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Group Analysis of Octahedral Librations Involved in Phonon-Induced Displacive Phase Transitions in Perovskite-Related ABX_4 Compounds*

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Abstract

The group-theoretical analysis of phase transitions in perovskite-related ABX_4 compounds using the framework of Landau's theory for second-order transitions is outlined. It is assumed that the only symmetry-reducing distortions during these transitions will be the tilting of rigid BX_6 octahedra as a consequence of the softening of a particular librational phonon mode. The analysis is applied to phase-transition sequences in $CsFeF_4$, $CsVF_4$, $RbFeF_4$, $RbVF_4$, $RbAlF_4$ and $TlAlF_4$ and compared with available experimental results. For many transitions the prediction of such a second-order transition is borne out by the experiments, which justifies the hypothesis of rigid tilting octahedra. General conclusions about the character of this type of transition are drawn and the allowed transition sequences are examined in terms of the diffraction features (*i.e.* diffraction typologies) of the involved phases.

Introduction

Soft-mode-induced displacive transitions are known to occur in perovskites such as $SrTiO_3$ and $NaNbO_3$ (Ahtee, Glazer & Megaw, 1972; Kay & Bailey, 1957). These transitions are carried by zone-boundary modes and involve the tilting of complete undistorted octahedra, which means that the octahedral librations will be the main components of the phonon eigenvector.

The perovskite-related ABX_4 compounds such as $CsVF_4$ and $RbFeF_4$ have an aristotype structure which is closely related to the perovskite aristotype structure since in the ABX_4 case two-dimensional arrays of vertex-linked BX_6 octahedra are formed as can be seen in Fig. 1.

As a consequence of these structural similarities it is expected that displacive transitions featuring tilting of octahedra will also occur in ABX_4 compounds. This has been confirmed by a large body of experimental evidence (Abrahams & Bernstein, 1972; Babel, Wall & Heger, 1974; Hidaka, Wood & Garrard, 1979; Hidaka, Wood, Wanklyn & Garrard, 1979; Hidaka, Inoue, Garrard & Wanklyn, 1982; Hidaka, Fujii, Garrard & Wanklyn, 1984; Bulou, Fourquet, Leble, Nouet, De Pape & Plet, 1982).

Only recently Bulou, Rousseau, Nouet, Loyzance, Mokhlisse & Couzi 1983) presented evidence for optical soft modes in displacive transitions in $RbAlF_4$.

Glazer (1972, 1975) proposed a structure classification and a general notation for ABX_3 structures which were recently extended by Deblieck, Van Tendeloo, Van Landuyt & Amelinckx (1985) for ABX_4 structures. Both classifications are based on the break down of a general tilt into component tilts around the tetrad axes of the octahedra. It will henceforth be assumed that the reader is familar with the accompanying symbolic structure notation of these classifications, which is described in the above-mentioned papers.

Because it is clear from the large amount of available experimental data for both ABX_3 and ABX_4 compounds that the new lattice period is never more than two basic periods, it is sufficient for both classifications to consider only such phases for which the basic period is doubled. In other words: only zone-centre or zone-boundary soft modes can be

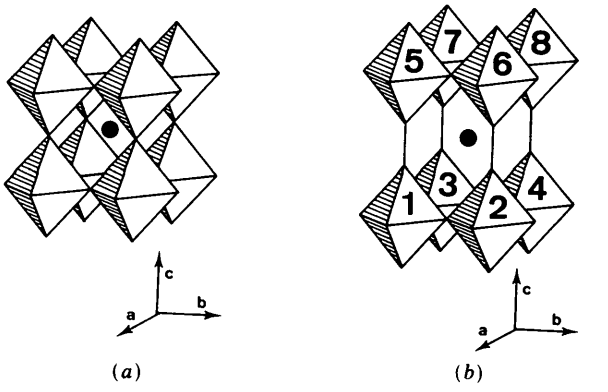

Fig. 1. The aristotype structures of (*a*) ABX_3 and (*b*) ABX_4. The BX_6 octahedra are hatched, the black circle is the *A* cation and the numbering of the octahedra is the one used for the labelling of the basis functions.

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involved and thus the present paper will be concerned with these modes solely.

The ABX_4 classification by Deblieck *et al.* (1985) features the group-to-subgroup relations between the 75 possible phases with tilted octahedra presented in the form of a family tree. These relations will be used later when the description of particular transitions is considered.

The aim of the present paper is to outline the group theoretical analysis of octahedral libration modes which are involved in phase transitions through the condensation of such modes. This analysis is made within the framework of the Landau theory for second-order phase transitions (Landau, 1937) and yields the eigenvector of the phonon transforming according to the active representation, that is, if a second-order transition is allowed in view of the Landau criteria.

Group theoretical aspects

The group theoretical aspects of the Landau theory can be summarized as follows:

If a crystal having a structure with space group G_0 undergoes a second-order phase transition to a structure having the space group G_1, where G_0 is of higher order than G_1, and $\Gamma_i^{\mathbf{k}}$ is the single irreducible representation of G_0 which drives this transition (*i.e.* the order parameter will transform according to this representation) then

(1) G_1 must be a subgroup of G_0;
(2) the transition corresponds only to that $\Gamma_i^{\mathbf{k}}$ which cannot be the totally symmetrical representation but according to (1) $\Gamma_i^{\mathbf{k}}$ must subduce the totally symmetrical representation of G_1;
(3) the symmetrized Kronecker cube of $\Gamma_i^{\mathbf{k}}$, which is denoted $[\Gamma_i^{\mathbf{k}}]^3$, must not contain the totally symmetrical representation of G_0. This criterion excludes a third-order invariant in the free-energy expansion;
(4) the antisymmetrized Kronecker square of $\Gamma_i^{\mathbf{k}}$, which is denoted $\{\Gamma_i^{\mathbf{k}}\}^2$, must not contain any polar vector representation.

