/mcm	740	Pnma	593	P2$_1$/n	Salje, 1977; Woodward *et al.*, 1995.
Na_xWO_3	423	P4/mbm	343	I4/mmm	293	Im$\bar{3}$	Clarke, 1977.
$MAPbBr_3$	236	I4/mcm	154	P4/mmm	149	Pna2$_1$	Onoda-Yamamuro *et al.*, 1992.

Just one oxide crystal of ReO_3-type which displays successive PT's is known: tungsten trioxide, WO_3. Its RT phase, δ-WO_3 is triclinic ($P\bar{1}$), with ($2a_c \times 2a_c \times 2a_c$) unit cell and tilt system ($\phi_1\phi_2\phi_3$). It transforms to monoclinic form γ-WO_3 (somewhere close to RT), conserving antipolar (aa0) displacements of W-atoms from the octahedra center. As a result the symmetry of the crystal passes through the $P2_1/m$ group, corresponding to the tilt system ($\phi_1\psi\phi_2$), see Table I, to the $P2_1/n$ group (Woodward, Sleight and Vogt, 1995). The structure of the orthorhombic β-WO_3 phase between approximately 600 and 970 K was first studied by X-ray diffraction on the twinned single crystal (Salje, 1977). It was assumed that the G_0 structure is distorted by ($\phi\phi\psi$)-tilts and belongs to $G_2 = D_{2h}^{16} = Pbnm$ Sp.Gr. Both high temperature α- and β-phases have been studied recently (Vogt, Woodward and Hunter, 1999). They have found that the orthorhombic β-phase belongs to $G_2 = D_{2h}^{14} = Pbcn$ Sp.Gr. between c.a. 620 and 980 K and its structure corresponds to ($0\psi\phi$)-tilts followed by antipolar (aa0) displacements. At 1073 K Rietveld refinements of the neutron powder diffraction data have led to the structure of α-WO_3, namely, tetragonal $G_1 = D_{4h}^{8} = P4/ncc$ Sp.Gr. with $Z = 4$ and (00ϕ)-tilt followed by (00a)-displacements along the main axis.

The non-stoichiometric compound Na_xWO_3 ($0.65 \leq x \leq 0.94$) has a unique sequence of PT's. Up to now among the known perovskites it is the only compound that belongs to the $a^+a^+a^+$ ($\psi\psi\psi$) tilt system below 293 K (G_3-phase), with only one type of cation on the A site. The number of ψ-tilts increases from $G_1 = P4/mbm$ ($a^0a^0c^+$) and further more $G_2 = I4/mmm$ ($a^+b^0a^+$) (see Tab. V), (Clarke, 1977).

Another group of oxide crystals has the $a^-b^+c^-$ ($\phi\psi\phi$) system of tilts; it is the so-called $GdFeO_3$-structure, the structure exhibited by this compound from decomposition temperature down to 0 K. Many examples of these crystals can be found in papers by Woodward (1997b) and Thomas (1996a) and reviews by Goodenough and Longo (1970) and Nomura (1978).

Most crystals that display successive PT's transform first, as a rule, to a tetragonal phase: $D_{4h}^{5} = P4/mbm$ or $D_{4h}^{18} = I4/mcm$ with unit cells $(\sqrt{2} \times \sqrt{2} \times 2)a_c^3$. The first case of such $G_0 \rightarrow G_1$ transition is preferred by some chlorides and bromides with large A-cations and polarizable anions, and also by fluorides and oxides with smaller A-ions (Na, K). Some examples are presented in Table V. These are

$CsPbCl_3$ and $CsPbBr_3$ (Fujii, Hoshino, Yamada and Shirane, 1974; Hirotsu, Harada *et al.*, 1974; Hua, 1991) and $NaNbO_3$ and $NaTaO_3$ (Ahtee, Glazer and Megaw 1972; Megaw, 1974; Ahtee and Glazer, 1976; Darlington and Knight, 1999).

The second PT is different in the crystals mentioned above; $CsPbBr_3$ transforms directly into $G_2 = D_{2h}^{16} = Pnma$, where two components of ϕ tilt appear at the second order PT (Hua, 1991). In the other three crystals $G_2 = D_{2h}^{17} = Cmcm$, with one ψ component conserved. A new ϕ component appears at the PT $G_2 \rightarrow G_3$ that brings these crystals either to $G_3 = D_{2h}^{16} = Pnma$ or to $G_3 = C_{2h}^{2} = P2_1/m$, when the temperature is lowered (see Tab. V). It seems very probable that the PT's in $CsSrCl_3$, $TlMnCl_3$ and $RbCdCl_3$ display the same sequences of PT's as the ones in $CsPbCl_3$ (Aleksandrov, Beznosikov and Posdnyakova, 1976; Hua, 1991).

Another group of ABX_3 crystals, oxides and fluorides, display a $G_0 \rightarrow G_1$ PT due to condensation of the R_{25}-mode, where just one ϕ tilt component appears below T_1 ($D_{4h}^{18} = I4/mcm$). $SrZrO_3$ and $RbCaF_3$ are examples of these PT's (Tab. V) (Hidaka, Maeda and Storey, 1985; Ahtee, Ahtee, Glazer and Hewat, 1976). Subsequent PT's in $SrZrO_3$ follow the sequence: $D_{4h}^{18} \rightarrow D_{2h}^{17} \rightarrow D_{2h}^{16}$ $(00\phi) \rightarrow (0\psi\phi) \rightarrow (\phi\psi\phi)$. At the same time the results on the symmetry changes in $RbCaF_3$ as well as in $KMnF_3$ are controversial. For both crystals two different Sp.Gr's of G_2 phase have been proposed: $D_{2h}^{13} = Pmmn(\psi_1\psi_2\phi)$ and $D_{4h}^{5}(00\Delta)$ for $SrZrO_3$ (Hidaka, Maeda and Storey, 1985), and D_{2h}^{16} and $D_{4h}^{5}(Z = 4)$ for $KMnF_3$ (Beckman and Knox, 1961; Gesi, Axe *et al.*, 1972 and references therein; Lockwood and Torrie, 1974).

At 186 K $KMnF_3$ undergoes a weak first order PT to tetragonal D_{4h}^{18} (Minckiewicz, Fujii and Yamada, 1970), and then at 91.5 K a second order PT changes its symmetry which Hidaka, Ohama *et al.* (1975a) propose as D_{4h}^{5}. However, this group is incompatible with Raman experiments and to explain the spectroscopic data the alternative D_{2h}^{17} Sp.Gr. was proposed by Lockwood and Torrie, 1975. The magnetic ordering transition that takes place at 87 K evidences the non-collinear antiferromagnetic ordered structure, that is consistent with the aforementioned D_{2h}^{17} group, as is proven by Bartolomé, Rojo, Navarro *et al.*, 1983. A strong magnetoelastic first order PT to a weak ferromagnetic phase happens at 81 K which is consistent with a PT to D_{4h}^{5} phase at low temperature, as described by Hidaka, 1975b.

For $KCaF_3$ it has been found that at T_1 the $G_0 \rightarrow G_1$ PT is connected with the simultaneous condensation of M_3^z and R_{25}^x soft modes, *i.e.*, $G_1 = D_{2h}^{17} = Cmcm$ $(\phi 0 \psi)$, and is followed by the $G_1 = \rightarrow G_2$ PT to the phase $G2 = D_{2h}^{16} = Pnma$, that develops from the appearance of a second ϕ-tilt component (Hidaka, Yamashita and Okamoto, 1984).

An interesting situation occurs with the symmetry changes of two related crystals: $BaPbO_3$ and $BaBiO_3$. Both crystals belong to $C_{2h}^3 =$ I2/m Sp.Gr. $(\phi_1 0 \phi_2)$. (see Tab. I), with the same tilt systems and the same unit cell parameters: $(\sqrt{2} \times 2 \times \sqrt{2})a_c^3$. In the Pb-compound a 2-fold axis is along $b = 2a_c || [001]_c$, the monoclinic angle is between [110] and $[\bar{1}10]$ and all PbO_6 octahedra are equivalent. On the other hand, in the Bi-compound this unique axis is along $b = \sqrt{2}a_c || [110]_c$ and the β angle is between the two other axes. Two types of BiO_6 octahedra exist in this compound (Ihringer, Maichle, Prandl *et al.*, 1991; Ritter, Ihringer, Maichle *et al.*, 1989). Such a difference is solved very simply by taking into account a previous paper by Cox and Sleight (1979), where it was shown that there are two types of Bi-atoms, Bi^{3+} and Bi^{5+}, fully ordered to form the elpasolite type structure. If we compare the $(\phi_1 0 \phi_2)$ systems shown in Tables I and VI it may be noticed that the Sp.Gr., unit cells and directions of the principal axes correspond to the experimental results, for the perovskite $BaPbO_3$ and the elpasolite $Ba_2Bi^{3+}Bi^{5+}O_6$ crystals, respectively. In the solid solution $BaPb_{0.75}Bi_{0.25}O_3$, which is a superconductor below 10 K (Sleight, Gillson and Bierstedt, 1975) the structure of $BaPbO_3$ is conserved and its superconductivity seems to be favored by equivalent octahedra (Ihringer, Maichle, Prandl *et al.*, 1991).

The most complicated phase diagram is displayed by the $Na_{1-x}K_xNbO_3$ system. For the pure $NaNbO_3$ seven distorted phases have been found (Megaw, 1974). The first three of them are distorted by ‘simple’ systems of tilts: $G_1(T_2)$, $G_2(T_1)$ and $G_3(S)$ tilts are (00ψ), $(\phi 0 \psi)$ and $(\phi \psi_1 \psi_2)$, respectively. Here T_2, T_1 and S in brackets are the accepted designations of these phases (Ahtee, Glazer and Megaw, 1972) (see Tab. V). Below about 700 K the more complex phases R and P appear. They consist of alternating slabs with different systems of tilts (Ahtee and Glazer, 1976). In addition, antiparallel displacements of B-ions have been found in these two phases: along $[001]_c$ in R-phase $(00a)$, and along $[110]_c$ in P-phase $(aa0)$. Below 446 K the phase N with

TABLE VI Symmetry changes in crystals with initial space group $G_0 = O_h^5 = Fm3m$, due to superposition of octahedral tilts

			Volume	*Unit cell parameters in a_0 units*		
Symbols	*Space group*	τ_i	*Z*	*a*	*b*	*c*
000	$O_h^5 = Fm\bar{3}m$	–	4	1	1	1
00ϕ	$C_{4h}^5 = I4/m$	τ_9	2	$1/\sqrt{2}$	$1/\sqrt{2}$	1
$\phi_1 0 \phi_2$	$C_{2h}^3 = C2/m$	τ_9	2	1	$1/\sqrt{2}$	$1/\sqrt{2}$
$\phi\phi\phi$	$C_{3i}^2 = R\bar{3}c$	τ_9	1	$1/\sqrt{2}$	$1/\sqrt{2}$	$1/\sqrt{2}$
00ψ	$D_{4h}^6 = P4/mnc$	τ_{10}	2	$1/\sqrt{2}$	$1/\sqrt{2}$	1
$\psi\psi 0$	$D_{4h}^{12} = P4_2/nnm$	τ_{10}	4	1	1	1
$\psi\psi\psi$	$T_h^2 = Pn\bar{3}$	τ_{10}	4	1	1	1
$\psi 0 \phi$	$C_{2h}^6 = C2/c$		4	1	1	1
00Δ	$D_{4h}^1 = P4/m$		2	$1/\sqrt{2}$	$1/\sqrt{2}$	1
$\psi_1\psi_2\phi$	$C_{4h}^4 = P4_2/n$		4	1	1	1
$\phi_1\phi_2\psi$	$C_{2h}^5 = P2_1/n$		2	$1/\sqrt{2}$	1	$1/\sqrt{2}$
$\Delta\Delta 0$	$C_{2h}^3 = B2/m$		8	$\sqrt{2}$	1	$\sqrt{2}$
$0\psi\Delta$	$C_{2h}^4 = P2/c$		4	1	1	1
$\psi_1\psi_2\Delta$	$C_{2h}^4 = P2/c$		4	1	1	1
$\phi_1\phi_2\Delta$	$C_i^1 = P\bar{1}$		2	$1/\sqrt{2}$	$1/\sqrt{2}$	1
$\Delta\Delta\Delta$	$C_{3i}^2 = R\bar{3}$		4	1	1	1

$\Delta = \phi \pm \psi$.

symmetry $D_{3h}^6 = R\bar{3}c$ (or R3c) exists; *i.e.*, the tilt system here is 'simple' again: $a^- a^- a^- = \phi\phi\phi$ (Darlington, 1971; cited by Glazer, 1972). At room temperature the symmetry of the crystal has been determined as $D_{2h}^9 = Pbma$ with $Z = 8$ and unit cell dimensions $(\sqrt{2} \times 4 \times \sqrt{2})a_c^3$ (Sakovsky-Cowley, Lukaszewitz and Megaw, 1969).

In solid solutions with potassium the superposition of tilts and polar displacements takes place. When the content of K is in the range $0.04 < x < 0.06$ the first three distorted phases have the same symmetry as in pure $NaNbO_3$. In G_4 (G-phase) one p-vector (p) component coexists with the same tilt system as in G_3; *i.e.* $(\psi_1\psi_2\phi)(00p)$ and the crystal belongs to $C_{2v}^1 = Pmm2$ Sp.Gr. (see Tab. II). For the next phase, Q, both tilts and polar displacements change to $(\phi_1\psi\phi_2)(p_1 0 p_2)$ and the crystal, according to data of Table II, belongs to $C_s^1 = Pm$, that exists at RT for $x = 0.02$ and 0.10 (Ahtee and Hewat, 1975). In the whole family of solid solutions there exist more than thirteen distorted phases (Ahtee and Glazer, 1976; Ahtee, Glazer and Hewat, 1978); most of them are ferro- and antiferro-electric phases. The symmetry of

F, H, K and L ferroelectric phases, with different combinations of tilts and displacements, also correspond to data of Table II.

The high temperature phases of $NaTaO_3$ as well as $NaNbO_3$ have been studied recently by Darlington and Knight, 1999. The symmetries of the G_1 and G_2 phases in $NaTaO_3$ are the same as in $NaNbO_3$ but the G_3 symmetry is different. The authors have stated that G_3 (three tilt phases) in both crystals have different symmetries and have promised to publish new data soon. So, in Table V we have left the "old" data for G_3 with signs (?) hoping to actualize it later. More recently, Kennedy and coworkers (1999) have studied the structures of successive phases of $NaTaO_3$ and $SrHfO_3$.

The $PbZrO_3$ structure studied by Glazer, Roleder and Dec (1993) consists of two substructures related by a shear $c/2$. Each component corresponds approximately to a tilt system $a^-a^-c^0$ $(\phi\phi0)$. The Sp.Gr. of the crystal was determined as D_{2h}^9 = Pbam with $(\sqrt{2} \times 2\sqrt{2} \times 2)a_c^3$, $Z=8$. At the same time $PbZr_{0.9}Ti_{0.1}O_3$ transforms into $G_1 = R3m$ due to a (ppp) displacements, and additional $(\phi\phi\phi)$ tilts change the symmetry to R3c (Glazer, 1975). One more example is known, namely $BiFeO_3$, which belongs to the same R3c Sp.Gr., due to the same superposition of tilts and displacements (Kubel and Schmid, 1990).

A relatively rare family of perovskites consists of $(NH_4)BF_3$ compounds (B = Cd, Zn, Co, Ni, Fe, Mn). The PT in these crystals take place directly from the cubic into the orthorhombic $G_1 = D_{2h}^{16}$ = Pnma-phase due to orientational ordering of the ammonia groups followed by $(\phi\phi\psi)$ tilts, but no soft modes have been observed (see for example Bartolomé, Navarro and Gonzalez, 1977; Le Bail, Fourquet, Rubín *et al.*, 1990; Laguna, Sanjuan, Orera *et al.*, 1993; Rubín, Palacios, Bartolomé *et al.*, 1995).

$MAPbX_3$ (X = Cl, Br, I; MA = CH_3NH_3) crystallize in the cubic perovskite structure and undergo two or three PT's. One of these crystals has been included in Table V. The phases G_2 in the chloride and bromide compounds disappear under moderate hydrostatic pressure, while the iodine substance displays a new unknown PT (Onoda-Yamamuro, Matsuo and Suga, 1992). The phase $G_1 = D_{4h}^1$ = P4/mmm, and the low-temperature phases in all three compounds have $P222_1$ symmetry. None of these Sp.Gr's correspond to pure tilts, since they are caused by orientational ordering of methylammonium groups (Maaej, Bahri, Abid *et al.*, 1998). It is also necessary to mention the distorted structures of some hydrides. These compounds, A_3PdD_3 (A = K, Rb) for example, have a tilted perovskite-like structure ABX_3 where the alkali cations are located at the X-ions sites, with the hydrogen or deuterium anions at the B site and PdD_2 complex ions acting as A (Thomas, 1996a, b).

3. CRYSTALS WITH INITIAL PHASE G_0=Fm$\bar{3}$m

Just a few series of perovskite-like crystals belong to the space group $G_0 = O_h^5 = Fm\bar{3}m$: elpasolites $A_2BB'X_6$, and partially ordered perovskites $AB_{1/2}B'_{1/2}X_3$, cryolites $A_3B'X_6$, the ReO_3-type ordered crystals $BB'X_6$, and antifluorites A_2BX_6. Here A = K, Rb, Cs, NH_4 and other univalent complex cations such as $[N(CH_3)]^+$ in halides X = F, Cl, Br, I; while A = Ca, Sr, Ba in oxides where B and B′ are middle sized cations of appropriate valence (see Fig. 1). These series of crystals often show PT's and sequences of PT's that arise chiefly by tilts of the $[BX_6]$ and $[B'X_6]$ octahedral groups.

