

## Phase transitions in the perovskitelike $A_2BX_4$ structure

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A comparison is made of two different approaches to the description of phase transitions in the  $A_2BX_4$  structure (space group  $D_{4h}^{17}$ ,  $I4/mmm$ ) due to rigid octahedral tiltings. The lower-symmetry subgroups due to coupling of the  $K_{13}\hat{\rho}^7$  ( $X_2^+$ ) and  $K_{12}\hat{\rho}^2$  ( $P_4$ ) representations ( $\Theta$  tilts) to other tilting modes are listed. All observed transitions in the  $A_2BX_4$  structure are of the octahedral tilting types. These are listed and correlated with the driving representations.

### I. INTRODUCTION

$A_2BX_4$  crystals with the structure of  $K_2MgF_4$  type are layered perovskitelike compounds. One of the main features of the perovskite structure, namely the flat square layers of  $BX_6$  octahedra corner linked within the layer plane, is preserved in the  $A_2BX_4$  structure. Layers neighboring along the  $c$  axis in these crystals are shifted by half of the body diagonal of the unit cell  $G_0=I4/mmm$  which has two formula units per conventional cell [Fig. 1(a)]. As a rule the  $A$  cations are arranged almost in the plane formed by the  $X$  atoms at the top (or bottom) of the octahedra and have nine nearest neighbors. Crystals with the structure of  $K_2MgF_4$  type are widely exhibited by fluorides and oxides  $A_2^{2+}B^{4+}O_4$  and  $A_2^{3+}B^{2+}O_4$  with large  $A$  cations. A large group of chlorides and bromides is also known, where the sites of the  $A$  cations in the general formula are occupied by organic chain alkylammonium cations  $(C_nH_{2n+1}NH_3)^{1+}$ ,  $n=1,2,\dots,5$ .<sup>1,2</sup> Many of the compounds listed above undergo phase transitions (PT's) or sequences of PT's.

It has been shown recently<sup>1-3</sup> that by considering the mutual tilts of  $BX_6$  octahedra (rotational distortions), one may describe all experimentally observed types of successive distortions within the  $A_2BX_4$  structure.

These investigations were performed independently by two research groups and the results were published in Refs. 1-3. However, each of these works has omissions and the philosophies of approach taken by the two groups are different. In this publication, we indicate the distinct approaches of the two groups, we provide data on the symmetry of rotationally distorted phases, and we make a comparison of the calculated results with existing experimental data. The latter two sets of information correct omissions of the previous papers.

### II. PHILOSOPHIES OF APPROACH

Aleksandrov *et al.*<sup>1,2</sup> have solved the problem of listing the possible symmetry changes of the  $A_2BX_4$  crystal structure using mainly a direct crystallographic method,

which consists of the determination of the space group for the distorted phase  $G_i$  by means of actually depicting its structure. The advantage of this method is physical clarity in the determination of the symmetry elements of the distorted structure when superpositions of definite types of distortions (in our case rotational ones) take place. Earlier, such a procedure was successfully used in the analysis of rotational distortions in perovskites and

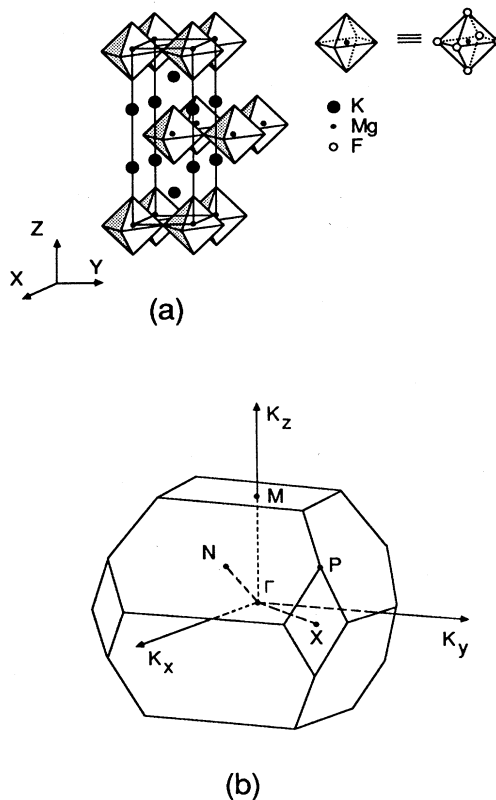


FIG. 1. (a) Crystal structure of  $K_2MgF_4$  type and (b) the first Brillouin zone of body-centered tetragonal unit cell.

elapsolites.<sup>4-6</sup> It was assumed that in the first approximation the  $BX_6$  octahedra for small tilts do not undergo any additional distortion, and the complex distortions may be treated as a superposition of either tilts of different kinds, or of those of the same kind but around the different axes of  $G_0$ . For the layered perovskitelike crystals  $A_2BX_4$ , it was shown<sup>1,2</sup> that in the square layers of octahedra three kinds of tilts are possible: a tilt around the normal to the layer plane ( $\Theta$  tilts) [Fig. 2(a)], and two kinds of tilts ( $\Phi$  and  $\Psi$ ) which can both occur around the  $a_0$  and/or  $b_0$  axes of  $G_0$ . For  $\Psi$  tilts around  $b_0$ , all octahedra in a column (looking down  $b_0$ ) are turned in the same direction [Fig. 2(b)]. The symbol of such a distortion is  $(0\Psi 0)$ , i.e.,  $\Psi$  tilts around the  $b_0$  axis. The simultaneous  $\Psi$  tilts around both  $a_0$  and  $b_0$  are also possible, which is indicated by the distortion symbol  $(\Psi\Psi 0)$ . The  $\Phi$  tilts are characterized by alternating tilt angles along the axis of rotation. Figure 2(c) corresponds to  $(0\Phi 0)$ .