This last condition is due to Lifshitz (1941) and can be stated otherwise: Out of the infinite number of representations of space groups this condition allows the selection of those that have $\mathbf{k}$ vectors at special positions (zone-centre or zone-boundary points) where $\mathbf{k}$ can be written as a simple fraction of a reciprocal-lattice vector.

Since in the present case zone-boundary modes are the only $\mathbf{k}\neq 0$ modes that might be involved, this fourth criterion is automatically fulfilled as will become clear later on.

The characters of the symmetrized cube and the antisymmetrized square of a particular representation are calculated as follows (Lyubarskii, 1960):

$$[\chi]^3(\hat{R})=\tfrac{1}{3}\chi(\hat{R}^3)+\tfrac{1}{2}\chi(\hat{R}^2)\chi(\hat{R})+\tfrac{1}{6}[\chi(\hat{R})]^3 \quad (1)$$

$$\{\chi\}^2(\hat{R})=\tfrac{1}{2}[\chi(\hat{R})]^2-\tfrac{1}{2}\chi(\hat{R}^2), \quad (2)$$

where $\hat{R}$ is the symmetry operation under consideration. These representations can then be reduced, if reducible, using the standard orthogonality relations between representations (Bradley & Cracknell, 1972). The representations of space groups are tabulated for special points of symmetry in the Brillouin zone in terms of the allowed small representations of Herring's little group ${}^H G^{\mathbf{k}}$; which is itself a factor group of the little group. The little group $G^{\mathbf{k}}$ contains all symmetry operations of the space group which leave $\mathbf{k}$ invariant, or bring it into an equivalent position $\mathbf{k}+\mathbf{g}$, where $\mathbf{g}$ is any reciprocal-lattice vector. The remaining symmetry operations form the star of $\mathbf{k}$, but since the isogonal point of all considered space groups is the holosymmetrical point group of the crystal system ($4/m\,2/m\,2/m$, $2/m\,2/m\,2/m$, $2/m$), the representation domain in the Brillouin zone will have the same volume as the basic domain and there is no need to study any wave vector outside the basic domain. This means that our attention may be restricted to the arm of the star of $\mathbf{k}$ situated in the representation domain and hence it is sufficient to consider only the little group belonging to this arm.

Herring's little group ${}^H G^{\mathbf{k}}$ is then defined as the factor group with respect to the invariant subgroup of translations $T^{\mathbf{k}}$ (Herring, 1942).

$${}^H G^{\mathbf{k}} = G^{\mathbf{k}}/T^{\mathbf{k}},$$

where $T^{\mathbf{k}}$ contains translations $\mathbf{t}$ for which

$$\exp(-i2\pi\mathbf{kt})=1.$$

Herring's little group has the advantage of being finite and of low order, which is not the case for space groups and their little groups. For a more complete treatment on this formalism the reader is referred to Bradley & Cracknell (1972). Once the representation for a particular transition is known, application of the full projection operator

$$\hat{O}^{\Gamma_i^{\mathbf{k}}}=(d_i/|G|)\sum_{\hat{R}}\chi_i^{\mathbf{k}}(\hat{R})\hat{R} \quad (3)$$

allows the construction of the phonon eigenvector in terms of the chosen base functions (*i.e.* atomic displacements, octahedral librations *etc.*).d_i is the dimension of the representation, $|G|$ the order of the group under consideration and $\chi_i^{\mathbf{k}}(\hat{R})$ the character of the considered representation for a symmetry operator $\hat{R}$.

As already mentioned, the base functions for the representation will be the octahedral libration coordinates

$$\theta_u^i, \quad (4)$$

where i denotes the number of the octahedron. The

numbering sequence is shown in Fig. 1(*b*). The first four octahedra are in the first two-dimensional layer at $z=0$ and the second set of four is situated in the second layer at $z=\frac{1}{2}$. The coordinates are then

octahedron number	1	2	3	4	5	6	7	8
position	000	$0\frac{1}{2}0$	$\frac{1}{2}00$	$\frac{1}{2}\frac{1}{2}0$	$00\frac{1}{2}$	$0\frac{1}{2}\frac{1}{2}$	$\frac{1}{2}0\frac{1}{2}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$

The index u in (4) indicates around which axis the libration coordinate is taken. $u=x$ stands for [100], $u=y$ for [010] and $u=z$ for [001].

Owing to the mechanical constraints not all 24 possible base functions are needed; only ten and most of the time even less are necessary for the complete description. The ten active base functions are

$$\theta_x^1, \theta_y^1, \theta_z^1, \theta_y^2, \theta_x^3, \theta_x^5, \theta_y^5, \theta_z^5, \theta_y^6, \theta_x^7. \qquad (5)$$

Because of the large number of possible group-to-subgroup relations which must be examined if the entire family tree of the 75 possible phases with tilted octahedra (Deblieck *et al.*, 1985) is to be investigated (subgroups of index 4, 6 and 8 included), the scope of the present work will be limited to sequences of phase transitions which were experimentally observed.

For each of the following symmetry analyses of transitions it is assumed that the transition is induced by a softening octahedral libration mode and the relevant normal coordinates are calculated according to the standard group theoretical projection (3).