3.1. Possible Distortions of G_0 Due to Tilts

O'Leary and Wheeler (1970) were the first to study the symmetry changes at PT's in antifluorites, to explain in a K_2ReCl_6 crystal the multiple phase transitions which take place above its antiferromagnetic PT at 12 K. The use of Landau (Landau and Lifshitz, 1958) and group theory altogether has allowed the authors to find that the second-order PT's can be determined by three irrep', which belong to $\Gamma(k_{11})$ and $X(k_{10})$ points of the G_0 Brillouin zone (see Fig. 3): $T_{1g}^{\Gamma}(\tau^{(9)})$, $A_{2g}^{X} = X^{4+}(\tau^{(3)})$ and $X^{2+}(\tau^{*})$. The latter corresponds to $[BX_6]$-octahedra internal vibrations, and can not be considered as a candidate for a soft lattice mode. The other two correspond to soft rotary modes at the center (Γ) and border (X) points of the zone (see Fig. 3b). Because both irrep's correspond to three-dimensional order parameters (X^{4+} mode is non-degenerate but there exist three equivalent X-points, three arms of the X-star in the zone) it may cover the octaheral tilts around the three cubic axes of G_0. If the PT conserves the volume of the initial unit cell; the irrep's components $\Gamma^{4+}{}_X$, $\Gamma^{4+}{}_Y$, $\Gamma^{4+}{}_Z$ ($a^0a^0c^-$, $a^0c^-a^0$, $c^-a^0a^0$, or 00ϕ, $0\phi0$, $\phi00$ in our notation) lead, of course, to the same $G_1 = C_{4h}^5 = I4/m$, $(Z=2)$ Sp.Gr. Similarly, X_Z^{4+}, X_Y^{4+}, X_X^{4+} are equivalent to $a^0a^0c^+$, $a^0c^+a^0$, $c^+a^0a^0$ or 00ψ, $0\psi 0$, $\psi 00$ and lead to $G_1 = D_{4h}^6 = P4/mnc$ $(Z = 4)$ Sp.Gr.

O'Leary and Wheeler (1970) have considered also the symmetry changes that appear when two or three components of the tilt take part in the PT (see Tab. VI). The most interesting case was the determination of the G_i symmetry when anti-phase (ϕ) and in-phase (ψ) tilts take place around different or the same axes. For example, when the first PT leads to $G_1 = C_{4h}^5 = I4/m$, with a ϕ-tilt around Z-axis, *i.e.* (00ϕ), and ψ-tilts around the X-axis, *i.e.* $(\psi 0\phi)$, the resulting symmetry is $G_2 = C_{2h}^6 = C2/c$ $(Z=4)$. But if the ψ-tilts take place around the same Z-axis, *i.e.* (00Δ) (see Tab. VI), one gets the $G_2 = C_{4h}^1 = P4/m$ Sp.Gr. For the first time the two types of tilts were allowed to exist around the same cubic axis. The same assumption for perovskites was considered by Aleksandrov (1976, 1978).

Ohe (1975) made a similar study on symmetry changes in order to explain the PT's in tetramethylammonium chloruranate and chlorstannate. But the author restricted his studies just to PT's due to a single irrep. He obtained for the Γ^{4+} and X^{4+} irrep's the same results as O'Leary and Wheeler (1970).

The first attempt to consider all the possible PT's in crystals having $G_0 = Fm3m$ in the framework of group theory was made by Zinenko and Misyul (1978), but their results were published as a report to the Russian Institute of Scientific Information and never reached a more widespread diffussion. Aleksandrov (1980) and Aleksandrov and Misyul (1981) have used some of the results in the course of the study of successive PT's due to tilts in elpasolite-type crystals. The results of the study are presented in Table VI. To the original data given by Aleksandrov and Misyul (1981) we have added the cases with non-equal, non-zero components of ψ- and ϕ-tilts, omitted by those authors but considered by O'Leary and Wheeler (1970), by Ohe (1975) and recently by Woodward (1997a). The tilt systems with two equal components, such as $(\phi\phi\psi)$ $(\psi\psi\Delta)$ and $(\phi\phi\Delta)$, listed previously by Aleksandrov (1980) and Aleksandrov and Misyul (1981), lead to monoclinic Sp.Gr's that are not compatible with the symmetry; consequently we have substituted them by systems having unequal tilt components. The same has been made for tilt systems corresponding to orthorhombic Sp.Gr's. In Table VI we have not included the cases with different Δ-tilts around different axes. We sincerely hope that now

Table VI, which contains tilt systems in crystals with $G_0 = Fm3m$ as initial phase, is the most complete one, as compared to those previously published.

Aleksandrov and Misyul (1981) published the possible sequences of successive PT's, when the assumption that the structural distortions increase with the decrease of temperature (or increase of external pressure) was taken. The same assumption had been considered earlier in the study of successive PT's in perovskites (Aleksandrov, 1976). The corresponding paths for elpasolites and other related crystals can be depicted in a scheme similar to Figure 4, but the space groups for any tilt system should be substituted with the help of Table VI.

It is necessary to mention here that group-subgroup relations for $G_0 = Fm3m$ have been published exhaustively in three other papers, by Sutton and Armstrong (1982), by Ben Ghosen and Mlik (1983) and by Misyul (1984). In each case the subgroups related to the action of IR's that belong to the Γ, X, L and W points of the Brillouin zone were analysed (Fig. 3b), while the superposition of different distortion types were not considered. In the paper by Misyul (1984) the irrep's leading to tilts of octahedra in distorted structures were deduced.

Aleksandrov and Misyul (1981) also mentioned that in antifluorite type crystals, where the octahedral units are not linked between each other, the octahedra which belong to layers orthogonal to the tilt axis may be turned, in principle, in the opposite direction. This may happen when the A-cation in the A_2BX_6 structure is a rather complex molecular cation.

Two simple cases of such types of tilts are shown on Figure 6e, f. These distortions named (00θ), $(\theta\theta 0)$ are determined by the six-dimensional irrep: $X^{5+} = E^X_{2g} = \tau^{(9)}$ of G_0. They belong to $D^{18}_{2h} =$ Cmca, $Z = 4$ and $D^{12}_{2h} =$ Pnnm, $Z = 2$ Sp.Gr.s, respectively. The representation X^{5+} determines the mixed rotary mode, where displacements of the A-cation follow the tilts (Linn, Patterson and Wheeler, 1978; Misyul, 1984).

3.2. Possible Distortions of G_0 Due to the Superposition of Tilts and Polar Displacements

Aleksandrov and Misyul (1981) enumerated the G_0 subgroups that arise due to the combined action of the main tilt systems listed in Table VI, and of polar displacements (Misyul, 1984). The polar

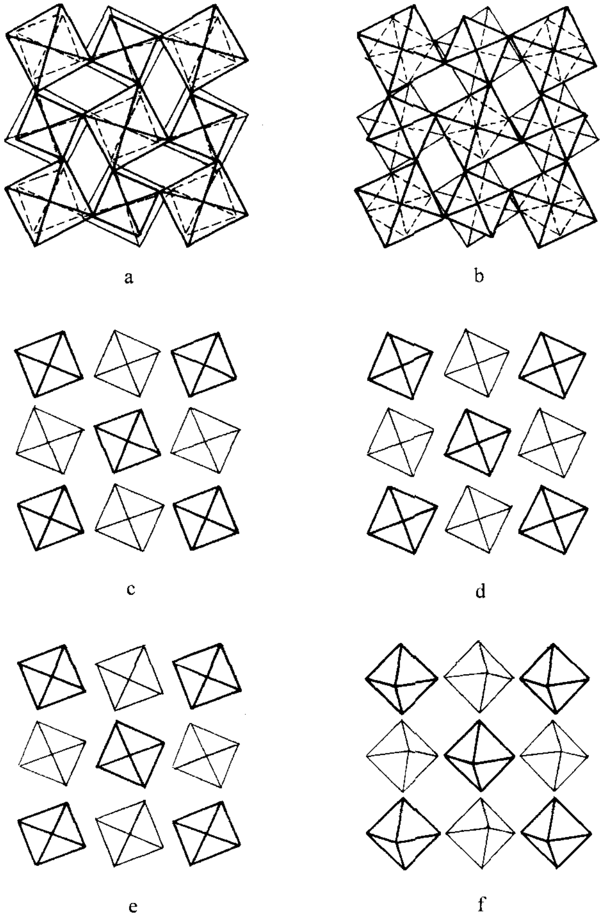

FIGURE 6 Octahedral tilts in elpasolites and antifluorites (A-cations are not shown). (a) (00ψ)- and; (b) (00ϕ)-tilts in elpasolite structure around [001] axis; (c) (00ψ)- and; (d) (00ϕ)-tilts in antifluorites. The octahedra of the lower layer are shown by thinner lines; (e) (00θ)- and; (f) $(\theta\theta0)$- tilts, unusual in antifluorite structure (see text).

distortions are characterized by p vector components along the proper cubic axes: (00p), (pp0), (ppp), *etc.* Symmetry changes of G_0 due to polar distortions alone are clearly seen in the first line of Table VII, where for each system just a tilt symbol and International space group symbol have been used for simplicity.

The symmetry of the complex distortions of G_0, caused by the combined actions of ψ- and ϕ-tilts and polar displacements of B- or

TABLE VII Symmetry of distorted phases, due to superposition of tilts and polar displacements, for crystals which belong to space group $G_0 = O_h^5$ = Fm3m in the initial phase

	Components of polar displacements								
Tilts	000	$00p$	$0p0$	$p00$	$pp0$	p_1p0	$p0p$	$p_1p_2p_3$	ppp
000	$Fm\bar{3}m$	$I4mm$	$I4mm$	$I4mm$	$Imm2$	Cm	$Imm2$	Cm	$R3m$
$\psi\psi\psi$	$Pn3$	$Pnn2$	$Pnn2$	$Pnn2$	Pc	Pc	Pc		$R3$
$\phi\phi\phi$	$R3$	$P1$	$P1$	$P1$	$P1$	$P1$	$P1$	$P1$	$R3$
$\Delta\Delta\Delta$	$R3$	$P1$	$P1$	$P1$	$P1$	$P1$	$P1$	$P1$	$R3$
00ψ	$P4/mnc$	$P4nc$	$Ama2$	$Ama2$	$Pmn2_1$	Pm	Pc	Cc	
$\psi\psi0$	$P4_2/nnm$	$P4_2nm$	$Pnn2$	$Pnn2$	$Abm2.$	Pc	Pc	Cm	
00ϕ	$I4/m$	$I4$	Cm	Cm	Cm	Cm	$P1$	$P1$	$P1$
00Δ	$P4/m$	$P4$	Pm	Pm	Pm	Pm	$P1$	$P1$	$P1$
$\psi\psi\phi$	$P4_2/n$	$P4_2$	Pc	Pc	Pc	Pc	$P1$	$P1$	$P1$
$\psi0\phi$	$C2_1/c$	$P2_1$	Pc	Pc	Pc	Pc	$P1$	$P1$	$P1$
$\psi0\Delta$	$P2/c$	$P2$	Pc	Pc	Pc	Pc	$P1$	$P1$	$P1$
$\phi\phi0$	$C2/m$	Cm	$P1$	$P1$	$C2$	$P1$	$P1$	$P1$	$P1$
$\Delta\Delta0$	$C2/m$	Cm	$P1$	$P1$	$C2$	$P1$	$P1$	$P1$	$P1$
$\phi\phi\psi$	$P2_1/n$	Pc	$P1$	$P1$	$P2_1$	$P1$	$P1$	$P1$	$P1$

A-cations, may be used to determine the nature of the distortion in the partially ordered complex ferroelectric perovskites.

3.3. Some Experimental Data on Crystals with Initial Phase G_0=Fm$\bar{3}$m

The number of works devoted to the study of PT's in the families of crystals mentioned above is very large and it is quite impossible to list them exhaustively. Therefore, it is inevitable to select some of the papers. We have restricted ourselves to those works where the symmetry changes at the successive PT's have been determined, and to the rather rare cases where the Sp.Gr. change at the $G_1 - G_2$ transitions cannot be described as a superposition of tilts, in contrast to the method used in Figure 4.

3.3.1. Elpasolites – Halides

Most studies on elpasolites have been devoted to $A_2BB'X_6$ crystals where X = F, Cl, Br, CN; A^+, B^+ = Li, Na, K, Rb, Tl, Cs, NH_4, Ag and B^{3+} = Al, Sc, V, Cr, Fe, Ga, In, Ln, Bi. Many complex oxide $AA'BB'O_6$ perovskites, with different combinations of the cations, also belong to Fm3m Sp.Gr. when B, B'-cations are (partially) ordered in the same manner as in the elpasolite structure (see Fig. 1b). Other types of ordering are also possible (Wang, Gu, Zhang, 1990). These together with the known examples of distorted phases will be mentioned below.

A detailed review of PT's in elpasolites, especially halides, has been published recently (Flerov, Gorev, Aleksandrov *et al.*, 1998). It summarizes many previous studies where it was shown that using the modified tolerance factor t (Tressaud, Khairaun, Chaminade *et al.*, 1986),

$$t = \frac{R_A + R_X}{\sqrt{2}[1/2(R_B + R_{B'}) + R_X]}$$

and the known experimental data (see cited review and references [8–26] therein) it is possible to determine limits of stability for different series of elpasolites. When the t value is above an upper limit the crystals, having the same general formula, transform to the polytypes of hexagonal or rhombohedral structure. Below a lower limit the cubic phase is unstable and the structure distorts (Flerov, Gorev, Aleksandrov *et al.*, 1998 and references therein).

Many halide elpasolites, which are cubic at RT, transform to a distorted phase with decreasing temperature (Landolt-Börnsten, 1973; Meyer and Dietzel, 1979). The chlorides $Rb_2LiB^{3+}Cl_6$ with $R_B > R_{Gd}$; $Rb_2NaB^{3+}Cl_6$ with $R_B > R_{Lu}$ and many others are tetragonal at RT, and belong to $D^6_{4h} = P4/mnc$ Sp.Gr. (Meyer and Dietzel, 1979). But most halides (chlorides, fluorides) display one PT, $G_0 - G_1$, and prefer $C^5_{4h} = I4/m$ Sp.Gr. for the low temperature phase; the compounds Rb_2NaLnF_6, Ln = Ho, Tm (Veenendaal, Brom and Ihringer, 1982; Selgert, Lingner and Luthi, 1984; Ihringer, 1982, 1984), Cs_2NaBCl_6, B = Nd, Pr, Tm, Bi (Anistratov, Beznosikov and Gusar, 1978; Knudsen 1984; Pelle, Blanzat and Chevalier, 1984), $Cs_2NaLnBr_6$, Ln = Tm, Dy, Ho (Buhrer and Gudel, 1987) may be mentioned.

There exist two series of halide elpasolites which display one or successive PT's depending on the size of B^{3+} cation. The first one is the well-studied $Rb_2KB^{3+}F_6$ series (Tressaud , Khairoun, Dance *et al.*, 1986; Couzi, Khairoun and Tressaud, 1986; Flerov, Gorev, Buhrer *et al.*, 1997). When the B^{3+} cation size grows from Al to La the t-factor diminishes from 0,894 (Al) to 0,805 (La). So, Rb_2KAlF_6, for example, does not display any PT above 77 K, and, on the contrary, the crystals with the B^{3+} radius equal or larger than Cr^{3+}($t = 0.878$) transform to distorted phases of lower symmetry that remain undetermined (Couzi, Khairoun and Tressaud, 1986). Below RT, the crystals with B^{3+} = Cr, Fe, Ga as well as Tl_2KInF_6 undergo strong first-order PT's followed by rather large entropy (S) changes $\Delta S/R \cong 2$ (Gorev, Flerov,Voronov *et al.*, 1994; Guengard, Grannec, Tressaud *et al.*, 1996). These crystals are destroyed at the PT due to a large volume change. On the other hand, the use of powder samples has not allowed to determine their Sp.Gr's below the PT (Couzi, Khairoun and Tressaud, 1986).

The $Rb_2KM^{3+}F_6$ crystals with M^{3+} = Sc, In, Lu undergo a sequence of two PT's; cubic-tetragonal-monoclinic. The temperature range where the tetragonal phase exists decreases in the trend Sc < In < Lu (Flerov, Tressaud, Aleksandrov *et al.*, 1991; Flerov, Gorev, Melnikova, 1992a, b; Flerov, Gorev, Buhrer *et al.*, 1997). For M^{3+} = RE, from Er down to La, a trigger-type PT appears, with the G_1 phase monoclinic $C_{2h}^5 = P12_1/n1$, $(\psi\phi_1\phi_2)$ tilts, the same as the G_2 phase for Sc, In, Lu (Couzi, Khairoun and Tressaud, 1986; Beznosikov, Flerov, Gorev *et al.*, 1983). The symmetry changes and PT temperatures for crystals of the series are presented in Table VIII.

Two special points in the transition temperature versus R_B diagram have been found for this system. When R_B is located somewhere between R_{Lu} and R_{Er} the crystal has a tricritical point, and when it is between R_{Sc} and R_{Fe} two successive PT's of the Sc-compound transform into a strong first-order PT in Fe-fluorelpasolite. An attempt to find the tricritical point in the $Rb_2KSc_{1-x}Ga_xF_6$ ($1.0 > x > 0.6$) system failed (Gorev, Bovina, Bondarenko *et al.*, 1995).

There exists another group of halides that display successive PT's. These are Cs_2RbDyF_6 (Aleksandrov, Melnikova and Misyul, 1987; Gorev, Iskornev, Kot *et al.*, 1985) and Cs_2RbHoF_6 (Ihringer, Wu, Hoppe and Hewat, 1984b). It can be seen in Table VIII and then in Table VI that the symmetry changes at the PT's correspond to the appearance of tilts.