Besides the symmetry equivalent  $(\Phi 0 0)$  and  $(0\Phi 0)$  distortions, also  $(\Phi\Phi 0)$ ,  $(\Phi, \Phi_2 0)$ , etc., are possible. In all, 15 variants result from distortions in a single layer. All of these were listed by Aleksandrov *et al.*<sup>1,2</sup> This method allowed the detection of one peculiarity inherent in layered crystals which is called polydistortion or distortional polytypism.<sup>7</sup> It distinguishes the variety of spatial symmetry variants in such crystals due to different combinations of kinds and amplitudes (or angles) of distortions in nearby layers, which are linked together comparatively weakly. An example of the phenomenon was found in the studied group of crystals.<sup>2</sup>

Experimental data on  $A_2BX_4$  structures (given in Refs. 1 and 2) indicated the absence of unit-cell multiplication along the  $c_0$  axis of the  $G_0$  phase [Fig. 1(a)]. As a result, Aleksandrov *et al.*<sup>1,2</sup> considered only the distortions  $G_i$  leading to unit-cell multiplication in the basic plane (001). This means that the irreducible representations responsible for PT's  $G_0 \rightarrow G_i$  were restricted to the two-armed  $K_{13}$  star (in terms of Kovalev<sup>8</sup>) or to the  $X$  point of the Brillouin zone of  $G_0$  (in terms of Miller and Love<sup>9</sup>) [Fig. 1(b)].

The partial group-theoretical analysis of distortions in  $A_2BX_4$  crystals was performed in Refs. 1 and 2 in order to obtain the correspondence between the kinds of tilts and the irreducible representations of  $G_0$  belonging to the  $K_{13}$  ( $X$ ) star of the wave vector. Those changes due to rotational distortions of  $\Phi$  and  $\Psi$  tilts were left out in the first paper.<sup>1</sup> Only after acquaintance with the work later published as Ref. 10 was this omission partially corrected in Ref. 2.

Hatch and Stokes<sup>3</sup> obtained the permissible rotational distortions in a manner distinct from Refs. 1 and 2. Previously they had implemented on computer a systematic method for obtaining subgroups resulting from a single irreducible physical distortion. This procedure is an extension of the Landau theory of continuous phase transitions (see Ref. 11 and references therein). The usual assumption in the Landau theory is that only one irreducible representation (irrep) drives the transition to the lower-symmetry (subgroup) phase. A listing of the al-

lowed subgroups for all Brillouin-zone points of symmetry had been obtained and the order parameter direction had been matched with the resulting lower-symmetry phase and the multiple domains.<sup>12</sup>

Together with the subgroup and order parameter listing, Hatch, Stokes, and Putnam<sup>13</sup> had also obtained a connection between the Wyckoff point-group representations and the resulting representations of  $G_0$  which could be induced from the representations of the Wyckoff point group. Thus, for a given group-subgroup change, the compatibility of this change with an assumed site distortion could be checked. By using projection operator techniques the specific sublattice displacements within a unit cell could then be obtained.<sup>13</sup>

However, for the perovskitelike structures, coupled parameters (direct sums of representations) are of interest. If  $G^\alpha$  denotes the subgroup symmetry for the order parameter  $\eta^{(\alpha)}$ , and  $G^\beta$  denotes the subgroup symmetry for the order parameter  $\eta^{(\beta)}$ , then an allowed subgroup for the bicoupled parametric transition will be the group-theoretical intersection of  $G^\alpha$  and  $G^\beta$ . By considering all possible domains for the  $G_0 \rightarrow G^\alpha$  and  $G_0 \rightarrow G^\beta$  transitions, a complete listing of all bicoupled (bireducible) representations can be found for these transitions.

In Refs. 3 and 10, Hatch and Stokes published a selected listing of coupled irreps. In Ref. 10 the subgroups of  $D_{4h}^1$  ( $P4/mmm$ ) were published restricting attention to the irreducible representations  $K_{15}\hat{\tau}^3$  ( $X_3^+$ ),  $K_{18}\hat{\tau}^3$  ( $M_3^+$ ),  $K_{18}\hat{\tau}^9$  ( $M_5^+$ ),  $K_{20}\hat{\tau}^9$  ( $A_5^+$ ), and  $K_{16}\hat{\tau}^3$  ( $R_3^+$ ). These were the only representations which those authors determined to be associated with tilting modes in the perovskitelike  $ABX_4$  structure, and all tilting configurations were obtained by projection operator methods. Specific examples of the tilting configurations were given in Ref. 10. In Ref. 3 they published similar work for the perovskitelike  $A_2BX_4$  structure. However, the two-dimensional representations  $K_{13}\hat{\tau}^7$  ( $X_2^+$ ) and  $K_{12}\hat{\tau}^2$  ( $P_4$ ) corresponding to the  $\Theta$  tilts were omitted in that publication.