(i) *The* $\mathbf{a^\circ a^\circ c^\circ \rightarrow a^\circ a^\circ c^+}$ *transition*

This transition is found in $RbAlF_4$ (Bulou *et al.*, 1982, 1983) at 553 K and it is assumed to occur in $RbVF_4$ above 700 K (Hidaka, Inoue, Garrard & Wanklyn 1982; Hidaka, Fujii, Garrard & Wanklyn, 1984). The change of symmetry

$$P4/mmm(D_{4h}^1) \rightarrow P4/mbm(D_{4h}^5)$$

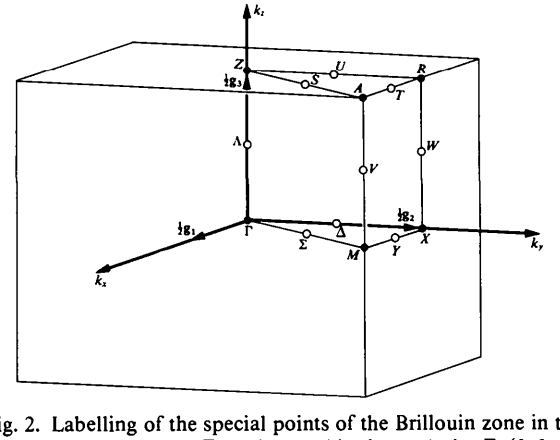

Fig. 2. Labelling of the special points of the Brillouin zone in the basic domain for the Γ_q lattice used in the analysis: Γ: (0, 0, 0); M: $(\frac{1}{2},\frac{1}{2},0)$; A: $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; Z: $(0,0,\frac{1}{2})$; X: $(0,\frac{1}{2},0)$ (from Bradley & Cracknell, 1972).

Table 1. *The allowed small representations for* D_{4h}^1/T^M *and* D_{4h}^1/T^A

The omitted symmetry elements can easily be obtained from those presented in the table. The translations $\mathbf{t}_i$ are $\mathbf{0}$ or $\mathbf{t}_1$ or $\mathbf{t}_2$ for the M point and $\mathbf{0}$ or $\mathbf{t}_1$ or $\mathbf{t}_2$ or $\mathbf{t}_3$ for the A point, where $\mathbf{t}_1$, $\mathbf{t}_2$ and $\mathbf{t}_3$ are basic translations of the tetragonal Γ_q Bravais lattice. p stands for x and y; q stands for a and b. The *ungerade* representations have been omitted because the inversion centre is conserved in the lower phase. All characters must be multiplied by a factor $\exp(-i2\pi\mathbf{k}\mathbf{t}_i)$.

$D_{4h}^1/T^{M,A}$	$\{E\|\mathbf{t}_i\}$	$\{C_{2z}\|\mathbf{t}_i\}$	$\{C_{4z}^+\|\mathbf{t}_i\}$	$\{C_{2p}\|\mathbf{t}_i\}$	$\{C_{2q}\|\mathbf{t}_i\}$	$\{I\|\mathbf{t}_i\}$
$M_1^+A_1^+A_{1g}$	1	1	1	1	1	1
$M_2^+A_2^+A_{2g}$	1	1	1	−1	−1	1
$M_3^+A_3^+B_{1g}$	1	1	−1	1	−1	1
$M_4^+A_4^+B_{2g}$	1	1	−1	−1	1	1
$M_5^+A_5^+E_g$	2	−2	0	0	0	2

is consistent with the group-to-subgroup relation in the ABX_4 family tree (Deblieck *et al.*, 1985), which means that it is unnecessary to assume any other structural deformation than the tilting octahedra. The symmetry reduction of index two is of the *klassengleich* type, which means that the isogonal point group remains unchanged in the transition and the lost symmetry elements will be purely translational. Indeed, the Γ_q Bravais lattice of $P4/mmm$ is transformed into a Γ_q' lattice in $P4/mbm$ according to

$$\Gamma_q: \begin{cases} \mathbf{t}_2=(a,0,0) \\ \mathbf{t}_2=(0,a,0) \\ \mathbf{t}_3=(0,0,c) \end{cases} \rightarrow \Gamma_q': \begin{cases} \mathbf{t}_1'=(a',\bar{a}',0) \\ \mathbf{t}_2'=(a',a',0) \\ \mathbf{t}_3'=(0,0,c), \end{cases}$$

where the components of the basic translations are taken along the base vectors **i**, **j**, **k** of an orthonormal right-handed base *Oxyz*, directed along the tetragonal axes of $P4/mmm$ and where $a'=a\cos\varphi_z$, with φ_z being the rotation angle around [001]. It is clear that such a transition may involve the condensation of a phonon at the M point of the Γ_q Brillouin zone, which is shown in Fig. 2 and hence the wave vector of such a phonon would be $\mathbf{q}=(\frac{1}{2},\frac{1}{2},0)$.

The allowed small representations for D_{4h}^1/T^M can be obtained from Bradley & Cracknell (1972) and they are shown in Table 1.

Since in the course of this transition the M point is transformed into a zone-centre point of $P4/mbm$, the M representations of $P4/mmm$ must subduce the identity representation Γ_1^+ of $P4/mbm$. For this purpose it is sufficient to consider the generating elements only and in the correct setting one obtains

$$\{C_{4z}^+|000\}, \quad \{C_{2x}|\tfrac{1}{2}\tfrac{1}{2}0\}, \quad \{I|000\}.$$

These generators $\{S_i|\mathbf{v}_i\}$ must satisfy the so-called Birman–Worlock condition:

$$\chi^{\Gamma_j^{\mathbf{k}}}(\{S_i|\mathbf{v}_i\})=1, \qquad (6)$$

for the $\Gamma_j^{\mathbf{k}}$ representation to subduce onto Γ_1^+. Clearly

M_2^+ fulfils condition (6) and this representation will now be examined more closely.

