Phase transitions in the perovskitelike A_2BX_4 structure

Dorian M. Hatch and Harold T. Stokes
Brigham Young University, Provo, Utah 84602

K. S. Aleksandrov and S. V. Misyul
L. V. Kirenskii Institute of Physics, Academy of Sciences of the U.S.S.R., Siberian Branch, Krasnoyarsk, U.S.S.R.

(Received 23 September 1988; revised manuscript received 23 January 1989)

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 $K_{13}\hat{\tau}^7$ (X_2^+) and $K_{12}\hat{\tau}^2$ (P_4) representations (Θ 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 $(C_nH_{2n+1}NH_3)^{1+}$, $n=1,2,\ldots,5$.[1,2] Many of the compounds listed above undergo phase transitions (PT's) or sequences of PT's.

It has been shown recently[1–3] 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.*[1,2] 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

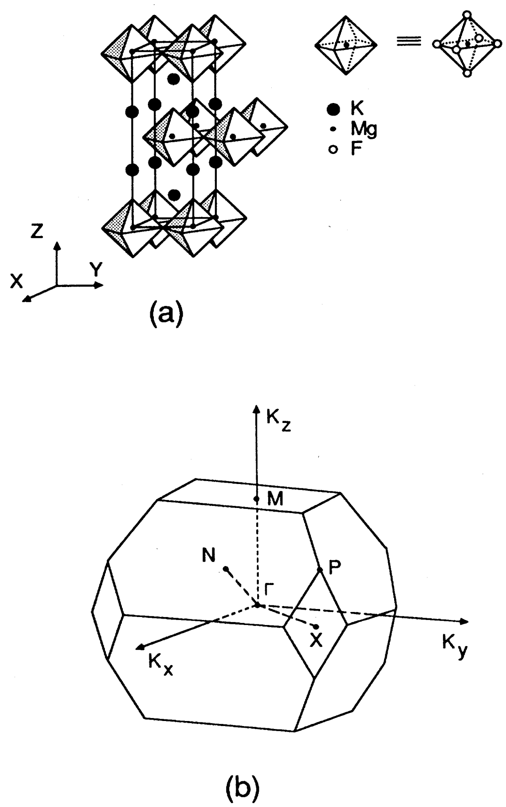

FIG. 1. (a) Crystal structure of K_2MgF_4 type and (b) the first Brillouin zone of body-centered tetragonal unit cell.

elapsolites.[4–6] 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[1,2] that in the square layers of octahedra three kinds of tilts are possible: a tilt around the normal to the layer plane (Θ tilts) [Fig. 2(a)], and two kinds of tilts (Φ and Ψ) which can both occur around the a_0 and/or b_0 axes of G_0. For Ψ 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., Ψ tilts around the b_0 axis. The simultaneous Ψ tilts around both a_0 and b_0 are also possible, which is indicated by the distortion symbol ($\Psi\Psi 0$). The Φ tilts are characterized by alternating tilt angles along the axis of rotation. Figure 2(c) corresponds to ($0\Phi 0$).

Besides the symmetry equivalent ($\Phi 00$) and ($0\Phi 0$) distortions, also ($\Phi\Phi 0$), ($\Phi_1\Phi_2 0$), etc., are possible. In all, 15 variants result from distortions in a single layer. All of these were listed by Aleksandrov *et al.*[1,2] This method allowed the detection of one peculiarity inherent in layered crystals which is called polydistortion or distortional polytypism.[7] 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.[2]

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.*[1,2] 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[8]) or to the X point of the Brillouin zone of G_0 (in terms of Miller and Love[9]) [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 Φ and Ψ tilts were left out in the first paper.[1] Only after acquaintance with the work later published as Ref. 10 was this omission partially corrected in Ref. 2.

Hatch and Stokes[3] 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 allowed 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.[12]

Together with the subgroup and order parameter listing, Hatch, Stokes, and Putnam[13] 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.[13]

However, for the perovskitelike structures, coupled parameters (direct sums of representations) are of interest. If G^{α} denotes the subgroup symmetry for the order parameter $\eta^{(\alpha)}$, and G^{β} 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^{α} and G^{β}. 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^1_{4h} ($P4/mmm$) 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 Θ tilts were omitted in that publication.

III. NEW RESULTS

Recognizing the need to include these representations (Θ 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

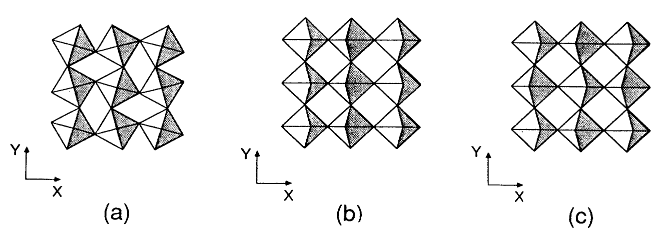

FIG. 2. Three types of octahedral tilting in layers of linked octahedra: (a) (00Θ); (b) ($0\Psi 0$); (c) ($0\Phi 0$).

coupling of Θ tilts with Φ and Ψ tilts, in this section we remedy the omissions of Refs. 1–3.