### III. NEW RESULTS

Recognizing the need to include these representations ( $\Theta$  tilts) in the listing of bicoupled transitions, and the need to give a more complete listing of the experimentally observed transitions in the  $A_2BX_4$  crystals due to the

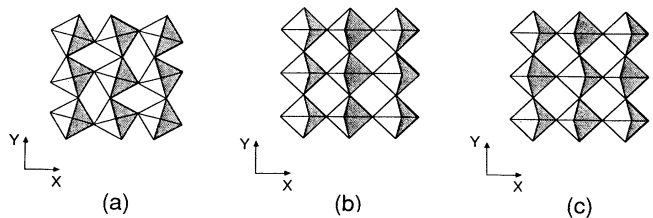


FIG. 2. Three types of octahedral tilting in layers of linked octahedra: (a)  $(00\Theta)$ ; (b)  $(0\Psi 0)$ ; (c)  $(0\Phi 0)$ .

coupling of  $\Theta$  tilts with  $\Phi$  and  $\Psi$  tilts, in this section we remedy the omissions of Refs. 1–3.

Using the approach of Hatch and Stokes,<sup>3,10</sup> we give in Table I the listing of transitions driven by uncoupled rep-

resentations of  $D_{4h}^{17}$ . We list only those corresponding to octahedral tilting modes. In Table II we list the transitions resulting from the coupling of the  $K_{13}\hat{\tau}^7(X_2^+)$  and  $K_{12}\hat{\tau}^2(P_4)$  representations with  $K_{13}\hat{\tau}^3(X_3^+)$ ,  $K_{13}\hat{\tau}^5$

TABLE I. Irreducible representations allowing octahedral tiltings in the  $A_2BX_4$  structure are listed. The subgroups resulting from the tilting are shown along with the conventional "basis" vectors and origins (in terms of the original conventional vectors of  $D_{4h}^{17}$ ). Numbers in parentheses are from Ref. 15. The order parameter orbit is also indicated for each subgroup.

Irrep	Subgroup	Orbit	Basis vectors	Origin
$X_2^+$	$D_{4h}^{5(127)}$	$P1$	(1,1,0),(-1,1,0),(0,0,1)	$(\frac{1}{2}, \frac{1}{2}, 0)$
	$D_{2h}^{18(64)}$	$P3$	(0,0,1),(1,1,0),(-1,1,0)	(0,0,0)
	$D_{2h}^9(55)$	$C1$	(1,1,0),(-1,1,0),(0,0,1)	(0,0,0)
$X_3^+$	$D_{4h}^{16(138)}$	$P1$	(1,1,0),(-1,1,0),(0,0,1)	(0,0,0)
	$D_{2h}^{18(64)}$	$P3$	(1,1,0),(0,0,1),(1,-1,0)	(0,0,0)
	$D_{2h}^{10(56)}$	$C1$	(1,1,0),(-1,1,0),(0,0,1)	(0,0,0)
$X_4^+$	$D_{4h}^{12(134)}$	$P1$	(1,1,0),(-1,1,0),(0,0,1)	$(\frac{1}{2}, \frac{1}{2}, 0)$
	$D_{2h}^{20(66)}$	$P3$	(0,0,1),(1,1,0),(-1,1,0)	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$
	$D_{2h}^2(48)$	$C1$	(1,1,0),(-1,1,0),(0,0,1)	(0,0,0)
$N_1^+$	$C_{2h}^3(12)$	$P5$	(0,-1,1),(1,0,0),(0,1,1)	(0,0,0)
	$D_{2h}^{19(65)}$	$P1$	(0,2,0),(0,0,2),(1,0,0)	$(0, \frac{1}{2}, \frac{1}{2})$
	$C_{2h}^3(12)$	$P11$	(0,0,2),(2,2,0), $(-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$	(0,0,0)
	$C_{2h}^1(10)$	$C3$	(0,1,1),(1,0,0),(0,1,-1)	(0,0,0)
	$C_1^1(2)$	$C12$	$(-1,1,1),(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}), (1,1,-1)$	(0,0,0)
	$D_{4h}^{19(141)}$	$P4$	(2,0,0),(0,2,0),(0,0,2)	(0,0,0)
	$D_{4h}^{17(139)}$	$P3$	(2,0,0),(0,2,0),(0,0,2)	$(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$
	$D_{2h}^{28(74)}$	$C2$	(2,0,0),(0,2,0),(0,0,2)	(0,0,0)
	$D_{2h}^{25(71)}$	$C1$	(2,0,0),(0,2,0),(0,0,2)	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
	$C_{2h}^6(15)$	$C10$	(0,0,-2),(-2,-2,0),(-1,1,1)	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
	$C_{2h}^3(12)$	$C8$	(0,0,-2),(-2,-2,0),(-1,1,1)	(0,0,0)
	$C_{2h}^3(12)$	$S1$	(2,0,-2),(0,2,0),(0,0,2)	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
	$C_1^1(2)$	$4D1$	$(-1,1,1), (1,-1,1), (1,1,-1)$	(0,0,0)
	$P_4$	$D_{4h}^{20(142)}$	$P1$	(1,10),(-1,1,0),(0,0,2)
$D_{4h}^{18(140)}$		$P3$	(1,1,0),(-1,1,0),(0,0,2)	(0,0,0)
$D_{2d}^{10(120)}$		$C1$	(1,1,0),(-1,1,0),(0,0,2)	(0,0,0)
$P_5$	$D_{2d}^{12(122)}$	$P1$	(1,1,0),(-1,1,0),(0,0,2)	$(\frac{1}{2}, 0, \frac{1}{4})$
	$D_{2d}^{11(121)}$	$P4$	(1,1,0),(-1,1,0),(0,0,2)	$(0, \frac{1}{2}, \frac{3}{4})$
	$D_{2h}^{28(74)}$	$P5$	(0,0,2),(1,-1,0),(1,1,0)	$(0, \frac{1}{2}, \frac{1}{2})$
	$D_{2h}^{26(72)}$	$P12$	(0,0,2),(1,-1,0),(1,1,0)	$(\frac{1}{4}, -\frac{1}{4}, \frac{3}{4})$
	$D_{2h}^{24(70)}$	$P3$	(2,0,0),(0,2,0),(0,0,2)	$(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$
	$D_{2h}^{23(69)}$	$P11$	(2,0,0),(0,2,0),(0,0,2)	$(0, \frac{1}{2}, \frac{1}{2})$
	$S_4^2(82)$	$C2$	(1,1,0),(-1,1,0),(0,0,2)	$(0, \frac{1}{2}, \frac{3}{4})$
	$C_{2v}^{22(46)}$	$C13$	(1,-1,0),(1,1,0),(0,0,2)	$(\frac{1}{2}, 0, 0)$
	$C_{2v}^{19(43)}$	$C1$	(2,0,0),(0,2,0),(0,0,2)	$(0, \frac{1}{2}, 0)$
	$C_{2v}^{18(42)}$	$C10$	(2,0,0),(0,2,0),(0,0,2)	$(0, \frac{1}{2}, 0)$
	$D_2^9(24)$	$C3$	(1,1,0),(-1,1,0),(0,0,2)	$(\frac{1}{4}, \frac{1}{4}, 0)$
	$D_2^8(23)$	$C11$	(1,1,0),(-1,1,0),(0,0,2)	$(0, \frac{1}{2}, \frac{3}{4})$
	$D_2^7(22)$	$C8$	(2,0,0),(0,2,0),(0,0,2)	$(0, \frac{1}{2}, \frac{1}{2})$
	$C_{2h}^6(15)$	$C9$	(0,2,0),(0,0,2),(1,-1,0)	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$
$C_{2h}^3(12)$	$C12$	(0,2,0),(0,0,2),(1,-1,0)	$(0, \frac{1}{2}, \frac{1}{2})$	
$C_2^3(5)$	$4D1$	(0,2,0),(0,0,2),(1,-1,0)	$(0, \frac{1}{2}, 0)$	