Another group of A_2BMX_6 crystals with successive PT's are oxifluorides A, B = Rb, Cs; M = Mo, W (Ravez, Peraudeau, Arend *et al.*, 1980; Abrahams, Bernstein and Ravez, 1981). These crystals, $Rb_2KMoO_3F_3$ for example ($T_c = 328\,K$), are interesting due to the existence of spontaneous polarization at RT, with $G_1 = C_3^4 = R3$

TABLE VIII Successive phase transitions in crystals with initial group $G_0 = O_h^5 = Fm3m$

Crystal	T_1, K	G_1	T_2, K	G_2	T_3, K	G_3	*References*
Rb_2KFeF_6	200	unknown	–	–	–	–	Tressaud, Khairoun, Dance *et al.*, 1986
Rb_2KGaF_6	123	unknown	–	–	–	–	Flerov, Gorev, Melnikova *et al.*, 1992b
Rb_2KScF_6	252	$C_{4h}^5 = I4/m$	223	$C_{2h}^5 = P2_1/n$	–	–	Flerov *et al.*, 1992a; Fayet *et al.*, 1996.
Rb_2KInF_6	283	$C_{4h}^5 = I4/m$	264	$C_{2h}^5 = P2_1/n$	–	–	Flerov, Gorev *et al.*, 1992b
Rb_2KLuF_6	360	$C_{4h}^5 = I4/m$	356	$C_{2h}^5 = P2_1/n$	–	–	Flerov, Gorev *et al.*, 1992b
Rb_2KYF_6	398	$C_{2h}^5 = P2_1/n$	–	–	–	–	Couzi, Khairoun and Tressaud, 1986.
Cs_2RbHoF_6	270	$C_{4h}^5 = I4/m$	197	$C_{2h}^5 = P2_1/n$	–	–	Ihringer, Wu and Hoppe, 1984.
$Rb_2MoO_3F_3$	538	C_3^1 or C_3^4	423	$C_i^1 = P\bar{1}$	–	–	Peraudeau, Ravez *et al.*, 1978; Ravez, 1981.
$Cs_2LiIr(CN)_6$	418	$D_{4h}^6 = P4/mnc$	335	(C_{2h})	–	–	Swanson and Lucas, 1978
$Ba_2Bi^{3+}Bi^{5+}O_6$	?	$R\bar{3}$	405	$C_{2h}^3 = I2/m$	–	–	Cox and Sleight, 1979
K_2ReCl_6	111	$C_{4h}^5 = I4/m$	103	$C_{2h}^6 = C2/c$	76	$C_{4h}^4 = P4/n$(¿)	O'Leary and Wheeler, 1970
K_2SnCl_6	261	$D_{4h}^6 = P4/mnc$	255	$C_{2h}^5 = P2_1/n$	–	–	Boysen *et al.*, 1973, 1978
K_2SeCl_6	238	$D_{4h}^6 = P4/mnc$	221	$C_{2h}^6 = C2/c$	212	$C_{2h}^5 = P2_1/n$	Noda, Ishii, Mori and Yamada, 1980.
K_2TeCl_6	434	$D_{4h}^6 = P4/mnc$	405	$C_{2h}^5 = P2_1/n$	243	?	Berg, Poulsen *et al.*, 1977; Abriel, 1984.
$(EA)_2PtCl_6$	?	C_{4h}^5 or D_{4h}^6	?	$C_{2h}^6 = C2/c$	–	–	Elyoubi and Ben Ghosen, 1986.
$(NH_4)_3ScF_6$	330	$D_{4h}^6 = P4/mnc$	291	$C_{2h}^5 = P2_1/n$	~240	$C_i^1 = P\bar{1}$	Tressaud, Khairoun, Rabardel *et al.*, 1986.
$CoZrF_6$	272	$R\bar{3}$	–	–	–	–	Rodriguez, Couzi *et al.*, 1990a, b, c.
Pb2MgTeO6	194	$R\overline{3/m}$, inc	142	$R\bar{3}$, inc	–	–	Baldinozzi, Grebille, Sciau *et al.*, 1998

Sp.Gr.. It might imply that some triple tilts: $(\psi\psi\psi)$, $(\phi\phi\phi)$ or $(\Delta\Delta\Delta)$, plus polar displacements (ppp) coexist in the ferroelectric-ferroelastic phase (see Tab. VII).

The compounds $Cs_2LiM(CN)_6$, M = Co, Ir, Cr, Fe also display two successive PT's above RT (Ryan and Swanson, 1978), (see Tab. VIII). At the high temperature first-order PT the tilts of $M(CN)_6$-octahedra are involved, while at the lower temperature second-order PT the participation of the Cs translational mode, belonging to the X-point of Brillouin zone, has been detected.

3.3.2. *Antifluorites*

Phase transitions in the antifluorite crystals, A_2BX_6 where A = K, Rb, Cs, NH_4 and more complex cations such as $[(CH_3)_4N]$, $[(C_2H_5)_4N]$, *etc.*, $B = M^{4+}$ and X = F, Cl, Br, I, were investigated much earlier than the PT's in other perovskite-like crystals with $G_0 = Fm3m$ as initial phase. Many experimental methods have been used: X-ray and neutron scattering, optics, calorimetry, Mössbauer and Raman spectroscopy, NMR and NQR. Armstrong (1980), published a review devoted to PT-studies in antifluorites, where abundant experimental data for these crystals were collected (see the review and references therein).

It is necessary to mention the opposite use of terms "in phase" and "anti-phase" tilts in many papers devoted to antifluorites with respect to the same terms applied to crystals with two- and three-dimensional octahedral constructions. For perovskites and elpasolites, the term "in phase" means $a^+(\psi)$ – tilt determined by the M_3 mode, and "anti-phase" $a^-(\phi)$ – tilt determined by the R_{25} mode. Though the terms are used in opposite fashion, the same modes and the same irrep's are responsible for corresponding PT's in antifluorites and lead to the same symmetry of the distorted phases.

The origin of the opposite use of the terms can be explained as follows. Imagine that ψ and ϕ tilts around $[001]_c$ exist in the elpasolite structure, Figure 6a, b, and then let us extract the largest octahedra from these pictures, Figure 6c, d, to get the antifluorite structure. It is seen that in the case of ψ-tilts for elpasolite (in-phase) the isolated octahedra in antifluorite have opposite tilt signs (anti-phase). On the contrary, for ϕ-tilts in elpasolite (anti-phase) similar tilts of octahedra appear, thus (in-phase) for the antifluorite structure.

Many substances with antifluorite structure are known that display successive PT's, like K_2PtCl_6 – five, K_2ReBr_6 – five, K_2SnCl_6 – two, *etc.* (Landolt-Börnstein, 1973; Armstrong, 1980). As a rule, it was considered that one or two PT's at T_1 and T_2 (for decreasing temperature) originate due to the condensation of one or two rotary modes: Γ^{4+} and then X^{4+}, or *vice versa.* A few representatives of these type of crystals are presented in Table VIII.

O'Leary and Wheeler (1970) determined the symmetry of the first two distorted phases of the K_2ReCl_6 crystal (Tab. VIII). It was studied later by Linn, Patterson and Wheeler, 1978 who found that the whole branch of lattice vibrations between the Γ and X points of the Brillouin zone, which corresponds to octahedral librations, is soft. At 111 K the Γ^{4+} mode is condensed and at 103 K the X^{4+} mode tends to zero frequency. As for the G_3-phase, the assumption made by O'Leary and Wheeler, 1970 and Berg, Poulsen and Bjerrum, 1977, that $G_3 = C_{4h}^4 = P4_2/n$, $(\psi\psi\phi)$ tilts, does not explain the appearance of three NQR Cl^{35} lines below 76 K. It is more natural to assume that in G_3 the crystal belongs to $C_{2h}^5 = P2_{1/n}$ $(\psi\phi_1\phi_2)$-tilts. The same Sp.Gr. was found in some other halide antifluorites (see Tab. VIII).

To explain the two successive PT's in K_2SnCl_6 at 261 and 255 K another path in Figure 4 is used. At 261 K the mode X^{4+} (ψ-tilt) is condensed first, and then at the first-order PT two components of ϕ-tilts appear which transform the crystal directly to monoclinic phase (Boysen, Ihringer, Prandl and Yelon, 1976; Boysen and Hewat, 1978), (see Tab. VIII).

In K_2TeBr_6 the sequence of the first two distorted phases is similar to that found in K_2SnCl_6 (Abriel, 1984), but in Rb_2TeBr_6 the mode condensing at T_1 is Γ^{4+} and the symmetry of G_1 is $C_{4h}^5 = I4/m$ (Abriel and Ihringer, 1984).

A less clear situation is that in antifluorites with molecular A-cations. For example Elyoubi, Ben Ghozen, Mlik and Daoud (1986) have determined G_2 at RT as $C_{2h}^3 = C2/c$ in $[(C_2H_5)_4N]_2PtCl_6$, and at rather high temperature the crystal belongs to G_0. The assumption made by the authors about the symmetry of the intermediate phase; either $P4_2/mmc$ or Cmmm, seems to be mistaken. In our opinion it is more logic to consider two other tetragonal phases; either I4/m or P4/mnc. For $[(CH_3)_4N]_2UCl_6$ and $[(CH_3)_4N]_2SnCl_6$ Ohe, 1975 reported $D_{2d}^{11} = I\bar{4}2m$ Sp.Gr. and assumed C_{4h}^5 or D_{4h}^6 Sp.Gr's for the intermediate phase. A transition between two tetragonal phases seems to be an exceptional case. Many other examples of a doubtful determination of symmetry could be presented.

Finally, it should be mentioned that not only in K_2ReCl_6 but also in some other antifluorites, K_2OsCl_6 and K_2TeBr_6 for example, the soft librational modes have been observed by means of inelastic and diffuse X-ray and neutron scattering (Mintz and Armstrong, 1979; Abriel, 1984; Abriel and Ihringer, 1984, *etc.*)

Bronger and Aufferman (1992) published some interesting data about the Rb_2PdH_4 and $CsPdH_4$ hydrides. These crystals belong also to the antifluorite structure, where four hydrogen atoms are randomly distributed in the structure over six X-sites.

3.3.3. Cryolites

The structural PT's in A_3BX_6 cryolites , where one of the A-cations is located inside the BX_6 octehedron ($Z = 6$), have been observed usually far above RT (for examples see Landolt-Börnstein, 1973; Aleksandrov, Anistratov, Beznosikov *et al.*, 1981). Most of the substances were studied by DTA technique in the course of phase diagram determination. Many substances that show successive PT's have been found, as for example, in Cs_3BiCl_6 and K_3LuF_6 (Aleksandrov, Anistratov, Beznosikov *et al.*, 1981 and refererences therein), and in Rb_3GaF_6 (Flerov, Gorev, Voronov and Bovina, 1996) for which three PT's are present. Other cryolites belong mostly to triclinic symmetry at RT, and transform directly to the cubic phase G_0 at high temperature. Some cryolites that present successive PT's were studied by X-ray diffraction, but the symmetries of the intermediate phases are in many cases either unknown or controversial.

Substances with ammonium groups have been studied in more detail because the PT's in these crystals take place in the temperature range 400–77 K (Tressaud, Khairoun, Rabardel *et al.*, 1986). Cryolites $(NH_4)_3B^{3+}F_6$ with small $B^{3+} = Al$, Ga, Cr, Fe, V are triclinic at RT: $G_1 = P\bar{1}$. The compounds with In, Fe and Sc display three PT's: $G_0 - G_1 - G_2 - G_3$. In the case of $(NH_4)_3ScF_6$ the symmetry of G_1 and G_2 phases have been proposed (Tressaud, Khairoun, Rabardel *et al.*, 1986) (see Tab. VIII). The nature of the PT's in this group of substances is most probably connected not only to tilts but also to ordering processes of the octahedral and tetrahedral units, as follows from the values of entropy changes, and from the NMR and NQR studies (Flerov, Gorev and Ushakova, 1999).

Oxifluorides of transition metals $A_3MeO_xF_{6-x}$ have been obtained by Pausewang and Rudorff, 1969. Many representatives of the group crystallyze in cubic, orthorhombic or monoclinic classes, but in most cases their Sp.Gr's have not been determined. The members of a series of oxifluorides with cryolite structure: $A_3MO_3F_3$ (A = K, Rb, Cs; M = Mo, W) display two successive first-order PT's above RT. The intermediate phase G_1 is again polar ($G_1 = C_3^1$ or C_3^4). Besides, the cryolite structure has been found in some hydrides such as Na_3RhH_6 and others (Bronger, Gehlen and Aufferman, 1991).

3.3.4. Elpasolites – Oxides

Many ordered (or partially ordered) complex $A(B_{1/2}B'_{1/2})O_3$ perovskites with distorted structures at RT are known (Landolt-Börnstein, 1973; Fesenko, 1972; Harrison, Reis, Jakobson *et al.*, 1995; Smolenskii, Bokov, Isupov *et al.*, 1984; Galasso, 1990). Some of the Ba_2MBiO_6, M = Ce, Pr, Nd, Tb, Yb (Harrison, Reis, Jacobson *et al.*, 1995) are partially ordered and if their Sp.Gr's and unit cell parameters are considered it may be conjectured that the distortions of the structures correspond to tilts. The Pb_2MgWO_6 crystal transforms into the orthorhombic phase $G_1 = D_{2h}^{16}$ below 312 K. The structure has been solved by Baldinozzi, Sciau *et al.*, 1995 and it was found that in addition to $(\phi_1\phi_2\psi)$ tilts there is an antiferroelectric displacement of the Pb-atoms along $[011]_c$.

The phase transitions in these crystals have been investigated mainly in ferroelectric and magnetic materials (Galasso, 1959, 1990; Fesenko, 1972). Far less data are available about structural transformations due to tilts. A few examples are noteworthy here: The group of $Ba(M^{3+}_{1/2}M^{5+}_{1/2})O_3$ perovskites, M^{3+} = Nd, Nd, Y, In and M^{5+} = Ta, Nb has been studied (Smolenskii, Bokov, Isupov *et al.*, 1984). Some of these crystals are paraelectric and display a PT to the $C_{4h}^5 = I4/m$ phase. $Ba(Y,Ta)O_3$ was studied by Raman spectroscopy in the backscattering geometry. A soft lattice mode was found in the G_1-phase (Gregora, Petzelt, Pokorny *et al.*, 1995).

The $BaBiO_3$ crystal is not commonly regarded as elpasolite, as it was mentioned above. Its structure was investigated by Cox and Sleight

(1979) and it was shown that the unit cell of this substance is monoclinic and contains four formula units with two sites for Bi-atoms, which differ in the Bi–O distances. It was concluded, therefore, that both Bi^{3+} and Bi^{5+} are ordered on octahedral sites and the formula of the substance should be written as $Ba_2Bi^{3+}Bi^{5+}O_6$ (elpasolite type). The structure at RT and up to the PT at 405 K corresponds to $\phi\phi0$ (or a^-a^-0) tilt system (see Section 2.3.1). This crystal is one of the rare exceptions in the sense that the tilt system above 405 K is $\phi\phi\phi$ (or $a^-a^-a^-$); *i.e.*, the number of tilt components increases with temperature, just opposite to the sequences shown in Figure 4.

There exists the group of ordered complex $Pb_2BB'O_6$ oxides; B = Mg, Co, Sc; B′ = W, Te, Ta. Some of them have PTs into an incommensurate phase (INC) (Sciau, Calvarin, Sun *et al.*, 1992; Baldinozzi, Sciau, Moret and Buffat, 1994; Baldinozzi, Grebille, Sciau *et al.*, 1998; Tamura, 1978; Sciau, Krusche, Buffat *et al.*, 1990). Thus, in Table VIII successive PTs $G_0-G_1-G_2$ for Pb_2MgTeO_6 are shown. Below $T_1 = 194\,K$ the crystal transforms into an INC phase; its averaged structure has been proposed to be $R\bar{3}m$, with the INC modulation along $[111]_0$. The structure of the low temperature phase has been solved by Baldinozzi, Grebille, Sciau *et al.*, 1998, yielding to an average structure $G_2 = R\bar{3}$ and the same direction of modulation. No indication of lock-in PT was found down to 6 K. It can be assumed that some kinds of tilts are associated with the symmetry changes. Two other crystals, Pb_2CoWO_6 and Pb_2ScTaO_6 (Sciau, Krusche, Buffat *et al.*, 1990; Tamura, 1978) also display two PTs below RT, the intermediate G_1 phase being of INC type. The space groups of G_1 (monoclinic, INC) and G_2 (orthorhombic) phases have not been described in the cited papers. On the other hand, no INC-modulation in Pb_2MgWO_6 has been found, which transforms into $G_1 = D_{2h}^{16} =$ Pnma at 312 K. In this phase antiferroelectric displacements of Pb ions exist, followed by a $(\phi_1\phi_2\psi)$ system of tilts.

3.3.5. *Ordered Crystals of ReO_3-type*

Crystals of $BB'X_6$ with B and B′ cations differing in their valence often belong to the ordered ReO_3-type structure. Some examples of these crystals have been recently studied. In $CoZrF_6$ and $ZnZrF_6$ which have structures related to elpasolite (see Fig. 1e), the low temperature phase belongs to $G_1 = R\bar{3}$, Z = 1 at RT. $CoZrF_6$ transforms to the cubic phase at 270 K (310 K for $ZnZrF_6$ as detected by DTA). In both cases the distorted phase corresponds to ($\phi\phi\phi$) tilts and a corresponding optical soft mode has been found in the $CoZrF_6$ Raman spectra (Rodríguez, Couzi, Tressaud *et al.*, 1990a, b, c; Gorev, Flerov, Tressaud *et al.*, 1992). Other substances of this type with rhombohedral or cubic structures, such as $LiSbF_6$, $BaSiF_6$, $KOsF_6$, had been prepared, and similar PT's had been observed in some of them. The crystal $NaSbF_6$ transforms into $R\bar{3}$ phase under pressure of about 0.1 Gpa (Sowa, 1997).

4. CRYSTALS WITH INITIAL PHASE $G_0=D^1_{4h}=P4/mmm$

It was mentioned in Section 1 that among the members of the "perovskite family tree" there exist many types of perovskite-like crystals with structures containing one or a few square layers of corner linked octahedra. Their undistorted phases can belong either to $G_0 = D^1_{4h} = P4/mmm$, to $G_0 = D^{17}_{4h} = I4/mmm$, or to some other Sp.Gr's, since their symmetry depend on the types of shifts between the neighboring octahedral layers (slabs) along the plane orthogonal to the main 4-fold axis of a slab.

Two broad families of crystals whose initial phase structure belongs to the P4/mmm Sp.Gr. are known. These are the ABX_4 crystals of $TlAlF_4$ type and the $AO_\delta(A'_2B'_{n-1}B_{2n}O_{2n+2})$ oxides, the so-called $12(n-1)n$ series, of high temperature superconductors (see below). Many ABF_4 fluorides have structural PT's due to tilts of octahedra in layers, or/and due to the Jahn-Teller effect. PT's to another family are seldom found. Both of these groups will be considered below, and again paramount attention will be paid to crystallographic studies of possible PT's due to tilts and to successive PT's.