The full projection operator (3) applied on a sufficient part of the basis (5) yields

$$\Phi^{M^+} = \hat{O}^{M^+} | \theta_x^1, \theta_y^1, \theta_z^1, \theta_y^2, \theta_x^3\rangle = |0, 0, \theta_z^1, 0, 0\rangle$$
$$= \theta_z^1.$$

This amplitude function represents an octahedral libration around [001] and it is clear that when softening this mode can generate a structural deformation with structure symbol $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^+$. Still the third Landau condition and the test for the presence of one or more Lifschitz invariants must be checked.

It is easy to show that for one-dimensional representations (1) and (2) simplify to

$$[\chi]^3(\hat{R}) = [\chi(\hat{R})]^3$$
$$\{\chi\}^2(\hat{R}) = 0$$

and hence any representation of that kind will fulfil the remaining conditions.

(ii) *The* $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^\circ \rightarrow \mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^-$ *transition*

This transition occurs at 514 K in $TlAlF_4$ (Bulou *et al.*, 1982) and the observed space group of the low-temperature phase is $F4/mmc$ (D_{4h}^{18}) (or $I4/mcm$ in the setting of *International Tables for Crystallography*, 1983) which is the same as the space group of the octahedral framework with tilt scheme $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^-$. Since the symmetry reduction of index two is of the *klassengleich* type only pure translations are lost. As a consequence the product Bravais lattice is Γ_q^v and the basic translations of the primitive unit cell are

$$\Gamma_p^v: \begin{cases} \mathbf{t}_1' = (\bar{a}', a', c) \\ \mathbf{t}_2' = (a', \bar{a}', c) \\ \mathbf{t}_3' = (a', a', \bar{c}). \end{cases}$$

Because a reflection will appear at the A point in the Brillouin zone of the high-symmetry phase, the wave vector of the phonon should be $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

Because D_{4h}^1/T^M is isomorphic with D_{4h}^1/T^A, Table 1 can be used again if allowance is made for the fact that the translation $\mathbf{t}_i$ now includes $\mathbf{t}_3$ as well.

The generating elements of $I4/mcm$ as described in the Γ_q^v basis are:

$$\{C_{4z}^+|000\}, \quad \{C_{2x}|\tfrac{1}{2}\tfrac{1}{2}0\}, \quad \{I|000\}$$

and subduction of A_2^+ is found. The octahedral libration coordinates transforming according to this representation are

$$\Phi^{A_2^+} = \theta_z^1 - \theta_z^5.$$

Clearly this libration eigenmode can lead to an $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^-$ tilting scheme because it is restricted to antiparallel libration around [001]. Since A_2^+ is real and one-dimensional, a second-order transition is again allowed.

Table 2. *The allowed small representations for* D_{4h}^1/T^X

The translations $\mathbf{t}_i$ are $\mathbf{0}$ or $\mathbf{t}_2 \in \Gamma_q$. All characters must be multiplied by a factor $\exp(-i2\pi\mathbf{k}\mathbf{t}_i)$.

D_{4h}^1/T^X	$\{E\|\mathbf{t}_i\}$	$\{C_{2z}\|\mathbf{t}_i\}$	$\{C_{2y}\|\mathbf{t}_i\}$	$\{C_{2x}\|\mathbf{t}_i\}$	$\{I\|\mathbf{t}_i\}$
$X_1^+A_{1g}$	1	1	1	1	1
$X_2^+B_{2g}$	1	−1	1	−1	1
$X_3^+B_{1g}$	1	1	−1	−1	1
$X_4^+B_{3g}$	1	−1	−1	1	1

(iii) *The* $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^\circ \rightarrow \mathbf{a}^+\mathbf{a}^\circ\mathbf{c}^\circ$ *transition*

The tilting scheme $\mathbf{a}_p^+\mathbf{a}^\circ\mathbf{c}^\circ$ is observed for $CsFeF_4$ below 508 K, $CsVF_4$ below 515 K and $RbFeF_4$ below 418 K (Hidaka, Wood & Garrard, 1979; Hidaka, Wood, Wanklyn & Garrard, 1979) and in all of these cases the observed space group is $Pmmb$ (D_{2h}^5) which indicates that tilting octahedra may be the only symmetry-reducing mechanism involved (Deblieck *et al.*, 1985). The symmetry reduction of index four is of mixed type (*i.e.* it consists of a *translationengleich* reduction followed by a *klassengleich* reduction) and the Bravais lattice transforms into an orthorhombic Γ_0 lattice:

$$\Gamma_0: \begin{cases} \mathbf{t}_1' = (a, 0, 0) \\ \mathbf{t}_2' = (a, 2b, 0) \\ \mathbf{t}_3' = (0, 0, c), \end{cases}$$

where $2b = 2a \cos\varphi_x$, $c' = c \cos\varphi_x$ and φ_x is the tilting angle around [100].

The active representation will thus be found at the X point of the Brillouin zone Γ_q and hence the wave vector of the corresponding librational mode should be $\mathbf{q} = (0, \frac{1}{2}, 0)$. The character table of D_{4h}^1/T^X is found in Table 2.

The generating elements of $Pmmb$ are

$$\{C_{2z}|0\tfrac{1}{2}0\}, \quad \{C_{2y}|0\tfrac{1}{2}0\}, \quad \{I|000\}$$

and it is found that the phonon eigenvector will thus transform according to X_4^+:

$$\Phi^{X_4^+} = \theta_x^1$$

and allowing for the phase relationships of the unit cell this mode shows in-phase oscillations of octahedra around the [100] axis and it is obvious that such a libration can generate a tilt scheme $\mathbf{a}_p^+\mathbf{a}^\circ\mathbf{c}^\circ$. Again a second-order transition is allowed.