TABLE II. The subgroups obtained from reducible representations of  $D_{4h}^{17}$  are listed. The irreps being coupled are shown as well as the order parameter orbits and stratum subspaces. The subgroup conventional basis vectors and origin are expressed in terms of the original conventional basis vectors of  $D_{4h}^{17}$ .

Irreps	Subgroup	Orbit	Subspace	Basis vectors	Origin
$X_2^+ \oplus X_3^+$	$C_{2h}^3$	$P1, P1$	1,1	(0,2,0),(2,0,0)(0,0,-1)	(0,0,0)
	$C_{2h}^5$	$P3, P3$	1,1	$(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}), (-1, 1, 0)(0, 0, 1)$	(0,0,0)
	$D_{2h}^{15}$	$P3, P3$	1,2	(1,1,0)(-1,1,0)(0,0,1)	(0,0,0)
	$C_{2h}^5$	$P3, C1$	1,1	(1,1,0),(-1,1,0),(0,0,1)	(0,0,0)
	$C_{2h}^5$	$C1, P3$	1,1	(0,0,1),(1,-1,0),(1,1,0)	(0,0,0)
	$C_i^1$	$C1, C1$	1,1	(1,1,0),(-1,1,0),(0,0,1)	(0,0,0)
$X_2^+ \oplus X_4^+$	$C_{2h}^3$	$P1, P1$	1,1	(0,2,0),(2,0,0),(0,0,-1)	(0,0,0)
	$C_{2h}^6$	$P3, P3$	1,1	(0,0,1),(1,1,0),(-1,1,0)	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$
	$D_{2h}^{10}$	$P3, P3$	1,2	(0,0,1),(1,-1,0),(1,1,0)	(0,0,0)
	$C_{2h}^4$	$P3, C1$	1,1	(1,-1,0),(1,1,0),(-1,1,1)	(0,0,0)
	$C_{2h}^5$	$C1, P3$	1,1	(0,0,1),(1,1,0),(-1,1,0)	(0,0,0)
	$C_i^1$	$C1, C1$	1,1	(1,1,0),(-1,1,0),(0,0,1)	(0,0,0)
$X_2^+ \oplus N_1^+$	$D_{2h}^{28}$	$P1, P1$	1,1	(2,0,0),(0,0,2),(0,-2,0)	(0,0,0)
	$C_{2h}^5$	$P1, P3$	1,1	(2,0,0),(0,2,0),(0,0,2)	$(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$
	$D_{2h}^{25}$	$P1, C1$	1,3	(2,0,0),(0,2,0),(0,0,2)	(0,0,0)
	$C_{2h}^3$	$P1, S1$	1,5	(2,0,-2),(0,2,0),(0,0,2)	(0,0,0)
	$C_{2h}^6$	$P3, C10$	1,1	(0,0,-2),(-2,-2,0),(-1,1,1)	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
	$C_{2h}^3$	$C1, C1$	1,1	(-2,2,0),(0,0,2),(2,0,0)	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
$X_2^+ \oplus P_4$	$C_i^1$	$C1, 4D1$	1,1	(-1,1,1),(1,-1,1),(1,1,-1)	(0,0,0)
	$D_{4h}^{13}$	$P1, P3$	1,1	(-1,-1,0),(1,-1,0),(0,0,2)	$(\frac{1}{2}, \frac{1}{2}, 0)$
	$D_{4h}^5$	$P1, P3$	1,2	(-1,-1,0),(1,-1,0),(0,0,2)	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
	$D_{2d}^7$	$P1, C1$	1,1	(-1,1,0),(-1,-1,0)(0,0,2)	$(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$
	$D_{2h}^8$	$P3, P1$	1,1	(-1,1,0),(0,0,-2),(-1,-1,0)	$(-\frac{1}{4}, -\frac{1}{4}, -\frac{3}{4})$
	$D_{2h}^9$	$C1, P3$	1,1	(-1,-1,0),(-1,1,0),(0,0,-2)	(0,0,0)
$X_2^+ \oplus P_5$	$C_{2v}^8$	$C1, C1$	1,1	(-1,-1,0),(-1,1,0),(0,0,-2)	(0,0,0)
	$D_{2h}^{17}$	$P1, P11$	1,1	(2,0,0),(0,2,0),(0,0,2)	(0,0,0)
	$D_{2h}^{17}$	$P1, P11$	1,3	(0,-2,0),(2,0,0),(0,0,2)	$(0, 0, \frac{1}{2})$
	$D_2^5$	$P1, C8$	1,1	(2,0,0),(0,2,0),(0,0,2)	(0,0,0)
	$C_{2v}^{12}$	$P1, C10$	1,1	(2,0,0),(0,2,0),(0,0,2)	(0,0,0)
	$D_{2h}^{10}$	$P3, P12$	1,1	(0,0,2),(1,-1,0),(1,1,0)	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$
$X_2^+ \oplus P_5$	$D_{2h}^{14}$	$P3, P12$	1,2	(0,0,2),(1,1,0),(-1,1,0)	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$
	$C_{2h}^5$	$P3, C9$	1,1	(-1,1,0),(0,0,2),(1,1,0)	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$
	$D_2^3$	$P3, C11$	1,1	(0,0,2),(1,-1,0),(1,1,0)	$(\frac{1}{4}, -\frac{1}{4}, \frac{3}{4})$
	$D_{2h}^{16}$	$C1, P5$	1,1	(-1,1,0),(0,0,2),(1,1,0)	(0,0,0)
	$D_2^4$	$C1, C3$	1,1	(1,1,0),(-1,1,0),(0,0,2)	$(\frac{1}{4}, \frac{1}{4}, 0)$
	$C_{2h}^2$	$C1, C12$	1,1	(-1,1,0),(0,0,2),(1,1,0)	(0,0,0)
$P_4 \oplus X_3^+$	$C_{2v}^9$	$C1, C13$	1,1	(1,-1,0),(1,1,0),(0,0,2)	(0,0,0)
	$C_2^2$	$C1, 4D1$	1,1	(-1,1,0),(0,0,2),(1,1,0)	(0,0,0)
	$D_4^4$	$P1, P1$	1,1	(-1,-1,0),(1,-1,0),(0,0,2)	$(\frac{1}{2}, 0, 0)$
	$D_{2h}^{15}$	$P1, P3$	1,1	(-1,-1,0),(0,0,-2),(1,-1,0)	$(-\frac{1}{4}, -\frac{1}{4}, -\frac{3}{4})$
	$D_2^4$	$P1, C1$	1,1	(-1,-1,0),(0,0,-2),(1,-1,0)	$(-\frac{1}{4}, -\frac{1}{4}, -\frac{3}{4})$
	$D_{2h}^{18}$	$P3, P1$	1,1	(0,-2,0),(2,0,0),(0,0,2)	$(\frac{1}{2}, \frac{1}{2}, 0)$
$P_4 \oplus X_3^+$	$D_{2h}^{14}$	$P3, P3$	1,1	(1,-1,0),(-1,-1,0),(0,0,-2)	(0,0,0)
	$C_{2h}^5$	$P3, C1$	1,1	(-1,1,0),(0,0,-2),(0,-2,0)	(0,0,0)
	$D_2^5$	$C1, P1$	1,1	(-2,0,0),(0,2,0),(0,0,-2)	$(-\frac{1}{2}, 0, -\frac{1}{2})$
	$C_{2v}^5$	$C1, P3$	1,1	(-1,-1,0),(-1,1,0),(0,0,-2)	$(-\frac{1}{2}, 0, 0)$

TABLE II. (Continued).