The ideal structure of $TlAlF_4$ type crystals is shown in Figure 7.1. Single layers of octahedra are located in juxtaposition, with a large A-cation in the symmetry center between the layers. The octahedra are slightly distorted and the coordination of A-cation ($Z = 8$) is different from the cubic one. Moreover, we should mention that instead of an A-cation the chain-like zigzag polyethylendi-ammonium groups $NH_3(CH_2)_mNH_3$, $m = 2-8$ can also be introduced (Arend and Granischer, 1976; Willet, 1977).

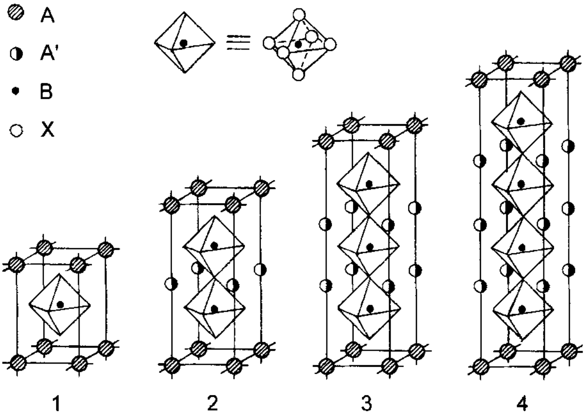

FIGURE 7 Unit cells of ABX_4 and n = 2, 3, 4 members of $AA'_{n-1}B_nX_{3n+1}$ series.

This group of crystals were considered as pseudo two-dimensional magnetic systems when the B-cations are paramagnetic, and long ($m = 2-8$) chains are located at the A-cation sites (Tichy, Benes and Kind, 1979). It was proposed by Aleksandrov and Beznosikov (1997), that more complex crystals may be found, with slabs of 2 and 3 octahedral layers instead of a single one (see Fig. 7.2, 3). New representatives with two octahedral layers in slabs have been actually found (Toda and Sato, 1996). The general formula of the family can be written as $AA'_{n-1}B_nX_{3n+1}$, where a large A-cation is located in between the slabs and the A′-cation in the slabs.

4.1. Symmetry Changes of G_0 Due to Octahedral Tilts

A group theoretical analysis of possible PT's in crystals belonging to $G_0 = D^1_{4h} = P4/mmm$ was published by Loyzance and Couzi (1984) limited to definite sequences of PT's in some ABF_4 crystals. The analysis was performed sequentially, for $G_0 \rightarrow G_1$, then for $G_1 \rightarrow G_2$, *etc.* These authors have used modified Glazer's symbols for the tilt systems. In summary, there exist three types of tilts in the tetragonal crystals: $a^+(\psi)$ and $a^-(\phi)$ tilts around the axis located in the octahedral layer and $c^+(\psi_z)$ tilts around the principal axis. The first two tilts are determined by two-dimensional irrep's of the G_0 Sp.Gr., while the last one is caused by a one-dimensional irrep. Since the layered structures loose the mechanical constraints between neighboring layers of octahedra separated by A-cations, each of these layers can be tilted independently. It means that the tilt systems in alternating layers can be different in sign; they can have either the same or opposite sign around [100], [010] and [001] axes in the alternate (001) layers, so the doubling of the unit cell c-parameter is possible. Deblieck, van Tandeloo *et al.* (1985) proposed a notation with subscripts and superscripts; the superscript has the same meaning as in Glazer's (1972, 1975) symbols, while the subscript indicates whether a tilt around an axis is the same (p) or opposite (a) in alternate (001) layers.

A more complete group theoretical study was done by Aleksandrov, Beznosikov and Misyul (1987a) and Aleksandrov (1987a) who used a method proposed by Gufan and Sakhnenko (1972). It was shown that irrep's τ_3, τ_9 and τ_5 which belong to M and X points (see Fig. 3c) correspond to ψ, ϕ and ψ_z tilts, respectively, when the same tilts take place in alternating octahedral layers. When the signs of the same tilts are opposite in alternating layers, $\psi_\pm$, $\phi_\pm$ symbols were used; these PT's are determined by irrep's belonging to R and A points of the Brillouin zone (see Fig. 3c). The superposition of different tilts can appear at successive PT's due to subsequent condensation of soft modes, which transform as the corresponding irrep's, at different temperatures. The vibrational representations for ABX_4 crystals have been analyzed partially, as far as we know, by Bulou, Rousseau, Nouet *et al.*, 1989. In some cases, especially for crystals with double octahedral layers, it is difficult to distinguish which one of the two irrep's corresponds to the actual soft mode.

The crystallographic analysis of possible changes from the initial structure due to tilts has been performed by Deblieck, van Tandeloo *et al.* (1985) and independently by Aleksandrov, Beznosikov and Misyul (1987a). Like previous authors (Hidaka, Inoue *et al.*, 1982; Bulou and Nouet, 1982), Deblieck and coworkers have used the symbols explained above; *i.e.*, super and subscripts in a notation similar to Glazer's. Up to 75 distorted phases have been enumerated, though many of these are incompatible with symmetry requirements. For example, in $a_p^+ a_a^+ c^0, a_p^- a_a^- c^0, a_p^- a_a^- c^0$ tilt systems and others, which lead to orthorhombic Sp.Gr's, the tilt angles can not be equal. We also mention that one example with opposite tilts in alternate layers was found by these authors (see below).

Aleksandrov, Beznosikov and Misyul (1987a, b) have used again their symbols; *i.e.*, ψ, ϕ and ψ_z tilts instead of a^+, a^- and c^+ and sign '$-$' as cap above the corresponding simbol when the tilt changes its sign in alternating layers. Instead of ψ_z used here the symbol θ was used in the cited papers. We introduce the same change here, the reason will be clear below. It takes into account that systems can exist where the same type of tilt takes place around different axes in the planes of alternating layers.

Later Aleksandrov and Bartolomé (1994) and Aleksandrov (1995) made a comprehesive analysis which took into account multilayered crystals of the same family. When these slabs contain odd $l = 2k + 1$ or even $l = 2k$ number of octahedral layers, it is necessary to use ψ_z and ϕ_z tilts which can exist around the main axis of the structure. Results of the analysis are shown in Tables IX and X for crystals having either odd or even number of octahedral layers. Possible PT's in multilayered crystals of the family shown in these Tables have not been observed yet, though multi-layered crystals exist, namely $HCa_2Nb_3O_{10}$ (Fang, Kim and Mallouk, 1999), $RbLaTa_2O_7$ and $RbCa_2Ta_3O_{10}$ (Toda and Sato, 1996).

For the purpose of the thermodynamic description of PT's it is useful to know which irrep of the initial space group is responsible for the PT experimentally found. These data are presented in Table XI where Kovalev's notation (1965, 1986) for irrep's is used.

4.2. Some Experimental Data

As we did above, we have selected some examples of successive PT's in crystals belonging to the Sp.Gr's. under study (Tab. XII). Tilts of ψ and ψ_z type may occur in crystals with atomic A-cations in successive PT's. In $CsVF_4$, $CsFeF_4$ and $CsScF_4$ ψ tilts appear at the $G_0 \rightarrow G_1$ PT, and at $G_1 \rightarrow G_2$ ψ_z-tilts transform the structure to the orthorhombic phase $G_2 = D_{2h}^{13} = Pmmn$, which corresponds to the tilt system $(\psi_1\psi_2\psi_z)$, $a_p^+ b_p^+ c^+$. The appearance of two additional tilts at the second PT implies that it is of first-order character, despite the fact that a second soft mode has been found (Hidaka, Fujii, Garrard and Wanklin, 1986). At the same time, in the crystals $RbAlF_4$ and $KAlF_4$, at the PT $G_0 \rightarrow G_1$ ψ_z tilts appear first ($G_1 = D_{4h}^5 = P4/mbm$). $RbAlF_4$ transforms into the same orthorhombic phase as $RbFeF_4$,

TABLE IX Symmetry of distorted phases due to tilts in crystals belonging to $G_0 = D_{4h}^1 = P4/mmm$ without doubling of the main axis parameter. OP – components of the order parameter

	Distortions in slabs	*Unit cell*				*Odd number layers in slab*				*Even number layers in slab*			
□		*a*	*b*	*c*	*Z*	*Space group*	*Star*	*Irrep*	*OP*	*Space group*	*Star*	*Irrep*	*OP*
1	000	a_0	a_0	c_0	1	$D_{4h}^1 - P4/mmm$				$D_{4h}^1 - P4/mmm$			
2	$00\psi_z$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	2	$D_{4h}^5 - P4/mbm$	$K18\text{-}M$	τ_3	μ	$D_{4h}^5 - P4/mbm$	$K18\text{-}M$	τ_3	μ
3	$00\phi_z$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	2	$D_{4h}^5 - P4/mbm$	$K18\text{-}M$	τ_3	μ'	$D_{4h}^3 - P4/nbm$	$K18\text{-}M$	τ_2, τ_8	μ'
4	$0\phi 0$	$2a_0$	$2a_0$	c_0	4	$D_{2h}^{21} - Cmma$	$K18\text{-}M$	τ_9	(μ, μ)	$D_{2h}^{19} - Cmmm$	$K18\text{-}M$	τ_{10}	(μ, μ)
5	$\phi\phi 0$	$\sqrt{2}a_0$	c_0	$\sqrt{2}a_0$	2	$D_{2h}^7 - Pmna$	$K18\text{-}M$	τ_9	$(\mu, 0)$	$D_{2h}^5 - Pmma$	$K18\text{-}M$	τ_{10}	$(\mu, 0)$
6	$\phi_1\phi_2 0$	$\sqrt{2}a_0$	c_0	$\sqrt{2}a_0$	2	$C_{2h}^4 - P112/n$	$K18\text{-}M$	τ_9	(μ_1, μ_2)	$C_{2h}^1 - P112/m$	$K18\text{-}M$	τ_{10}	(μ_1, μ_2)
7	$0\psi 0$	$2a_0$	a_0	c_0	2	$D_{2h}^5 - Pmma$	$K15\text{-}X$	τ_3	$(\mu', 0)$	$D_{2h}^1 - Pmmm$	$K15$	τ_1, τ_6	$\mu', 0$
8	$\psi\psi 0$	$2a_0$	$2a_0$	c_0	4	$D_{4h}^7 - P4/nmm$	$K15\text{-}X$	τ_3	(μ', μ')	$D_{4h}^1 - P4/mmm$	$K15$	τ_1, τ_6	μ', μ'
9	$\psi_1\psi_2 0$	$2a_0$	$2a_0$	c_0	4	$D_{2h}^{13} - Pmmn$	$K15\text{-}X$	τ_3	(μ'_1, μ')	$D_{2h}^1 - Pmmm$	$K15$	τ_1, τ_6	μ'_1, μ'_2
10	$0\phi\psi_z$	c_0	$2a_0$	$2a_0$	4	$C_{2h}^3 - A112/m$	M	τ_3, τ_9		$C_{2h}^{14} - Amm2$	$K18\text{-}M$	τ_3, τ_{10}	
11	$0\phi\phi_z$	c_0	$2a_0$	$2a_0$	4	$C_{2h}^3 - A112/m$		τ_3, τ_9		$C_{2h}^3 - A12/m1$	M	τ_{10}, τ_8	
12	$\phi\phi\psi_z$	c_0	$2a_0$	$2a_0$	4	$C_{2h}^5 - P112_1/b$		τ_3, τ_9		$C_{2v}^2 - Pmc2_1$	M	τ_{10}, τ_8	
13	$\phi\phi\phi_z$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	2	$C_{2h}^5 - P112_1/b$		τ_3, τ_9		$C_{2h}^4 - P112/b$	M	τ_{10}, τ_8	
14	$\phi_1\phi_2\psi_z$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	2	$C_i^1 - P\bar{1}$		τ_3, τ_9		$C_s^1 - P11m$	M	τ_{10}, τ_8	
15	$\phi_1\phi_2\phi_z$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	2	$C_1^1 - P1$		τ_3, τ_9		$C_1^1 - P1$	M	τ_{10}, τ_8	
16	$\psi 0\psi_z$	$2a_0$	$2a_0$	c_0	4	$D_{2h}^{13} - Pmmn$	X, M	τ_3, τ_3		$D_{2h}^1 - Pmmm$	X, M	τ_6, τ_3	
17	$\psi_1\psi_2\psi_z$	$2a_0$	$2a_0$	c_0	4	$D_{2h}^{13} - Pmmn$		τ_3, τ_3		$D_{2h}^1 - Pmmm$	X, M	τ_6, τ_3	
18	$\psi 0\phi_z$	$2a_0$	$2a_0$	c_0	4	$D_{2h}^{13} - Pmmn$	M, X	τ_3, τ_3		$D_{2h}^5 - Pmma$	X, M	τ_6, τ_8	
19	$\psi\psi\phi_z$	$2a_0$	$2a_0$	c_0	4	$D_{2h}^{13} - Pmmn$		τ_3, τ_3		$D_{2d}^5 - P\bar{4}m2$		τ_6, τ_8	
20	$\psi_1\psi_2\phi_z$	$2a_0$	$2a_0$	c_0	4	$D_{2h}^{13} - Pmmn$		τ_3, τ_3		$C_{2v}^1 - Pmm2$		τ_6, τ_8	
21	$\phi\psi 0$	c_0	$2a_0$	$2a_0$	4	$D_{2h}^{11} - Pbcm$	X,M	τ_3, τ_3		$D_{2h}^5 - Pmma$	X, M	τ_6, τ_{10}	

TABLE X Symmetry of distorted phases due to tilts in crystals belonging to $G_0 = D_{4h}^1 = P4/mmm$ with doubling of the main axis of G_0

	Distortions in slabs		*Unit cell*				*Odd number layers in slab*			*Even number layers in slab*		
☐	I	II	*a*	*b*	*c*	*Z*	*Space group*	*Star*	*Irrep*	*Space group*	*Star*	*Irrep*
1	$00\psi_z$	$00\bar{\psi}_z$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	$2c_0$	4	$D_{4h}^{18} - I4/mcm$	*K*20-*A*	τ_5	$D_{4h}^{18} - I4/mcm$	*K*20-*A*	τ_5
2	$00\phi_z$	$00\bar{\phi}_z$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	$2c_0$	4	$D_{4h}^{18} - I4/mcm$	*K*20-*A*	τ_5	$D_{4h}^{18} - I4/mcm$	*K*20-*A*	τ_7
3	$\phi00$	$\bar{\phi}00$	$2a_0$	$2a_0$	$2c_0$	8	$D_{2h}^{23} - Fmmm$	*K*20-*A*	τ_9	$D_{2h}^{23} - Fmmm$	*K*20-*A*	τ_{10}
4	$\phi\phi0$	$\bar{\phi}\bar{\phi}0$	$\sqrt{2}a_0$	$2c_0$	$\sqrt{2}a_0$	4	$D_{2h}^{28} - Imma$	*K*20-*A*	τ_9	$D_{2h}^{28} - Imma$	*K*20-*A*	τ_{10}
5	$\psi00$	$\bar{\psi}00$	$2a_0$	$2c_0$	$2a_0$	8	$D_{2h}^{19} - Cmmm$	*K*16-*R*	τ_3	$D_{2h}^{19} - Cmmm$	*K*16-*R*	τ_6
6	$\psi\psi0$	$\bar{\psi}\bar{\psi}0$	$2a_0$	$2a_0$	$2c_0$	8	$D_{4h}^{17} - I4/mmm$	*K*16-*R*	τ_3	$D_{4h}^{17} - I4/mmm$	*K*16-*R*	τ_6
7	$\phi0\psi_z$	$\bar{\phi}0\psi_z$	$2a_0$	$2a_0$	$2c_0$	8	$D_{2h}^{17} - Cmcm$	*A*, *M*	τ_9, τ_3	$D_{2h}^{17} - Cmcm$	*A*, *M*	τ_{10}, τ_3
8	$0\phi\phi_z$	$0\bar{\phi}\phi_z$	$2a_0$	$2a_0$	$2c_0$	8	$D_{2h}^{17} - Cmca$	*A*, *M*	τ_9, τ_3	$D_{2h}^{18} - Cmca$	*A*, *M*	τ_{10}, τ_8
9	$\phi\phi\psi_z$	$\bar{\phi}\bar{\phi}\psi_z$	$\sqrt{2}a_0$	$2c_0$	$\sqrt{2}a_0$	4	$D_{2h}^{16} - Pnma$	*A*, *M*	τ_9, τ_3	$D_{2h}^{16} - Pnma$	*A*, *M*	τ_9, τ_3
10	$\phi\phi\phi_z$	$\bar{\phi}\bar{\phi}\phi_z$	$\sqrt{2}a_0$	$2c_0$	$\sqrt{2}a_0$	4	$D_{2h}^{16} - Pnma$	*A*, *M*	τ_9, τ_3	$D_{2h}^{6} - Pnna$	*A*, *M*	τ_{10}, τ_8
11	$\phi0\psi_z$	$\phi0\bar{\psi}_z$	$2a_0$	$2a_0$	$2c_0$	8	$D_{2h}^{18} - Cmca$	*M*, *A*	τ_9, τ_5	$D_{2h}^{17} - Cmcm$	*M*, *A*	τ_{10}, τ_5
12	$0\phi\phi_z$	$0\phi\bar{\phi}_z$	$2a_0$	$2a_0$	$2c_0$	8	$D_{2h}^{18} - Cmca$	*M*, *A*	τ_9, τ_5	$D_{2h}^{17} - Cmcm$	*M*, *A*	τ_{10}, τ_7
13	$\phi\phi\psi_z$	$\phi\phi\bar{\psi}_z$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	$2c_0$	4	$D_{2h}^{14} - Pbcn$	*M*, *A*	τ_9, τ_5	$D_{2h}^{11} - Pbcm$	*M*, *A*	τ_{10}, τ_5
14	$\phi\phi\phi_z$	$\phi\phi\bar{\phi}_z$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	$2c_0$	4	$D_{2h}^{14} - Pbcn$	*M*, *A*	τ_9, τ_5	$D_{2h}^{11} - Pbcm$	*M*, *A*	τ_{10}, τ_7
15	$\psi0\psi_z$	$\bar{\psi}0\psi_z$	$2a_0$	$2a_0$	$2c_0$	8	$D_{2h}^{25} - Immm$	*R*, *M*	τ_3, τ_3	$D_{2h}^{28} - Imma$	*R*, *M*	τ_6, τ_3
16	$\psi\psi\psi_z$	$\bar{\psi}\bar{\psi}\psi_z$	$2a_0$	$2a_0$	$2c_0$	8	$D_{2h}^{25} - Immm$	*R*, *M*	τ_3, τ_3	$D_{2h}^{28} - Imma$	*R*, *M*	τ_6, τ_3
17	$\psi0\psi_z$	$\bar{\psi}0\bar{\psi}_z$	$2c_0$	$2a_0$	$2a_0$	8	$D_{2h}^{17} - Cmcm$	*R*, *A*	τ_3, τ_5	$D_{2h}^{19} - Cmmm$	*R*, *A*	τ_6, τ_5
18	$\psi\psi\psi_z$	$\bar{\psi}\bar{\psi}\bar{\psi}_z$	$2a_0$	$2a_0$	$2c_0$	8	$D_{2h}^{13} - Pmmn$	*R*, *A*	τ_3, τ_5	$D_{2h}^{13} - Pmmn$	*R*, *A*	τ_6, τ_5
19	$\psi\psi\phi_z$	$\bar{\psi}\bar{\psi}\bar{\phi}_z$	$2a_0$	$2a_0$	$2c_0$	8	$D_{2h}^{13} - Pmmn$	*R*, *A*	τ_3, τ_5	$D_{2h}^{13} - Pmmn$	*R*, *A*	τ_6, τ_7
20	$\psi0\phi_z$	$\psi0\bar{\phi}_z$	$2c_0$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$D_{2h}^{17} - Cmcm$	*X*, *A*	τ_3, τ_5	$D_{2h}^{19} - Cmmm$	*X*, *A*	τ_6, τ_7
21	$\psi\psi\psi_z$	$\psi\psi\bar{\psi}_z$	$2a_0$	$2a_0$	$2c_0$	8	$D_{2h}^{13} - P4_2/nmc$	*X*, *A*	τ_3, τ_5	$D_{2h}^{13} - P4_2/nmc$	*X*, *A*	τ_6, τ_5