(iv) *The* $\mathbf{a}_p^+\mathbf{a}^\circ\mathbf{c}^\circ \rightarrow \mathbf{a}_p^+\mathbf{a}_p^+\mathbf{c}^\circ$ *and* $\mathbf{a}_p^+\mathbf{a}^\circ\mathbf{c}^\circ \rightarrow \mathbf{a}_p^+\mathbf{a}_p^+\mathbf{c}^+$ *transitions*

The former transition is proposed for $CsFeF_4$ to occur at 423 K and for $RbFeF_4$ at 378 K (Hidaka, Wood, Wanklyn & Garrard, 1979). The latter is found in $CsVF_4$ at 425 K (Hidaka, Wood & Garrard, 1979). In all cases the low-temperature symmetry is $Pmmn$ (D_{2h}^{13}) except for $RbFeF_4$, where it is $P2_12_12$ (D_2^3),

which indicates that the centre of symmetry is lost, probably through additional deformation of the octahedra (*i.e.* displacement of the Fe cation).

The Bravais lattice remains primitive orthorhombic but all symmetry reductions, except for $RbFeF_4$, are of the *klassengleich* type of index two and the new cell is now doubled along the [100] axis as well:

$$\Gamma_0: \begin{cases} \mathbf{t}_1' = (2a', 0, 0) \\ \mathbf{t}_2' = (0, 2b, 0) \\ \mathbf{t}_3' = (0, 0, c''), \end{cases}$$

where $2a' = 2a \cos \varphi_y$, $c'' = c' \cos \varphi_y$ and φ_y is the tilting angle around [010].

From the schematic representation of the Γ_0 Brillouin zone in Fig. 3 it is clear that the librational mode which could induce this transition will transform according to a Y-point representation and hence $\mathbf{q} = (\frac{1}{2}, 0, 0)$. The irreducible representations for this wave vector of *Pmmb* are reproduced in Table 3 and the generating elements for *Pmmn* are

$$\{C_{2z}|\tfrac{1}{2}\tfrac{1}{2}0\}, \quad \{C_{2y}|0\tfrac{1}{2}0\}, \quad \{I|000\}.$$

Y_3^+ is found to subduce onto L_1^+. Since two transitions are consistent with the present symmetry reduction, two corresponding librational modes can be found. The mechanical representation of the octahedral librations, limited to one layer, reduces to:

$$2Y_1^+ \oplus 2Y_3^+ \oplus Y_4^+,$$

which indeed means that two librational modes will transform according to Y_3^+:

$$\Phi^{Y_3^+} = \hat{O}^{Y_3^+} |\theta_x^1, \theta_y^1, \theta_z^1, \theta_y^2, \theta_x^3\rangle$$
$$= |0, \theta_y^1 + \theta_y^2, \theta_z^1 + \theta_z^2, 0, \theta_y^1\rangle$$

and choosing two orthogonal linear combinations of the base, one gets

$$\Phi_1^{Y_3^+} = \theta_z^1$$
$$\Phi_2^{Y_3^+} = \theta_y^1 + \theta_y^2 + \theta_z^1.$$

These eigenvectors result in tilt schemes $\mathbf{a}_p^+\mathbf{a}_p^\circ\mathbf{c}^+$ and $\mathbf{a}_p^+\mathbf{a}_p^+\mathbf{c}$ respectively. The former is represented schematically in Fig. 4 as an example. Since Y_3^+ is real and one dimensional, a second-order transition is again symmetrically allowed.

Although in $RbFeF_4$ the structural deformation involves more than mere octahedral tilting it is always possible to check whether the same Y_3^+ representation can be responsible for the symmetry reduction which is now of index four and of a mixed type. Indeed, the point-group symmetry is also affected and, because the inversion centre is lost, there is additional subduction of the Y_3^- representation. However, since Y_3^- does not appear in the mechanical representation, Y_3^+ remains the only possible active representation. This transition is expected to be of first order, in view of the obvious presence of other distortion mechanisms.

Table 3. *The allowed small representations for* D_{2h}^5/T^Y

The translations $\mathbf{t}_i$ are $\mathbf{0}$ or $\mathbf{t}_1$, where $\mathbf{t}_1$ is the basic translation along [010] of the primitive Γ_0 Bravais lattice. All characters must be multiplied by a factor $\exp(-i2\pi\mathbf{k}\mathbf{t}_i)$.

D_{2h}^5/T^Y	$\{E\|\mathbf{t}_i\}$	$\{C_{2y}\|\frac{1}{2}0+\mathbf{t}_i\}$	$\{C_{2x}\|\mathbf{t}_i\}$	$\{C_{2z}\|0\frac{1}{2}0+\mathbf{t}_i\}$	$\{I\|\mathbf{t}_i\}$
$Y_1^+A_{1g}$	1	1	1	1	1
$Y_2^+B_{2g}$	1	−1	1	−1	1
$Y_3^+B_{1g}$	1	1	−1	−1	1
$Y_4^+B_{3g}$	1	−1	−1	1	1

(v) *The* $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^+ \rightarrow \mathbf{a}_p^+\mathbf{a}_p^+\mathbf{c}^+$ *and* $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^+ \rightarrow \mathbf{a}_p^+\mathbf{a}^\circ\mathbf{c}^+$ *transitions*