Irreps	Subgroup	Orbit	Subspace	Basis vectors	Origin
$P_4 \oplus X_4^+$	$C_2^2$	$C1, C1$	1,1	$(-1, 1, 0), (0, 0, -2), (0, -2, 0)$	$(0, -\frac{1}{2}, 0)$
	$D_4^7$	$P1, P1$	1,1	$(-1, -1, 0), (1, -1, 0), (0, 0, 2)$	$(\frac{1}{2}, 0, \frac{3}{4})$
	$D_{2h}^8$	$P1, P3$	1,1	$(0, 0, -2), (-1, -1, 0), (-1, 1, 0)$	$(-\frac{1}{4}, -\frac{1}{4}, -\frac{3}{4})$
	$D_2^2$	$P1, C1$	1,1	$(-1, -1, 0), (-1, 1, 0), (0, 0, -2)$	$(-\frac{1}{2}, 0, -\frac{3}{4})$
	$D_{2h}^{18}$	$P3, P1$	1,1	$(0, -2, 0), (2, 0, 0), (0, 0, 2)$	$(\frac{1}{2}, \frac{1}{2}, 0)$
	$D_{2h}^{14}$	$P3, P3$	1,1	$(-1, -1, 0), (-1, 1, 0), (0, 0, -2)$	$(0, 0, 0)$
	$C_{2h}^5$	$P3, C1$	1,1	$(-1, 1, 0), (0, 0, -2), (0, -2, 0)$	$(0, 0, 0)$
	$D_2^5$	$C1, P1$	1,1	$(-2, 0, 0), (0, 2, 0), (0, 0, -2)$	$(-\frac{1}{2}, 0, -\frac{1}{2})$
	$C_{2v}^5$	$C1, P3$	1,1	$(1, -1, 0), (-1, -1, 0), (0, 0, -2)$	$(0, -\frac{1}{2}, 0)$
	$C_2^2$	$C1, C1$	1,1	$(-1, 1, 0), (0, 0, -2), (0, -2, 0)$	$(0, -\frac{1}{2}, 0)$
$P_4 \oplus N_1^+$	$D_4^8$	$P1, P_4$	1,1	$(-2, 0, 0), (0, -2, 0), (0, 0, 2)$	$(\frac{1}{2}, 0, \frac{1}{4})$
	$C_{2h}^5$	$P1, P_5$	1,1	$(0, -1, -1), (-2, 0, 0), (0, 1, -1)$	$(-\frac{1}{4}, \frac{1}{4}, -\frac{1}{4})$
	$C_{2h}^6$	$P1, P_{11}$	1,1	$(2, -2, 0), (-2, -2, 0), (0, 0, -2)$	$(-\frac{1}{4}, -\frac{3}{4}, -\frac{1}{4})$
	$C_2^3$	$P1, C_{10}$	1,1	$(2, -2, 0), (-2, -2, 0), (0, 0, -2)$	$(0, \frac{3}{2}, -\frac{3}{4})$
	$C_i^1$	$P1, C_{12}$	1,1	$(0, -2, 0), (0, 0, -2), (2, -2, 0)$	$(\frac{3}{4}, -\frac{3}{4}, -\frac{1}{4})$
	$D_{2h}^{17}$	$P3, P1$	1,1	$(0, -2, 0), (0, 0, 2), (-2, 0, 0)$	$(0, \frac{1}{2}, \frac{1}{2})$
	$D_{2h}^{17}$	$P3, P1$	1,3	$(0, 0, -2), (0, -2, 0), (-2, 0, 0)$	$(0, 0, 0)$
	$D_{4h}^{15}$	$P3, P3$	1,1	$(-2, 0, 0), (0, -2, 0), (0, 0, 2)$	$(2, 0, -1)$
	$D_{4h}^6$	$P3, P3$	1,2	$(-2, 0, 0), (0, -2, 0), (0, 0, 2)$	$(1, 0, 0)$
	$D_{2h}^{13}$	$P3, C1$	1,1	$(-2, 0, 0), (0, -2, 0), (0, 0, 2)$	$(0, 0, 0)$
	$D_{2h}^{12}$	$P3, C1$	1,3	$(-2, 0, 0), (0, -2, 0), (0, 0, 2)$	$(0, 0, 0)$
	$D_{2h}^{16}$	$P3, C2$	1,1	$(-2, 0, 0), (0, -2, 0), (0, 0, 2)$	$(0, 0, 0)$
	$C_{2h}^2$	$P3, C3$	1,1	$(0, -1, 1), (-2, 0, 0), (0, -1, -1)$	$(0, 0, 0)$
	$C_{2h}^6$	$P3, C8$	1,1	$(2, -2, 0), (-2, -2, 0), (0, 0, -2)$	$(0, 1, 0)$