TABLE X (Continued)

	Distortions in slabs		*Unit cell*				*Odd number layers in slab*			*Even number layers in slab*		
□	I	II	*a*	*b*	*c*	*Z*	*Space group*	*Star*	*Irrep*	*Space group*	*Star*	*Irrep*
22	$\psi\psi\phi_z$	$\psi\psi\bar{\phi}_z$	$2a_0$	$2a_0$	$2c_0$	8	$D_{4h}^{15} - P4_2/nmc$	X, A	τ_3, τ_5	$D_{4h}^{15} - P4_2/nmc$	X, A	τ_6, τ_7
23	$\psi 0\phi_z$	$\bar{\psi}0\bar{\phi}_z$	$2c_0$	$2a_0$	$2a_0$	8	$D_{2h}^{21} - Cmma$	R, A	τ_3, τ_5	$D_{2h}^{21} - Cmma$	R, A	τ_6, τ_7
24	$\phi\psi 0$	$\bar{\phi}\psi 0$	$2c_0$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$D_{2h}^{5} - Pmma$	A, X	τ_9, τ_3	$D_{2h}^{5} - Pmma$	A, X	τ_{10}, τ_6
25	$\phi\psi 0$	$\phi\bar{\psi}0$	$2c_0$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$D_{2h}^{28} - Imma$	M, R	τ_9, τ_3	$D_{2h}^{28} - Imma$	M, R	τ_{10}, τ_6
26	$\phi\psi 0$	$\bar{\phi}\bar{\psi}0$	$2c_0$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$D_{2h}^{5} - Pbam$	A, R	τ_9, τ_3	$D_{2h}^{9} - Pbam$	A, R	τ_{10}, τ_6

TABLE XI Symmetry of distorted phases induced by two-dimentional irreps τ_i of $G_0 = P4/mmm$ due to one kind of tilt

Star	τ_l	*Order parameter* η	*Space group* G_i	*Orientation of symmetry planes* G_i *in* G_0	*Octahedral tilt leading to the same symmetry changes in crystals with n-layers*
	τ_3	$(0, \eta)$	$D_{2h}^5 - Pmma$	$a\|(001)_0$	ψ, ψ-tilts
		(η, η)	$D_{4h}^7 - P4/nmm$	$m\|(100)_0$	for $n = 2l + 1$
		(η_1, η_2)	$D_{2h}^{13} - Pmmn$	$n\|(001)_0$	
$K15$-X	τ_6	$(0, \eta)$	$D_{2h}^1 - Pmmm$		ψ, ψ-tilts
		(η, η)	$D_{4h}^1 - P4/mmm$	$m\|(100)_0$	for $n = 2l$
		(η_1, η_2)	$D_{2h}^1 - Pmmm$		
	τ_9	$(0, \eta)$	$D_{2h}^7 - Pman$	$n\|(001)_0$	ϕ, ϕ-tilts
		(η, η)	$D_{2h}^{21} - Cmma$	$a\|(001)_0$	for $n = 2l + 1$
		(η_1, η_2)	$C_{2h}^4 - P112/n$	$n\|(001)_0$	
$K18$-M	τ_{10}	$(0, \eta)$	$D_{2h}^5 - Pmam$	$a\|(110)_0$	ϕ, ϕ-tilts
		(η, η)	$D_{2h}^{19} - Cmmm$	$m\|(110)_0$	for $n = 2l$
		(η_1, η_2)	$C_{2h}^1 - P112/m$	$m\|(001)_0$	
	τ_3	$(0, \eta)$	$D_{2h}^{19} - Cmmm$		ψ, $\bar{\psi}$-tilts
		(η, η)	$D_{4h}^{17} - I4/mmm$		for $n = 2l + 1$
		(η_1, η_2)	$D_{2h}^{25} - Immm$	$m\|(100)_0$	
$K16$-R	τ_6	$(0, \eta)$	$D_{2h}^{19} - Cmmm$		ψ, $\bar{\psi}$-tilts
		(η, η)	$D_{4h}^{17} - I4/mmm$		for $n = 2l$
		(η_1, η_2)	$D_{2h}^{25} - Immm$		
	τ_9	$(0, \eta)$	$D_{2h}^{28} - Imma$	$a\|(110)_0$	ϕ, $\bar{\phi}$-tilts
		(η, η)	$D_{2h}^{23} - Fmmm$	$m\|(100)_0$	for $n = 2l + 1$
		(η_1, η_2)	$C_{2h}^3 - B112/m$	$m\|(001)_0$	
$K20$-A	τ_{10}	$(0, \eta)$	$D_{2h}^{28} - Imma$	$a\|(110)_0$	ϕ, $\bar{\phi}$-tilts
		(η, η)	$D_{2h}^{23} - Fmmm$	$m\|(100)_0$	for $n = 2l$
		(η_1, η_2)	$C_{2h}^3 - B112/m$	$m\|(001)_0$	

but $KAlF_4$ changes its structural type as it transforms into the $KFeF_4$ structure, where octahedral layers are shifted by $1/2b_t$ in the basal plane (Launay, Bulou, Hewat *et al.*, 1985). The crystals KBF_4 (B = Fe, V, Ti) display also successive PT's due to tilts (Hidaka, Garrard and Wanklin, 1979).

Soft lattice modes have been observed in optically transparent $RbAlF_4$ (Bulou, and Nouet, 1982), and a similar sequence of PT's has been found in $CsScF_4$ (Aleksandrov, Voronov, Kruglik *et al.*, 1988; Flerov, Aleksandrov, Melnikova *et al.*, 1989) (see Tab. XII).

TABLE XII Some experimental data on successive PT's in the layered perovskite-like crystals which belong to $G_0 = D_{4h}^1 = P4/mmm$

Crystal	G_i	T_i, K	*Space group*	*Distortions in layers*	*References*
$TlAlF_4$	G_1	514	$D_{4h}^{18} = I4/mcm$	$(00\psi_z)(00\bar{\psi}_z)$	Bulou, Fourquet, Leble *et al.*, 1982a
	G_2	435	$C_{2h}^{6} = I2/a$	$(\phi_1\phi_2\psi_z)(\phi_1\phi_2\bar{\psi}_z)$	
$(NH_4)AlF_4$	G_1		$D_{4h}^{18} = I4/mcm$	$(00\psi)(00\bar{\psi}_z)$	Bulou, Leble, Hewat *et al.*, 1982
	G_2	145	$D_{4h}^{13} = P4_2/mbc$	ordering of NH_4	
$RbAlF_4$	G_1	553	$D_{4h}^{5} = P4/mbm$	$(00\psi_z)$	Bulou, Rousseau, Nouet *et al.*, 1989
	G_2	282	$D_{2h}^{13} = Pmmn$	$(\psi_1\psi_2\psi_z)$	Bulou and Nouet, 1982
$RbFeF_4$	G_1	923	$D_{4h}^{5} = P4/mbm$	$(00\psi_z)$	Hidaka, Akiyama and Wanklin, 1986;
	G_2	483	$D_{2h}^{13} = Pmmn$	$(\psi 0\psi_z)$	Moron, Bulou, Pique *et al.*, 1990
	G_3	380	$D_{2h}^{11} = Pmab$	$(\psi\varphi\psi_z)$	Pique, Bulou, Moron *et al.*, 1990.
$RbVF_4$	G_1	482	$D_{4h}^{5} = P4/mbm$	$(00\psi_z)$	Hidaka, Inoue, Garrard and Wanklin, 1982
	G_2	413	$D_{2h}^{13} = Pmmn$	$(\psi_1\psi_2\psi_z)$	
	G_3	135	$D_2^3 = P2_12_12_1$	?	Dubliek, Landuyt and Amelinckx, 1986
$CsVF_4$	G_1	515	$D_{2h}^{5} = Pmma$	$(0\psi 0)$	Hidaka, Wood and Garrard, 1979;
	G_2	425	$D_{2h}^{13} = Pmmn$	$(\psi_1\psi_2\psi_z)$	Deblieck, Van Tandeloo *et al.*, 1985.
	G_3	140	$D_2^3 = P2_12_12_1$	?	
$CsFeF_4$	G_1	508	$D_{2h}^{5} = Pmma$	$(0\psi 0)$	Hidaka, Wood and Wondre, 1979
	G_2	423	$D_{2h}^{13} = Pmmn$	$(\psi_1\psi_2\psi_z)$	
	G_3	250			
$CsScF_4$	G_1	475	$D_{4h}^{5} = P4/mbm$	$(00\psi_z)$	Flerov, Aleksandrov, Melnikova *et al.*, 1989
	G_2	317	$D_{2h}^{13} = Pmmn$	$(\psi_1\psi_2\psi_z)$	

$KAlF_4$	G_1		$D_{4h}^5 = P4/mbm$	$(00\psi_z)$	Bulou, Gibaud, Debieche *et al.*, 1989
	G_2	250	$C_{2h} = P2_1/m$	other structure	
$NH_3(CH_2)_2NH_3MnCl_4$	G_1	–	$C_{2h}^5 = P2_1/b$	$(\phi_1\phi_2\psi_z)$	Arend, Tichy, Baberschke and Rys, 1976
$NH_3(CH_2)_3NH_3MnCl_4$	G_1	?	$D_{2h}^{28} = Imma$	$(\phi_1\phi_2 0)\ (\phi_1\phi_2 0)$	Kind, Plesko and Roos, 1978
	G_2	336	$D_{2h}^{23} = Fmmm$	$(0\phi 0)\ (0\bar{\phi}0)$	
	G_3	305	$D_{2h}^{16} = Pnma$	$(\phi_1\phi_2\psi_z)\ (\bar{\phi}_1\bar{\phi}_2\psi_z)$	
$NH_3(CH_2)_4NH_3MnCl_4$	G_1	?	$D_{2h}^{16} = Pnma$	$(\phi_1\phi_2\psi_z)\ (\bar{\phi}_1\bar{\phi}_2\psi_z)$	Tichy, Benes and Kind, 1979
	G_2	382	$C_{2h}^5 = P2_1/b$	$(\phi_1\phi_2\psi)$	

Among the family under study, it was found in two cases, NH_4AlF_4 (Bulou, Leble, Hewat and Fourquet, 1982) and $TlAlF_4$ (Deblieck, van Tendeloo, Landuyt and Amelinckx, 1985), that at $G_0 \rightarrow G_1$ ψ_z tilts have opposite signs in alternate layers; *i.e.*, the tilt system is $(00\psi_z)$ $(00\bar{\psi}_z)$ with $G_1 = D_{4h}^{18} = I4/mcm$, as it is shown in Tables X and XII, and the unit cell parameter c is doubled at the transition. The second PT in the ammonium compound is driven by the order of ammonia groups, and results in $G_2 = D_{4h}^{15} = P4_2/mbc$, with unit cell $(2a \times 2a \times 2c)$. The ordering is followed by ψ tilts around both axes in the layers (see Tab. X), distortion $(\bar{\psi}\bar{\psi}\bar{\psi}_z)$; *i.e.*, ψ_z-tilts in neighboring layers also have opposite signs. Tallium fluoroaluminate has another tilt system in the G_2 phase; in the layers two components of ϕ tilt appear at T_2. In this case the structure should belong either to $G_2 = C_{2h}^5 = P112_1/n$ Sp.Gr. if ψ_z tilts are equivalent in all layers, or to $G_2 = C_{2h}^6 = I12/a1$ Sp.Gr. if they have opposite signs. However, the C_{2h}^3 group was assigned to explain the experimental results (Bulou, Fourquet, Leble *et al.*, 1982).

The crystals $RbFeF_4$ and $RbVF_4$ display one additional PT which lead to a G_3 phase. This structure was determined for both crystals as $G_3 = P2_12_12$ with $2a_t \times 2a_t \times 2c_t$, $Z = 8$ (Hidaka, Fujii, Garrard *et al.*, 1986; Hidaka, Akiyama and Wanklin, 1986; Hidaka, Inoue, Garrard *et al.*, 1982). This phase is absent in Tables X and XI since the nature of $G_2 \rightarrow G_3$ PT remains unclear.

Morón, Bulou, Piqué and Fourquet, 1990; Piqué, Bulou, Morón *et al.* (1990) have studied $RbFeF_4$ by means of X-ray diffraction and Raman scattering. They have obtained $G_3 = D_{2h}^{11} = Pmab$ corresponding to the tilt system $(\phi\psi 0)$ or $a_p^+ b_p^- c^0$, Table XII. Phases G_2 of $P2_12_12$ symmetry have been found in NH_4FeF_4 and $CsFeF_4$ (Babel and Tressaud, 1985; Hidaka, Fujii, Garrard *et al.*, 1986), but it can be conjectured that the structures are also centrosymmetric.

Special attention should be paid to PT's in crystals containing Jahn-Teller ions in their structure. The series $AMnF_4$ ($A = Cs$, Rb, K), which contain Jahn-Teller distorted octahedra at room temperature, belong to P4/n (Cs), Pmab (Rb), as determined by energy dispersive synchrotron X-ray diffraction (Morón, Palacio and Clark, 1996), or to $P2_1/a$ (K, Rb) by neutron. At lower temperatures (down to 4 K), non-structural PT's have been found. Ferromagnetic and antiferromagnetic (collinear and non-collinear) PT's have been studied (Morón, Palacio and Rodríguez-Carvajal, 1993 and references therein).

Under hydrostatic high-pressure the structures of these series change to lower symmetries. For increasing pressure the Cs compound transforms from tetragonal to orthorhombic and in a subsequent PT to monoclinic. The Rb compound transforms from orthorhombic to monoclinic, while the K compound undergoes no transition with pressure. Thus, the space group sequence induced by hydrostatic pressure is analogous to the effect of chemical pressure caused by the decrease of the effective A-ions radii (Morón, Palacio and Clark, 1996).

The complex oxide perovskite La_2CuSnO_6 has an unusual arrangement of B-cations, since Cu and Sn ions are distributed in alternate $(001)_t$ planes. The structure of the crystal was determined as $G = C_{2h}^3 = P2/m$ with unit cell $(2a_p \times 2a_p \times 2a_p)$ with respect to the simple perovskite parameter (Anderson and Poeppelmeier, 1991). Such distribution of cations allows to correlate the ideal structure of the crystal to $G_0 = D_{4h}^1 = P4/mmm$, with unit cell $a_p \times a_p \times c_t = 2a_p$. The distorted structure can be imagined as due to $(0\phi\psi)$ tilt, which leads to the same C_{2h}^3 Sp.Gr. and to the cell $(2a_p, 2a_p, 2a_p)$, as found in the experiment, though the predicted C-center was not observed (see No. 10 in Tab. IX).

The structural distortions in ABX_4 crystals where A-cations are replaced by propylendiammonium ones are very interesting examples. The general formula is $[NH_3(CH_2)_mNH_3]$ BCl_4, with odd and even m, here $B = Mn$, Cd, Cu, Fe (Tichy, Benes, Halg and Arend, 1978 and references therein; Kind, 1980). For propylenediammonium manganese chloride at RT the symmetry $(D_{2h}^{28} = Imma)$ and unit cell parameters allow to attribute its orthorhombic distortion to the tilt system $(\phi_1\phi_2\psi_z)$ $(-\phi_1 - \phi_2\psi_z)$ with different signs of antiphase tilts in alternate layers (Kind, Plesko and Roos, 1978). With temperature increase, at 305 K, another orthorhombic phase appears such that one component of the ϕ- and ψ_z-tilts disappear. Above 336 K, a new orthorhombic phase shows up, where the second ϕ-component reappears (see Tab. XII). Moreover, both PT's are of first-order character. In the Cd-analog the intermediate phase is absent and a PT takes place at 375 K between the G_1 and G_3 phases of the Mn substituted crystal (Willet, 1977). In crystals with $m = 2, 4, \ldots$ PT's into G_0 have not been observed and in these structures the c-parameter does not double. Finally, in $[NH_3(CH_2)_4$ $NH_3]$ $MnCl_4$ the symmetry of the G_1 phase implies that the PT at 382 K should show doubling of the *c*-parameter, a fact that, however, was not found (Tichy, Benes and Kind, 1979).