The former transition is observed in $RbAlF_4$ at 282 K (Bulou *et al.*, 1982, 1983). The latter is found in $RbVF_4$ at 483 K (Hidaka *et al.*, 1982, 1984) and the low-temperature space group is $Pmmn(D_{2h}^{13})$ in both cases. The symmetry reduction of index four is of a mixed type and the Bravais lattice changes from

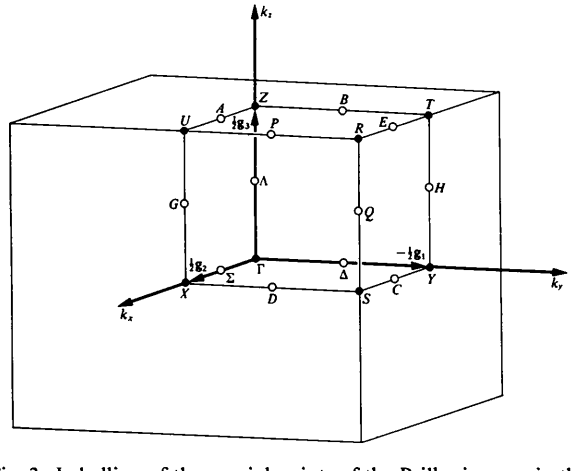

Fig. 3. Labelling of the special points of the Brillouin zone in the basic domain for the Γ_0 lattice used in the analysis. Γ: (0, 0, 0); Y: $(\frac{1}{2}, 0, 0)$ (from Bradley & Cracknell, 1972).

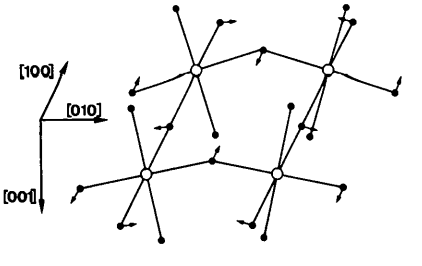

Fig. 4. Schematic representation of a Y_3^+/B_{1g} mode leading to the $\mathbf{a}_p^+\mathbf{a}^\circ\mathbf{c}^+$ tilt scheme. Only the octahedra of one layer are displayed. The circles indicate the B cations and the small dots are the fluorine atoms. The axial setting of the aristotype is also indicated.

Table 4. *The allowed small representations for* D_{4h}^5/T^M

The translations $\mathbf{t}_i$ are $\mathbf{0}$ or $\mathbf{t}_1$ or $\mathbf{t}_2(\mathbf{t}_1, \mathbf{t}_2 \in \Gamma_q)$. The symmetry elements are shifted by $\frac{1}{2}\mathbf{t}_1$ with respect to the setting in *International Tables for Crystallography* (1983). The *ungerade* representations are selected because only the inversion centre $\{I|\mathbf{t}_i\}$ with $\mathbf{t}_i \neq 0$ is conserved. All characters must be multiplied by a factor $\exp(-i2\pi\mathbf{k}\mathbf{t}_i)$.

D_{2h}^5/T^M	$\{E\|\mathbf{t}_i\}$	$\{C_{2z}\|\mathbf{t}_i\}$	$\{C_{2p}\|\frac{1}{2}\frac{1}{2}0+\mathbf{t}_i\}$	$\{C_{2p}\|\mathbf{t}_i\}$	$\{C_{4z}^{\pm}\|\frac{1}{2}\frac{1}{2}0+\mathbf{t}_i\}$	$\{I\|\mathbf{t}_i\}$
${}^2E_u'$	1	1	i	-1	$-i$	-1
${}^1E_u'$	1	1	$-i$	-1	i	-1
${}^1E_u''$	1	1	$-i$	1	$-i$	-1
${}^2E_u''$	1	1	i	1	i	-1
E_u	2	2	0	0	0	2

Table 5. *The allowed small representations for* D_{4h}^{18}/T^Γ

The setting of the axes and the choice of the origin correspond with *International Tables for Crystallography* (1983). The *ungerade* representations are omitted because the inversion centre at the origin is conserved.

D_{4h}^5/T^Γ	$\{E\|0\}$	$\{C_{2z}\|000\}$	$\{C_{2xy}\|\frac{1}{2}\frac{1}{2}0\}$	$\{I\|0\}$	$\{S_{4z}^{\pm}\|000\}$	$\{\sigma_{ab}\|\frac{1}{2}\frac{1}{2}0\}$
Γ_1^+/A_{1g}	1	1	1	1	1	1
Γ_2^+/A_{2g}	1	1	$\bar{1}$	1	1	$\bar{1}$
Γ_3^+/B_{1g}	1	1	1	1	$\bar{1}$	$\bar{1}$
Γ_4^+/B_{2g}	1	1	$\bar{1}$	1	$\bar{1}$	1
Γ_5^+/E_g	2	$\bar{2}$	0	2	0	0

Γ_q to Γ_0 and the Brillouin zone point involved will clearly be the M point with $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0)$.

The irreducible representations of D_{4h}^5/T^M are shown in Table 4 and using the proper generators of *Pmmn* it is found that two complex-conjugate representations subduce Γ_1^+:

$$^2E_u' \quad \text{and} \quad {}^1E_u'.$$

As a consequence, ${}^2E_u'$ and ${}^1E_u'$ must be regarded as a two-dimensional physically irreducible representation E_u' (Lyubarskii, 1960). The corresponding librational eigenmodes are

$$\Phi_1^{E_u'} = \theta_x^1 + \theta_x^3$$
$$\Phi_2^{E_u'} = \theta_x^1 + \theta_x^3 + \theta_y^1 + \theta_y^2.$$

Both modes bear out the following tilt schemes:

$$\Phi_1^{E_u'} \rightarrow \mathbf{a}_p^+\mathbf{a}^\circ\mathbf{c}^+ \quad (\text{or } \mathbf{a}^\circ\mathbf{a}_p^+\mathbf{c}^+)$$
$$\Phi_2^{E_u'} \rightarrow \mathbf{a}_p^+\mathbf{a}_p^+\mathbf{c}^+.$$

The remaining Landau conditions are fulfilled and hence this transition can again be of second order.