	$C_{2h}^2$	$P3, S1$	1,1	$(0, 0, -2), (0, -2, 0), (-2, 0, 0)$	$(0, 0, 0)$
	$C_{2h}^5$	$P3, S1$	1,5	$(0, 0, -2), (0, -2, 0), (-2, 0, -2)$	$(0, 0, 0)$
	$C_i^1$	$P3, 4D1$	1,1	$(0, -2, 0), (0, 0, -2), (2, -2, 0)$	$(0, 0, 0)$
	$D_2^5$	$C1, P1$	1,1	$(0, 0, -2), (0, -2, 0), (-2, 0, 0)$	$(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$
	$D_{2d}^4$	$C1, P3$	1,1	$(-2, 0, 0), (0, -2, 0), (0, 0, 2)$	$(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$
	$D_2^3$	$C1, C1$	1,1	$(-2, 0, 0), (0, -2, 0), (0, 0, 2)$	$(-\frac{1}{2}, -\frac{1}{2}, 0)$
	$D_2^4$	$C1, C2$	1,1	$(0, 0, -2), (0, -2, 0), (-2, 0, 0)$	$(-\frac{1}{2}, -\frac{1}{2}, 0)$
	$C_2^2$	$C1, C3$	1,1	$(0, -1, 1), (-2, 0, 0), (0, -1, -1)$	$(0, 0, 0)$
	$C_s^4$	$C1, C8$	1,1	$(2, -2, 0), (-2, -2, 0), (0, 0, -2)$	$(0, -1, 0)$
	$C_2^2$	$C1, S1$	1,1	$(0, 0, -2), (0, -2, 0), (-2, 0, 0)$	$(0, 0, 0)$
	$C_1^1$	$C1, 4D1$	1,1	$(0, -2, 0), (0, 0, -2), (2, -2, 0)$	$(0, 0, 0)$
$P_4 \oplus P_5$	$C_{2h}^6$	$P1, P3$	1,1	$(0, 0, -2), (0, -2, 0), (-1, 0, 1)$	$(-\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$
	$C_{2v}^{19}$	$P1, P3$	1,2	$(0, 0, -2), (0, -2, 0), (-2, 0, 0)$	$(-\frac{1}{2}, 0, -\frac{1}{2})$
	$C_{2h}^6$	$P1, P_{12}$	1,1	$(1, 1, -2), (1, -1, 0), (0, 0, -2)$	$(-\frac{1}{4}, -\frac{1}{4}, \frac{1}{4})$
	$C_{2v}^{21}$	$P1, P_{12}$	1,5	$(-1, 1, 0), (0, 0, 2), (1, 1, 0)$	$(-\frac{1}{2}, 0, \frac{1}{4})$
	$C_{2v}^{21}$	$P1, P_{12}$	2,2	$(-1, -1, 0), (0, 0, 2), (-1, 1, 0)$	$(0, -\frac{1}{2}, \frac{1}{4})$
	$C_{2h}^6$	$P1, P_{12}$	2,6	$(-1, 1, -2), (-1, -1, 0), (-1, 1, 0)$	$(-\frac{3}{4}, \frac{1}{4}, -\frac{1}{4})$
	$C_s^4$	$P1, C1$	1,1	$(0, 0, -2), (0, -2, 0), (-1, 0, 1)$	$(0, -\frac{3}{4}, -\frac{3}{4})$
	$C_i^1$	$P1, C_9$	1,1	$(0, -1, 1), (0, 0, -2), (1, -1, 0)$	$(\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$
	$C_s^4$	$P1, C_9$	1,3	$(0, 2, 0), (0, 0, 2), (1, -1, 0)$	$(0, \frac{3}{4}, \frac{3}{4})$
	$C_2^3$	$P1, C_{11}$	1,1	$(1, 1, -2), (1, -1, 0), (0, 0, -2)$	$(-\frac{1}{2}, 0, -\frac{1}{4})$
	$C_2^3$	$P1, C_{11}$	2,1	$(-1, 1, -2), (-1, -1, 0), (-1, 1, 0)$	$(\frac{5}{8}, \frac{1}{8}, \frac{3}{4})$
	$C_{2h}^6$	$P3, P_5$	1,1	$(-1, 1, -2), (-1, -1, 0), (-1, 1, 0)$	$(\frac{1}{2}, 0, \frac{1}{2})$