A question arises: What is the reason for the different distortions between the odd and even members of the series? It has been assumed that the difference arises due to the different configurations of the zigzag polypropylendiammonium chains. In all members of the series C and N atoms lie on a plane, but in crystals with even *m* the NH_3 groups are located on opposite sides with respect to the chain axis. The hydrogen bonds N—H···Cl attract the apical chlorines from neighboring layers and in any layer equivalent distortions are promoted. On the contrary, when *m* is odd the NH_3 groups lie on the same side of the plane and, therefore, the apical chlorine atoms in the upper and in the lower neighboring layers are shifted in the same direction. This leads to the multiplication of the *c*-parameter in the distorted phases (Aleksandrov, Beznosikov and Misyul, 1987a; Aleksandrov, 1987a).

5. CRYSTALS BELONGING TO $G_0=D_{4h}^{17}=I4/mmm$ IN THEIR INITIAL PHASE

Two broad series of crystals belong to $G_0 = D_{4h}^{17} = I4/mmm$ Sp.Gr. in their initial phase. The first are the Ruddlesden-Popper series (1957, 1958), which have general formula $AX(A'BX_3)_n$ and their anion deficient relatives. Only crystals of the first three members of the series have been obtained, and the structures are shown in Figure 8. In these structures perovskite-like layers or slabs are shifted by half the body diagonal of the unit cell, and inter-grow with AX-blocks of the so-called NaCl-type. A-cations are usually located in the same plane as the apical anions. Their coordination number is $Z=9$. A number of chlorides and bromides A_2BX_4 exist in which long chain organic alkylammonium groups $(C_mH_{2m+1}NH_3)^{1+}$, $m=1-5$ substitute A-cations in the structure, and the NH_3- groups of the molecules are linked by octahedral layers. Many PT's are known in crystals of these series.

The second are the Aurivillius's series (1952). The general formula of the crystals is: $A_2X_2(A'_nB_nX_{3n+1})$, and many representatives with $n=1-8$ have been found. The structures of the first three members of

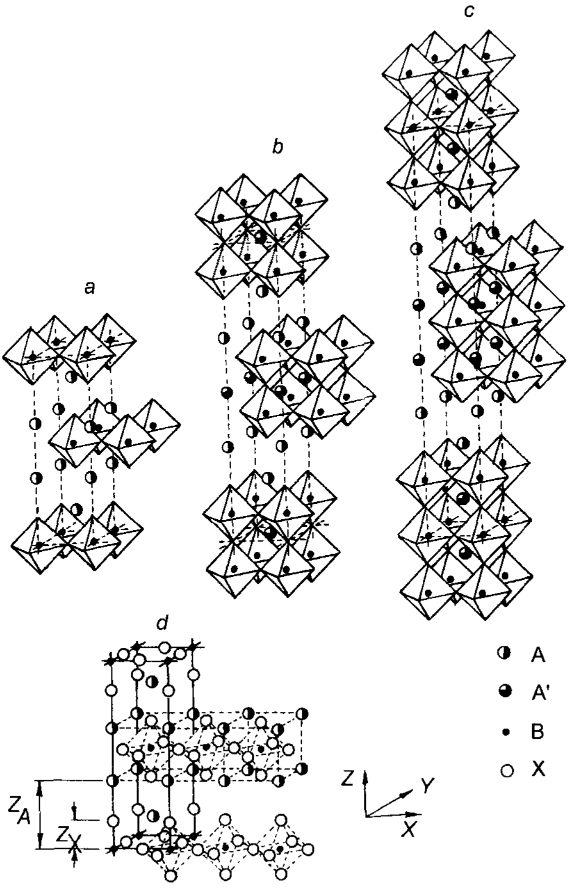

FIGURE 8 Unit cells of the first three members of Ruddlesden-Popper's series. (a) A_2BX_4; (b) $A_3B_2X_7$; (c) $A_4B_3X_{10}$.

the series are schematically shown in Figure 9. Perovskite-like slabs are shifted again and a body-centered lattice is formed. The A$'$-cations are incorporated into the slab when $n = 2, 3, 4\ldots$, while the A-cations are located out of the slabs and have $Z = 8$. Crystals of Aurivillius series are known in many oxides and oxihalogenides. Many ferroelectric crystals belong to the stoichiometric members of the series. Their anion deficient relatives form well known families of high temperature superconductors of $22(n-1)n$ type, where A = Tl, Bi, Hg, *etc.*, and B = Cu.

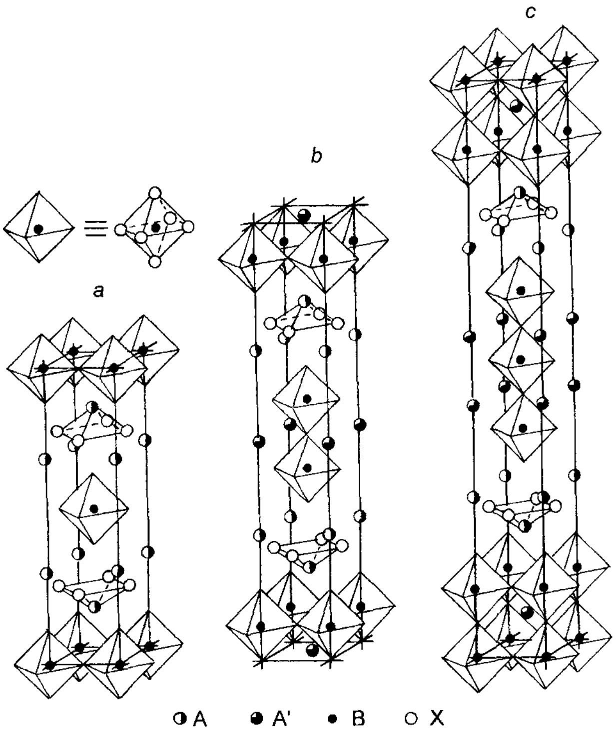

FIGURE 9 Undistorted unit cells of the first three members of Aurivillius series. (a) A_2BX_6; (b) $A_2A'B_2X_9$; (c) $A_2A'_2B_3X_{12}$.

5.1. Possible Distortions Due to Octahedral Tilts

The first attempt to study the symmetry changes and lattice dynamical aspects of structural PT's in A_2BX_4 crystals with $G_0 = I4/mmm$ was made by Petzelt (1975) to explain an unusual PT sequence in $(MA)_2BX_4$ crystals, where $MA = CH_3NH_3$ – methylammonium, $B = Mn$, Cd, Cu and $X = Cl$, Br. The crystals display PT's from tetragonal (G_0) to orthorhombic and again to tetragonal phase. At that time it was regarded as a possible contradiction of Landau's thermodynamical theory of PT's.

Petzelt had considered both the group-theoretical analysis of possible PT's due to active irreps of G_0 and the vibrational representation of the A_2BX_4-structure. The study was made for the Γ, Z, X, N and P symmetry points of the Brillouin zone, see Figure 3d. It was found that the PT $G_1 \rightarrow G_2$: $D_{4h}^{17} \rightarrow D_{2h}^{18}$ observed in some crystals of this group (see below) is determined by irrep τ_5^x, belongs to the X boundary point of the Brillouin zone. It corresponds mainly to $a^-a^-c^0$ ($\phi\phi0$) tilts in octahedral layers followed by rotations of the MA-cations. The same conclusion was obtained by Heger, Mullen and Knorr (1975). Though at that time it was widely accepted that the nature of PT's in $(MA)_2BX_4$ crystals was determined by the hydrogen bond ordering of MA-groups followed by octahedral tilting in layers (Petzelt, 1975; Heger, Mullen and Knorr, 1976; Blinc, Zeks and Kind, 1978), we shall return to this point later (Section 5.2.1). Depmeier, Felsche and Widdermuth (1977) found an incommensurate phase in other compounds of the series with $A = C_3H_5NH_3$ – propylammonium (PA). The averaged and the incommensurate structure of $(PA)_2MnCl_4$ was solved later (Depmeier, 1979, 1981).

Geick and Strobel (1977) have studied the group theoretical and the lattice dynamical properties of G_0 group in order to explain the appearance of $G_1 = D_{2h}^{18}$ = Abma, $G_2 = D_{4h}^{15}$ = $P4_2/ncm$ and $G_2 = D_{2h}^{15}$ = Pbca Sp.Gr's , which have been found experimentally in different halide compounds of the series $(C_nH_{2n+1}NH_3)_2BX_4$ with B = Mn, Cd, Cu and X = Cl, Br. Compatibility relations between the symmetry types of the lattice vibrations and the symmetry coordinates were obtained for these groups, however, the known PT $D_{2h}^{18} - D_{4h}^{15}$ could not be explained.

Hatch and Stokes (1987) made the complete classification of possible subgroups of G_0, which may arise due to "simple" octahedral tilting. The group theoretical method was used to obtain the Sp.Gr's of the distorted phases which appear at $G_0 - G_1$ PT's. However, if one aims to understand the successive PT's it is necessary, either to assume that they appear due to the same irrep of G_0, with a change of the number of components of the order parameter, or to repeat the group theoretical considerations for the G_1 group to explain the $G_1 - G_2$ PT to the next lower symmetry. This rigorous group theoretical method was used by Petzelt (1975) and Geick and Strobel (1977). Another procedure consists in the analysis of direct products of irreps for the coupled order parameter, but in this case and if only these irreps are used it is not easy to unravel the real changes of atomic positions in G_i.

Aleksandrov (1987b) and Aleksandrov, Beznosikov and Misyul (1987b) used another method. These authors took into account that in the layered structures under consideration three kinds of tilts can exist: ψ and ϕ tilts around [100] and [010] in octahedral layers, and ψ_z tilts around the main axis [001] of G_0. For the last tilt the symbol ψ_z is used here, instead of θ in the cited papers. When the G_0 structure contains octahedral slabs, $n \neq 1$, in its general formula a fourth kind of tilt may exist: ϕ_z tilt around [001]. Distortions due to "simple" tilts and their superposition were depicted and then the symmetry of the distorted phases determined just checking their symmetry elements. It must be stressed that the G_i symmetry determined using the depicted structure, distorted by any kind of tilt, does not necessarily correspond to a possible active irrep of G_0 obtained by the group theoretical method. Examples will be mentioned below.

Later, in a common work (Hatch, Stokes, Aleksandrov and Misyul, 1989) a computer program was used to determine the subgroups resulting both from "simple" tilts (one irrep) and from the direct product of two irreps $\tau_i \otimes \tau_j$ (two kinds of tilts). These results were compared with those obtained from the depicted structures. Both methods lead to the same changes in symmetry and their combination gives the most clear and rigorous results.

The distorted phases in multi-layered structures containing both odd and even number of octahedral layers in the slabs have been determined by Aleksandrov and Bartolomé (1994) and Aleksandrov (1995). For the multi-layered slabs the authors have also used the direct symmetry determination from depicted structures. As it can be seen from Figure 10a, the introduction of octahedral tilts leads to the complication of the picture, especially if it is necessary to introduce ϕ_z tilts in the slabs. The determination of the resulting symmetry may end being a sophistic problem. Therefore, to simplify the problem an artificial method was used. Each octahedron was contracted by half with respect to its center (Fig. 10b) and in this figure the points between contracted octahedra indicate the contact points of the octahedral vertices. The method simplifies the conception of the structure and does not change the symmetry of the G_0 phase. With this artificially simplified "structure" it is much easier to introduce any kind of tilt and consider their superposition. Of course, it is necessary to remember that the octahedra are corner linked in both slabs. Therefore, the phases of the tilts in the neighboring octahedra should correspond to those in the linked slab for each ψ, ϕ, ψ_z or ϕ_z definite kind of tilt.

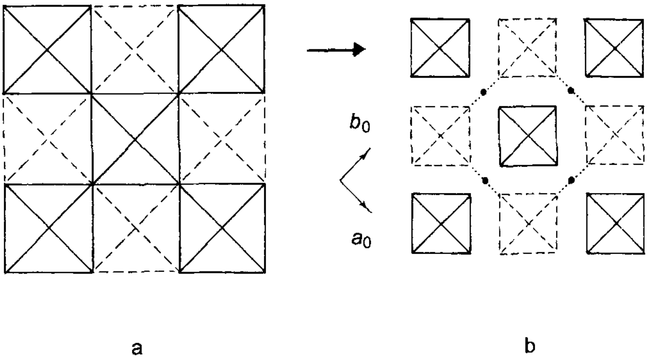

FIGURE 10 Accepted method to simplify of the crystallographic analysis of distortions due to tilts. The (001) projection of two neighbor slabs is shown; A and A′ cations are omitted. The upper slab octahedra of are drawn by full lines; those of the lower slab by broken lines. (a) Real structure; (b) simplified octahedral structure (see text).

In this case the appearance of a fourth kind of tilt (ϕ_z) leads to different Sp.Gr's for crystals with even layers, because a ($00\phi_z$) distortion does not keep the mirror plane orthogonal to the main axis of G_0. On the other hand, in cases of ψ and ϕ tilts the same mirror plane (between the octahedral layers of a slab) is maintained. This situation is exactly opposite to the slabs with odd number of layers, where the mirror plane is lost for ψ and ϕ tilts around a_0 and b_0 axes, but exists when ψ_z and ϕ_z tilts appear. It has been found earlier, for crystals with $n = 1$, that distortions due to ϕ and ψ_z tilts are determined by irreps $\tau_5(X_4^+)$, $\tau_3(X_3^+)$ and $\tau_7(X_2^+)$. Distortions due of ψ tilts, which were considered by Aleksandrov, Beznosikov and Misyul (1987b) do not correspond to any irrep of G_0. They have never been met for any real crystal and, as a consequence, we have omitted these cases from the Tables shown below. In slabs with $n = 2l + 1$ the symmetry of distorted phases is the same as for $n = 1$.

In all cases the ϕ-tilts around axes contained in the plane of the slab take place around orthogonal axes in neighboring slabs, which implies that the symmetry of the final structure depends on the signs of the tilts in the slabs. This can be seen in Figure 11 for the case with one ϕ tilt component, where the octahedra of the upper slab are drawn by full lines and those of the lower slab by broken lines. The structure drawn in Figure 11a belongs to $G_1 = D_{4h}^{16} = P4_2/ncm$ (irrep τ_3) and the one in Figure 11b to $G_1 = D_{4h}^{12} = P4_2/nnm$ (irrep τ_5). In the case of even

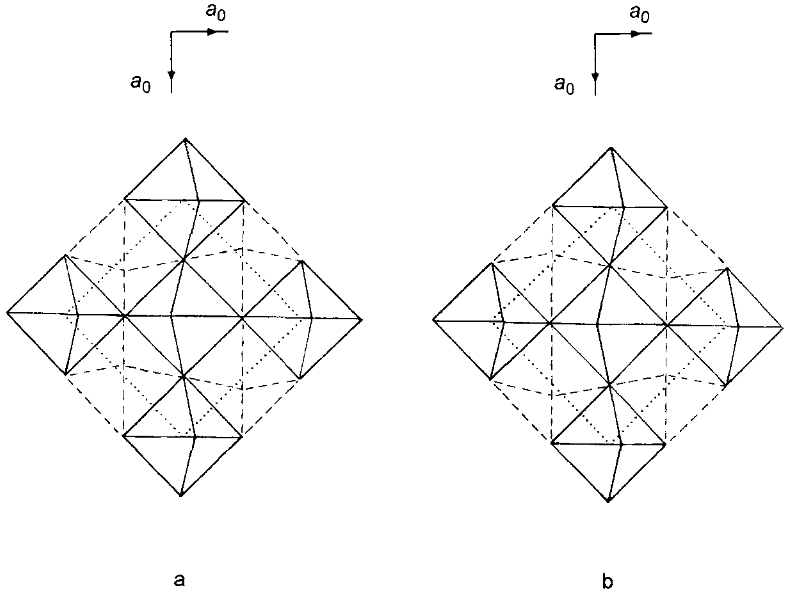

FIGURE 11 Illustration, for crystals which belong to $G_0 = I4/mmm$, of the symmetry change when a ϕ tilt changes its sign in the lower layer. Full lines and broken lines represent octahedra of the upper and lower layer, respectively. Unit cells are shown by dotted lines, A cations are omitted and the symmetry of (a) and (b) is stated in the text.

layered slabs the irreps corresponding to ψ_z, ϕ_z and ϕ tilts are the two-dimensional irreps $\tau_7(X)$, $\tau_2(X)$ and $\tau_6(X)$ respectively. This means that the PT parameters which transform according to these irreps are two-component ones. It is easy to guess for ϕ and ϕ' tilts that they can correspond to the cases $(\eta, 0)$ (η, η) and (η_1, η_2) which belong to different Sp.Gr.'s. The results of the analysis are presented in Table XIII for 'simple' tilts and in Table XIV for the superposition of two kinds of tilts, both for crystals with odd and even number of octahedral layers in the slabs. The orientation of the symmetry planes in the distorted structure due to "simple" tilts is also given in Table XV.