(vi) *The* $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^- \rightarrow \mathbf{a}_a^-\mathbf{a}_a^-\mathbf{c}^-$ *transition*

This transition was observed in $TlAlF_4$ at 435 K and the low-temperature symmetry was designated as $C2/m$ (C_{2h}^3) (Bulou *et al.*, 1982). However, the space group of a structure with tilt scheme $\mathbf{a}_a^-\mathbf{a}_a^-\mathbf{c}^-$ must be $C2/c$ (C_{2h}^6) which is a subgroup of $C2/m$ and hence the latter is excluded because additional deformations could never explain an ascent in symmetry. Because there is no change in the volume of the unit cell (*translationengleich*) the active representation will be found at the zone centre and the allowed small representations of $I4/mcm$ at the Γ point are shown in Table 5.

The generators for $I2/b11(C_{2h}^6)$ in the correct setting are

$$\{C_{2x}|\tfrac{1}{2}\tfrac{1}{2}0\}, \{I|000\}.$$

Γ_3^+ and Γ_5^+ subduce and the corresponding phonon eigenvectors are

$$\Phi^{\Gamma_3^+} = 0$$
$$\Phi^{\Gamma_5^+} = \theta_x^1 + \theta_y^1.$$

The normal coordinates of the remaining octahedra follow from phase relationships in the unit cell. The resulting librational eigenmode generates a structure with tilt scheme $\mathbf{a}_a^-\mathbf{a}_a^-\mathbf{c}^-$ and since the remaining conditions are fulfilled this transition can be of second order.

Discussion

The $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^\circ \rightarrow \mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^+$ transition in $RbAlF_4$ at 553 K as found by Bulou *et al.* (1982, 1983) is of first order although Toledano & Toledano (1982) and the present work predict it to be of second order according to the Landau criteria. This indicates that the softening of an M_2^+ mode in a perfect structure is a too simple explanation. Bulou *et al.* assume that interlayer disorder and structural disorder concerning the fluorine ions may be responsible and their hypothesis is substantiated by the observation of diffuse X-ray scattering and a modulated background in neutron diffraction patterns.

In an attempt to analyse the sequence of transitions observed for $RbAlF_4$ and $RbVF_4$, Loyzance & Couzi (1984) find two representations M_3^+ and M_2^+ subducing onto Γ_1^+ of $P4/mbm$ but M_3^+ leads to a setting of the symmetry elements which is inconsistent with the observed structure. In our opinion the family tree presented by these authors should bifurcate at the

M_2^+-generated $P4/mbm$ and not at the M_3^+-generated $P4/mmb$.

As for the $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^\circ \rightarrow \mathbf{a}_p\mathbf{a}^\circ\mathbf{c}^\circ$ transition, it is found to be of second order as predicted in $RbFeF_4$, whereas for $CsFeF_4$ and $CsVF_4$ this transition is of first order (Hidaka, Wood & Garrard, 1979; Hidaka, Wood, Wanklyn & Garrard, 1979; Hidaka *et al.*, 1982). Probably a coupled steric displacement of the larger Cs^+ ion causes this first-order character. Hidaka indicates that this transition could be induced by an X-point mode with B_{2g} symmetry and $\mathbf{q}=(\frac{1}{2},0,0)$, which is confirmed by the present work since the B_{2g}/X_2 mode is symmetrically equivalent with the B_{3g}/X_4^+ mode (*i.e.* it is sufficient to interchange the tetragonal a and b axes).

The $\mathbf{a}_p^+\mathbf{a}^\circ\mathbf{c}^\circ \rightarrow \mathbf{a}_p^+\mathbf{a}_p^+\mathbf{c}^\circ$ (or $\mathbf{a}_p^+\mathbf{a}_p^+\mathbf{c}^+$) transition in $CsFeF_4$ is found to be of second order and a mode with B_{3g} symmetry and $\mathbf{q}=(0,\frac{1}{2},0)$ is said to be probably responsible (Hidaka, Wood, Wanklyn & Garrard, 1979). This second-order character is confirmed by the present analysis but rather than a B_{3g} mode, a B_{1g}/Y_3^+ mode with $\mathbf{q}$: $(\frac{1}{2},0,0)$ is involved.

In $RbFeF_4$, on the contrary, a first-order character is found (Hidaka, Wood, Wanklyn & Garrard, 1979) as expected.

The transitions $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^\circ \rightarrow \mathbf{a}_p^+\mathbf{a}_p^+\mathbf{c}^+$ in $RbAlF_4$ and the $\mathbf{a}^\circ\mathbf{a}^\circ\mathbf{c}^+ \rightarrow \mathbf{a}_p^+\mathbf{a}^\circ\mathbf{c}^\circ$ in $RbVF_4$ are both of second order (Bulou *et al.*, 1983; Hidaka *et al.*, 1982) as predicted.

Loyzance & Couzi (1984) also indicate the same two complex-conjugate representations to be active in this transition and the present work confirms their conclusion about the order.

The present analysis is summarized in a transition diagram shown in Fig. 5.