TABLE II. (Continued).

Irreps	Subgroup	Orbit	Subspace	Basis vectors	Origin
	$C_{2v}^{22}$	$P3, P5$	1,5	$(0,0,2), (-1, -1, 0), (1, -1, 0)$	$(-\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$
	$C_2^3$	$P3, C3$	1,1	$(-1, 1, -2), (-1, -1, 0), (-1, 1, 0)$	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$
	$C_2^3$	$P3, C3$	2,1	$(1, 1, -2), (1, -1, 0), (0, 0, -2)$	$(0, 0, 0)$
	$C_s^3$	$P3, C10$	1,1	$(0, 0, -2), (0, -2, 0), (-1, 0, 1)$	$(0, -\frac{1}{2}, -\frac{1}{2})$
	$C_i^1$	$P3, C12$	1,1	$(0, -1, 1), (0, 0, -2), (1, -1, 0)$	$(0, 0, 0)$
	$C_s^3$	$P3, C12$	1,9	$(0, 2, 0), (0, 0, 2), (1, -1, 0)$	$(0, 0, 0)$
	$C_2^3$	$C1, C8$	1,1	$(0, 0, -2), (0, -2, 0), (-1, 0, 1)$	$(0, \frac{1}{2}, \frac{1}{2})$
	$C_s^4$	$C1, C13$	1,1	$(-1, 1, -2), (-1, -1, 0), (-1, 1, 0)$	$(-\frac{1}{2}, 0, -\frac{1}{2})$
	$C_i^1$	$C1, 4D1$	1,1	$(0, -1, 1), (0, 0, -2), (1, -1, 0)$	$(0, 0, 0)$

TABLE III. Symmetry of distorted phases arising due to octahedral tilts in crystals of  $K_2MgF_4$  type. Distortions connected with representations  $N_1^+, P_5$  are not covered. MA is  $CH_3NH_3$ ; EA is  $C_2H_5NH_3$ ; PA is  $C_3H_7NH_3$ .