As it can be seen in Table XIV the superposition of different kinds of tilts in crystals with slabs containing an even number of octahedral layers often lead to the loss of a symmetry center. Two examples are shown in Figure 12(a,b) for $(\phi 0 \psi_z)$ $(0 \phi \psi_z)$ and $(\phi \phi \psi_z)$ $(\phi \phi \psi_z)$ tilt systems, respectively. Both structures are polar with the main axes along $b = \sqrt{2} a_0$. These structures may appear in successive (or

TABLE XIII Distortions due to one kind of tilt in the layered perovskite-like crystals, which belong to $G_0 = D_{4h}^{17} = I4/mmm$ and have odd or even layers in the octahedral slabs

	Distortions						*Numbers of layers in slabs*			
	in slabs		*Unit cell*				$n = 2l + 1$		$n = 2l$	
☐	I	II	a	b	c	Z	*Space group*	*Irrep*	*Space group*	*Irrep*
1	000	000	a_0	a_0	c_0	2	$D_{4h}^{17} - I4/mmm$	–	$D_{4h}^{17} - I4/mmm$	–
2	$00\psi_z$	$00\psi_z$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$D_{2h}^{18} - Cmca$	τ_7	$D_{2h}^{18} - Cmca$	τ_7
3	$00\psi_z$	000	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$D_{4h}^{5} - P4/mbm$	τ_7	$D_{4h}^{5} - P4/mbm$	τ_7
4	$00\psi_{z1}$	$00\psi_{z2}$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$D_{2h}^{9} - Pbam$	τ_7	$D_{2h}^{9} - Pbam$	τ_7
5	$00\phi_z$	$00\phi_z$	$\sqrt{2}a_0$	c_0	$\sqrt{2}a_0$	4	$D_{2h}^{18} - Cmca$	τ_7	$D_{2h}^{22} - Ccca$	τ_2
6	$00\phi_z$	000	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$D_{4h}^{5} - P4/mbm$	τ_7	$D_{4h}^{3} - P4/nbm$	τ_2
7	$00\phi_{z1}$	$00\phi_{z2}$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$D_{2h}^{9} - Pbam$	τ_7	$D_{2h}^{4} - Pban$	τ_2
8	$\phi 00$	$0\phi 0$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$D_{4h}^{12} - P4_2/nnm$	τ_5	$D_{4h}^{14} - P4_2/mnm$	τ_4
9	$\phi\phi 0$	$\phi\phi 0$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$D_{2h}^{20} - Cccm$	τ_5	$D_{2h}^{17} - Cmcm$	τ_4
10	$\phi_1\phi_2 0$	$\phi_2\phi_1 0$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$D_{2h}^{2} - Pnnn$	τ_5	$D_{2h}^{12} - Pnnm$	τ_4
11	$\phi 00$	$0\bar{\phi} 0$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$D_{4h}^{16} - P4_2/ncm$	τ_3	$D_{4h}^{10} - P4_2/mcm$	τ_6
12	$\phi\phi 0$	$\bar{\phi}\bar{\phi} 0$	$\sqrt{2}a_0$	c_0	$\sqrt{2}a_0$	4	$D_{2h}^{18} - Cmca$	τ_3	$D_{2h}^{21} - Cmma$	τ_6
13	$\phi_1\phi_2 0$	$\bar{\phi}_2\bar{\phi}_1 0$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$D_{2h}^{10} - Pccn$	τ_3	$D_{2h}^{3} - Pccm$	τ_6

TABLE XIV Symmetry of distorted phases due to superposition of two kinds of tilts, for layered perovskite-like crystals which belong to $G_0 = I4/mmm$

	Tilts		*Odd number of layers in slabs*						*Even number of layers in slabs*					
	in slab		*Unit cell*						*Unit cell*					
□	I	II	*a*	*b*	*c*	*Z*	*Space group*	*Irrep*	*a*	*b*	*c*	*Z*	*Space group*	*Irrep*
1	$\phi 0 \psi_z$	$0 \phi \psi_z$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$C_{2h}^5 - P12_1/c1$	$\tau_5 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2v}^4 - Pma2$	$\tau_4 \otimes \tau_7$
2	$\phi 0 \phi_z$	$0 \phi \phi_z$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$C_{2h}^5 - P12_1/c1$	$\tau_5 \otimes \tau_7$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$C_{2h}^4 - P12/c1$	$\tau_4 \otimes \tau_2$
3	$\phi 0 \psi_z$	$0 \bar{\phi} \psi_z$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^4 - P12/n1$	$\tau_3 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2v}^7 - Pmn2_1$	$\tau_6 \otimes \tau_7$
4	$\phi 0 \phi_z$	$0 \bar{\phi} \phi_z$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^4 - P12/n1$	$\tau_3 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^5 - P12_1/n1$	$\tau_6 \otimes \tau_2$
5	$\phi 0 \psi_z$	$0 \phi 0$	c_0	$2a_0$	$2a_0$	8	$C_{2h}^3 - C12/m1$	$\tau_5 \otimes \tau_7$	c_0	$2a_0$	$2a_0$	8	$C_{2v}^{14} - Amm2$	$\tau_4 \otimes \tau_7$
6	$\phi 0 \phi_z$	$0 \phi 0$	c_0	$2a_0$	$2a_0$	8	$C_{2h}^3 - C12/m1$	$\tau_5 \otimes \tau_7$	c_0	$2a_0$	$2a_0$	8	$C_{2v}^{14} - Amm2$	$\tau_4 \otimes \tau_2$
7	$\phi 0 \psi_z$	$0 \bar{\phi} 0$	c_0	$2a_0$	$2a_0$	8	$C_{2h}^3 - C12/m1$	$\tau_3 \otimes \tau_7$	c_0	$2a_0$	$2a_0$	8	$C_{2h}^3 - C12/m1$	$\tau_6 \otimes \tau_7$
8	$\phi 0 \phi_z$	$0 \bar{\phi} 0$	c_0	$2a_0$	$2a_0$	8	$C_{2h}^3 - C12/m1$	$\tau_3 \otimes \tau_7$	c_0	$2a_0$	$2a_0$	8	$C_{2h}^3 - C12/m1$	$\tau_6 \otimes \tau_2$
9	$\phi \phi \psi_z$	$\phi \phi \psi_z$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^6 - C12/c1$	$\tau_5 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2v}^{12} - Cmc2_1$	$\tau_4 \otimes \tau_7$
10	$\phi \phi \phi_z$	$\phi \phi \phi_z$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^6 - C12/c1$	$\tau_5 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^6 - C12/c1$	$\tau_4 \otimes \tau_2$
11	$\phi \phi \psi_z$	$\phi \phi \bar{\psi}_z$	$\sqrt{2}a_0$	c_0	$\sqrt{2}a_0$	4	$D_{2h}^{10} - Pccn$	$\tau_5 \otimes \tau_7$	$\sqrt{2}a_0$	c_0	$\sqrt{2}a_0$	4	$D_{2h}^{16} - Pnma$	$\tau_4 \otimes \tau_7$
12	$\phi \phi \phi_z$	$\phi \phi \bar{\phi}_z$	$\sqrt{2}a_0$	c_0	$\sqrt{2}a_0$	4	$D_{2h}^{10} - Pccn$	$\tau_5 \otimes \tau_7$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$D_{2h}^{14} - Pbcn$	$\tau_4 \otimes \tau_2$
13	$\phi \phi \psi_z$	$\bar{\phi} \bar{\phi} \psi_z$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$D_{2h}^{15} - Pbca$	$\tau_3 \otimes \tau_7$	$\sqrt{2}a_0$	$\sqrt{2}a_0$	c_0	4	$D_{2h}^{11} - Pbcm$	$\tau_6 \otimes \tau_7$
14	$\phi \phi \phi_z$	$\bar{\phi} \bar{\phi} \phi_z$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$D_{2h}^{15} - Pbca$	$\tau_3 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$D_{2h}^{8} - Pcca$	$\tau_6 \otimes \tau_2$
15	$\phi \phi \psi_z$	$\bar{\phi} \bar{\phi} \bar{\psi}_z$	$\bar{a}^*$	$\sqrt{2}a_0$	c_0	4	$C_{2h}^5 - P12_1/c1$	$\tau_3 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2v}^{15} - Abm2$	$\tau_6 \otimes \tau_7$
16	$\phi \phi \phi_z$	$\bar{\phi} \bar{\phi} \bar{\phi}_z$	$\bar{a}^*$	$\sqrt{2}a_0$	c_0	4	$C_{2h}^5 - P12_1/c1$	$\tau_3 \otimes \tau_7$	$\bar{a}$	$\sqrt{2}a_0$	c_0	4	$C_{2h}^4 - P12/c1$	$\tau_6 \otimes \tau_2$
17	$\phi \phi \psi_z$	$\phi \phi 0$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^5 - P12_1/c1$	$\tau_5 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2v}^2 - Pmc2_1$	$\tau_4 \otimes \tau_7$
18	$\phi \phi \psi_z$	$\bar{\phi} \bar{\phi} 0$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^5 - P12_1/c1$	$\tau_3 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2v}^2 - Pmc2_1$	$\tau_6 \otimes \tau_2$
19	$\phi \phi \phi_z$	$\phi \phi 0$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^5 - P12_1/c1$	$\tau_5 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^4 - P12/c1$	$\tau_4 \otimes \tau_2$
20	$\phi \phi \phi_z$	$\bar{\phi} \phi 0$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^5 - P12_1/c1$	$\tau_3 \otimes \tau_7$	c_0	$\sqrt{2}a_0$	$\sqrt{2}a_0$	4	$C_{2h}^4 - P12/c1$	$\tau_6 \otimes \tau_2$

$\bar{a}^* = (\bar{a}_0 + \bar{b}_0 + \bar{c}_0)1/2.$

TABLE XV Symmetry of distorted phases in crystals with $G_0 = D_{4h}^{17} = I4/mmm$, induced by two-dimentional irreps τ_i which belong to X-point of Brillouin zone

τ_I	*Order parameter* η	*Space group* G_i	*Orientation of* G_I *symmetry planes in* G_0	*Octahedral tilts leading to the same symmetry changes for crystals with n-layers*
τ_2	$(0, \eta)$	$D_{2h}^{22} - Ccca$	c_1-$(001)_0$, c_2-$(110)_0$	ϕ_z for $n=2l$
	(η, η)	$D_{4h}^{3} - P4/nbm$	b-$(110)_0$, m-$(100)_0$	
	(η_1, η_2)	$D_{2h}^{4} - Pban$	b-$(110)_0$, a-$(110)_0$	
τ_3	$(0, \eta)$	$D_{2h}^{18} - Ccma$	c-$(001)_0$, m-$(110)_0$	ϕ, ϕ for $n=2l+1$
	(η, η)	$D_{4h}^{16} - P42/ncm$	c-$(110)_0$, m-$(100)_0$	
	(η_1, η_2)	$D_{2h}^{10} - Pccn$	c_1-$(110)_0$, c_2-$(110)_0$	
τ_4	$(0, \eta)$	$D_{2h}^{17} - Cmcm$	m_1-$(001)_0$,$(110)_0$, c_2-$(110)_0$	ϕ, ϕ for $n=2l$
	(η, η)	$D_{4h}^{14} - P42/mnm$	n-$(110)_0$, m-$(100)_0$, $(001)_0$	
	(η_1, η_2)	$D_{2h}^{12} - Pnnm$	n-$(110)_0$, $(110)_0$, m-$(001)_0$	
τ_5	$(0, \eta)$	$D_{2h}^{20} - Cccm$	c-$(001)_0$, $(110)_0$, m-$(110)_0$	$\phi, \bar{\phi}$ for $n=2l+1$
	(η, η)	$D_{2h}^{12} - P42/\mathrm{nnm}$	n-$(110)_0$, $(001)_0$, m-$(100)_0$	
	(η_1, η_2)	$D_{2h}^{2} - Pnnn$	n-$(110)_0$,$(110)_0$, $(001)_0$	
τ_6	$(0, \eta)$	$D_{2h}^{21} - Cmma$	m-$(001)_0$, $(110)_0$, a-$(110)_0$	$\phi, \bar{\phi}$ for $n=2l$
	(η, η)	$D_{4h}^{10} - P42/mcm$	m-$(100)_0$, $(001)_0$, n-$(110)_0$	
	(η_1, η_2)	$D_{2h}^{3} - Pccm$	c-$(110)_0$, $(110)_0$, $m \parallel (001)_0$	
τ_7	$(0, \eta)$	$D_{2h}^{18} - Ccma$	m-$(001)_0$, c-$(110)_0$	ψ_z, ϕ_z for $n=2l+1$, ψ_z for $n=2l$
	(η, η)	$D_{4h}^{5} - P4/mbm$	m-$(100)_0$, $(001)_0$, b-$(110)_0$	
	(η_1, η_2)	$D_{2h}^{9} - Pbam$	m-$(001)_0$, b-$(110)_0$	

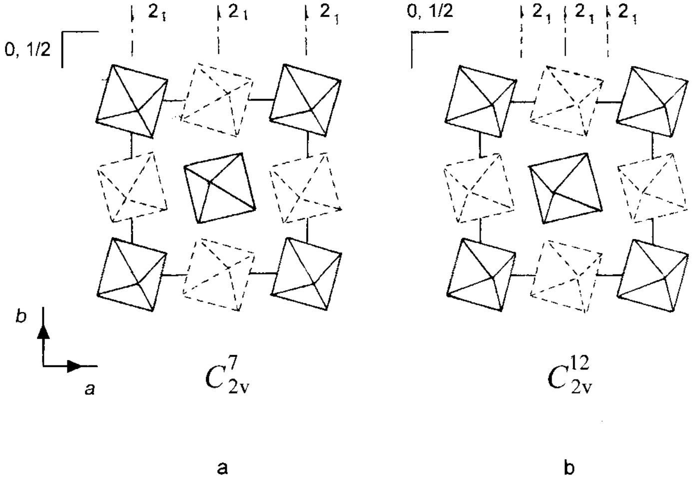

FIGURE 12 Two polar structures due to superpositions of (a) $(\phi 00)(0\phi 0)$ and (b) $(\phi\phi 0)(\phi\phi 0)$, with $(00\psi_z)(00\psi_z)$ tilt systems (see text).

triggered) PTs where two order parameters participate (Holakovsky, 1973). As it was mentioned above, often the tilts can be rationalized as due to the condensation of a soft librational lattice mode of G_0. Some other polar phases can be found in Table XIV. The symmetry corresponding to Figure 12b will be discussed below in more detail.

5.2. Some Experimental Data

In this Section we discuss experimental studies on crystals which contain single and multiple octahedral layers in their G_0 phases and undergo successive PTs. The great amount of existing studies compels us to select some representative data where the structural studies proved unambiguously that the PTs are definitely determined by tilting in octahedral layers and slabs.

5.2.1. Crystals with Single and Odd Octahedral Layers

Extensive sets of the data were collected for $(C_nH_{2n+1}NH_3)_2BX_4$ crystals where B = Mn, Cd, Fe, Cu and X = Cl, Br. The compounds with A = CH_3NH_3 (MA) groups display two different sequences of PTs. Distorsions in $(MA)_2MnCl_4$ lead to the appearance of $(\phi\phi 0)$ tilts in both layers for the G_1 phase, which correspond to a one-component order parameter $(\eta, 0)$ or $(0, \eta)$ (Heger, Mullen and Knorr, 1975, 1976). In the G_2 phase the tilting scheme changes to $(\phi 00)(0\phi 0)$ and the second component of the order parameter (η, η) appears. At the third PT, which has first order character, the tilting is reconstructed by $(\phi\phi\psi_z)(\phi\phi\bar{\psi}_z)$ due to tilts around the main axis of G_0. MA cadmium chloride displays the same sequence of PTs (Chapius, Kind and Arend, 1976; Kind, 1977). An unusual behavior of the elastic stiffness c_{66}, which tends to zero on approaching the PT G_2-G_1 from low temperature (Goto, Luthi, Geick *et al.*, 1980), was explained by Ishibashi and Suzuki (1984).

The first distorted phases in $(EA)_2MnCl_4$ and $(EA)_2FeCl_4$, EA = Ethylammonium (Brunskill and Depmeier, 1982; Suzuki, Yoshizawa, Goto *et al.*, 1983) belong to $G_1 = D_{2h}^{18}$ = Abma Sp.Gr. However, $G_2 = D_{2h}^{15}$ = Pbca in the Mn-compound is different to the G_2 phase in the the MA – Mn crystal due to the fact that ψ_z tilts are now "in phase" in both slabs, see Table XVI. The same D_{2h}^{15} Sp.Gr. exists in G_2 phase of $(PA)_2CdCl_4$ (Depmeier, Felsche and Widdemuth, 1977). As it was mentioned above $(PA)_2MnCl_4$ displays five PTs and one of the distorted phases has an incommensurate modulation of the structure (Depmeier, 1979, 1981). For other crystals of the series structural data are either similar or less complete and were not included in Table XVI.