Using the approach of Hatch and Stokes,[3,10] we give in Table I the listing of transitions driven by uncoupled representations 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_i^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_i^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)	(−$\frac{1}{4}$,$\frac{1}{4}$,$\frac{3}{4}$)
	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_{4h}^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)	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
	C_i^1	$C1,4D1$	1,1	(−1,1,1),(1,−1,1),(1,1,−1)	(0,0,0)
$X_2^+ \oplus P_4$	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)
	C_{2v}^8	$C1,C1$	1,1	(−1,−1,0),(−1,1,0),(0,0,−2)	(0,0,0)
$X_2^+ \oplus P_5$	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)	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})$
	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),(1,10)	$(\frac{1}{4},-\frac{1}{4},\frac{3}{4})$
	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)
	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)
$P_4 \oplus X_3^+$	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)	$(\frac{1}{2},\frac{1}{2},0)$
	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
	C_2^2	$C1,C1$	1,1	$(-1,1,0),(0,0,-2),(0,-2,0)$	$(0,-\frac{1}{2},0)$
$P_4 \oplus X_4^+$	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	$P1,P5$	1,1	$(0,-1,-1),(-2,0,0),(0,1,-1)$	$(-\frac{1}{4},\frac{1}{4},-\frac{1}{4})$
	C_{2h}^6	$P1,P11$	1,1	$(2,-2,0),(-2,-2,0),(0,0,-2)$	$(-\frac{1}{4},-\frac{3}{4},-\frac{1}{4})$
	C_2^3	$P1,C10$	1,1	$(2,-2,0),(-2,-2,0),(0,0,-2)$	$(0,\frac{3}{2},-\frac{3}{4})$
	C_i^1	$P1,C12$	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	$P1,P12$	1,1	$(1,1,-2),(1,-1,0),(0,0,-2)$	$(-\frac{1}{4},-\frac{1}{4},\frac{1}{4})$
	C_{2v}^{21}	$P1,P12$	1,5	$(-1,1,0),(0,0,2),(1,1,0)$	$(-\frac{1}{2},0,\frac{1}{4})$
	C_{2v}^{21}	$P1,P12$	2,2	$(-1,-1,0),(0,0,2),(-1,1,0)$	$(0,-\frac{1}{2},\frac{1}{4})$
	C_{2h}^6	$P1,P12$	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	$P1,C9$	1,1	$(0,-1,1),(0,0,-2),(1,-1,0)$	$(\frac{1}{4},-\frac{1}{4},-\frac{1}{4})$
	C_s^4	$P1,C9$	1,3	$(0,2,0),(0,0,2),(1,-1,0)$	$(0,\frac{3}{4},\frac{3}{4})$
	C_2^3	$P1,C11$	1,1	$(1,1,-2),(1,-1,0),(0,0,-2)$	$(-\frac{1}{2},0,-\frac{1}{4})$
	C_2^3	$P1,C11$	2,1	$(-1,1,-2),(-1,-1,0),(-1,1,0)$	$(\frac{5}{8},\frac{1}{8},\frac{3}{4})$
	C_{2h}^6	$P3,P5$	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_1^1	$C1,4D1$	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	(00Θ)	(00Θ)	D_{2h}^{18}	4	τ_7 (X_2^+)	
	(00Θ)	$(00\bar{\Theta})$				
2	(00Θ)	(000)	D_{4h}^{5}	4	τ_7 (X_2^+)	
3	$(00\Theta_1)$	$(00\Theta_2)$	D_{2h}^{9}	4	τ_7 (X_2^+)	
4	$(0\Phi 0)$	$(0\Phi 0)$	C_{2h}^{6}	4	$\tau_3\oplus\tau_5$ $(X_3^+\oplus X_4^+)$	
	$(\Phi_1\Phi_2 0)$	$(\Phi_1\Phi_2 0)$				
5	$(0\Phi 0)$	$(\Phi 00)$	D_{4h}^{16}	4	τ_3 (X_3^+)	$(MA)_2MnCl_4$,[a] $(MA)_2CdCl_4$,[b]
6	$(0\Phi 0)$	$(\bar{\Phi}00)$	D_{4h}^{12}	4	τ_5 (X_4^+)	
7	$(\Phi\Phi 0)$	$(\Phi\Phi 0)$	D_{2h}^{18}	4	τ_3 (X_3^+)	$(MA)_2MnCl_4$,[c]$(MA)_2CdCl_4$[b] $(EA)_2MnCl_4$,[d]$(PA)_2MnCl_4$[d] $(PA)_2CdCl_4$[e],$CaYCrO_4$[f]
8	$(\Phi\Phi 0)$	$(\bar{\Phi}\bar{\Phi}0)$	D_{2h}^{20}	4	τ_5 (X_4^+)	
9	$(\Phi\Phi 0)$	$(\Phi\bar{\Phi}0)$	C_{4h}^{4}	4	$\tau_3\oplus\tau_5$ $(X_3^+\oplus X_4^+)$	
	$(\Phi_1\Phi_2 0)$	$(\Phi_2\bar{\Phi}_1 0)$				
10	$(\Phi_1\Phi_2 0)$	$(\Phi_1\bar{\Phi}_2 0)$	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	τ_3 (X_3^+)	Rb_2CdCl_4[g]
12	$(\Phi_1\Phi_2 0)$	$(\bar{\Phi}_2\bar{\Phi}_1 0)$	D_{2h}^{2}	4	τ_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	τ_5 (X_4^+)	
15	$(0\Phi\Theta)$	$(\Phi 0\Theta)$	C_{2h}^{5}	4	$\tau_3\oplus\tau_7$ $(X_3^+\oplus X_2^+)$	
	$(\Phi_1\Phi_2\Theta)$	$(\Phi_2\Phi_1\Theta)$				
16	$(0\Phi\Theta)$	$(\bar{\Phi}0\Theta)$	C_{2h}^{4}	4	$\tau_5\oplus\tau_7$ $(X_4^+\oplus X_2+)$	
	$(\Phi_1\Phi_2\Theta)$	$(\bar{\Phi}_2\Phi_1\Theta)$				
17	$(\Phi_1\Phi_2\Theta)$	$(\bar{\Phi}_1\bar{\Phi}_2\Theta)$	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	$\tau_3\oplus\tau_7$ $(X_3^+\oplus X_2^+)$	$(EA)_2MnCl_4$,[d]$(PA)_2CdCl_4$[e] $CaYCrO_4$[f]
19	$(\Phi\Phi\Theta)$	$(\Phi\Phi\bar{\Theta})$	C_{2h}^{5}	4	$\tau_3\oplus\tau_7$ $(X_3^+\oplus X_2^+)$	$(MA)_2MnCl_4$,[c]$(MA)_2CdCl_4$[b]
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	$\tau_3\oplus\tau_5\oplus\tau_7$ $(X_3^+\oplus X_4^+\oplus X_2^+)$	