No.	Tilts (in layers)		Space group		Irreducible representations of $K_{13}(X)$ star	Examples
	I layer	II layer	$G_i$	Z		
1	(00 $\Theta$ )	(00 $\Theta$ )	$D_{2h}^{18}$	4	$\tau_7(X_2^+)$	
2	(00 $\Theta$ )	(000)	$D_{4h}^5$	4	$\tau_7(X_2^+)$	
3	(00 $\Theta_1$ )	(00 $\Theta_2$ )	$D_{2h}^9$	4	$\tau_7(X_2^+)$	
4	(0 $\Phi$ 0)	(0 $\Phi$ 0)	$C_{2h}^6$	4	$\tau_3 \oplus \tau_5(X_3^+ \oplus X_4^+)$	
5	( $\Phi_1\Phi_2$ 0)	( $\Phi_1\Phi_2$ 0)	$D_{4h}^{16}$	4	$\tau_3(X_3^+)$	(MA) $_2$ MnCl $_4$ , <sup>a</sup> (MA) $_2$ CdCl $_4$ , <sup>b</sup>
6	(0 $\Phi$ 0)	( $\bar{\Phi}$ 00)	$D_{4h}^{12}$	4	$\tau_5(X_4^+)$	
7	( $\Phi\Phi$ 0)	( $\Phi\Phi$ 0)	$D_{2h}^{18}$	4	$\tau_3(X_3^+)$	{(MA) $_2$ MnCl $_4$ , <sup>c</sup> (MA) $_2$ CdCl $_4$ , <sup>b</sup> (EA) $_2$ MnCl $_4$ , <sup>d</sup> (PA) $_2$ MnCl $_4$ , <sup>d</sup> (PA) $_2$ CdCl $_4$ , <sup>e</sup> CaYCrO $_4$ , <sup>f</sup>
8	( $\Phi\Phi$ 0)	( $\bar{\Phi}\bar{\Phi}$ 0)	$D_{2h}^{20}$	4	$\tau_5(X_4^+)$	
9	( $\Phi\Phi$ 0)	( $\Phi\bar{\Phi}$ 0)	$C_{4h}^4$	4	$\tau_3 \oplus \tau_5(X_3^+ \oplus X_4^+)$	
10	( $\Phi_1\Phi_2$ 0)	( $\Phi_2\bar{\Phi}_1$ 0)	$C_{2h}^4$	4	$\tau_3 \oplus \tau_5(X_3^+ \oplus X_4^+)$	
11	( $\Phi_1\Phi_2$ 0)	( $\Phi_2\Phi_1$ 0)	$D_{2h}^{10}$	4	$\tau_3(X_3^+)$	Rb $_2$ CdCl $_4$ , <sup>g</sup>
12	( $\Phi_1\Phi_2$ 0)	( $\bar{\Phi}_2\bar{\Phi}_1$ 0)	$D_{2h}^7$	4	$\tau_5(X_4^+)$	
13	(0 $\Phi\Theta$ )	(0 $\Phi\Theta$ )	$C_{2h}^5$	4	$\tau_3 \oplus \tau_5 \oplus \tau_7(X_3^+ \oplus X_4^+ \oplus X_2^+)$	
14	( $\Phi$ 0 $\Theta$ )	( $\bar{\Phi}$ 0 $\Theta$ )	$C_i^1$	4	$\tau_5(X_4^+)$	
15	(0 $\Phi\Theta$ )	( $\Phi$ 0 $\Theta$ )	$C_{2h}^5$	4	$\tau_3 \oplus \tau_7(X_3^+ \oplus X_2^+)$	
16	( $\Phi_1\Phi_2\Theta$ )	( $\Phi_2\Phi_1\Theta$ )	$C_{2h}^4$	4	$\tau_5 \oplus \tau_7(X_4^+ \oplus X_2^+)$	
17	( $\Phi_1\Phi_2\Theta$ )	( $\bar{\Phi}_2\bar{\Phi}_1\Theta$ )	$C_i^1$	4	$\tau_5 \oplus \tau_7(X_4^+ \oplus X_2^+)$	
18	( $\Phi\Phi\Theta$ )	( $\Phi\Phi\Theta$ )	$D_{2h}^{15}$	4	$\tau_3 \oplus \tau_7(X_3^+ \oplus X_2^+)$	(EA) $_2$ MnCl $_4$ , <sup>d</sup> (PA) $_2$ CdCl $_4$ , <sup>e</sup> CaYCrO $_4$ , <sup>f</sup>
19	( $\Phi\Phi\Theta$ )	( $\Phi\Phi\bar{\Theta}$ )	$C_{2h}^5$	4	$\tau_3 \oplus \tau_7(X_3^+ \oplus X_2^+)$	(MA) $_2$ MnCl $_4$ , <sup>c</sup> (MA) $_2$ CdCl $_4$ , <sup>b</sup>
20	( $\Phi\Phi\Theta$ )	( $\bar{\Phi}\bar{\Phi}\Theta$ )	$D_{2h}^{10}$	4	$\tau_5 \oplus \tau_7(X_4^+ \oplus X_2^+)$	
21	( $\Phi\Phi\Theta$ )	( $\bar{\Phi}\bar{\Phi}\bar{\Theta}$ )	$C_{2h}^4$	4	$\tau_5 \oplus \tau_7(X_4^+ \oplus X_2^+)$	
22	( $\Phi\Phi\Theta$ )	( $\Phi\bar{\Phi}\Theta$ )	$C_i^1$	4	$\tau_3 \oplus \tau_5 \oplus \tau_7(X_3^+ \oplus X_4^+ \oplus X_2^+)$	

<sup>a</sup>Ref. 15.<sup>b</sup>Ref. 16.<sup>c</sup>Ref. 17.<sup>d</sup>Ref. 18.<sup>e</sup>Ref. 19.<sup>f</sup>Ref. 20.<sup>g</sup>Ref. 21.

$(X_4^+)$ ,  $K_{11}\hat{\tau}^1(N_1^+)$ , and  $K_{12}\hat{\tau}^5(P_5)$  representations. In Tables I and II we give the subgroup, the orbit, and domain orientations (i.e., stratum subspace, see Ref. 3 for more details), the new lattice basis vectors in terms of the parent conventional basis, and the origin of the subgroup in terms of the parent conventional basis. The irrep labels in both tables follow the convention of Miller and Love<sup>9</sup> and we use the space-group settings of Hahn.<sup>14</sup>

In Table III we list experimentally observed transitions for the  $A_2BX_4$  structure. In this table we give the sub-

group, the primitive cell size change, the representation corresponding to the transition (see Tables I and II), and in the last column we give the experimentally observed crystals undergoing the associated transition.

Tables I, II, and III augment the information given in Refs. 1–3. Tables I and II, when used with similar tables in Ref. 3, give the complete listing of tilting modes in the  $A_2BX_4$  structure. Table III, when used with a similar table in Ref. 2, gives the complete correspondence with the experimentally observed transitions in this structure.

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