It is necessary to point out that the entropy changes $(\Delta S/R)$ at some of the mentioned PTs are too small in comparison with the same values for PTs of order – disorder type. Thus, the PTs $G_0-G_1-G_2$ in $(MA)_2MnCl_4$ $(MA)_2CdCl_4$ and the PT G_0-G_1 in $(EA)_2BCl_4$, B = Mn, Fe, Cd have $\Delta S/R \leq 0.10$. It contradicts the accepted point of view that the whole sequence of PTs in crystals of these series is determined by the consecutive ordering of NH_3 groups (Blinc, Zeks and Kind, 1978). On the other hand, the values of $\Delta S/R$ at PT G_1-G_2 in $(EA)_2BCl_4$ crystals are much larger, namely 0.42, 0.73 and 1.17, respectively, for B = Mn, Fe and Cd (Yoshizava, Suzuki, Goto *et al.*, 1984). These values are close to ln2 for B = Mn and Fe and to ln3 for B = Cd. So, it is reasonable to conclude that that those PTs, in which a rather small entropy change is involved, are driven by lattice instability (tilting). At the PTs into $C2_1/a$ or Pbca phases of hydrogen bonds order and the ψ_z tilts follow from the process (Aleksandrov, Beznosikov and Misyul, 1987). The reason for this conclusion was the

TABLE XVI Successive phase transitions in crystals which belong to $G_0 = D_{4h}^{17} = I4/mmm$ space group

Crystal	G_i	T_i	*Space group*	*Distortions in layers*	*References*
$(MA)_2MnCl_4$	G_1	398	Amba	$(\phi\phi0)(\phi\phi0)$	Heger, Mullen and Knorr, 1975
	G_2	257	$P4_2/bma$	$(0\phi0)(\phi00)$	Heger, Mullen and Knorr, 1976
	G_3	92	$P2_1/a$	$(\phi\phi\psi_z)(\phi\phi\bar{\psi}_z)$	
$(EA)_2MnCl_4$	G_1	424	Amba	$(\phi\phi0)(\phi\phi0)$	Knorr, Jahn, Heger, 1974
		225	Pbca	$(\phi\phi\theta)(\phi\phi\theta)$	Depmeier, 1979
					Depmeier, Felsche *et al.*, 1977
$(PA)_2MnCl_4$	G_1	446	Abma	$(\phi\phi0)(\phi\phi0)$	Depmeier, Felsche and Widdermuth, 1977
	G_2	396	Incommen		
	G_3	344	Abma	$(\phi\phi0)(\phi\phi0)$	Depmeier, 1981
	G_4	165	Pbma		Depmeier, 1979
	G_5	110	Pbca		
Rb_2CdCl_4	G_1	143	Abma or	$(\phi\phi0)(\phi\phi0)$	Aleksandrov, Emelyanova, Mishul *et al.*, 1985
			Pccn	$(\phi_1\phi_20)(\phi_2\phi_10)$	
					Kruglik, Vasilyev and Aleksandrov, 1989
$Rb_3Cd_2Cl_7$	G_1	213	Bbmm	$(\phi\phi0)(\phi\phi0)$	Aleksandrov, Kokov, Melnikova *et al.*, 1988
	G_2	172	$P4_2/mnm$	$(\phi00)(0\phi0)$	
$Rb_4Cd_3Cl_{10}$	G_1	237	(Abma)	$(\phi\phi0)(\phi\phi0)$	Bovina, Kokov, Melnikova *et al.*, 1990
	G_2	194	$(P4_2/ncm)$	$(\phi00)(0\phi0)$	
		137	$(C2_1/a)$	$(\phi\phi\psi)(\phi\phi\psi)$	
La_2CuO_4	G_1	490	Abma	$(\phi\phi0)(\phi\phi0)$	Axe, Cox, Mohenty *et al.*, 1989
	G_2	36	$P4_2/ncm$	$(\phi00)(0\phi0)$	
Bi_2WO_6	G_1	1223	(Abma)	$(\phi\phi0)(\phi\phi0)$	Knight, 1993
	G_2	933	$Pca2_1$	$(\phi\phi\psi_z)(\phi\phi\psi_z)$	Rae, Thompson and Withers 1991
$Bi_2SrTa_2O_9$	G_1	608	$A2_1am$	$(\phi\phi\psi)(\phi\phi\psi)$	Rae, Thompson and Withers 1991
$Ca_3Ti_2O_7$	G_1	?	$Ccm2_1$	$(\phi\phi\psi)(\phi\phi\psi)$	Elcombe, Kisi, Hawkins *et al.*, 1991
$SrTb_2Fe_2O_7$	G_1	?	$P4_2/mnm$	$(\phi00)(0\phi0)$	Samaras, Collomb and Joubert, 1973
$Bi_4Ti_3O_{12}$	G_1	?	B1b1	?	Rae, Thompson, Withers *et al.*, 1990
$Ca_4Ti_3O_{12}$	G_1		Pcab	$(\phi\phi\phi)(\bar{\phi}\bar{\phi}\phi)$	Elcombe, Kisi, Hawkins *et al.*, 1991

observations of structural PTs in La_2CuO_4 and its solid solutions, and in Rb_2CdCl_4, which in all cases are determined by the lattice instabilities of G_0 phases respect to octahedral librations in the layers (Axe, Moudden and Holwein, 1989; Aleksandrov, Emelyanova, Misyul *et al.*, 1985a, b). Soft lattice modes have been found by neutron inelastic scattering in La_2CuO_4, and the G_1 phase symmetry of Rb_2CdCl_4 (Schafer, Shabanov and Aleksandrov, 1986) was determined by Raman spectroscopy. Later, crystals with double and triple octahedral layers have been grown in the systems $CdCl_2-RbCl: Rb_3Cd_2Cl_7$ and $Rb_4Cd_3Cl_{10}$ (Aleksandrov, Kokov, Melnikova *et al.*, 1988; Bovina, Kokov, Melnikova *et al.*, 1990). Both crystals display sequences of PTs due to tilts, but their structures have not been solved by direct methods. The tilting systems of the G_1 and G_2 phases were determined by X-ray diffraction, just studying the appearance of superstructure reflections, combined with optical birefrigence studies. The space groups of these phases are shown in brackets in Table XVI. Efforts to grow a $Rb_4Cd_3Cl_{10}$ single-phase crystal failed: the boules, grown by the Bridgman method, contain the desired compound together with $Rb_3Cd_2Cl_7$ (Bovina, Kokov, Melnikova *et al.*, 1990). However, it has been possible to determine the PT temperatures, since the corresponding values for pure $Rb_3Cd_2Cl_7$ are known, see Table XVI. It is seen that the distorted phases in this crystal correspond to the data of Table XIII.

In the last decade intensive attention has been drawn to the structural PTs in A_2BX_4 oxide crystals which have the so-called T-type of structure: La_2CuO_4, La_2NiO_4 and others, both as pure compounds and crystals with partial substitution of B^{2+}= Ba, Sr, Ca ions by A ions. Solid solutions $La_{1-x}B_xCuO_4$ are high temperature superconductors (Gangaly and Rao, 1984; Bednorz and Muller, 1986; Cava, Dover, Batloggg *et al.*, 1987a; Cava, Santoro, Johnson *et al.*, 1987b; Axe, Moudden, Holwein *et al.*, 1987; Rodríguez-Carvajal, Martínez *et al.*, 1988; Axe, Cox, Mohenty *et al.*, 1989; Burns, Dacol, Rice *et al.*, 1990; Rodriguez-Carvajal, Fernández-Díaz and Martínez, 1991). Structural PTs have been found in these crystals; $G_0-G_1-G_2$ with the same symmetry changes as for the two distorted phases of $(MA)_2MnCl_4$: Abma and $P4_2/ncm$. It has been conjectured that in the G_2 phase of La_2CuO_4 the coherent superposition of twins related to the G_1 (orthorhombic) phase may lead to tetragonal symmetry (Axe, Cox, Mohenty *et al.*, 1989). Pr_2NiO_4 is orthorhombic at RT with $G_1 = Bmab$ and $G_2 = P4_2/mcb$ ($T_2 = 115\,K$) which correspond to the same tilting scheme as the two above-mentioned crystals (Fernández-Diaz, Rodríguez-Carvajal, Martínez *et al.*, 1991).

It is worthwhile to mention here that Nd_2CuO_4 is a unique crystal, which belongs to the so called T′-type of A_2BX_4 structures, that lacks the apical oxygen atoms of the octahedral layers, shown on Figure 8a, and square CuO_2 lattices are separated by A_2O_2 blocks of CaF_2-type. The softening of a librational lattice mode with decreasing temperature was found (Pyka, Mitrofanov, Bourges *et al.*, 1992). Later, Braden, Paulus, Cousson *et al.*, 1994 using neutron diffraction have found that CuO_2 layers have ψ_z tilts (5,2°). The distorted structure belongs to $G_1 = Acam$ (Cmca) Sp.Gr. The T′ type crystals are formed with A = Rare Earth ions ranging from Nd to Tm. Furthermore tilting can be found in other crystals of this type.

In the course of the study of structural changes due to tilts (Aleksandrov, Beznosikov and Misyul, 1987b) the authors restricted themselves to the cases leading to the multiplication of the G_0 unit cell without doubling of the main c_t axis. However, some crystals, like Sr_2IrO_4, Sr_2RhO_4, Ca_2MnO_4 and others (Subramanian, Crawford, Harlow *et al.*, 1994a, b; Takahashi and Camagashira, 1993), were found which double their c_t axis. The structural data (Crawford, Subramanian and Harlow, 1994) show that the tilting scheme, in Sr_2IrO_4 for example, is the following: in the first G_0 unit cell the octahedra in both layers are tilted as $(00\psi_z)(00\psi_z)$ but in the second cell these tilts change sign $(00\bar{\psi}_z)(00\bar{\psi}_z)$. It leads to $G_1 = D_{4h}^{20} = I4_1/acd$ Sp.Gr. with $Z = 4$ and at 13 K the value of the tilt angle is 11°. The analysis by Hatch, Stokes, Aleksandrov *et al.* (1989) indicates that this distortion is determined by irrep P_4, which belongs to the P point of the Brillouin zone (Fig. 3d).

The presence of phase transitions in crystals of the Aurivillius series is less widespread, but many crystals have distorted and polar structures at RT. Aurivillius (1950, 1951, 1952) studied the structures and properties of some undistorted crystals, $BaNbO_5F$, $CaBi_2Nb_2O_8$, $Bi_4Ti_3O_{12}$, and others. Later, a large amount of new representatives of the series have been studied (Galasso, 1959, 1990; Isupov, 1995 and references therein), and many of the crystals have polar structures and high temperature PTs, see Table XVI. As an example we consider Bi_2WO_6 for which the published structural data are contradictory.

Thus, Knight, 1993 has reported that in the sequence of PTs $G_0-G_1-G_2$ the change of Sp.Gr's is the following: (I4/mmm)$-$Aba2_1-Pca2_1, *i.e.*, the PT G_1-G_2 takes place between two orthorhombic polar phases with $(\phi\phi 0)(\phi\phi 0)$ tilt system in G_1 plus polar displacements (pp0), and in the G_2 phase, in addition, the ψ_z tilt appears. On the other hand, Utkin, Roginskaya, Voronkova *et al.* (1980) showed that the generation of optical second harmonics is quenched above 933 K, which means that the G_1 phase is centro-symmetrical. In our opinion it is better to consider G_1 as belonging to Abam Sp.Gr. without polar displacements and $G_2=$Pca2_1 with the tilts found by Knight (Aleksandrov and Beznosikov, 1997).

5.2.2. Crystals with Even Number of Octahedral Layers in the Structure

Examples of well studied PTs in perovskite-like crystals with an even number of octahedral layers in slabs are very limited, in spite of the large number of crystals belonging to the considered series, and specially to the anion deficient related crystals. It was found that many representatives of the Aurivillius-type crystals have distorted and polar structures at room temperature and display PTs of unknown nature both above and below RT (Subbarao, 1973; Smolensky, Bokov, Isupov *et al.*, 1984). These PTs have not been studied in detail. It was also found that many crystals of both series have the unit-cell parameters a and b nearly equal to $\sqrt{2}a_t$ of G_0 and $Z=4$, but the X-ray diffraction data did not allow to distinguish the type of distortion. Sometimes the distorted structures have been considered as having an F-centered unit cell with additional polar distortions.

Among crystals with double layers in the slabs we mention a few examples. One of them is $Rb_3Cd_2Cl_7$ (Aleksandrov, Kokov, Melnikova *et al.*, 1988; Flerov, Aleksandrov, Melnikova *et al.*, 1989). The crystal displays two structural PTs $G_0-G_1-G_2$ and its distorted phases are $G_1 = D_{2h}^{17} =$ Cmcm and $G_2 = D_{4h}^{14} ==$ P4_2/mnm. The tilting schemes and transition temperatures are shown in Table XVI and correspond to the action of irrep τ_4 in Table XV.

Kim, Kawaji, Itoh *et al.* (1992) studied on powder samples the structure of $SrLa_2Sc_2O_7$. They have found that the substance has two PTs: tetragonal-orthorhombic-orthrhombic phase, but the actual

Sp.Gr's could not be determined. If the known unit-cell parameters are taken into account Table XIII and Table XIV give many possibilities to describe such structural changes. This crystal, as well as $Sr_3Ir_2O_7$ (Subramanian, Crawford and Harlow, 1994b), has not been included in Table XVI. For the last crystal the authors have found a rather large (11°) tilt angle in the octahedra belonging to the slabs, but concluded that the tilts are uncorrelated(!), and have described the structure as belonging to G_0. Elcombe, Kisi, Hawkins *et al.*, 1991) have studied the structure of $Ca_3Ti_2O_7$ and found that at RT the crystal has the polar $G_I = C_{2v}^{12} = Ccm2_1$ Sp.Gr. (see Fig. 12b). According to the data by Samaras, Collomb and Joubert, 1973, who studied some complex ferrites with perovskite double layered structures, the crystal $SrTb_2Fe_2O_7$ has a slightly distorted structure. The Rietveld analysis gave the best results for $D_{4h}^{14} = P4_2/mnm$, the same Sp.Gr. as for G_2 in $Rb_3Cd_2Cl_7$. A similar structure was found in $Sr_2HoMn_2O_7$ and $Sr_2YMn_2O_7$ (Battle, Millburn, Rosseinsky *et al.*, 1997), substances which may have high temperature PTs.

Many ferroelectric crystals, with even number of octahedral layers in the slabs, belong to the Aurivillius series. Thus the structure of $Bi_2SrTa_2O_9$ (Rae, Thompson and Withers, 1992) has been described as $G_I = A2_1am$. As it can be derived from Table XIV (No. 9), it is the same Sp.Gr., C_{2v}^{12}, that appears as the result of the superposition of the $(\phi\phi0)(\phi\phi0)$ and $(00\psi_z)(00\psi_z)$ tilt systems (compare with Fig. 12b). Indeed, the structures of the crystals mentioned above really contain the anion displacements corresponding to these tilt systems. There may be polar distortions in the case that polar shifts of the central ions in the octahedra and displacements of A-atoms in the perovskite-like slabs along the polar $[110]_t$ direction are superposed to the tilt system. The values of the tilts are usually less than 10°. Some other crystals of the series, included the cation deficient $Bi_2W_2O_9$, have been studied by Champanaud-Mesjard, Frit and Watanabe (1999). The structure of $Bi_2W_2O_9$ at RT has been described as belonging to $Pna2_1$ Sp.Gr., and the authors showed that the tilting scheme is the same as for $Bi_2SrTa_2O_9$.

The tolerance factors introduced in Sections 2 and 3 for perovskites and elpasolites were modified for the layered A_2BO_4 oxide crystals. Poix (1980), introduced two empirical coefficients, calculated from the known experimental data, but the method has restricted application for A_2BX_4 structures with other anions and specially for structures with two or more octahedral layers. Anyhow, it can conjectured that some other layered crystals having a "tolerance factor" beyond the stability range of G_0, may have distorted structures in a certain temperature region.

6. SUMMARY AND CONCLUSION

Many authors, during the last three decades, have made the crystallographic and group theoretical analysis of the structural distortions caused by octahedral tilts in perovskites and their relatives: ($G_0 = Pm\bar{3}m$), elpasolites, cryolites, $BB'X_6$ and A_2BX_6 crystals of K_2PtCl_6 structures ($G_0 = Fm\bar{3}m$), and also in layered perovskite-like crystals belonging to $G_0 = P4/mmm$ and $G_0 = I4/mmm$. In Tables I–XVI we have collected the theoretical and some experimental data.

For perovskites and their nearest relative structures the tilts are determined by two "simple" kinds of tilts, which correspond to two active irreps of G_0: M_3 and R_{25}. Both irreps determine the three components order parameter and the main paths of successive PTs to structures of lower symmetry, due to the appearance of additional tilt components. But some exceptions exist which are determined in the frame of the Landau thermodynamic theory of PTs by definite relations between some coefficients of the thermodynamic potential. Successive PTs, where only one of the irreps participates (one kind of tilt), are easily described by the group theoretical analysis. When two kinds of tilt appear it is necessary either to repeat the analysis for G_1, G_2, *etc*, or to consider the direct product of two irreps. The procedure becomes more complicated for the layered crystals where three and four kinds of tilt may exist. There is another way to determine the symmetry of a distorted phase, just by depicting the distorted structure and checking its symmetry in comparison with the results of the group theory. It was shown that such combined procedure gives the most reliable results.

In layered crystals with $G_0 = P4/mmm$ the third kind of tilt (ψ_z tilt around the main axis) appears for crystals of $TlAlF_4$ type. Furthermore, in crystals with multiple octahedral layers the fourth kind of tilt (ϕ_z around the main axis) appears. It implies that there are three or four irreps associated with the tilts and, as a result, the group theoretical method becomes too complicated. Moreover, the signs of ψ_z and ϕ_z tilts can be opposite in neighboring layers or slabs and then two more irreps have to be taken into consideration.

Many examples of the considered series of perovskite-like crystals display structures distorted by different kinds of tilt. A restricted number of representatives and the corresponding experimental data were presented in the Tables: crystals having successive PTs, and those where different paths of the symmetry changes occur. As a rule these PTs are associated with the lattice instability of the initial structure, and, often, soft lattice modes were experimentally observed. The second phenomenon, which was studied for some perovskites and elpasolites, is that the pronounced X ions anharmonicity in G_0 phases tend, below the PT, to displace them from the right positions.

It was mentioned also that the values of tolerance factors are a rather crude measure of crystal stability in the G_0 phase. Moreover, even if the t value is known, it is impossible to predict, below PT, to which distorted phase the crystal will transform . As it was shown by Woodward (1997b) for oxides, the main role in the perovskite structure is played by the interrelation between covalent bonding, coulomb forces, short-range interactions, and the particular nature of the A and B ions.

It is well known that the structures of many high temperature superconductors are similar to the stoichiometric phases of the Aurivillius's, Ruddlesden-Popper's and $AA'_{m-1}B_mX_{3m+1}$ series. In these anion deficient compounds distortions from a tetragonal structure have been found in some cases. The appearance of weak superstructure reflections is determined mainly either by inter-growth of different m-members of the studied series in the given sample or by a different anion deficiency. At the same time, many examples may be found in the current literature in which the structure, studied on a powder sample, is considered to belong to the highest tetragonal space group. However, some atoms in these structures move away from the right positions and are distributed on shifted, partially occupied, sites. It may be assumed that probably some tilts exist in these structures. Then, using the crystallographic data presented in this review, it would be possible to select a few trial models of proper distortions and to repeat the fitting procedure of the experimental data collected earlier.

Some of these anion deficient substances may also display the structural PTs described above.

As it was mentioned in the Introduction, there exist three ways to cut the three-dimensional octahedral frame: by (001), (110) and (111) planes. In the first case, the distortions due to tilts in layered crystals with square lattices of octahedra have been considered in the review. But similar kinds of tilts exist in structures $A_nB_nX_{3n+2}$, $2 \leq n \leq 7$, where the octahedral frame is cut by (110) planes. The crystallography of their distortions has been considered recently by Levin and Bendersky (1999). They have shown that the symmetry changes in most crystals of the series are fully determined by the 27 tilt systems associated with the rigid BX_6 octahedra. The authors are unaware of any publication about similar distortions in crystals formed by (111) slabs of the linked octahedra.

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