Although the complete analysis of all possible transitions found in the ABX_4 family tree would lead us too far, some general remarks can be made. It is interesting to find out whether these transitions, involving only tilting octahedra, are always allowed to be of second order. Obviously, when the representation which is active according to the Birman–Worlock theorem is one dimensional, third-order invariants in the free-energy expansion will be discarded. The symmetrized cubes of two-dimensional representations, on the other hand, will only contain the totally symmetrical representation for the case of trigonal and cubic point groups (Cracknell & Joshua, 1968) and because the factor group $G^{\mathbf{k}}/T^{\mathbf{k}}$ is isomorphic with the little co-group it is certain that none of the two-dimensional active representations under consideration could ever yield third-order invariants in the free-energy expansion. Furthermore, since only zone boundary and zone-centre representations are considered, the Lifshitz condition will always be fulfilled as was mentioned before. It is therefore clear that, if the Birman–Worlock theorem is satisfied, the transition will always be allowed to be of second order.

An interesting alternative for drawing general conclusions about the order of transitions between phases with tilted octahedra in ABX_4 compounds from the observed changes in the reciprocal space lies in the use of the so-called diffraction typology (DT) of the involved phases. The DT describes the features of the reciprocal space in a shorthand way making use of a code based on the labelling of special high-symmetry points of the Γ_q Brillouin zone (Deblieck *et al.*, 1985). Obviously the pure *translationengleich*

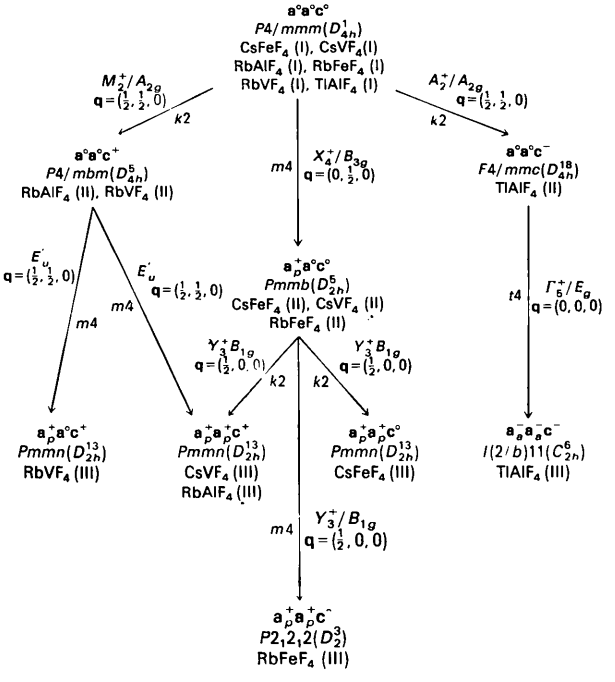

Fig. 5. Family-tree representation of the results of the present work. The indication of the phase number following each compound name is the same as that used by Bulou *et al.* and Hidaka *et al.* The occurring phases are grouped in levels according to the index of the symmetry reduction. This symmetry reduction is indicated by a letter *t*, *k* or *m* (*translationengleich*, *klassengleich* or mixed) followed by the index.

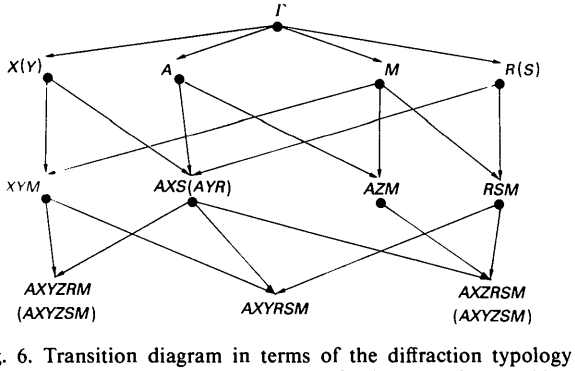

Fig. 6. Transition diagram in terms of the diffraction typology derived from the group-to-subgroup family tree of perovskite-related ABX_4 compounds (Deblieck *et al.*, 1985). The symmetrically related typologies are given between brackets.

transitions will not yield a difference in the DT and hence only transitions involving a *klassengleich* or mixed-type symmetry reduction have to be considered. The allowed transitions between the different possible DT's are derived from the ABX_4 family tree and they are summarized in Fig. 6 where the symmetrically related typologies are enclosed between brackets.

Concluding remarks

For some of the transition sequences analysed in the present work, the Landau theory with the tilting of regular octahedra as the only order parameter occurring predicts the observed second-order character. This supports the hypothesis that in most of these transitions no other major structural distortions are present.

In those cases where a first-order character is found, either supplementary symmetry-reducing distortions or another possibility such as the lack of long-range order between octahedral layers may have to be considered. The presence of diffuse X-ray scattering in $RbAlF_4$ (Bulou *et al.*, 1983) supports the latter assumption.

For those transitions which were not mentioned in the discussion the second-order character has not yet been observed experimentally.

Finally, it may be concluded that the mere existence of a group-to-subgroup relation, according to the Birman-Worlock theorem, between ABX_4 phases which differ only in their tilt schemes is a sufficient condition for a second-order transition to be allowed.

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Comparison of Vector Search and Feedback Methods for Finding Heavy-Atom Sites in Isomorphous Derivatives

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Abstract

Heavy-atom sites in an isomorphous replacement derivative are usually found by inspection of a difference Patterson map. A systematic search procedure is necessary in the presence of high non-crystallographic symmetry as in a crystalline virus. A reciprocal-space equivalent of the Patterson search procedure has been developed. Furthermore, it is shown that the Patterson search is closely analogous to the usual 'feedback' tests applied in checking a proposed site. The separation of self and cross vectors

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