[a]Ref. 15.
[b]Ref. 16.
[c]Ref. 17.
[d]Ref. 18.
[e]Ref. 19.
[f]Ref. 20.
[g]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[9] and we use the space-group settings of Hahn.[14]

In Table III we list experimentally observed transitions for the A_2BX_4 structure. In this table we give the subgroup, 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.

[1]K. S. Aleksandrov, Kristallografiya **32**, 937 (1987).

[2]K. S. Aleksandrov, B. V. Beznosikov, and S. V. Misyul, Phys. Status Solidi A **104**, 529 (1987).

[3]D. M. Hatch and H. T. Stokes, Phys. Rev. B **35**, 8509 (1987).

[4]K. S. Aleksandrov, A. T. Anistratov, B. V. Beznosikov, and N. V. Fedoseeva, *Phase Transitions in Crystals of Halide ABX_3 Compounds* (Nauka, Novosibirsk, 1981), p. 264.

[5]K. S. Aleksandrov, V. N. Voronov, S. V. Misyul, and I. N. Flerov, in *Problems of Crystallography* (Nauka, Moscow, 1987), p. 247.

[6]K. S. Aleksandrov and S. V. Misyul, Kristallografiya **26**, 1074 (1981).

[7]K. S. Aleksandrov, Kristallografiya **32**, 661 (1987).

[8]O. V. Kovalev, *Irreducible and Induced Representations and Co-representations of Fedorov Groups* (Nauka, Moscow, 1986), p. 367.

[9]S. C. Miller and W. F. Love, *Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups* (Pruett, Boulder, 1967).

[10]D. M. Hatch and H. T. Stokes, in the *XV International Colloquium on Group Theoretical Methods in Physics,* edited by R. Gilmore (World-Scientific, Singapore, 1987), p. 710.

[11]D. M. Hatch and H. T. Stokes, Phys. Rev. B **31**, 2908 (198); **30**, 4962 (1984).

[12]H. T. Stokes and D. M. Hatch, *Isotropy Subgroups of the 230 Crystallographic Space Groups* (World-Scientific, Singapore, 1988).

[13]D. M. Hatch, H. T. Stokes, and R. M. Putnam, Phys. Rev. B **35**, 4935 (1987); in the *XVI International Colloquium on Group Theoretical Methods in Physics,* edited by H. Doebner and T. D. Palev (World-Scientific, Singapore, in press).

[14]T. Hahn, *International Tables for Crystallography* (Reidel, Boston, 1983), Vol. A.

[15]G. Heger, D. Mullen, and K. Knorr, Phys. Status Solidi A **35**, 627 (1976).

[16]R. Kind, G. Chapius, and H. Arend, Phys. Status Solidi A **31**, 449 (1975).

[17]G. Heger, D. Mullen, K. Knorr, Phys. Status Solidi A **31**, 455 (1975).

[18]W. J. Depmeier, Solid State Chem. **29**, 15 (1979).

[19]W. J. Depmeier, J. Felsche, and G. J. Widdermuth, Solid State Chem. **21**, 57 (1977).

[20]P. Gungaly, and C. J. Rao, Solid State Chem. **53**, 193 (1984).

[21]A. I. Kruglik, A. D. Vasilyev, and K. S. Aleksandrov (unpublished).