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Quantitative description of the tilt of distorted octahedra in ABX_3 structures

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A description of the tilt of octahedra in ABX_3 perovskite-related structures is proposed that can be used to extract the unique values for the tilt parameters φ, θ and δ of ABX_3 structures with regular and distorted octahedra up to the point symmetry $\bar{1}$, from atomic coordinates and lattice parameters. The geometry of the BX_6 octahedron is described by three $B-X$ bond lengths (r_1, r_2, r_3) and three $X-B-X$ bond angles (ψ_{12}, ψ_{13} and ψ_{23}) or alternatively by a local strain tensor together with an average $B-X$ bond length. Connections between the proposed method and Glazer's tilt system are discussed. The method is used to analyze structural transformations of $I2/c$, $Pbnm$ and $Immm$ structures. The proposed description allows the analysis of group–subgroup relations for the ABX_3 structures with distorted octahedra, in terms of octahedral deformations and tilting. The method might also be of interest in the study of the phase transitions in the family of ABX_3 structures.

1. Introduction

Interest in ABX_3 compounds with the perovskite-type structure arises from the wide variety of physical phenomena that have been observed in them. These phenomena include the ferroelectric and piezoelectric properties of $BaTiO_3$ and $Pb(Zr,Ti)O_3$ (Newnham, 1998), superconductivity in $BaBiO_3$ (Sleight *et al.*, 1975) and colossal magnetoresistance (CMR) in doped manganites $Ln_{1-x}A_xMnO_3$ (Ln = lanthanide ion, A = alkaline earth ion; Goodenough, 2004). For perovskite-related structures, temperature- and composition-dependent phase transitions have been observed between different electronic and magnetic states. Moreover, in some cases these phase transitions are accompanied by structural phase transitions which are caused by distortions and tilting of octahedral groups BX_6 (Howard *et al.*, 2000). The quantitative description of these structural changes seems to be a useful tool for the understanding of the correlation between physical properties and crystal structures of these materials.

The ideal ABX_3 perovskite structure is cubic (space group $Pm\bar{3}m$) and is composed of a three-dimensional network of vertex-sharing BX_6 octahedra. The A-site cation fills the 12-coordinated cavities (cuboctahedra) of the three-dimensional network (Glazer, 1972). This structure is very flexible and it can accommodate most of the metallic elements of the periodic table. Depending on the ionic radii of A and B, octahedra are tilted, thus reducing the volume of the cuboctahedron until it fits the size of the A cation. Tilting of octahedra reduces the symmetry of structure. Analysis of perovskite-related structures has shown that in many cases the BX_6 octahedra are

distorted, which may be a cause for the reduction of symmetry by itself. There are many ways in which the octahedra can tilt and distort, each leading to a different symmetry.

The discussion on octahedral tilting in the ABX_3 structures was initiated by Megaw (1966). Different tilt schemes are usually described according to a notation developed by Glazer (1972). In that work, regular BX_6 octahedra were assumed and all tilts were considered to be combinations of three independent rotations about the three cubic axes. It was shown that the space group may be determined by the pattern of octahedral tilting and a classification of octahedral tilting in terms of 23 alternative tilt systems was given. Some of these 23 tilt systems describe the same structures with identical space groups. Therefore, the 23 tilt systems give rise to only 15 different structures. A group-theoretical analysis has shown that only 15 space groups need be used for the description of perovskite-related structures with regular octahedra (Howard & Stokes, 1998, 2004). An analysis of the geometrical aspects of the tilting schemes of Glazer (1975) showed that six out of 23 tilting schemes, representing two of the 15 space groups, cannot be realised by regular octahedra and distortions of the octahedra are inherent in these structures (Woodward 1997*a*,*b*). An analysis of the group–subgroup relations between ABX_3 structures with distorted octahedra has been carried out by Bock & Müller (2002). Taking into account the possibility of octahedral distortions they derived ten additional space groups for the ABX_3 structures.

A quantitative description of octahedral tilts of peroskite-based compounds has been of continued interest amongst crystallographers, and a mathematical description has been given for the relation between tilt angles of so-called one-tilt structures of regular octahedra and lattice parameters (Megaw, 1969; Megaw & Darlington, 1975; O'Keeffe & Hyde, 1977). However, symmetry requires regular octahedra only in the ideal $Pm\bar{3}m$ structure. Low-symmetry structures that can be realised by pure tilts may have distortions of octahedra in addition, while distortions of BX_6 octahedra are inherent to other symmetries (cited above). In several structures these distortions are so large that they cannot be neglected. The first attempt to describe perovskite-related structures with distorted octahedra was made by Thomas & Beitollahi (1994). Six variables were used for a parametrization of the structure with the space group *Pbnm* on the $2^{1/2}a_c \times 2^{1/2}a_c \times 2a_c$ lattice: three $B-X$ bond lengths assumed to be orthogonal to each other, and three angles, θ_1, θ_2 and θ_3, between corresponding bonds and the nearest pseudo-cubic lattice translation vectors. Later, introducing additional parameters such as Γ_i, describing the angles between planes formed by chains of octahedral stalks and the corresponding pseudo-cubic lattice axes, the orthogonal approximation of $B-X$ bonds was removed and a new global parameterization of perovskite structures was developed (Thomas, 1998). The angular parameters θ_i and Γ_i in Thomas's model are defined relative to pseudo-cubic lattice translation vectors. On the other hand, the orientations of pseudo-cubic lattice translation vectors depend on the tilting angles themselves, therefore the angles θ_i reflect not only tilting but also the deformations of the lattice and octahedra.

The description of octahedral tilt, while also allowing for the calculation of tilt angles from the crystallographic data in the presence of octahedral distortions, is an unsolved problem. In this contribution a method is proposed that uniquely decomposes any ABX_3 derived structure into a description by tilts and deformations of BX_6 octahedral groups. Mathematical formulae are presented for the calculation of tilt angles from crystallographic data.

2. Deformations and tilting angles

In ABX_3 structures octahedral distortions and tilts can be described by shifts of the X atoms. The relative shifts of X atoms which are transverse to the $B-X$ bonds cause shear-like deformations of the octahedra (deviations of $X-B-X$ bond angles from 90°), longitudinal relative shifts cause Jahn–Teller-type deformations (difference in $B-X$ bond lengths), while cooperative shifts of X atoms give rise to rotations or tilting of the octahedra. To analyze the three-dimensional network of deformed and tilted octahedra it is necessary to define deformations and tilting of octahedra in such a way that they satisfy the following conditions:

(i) Octahedral tilting should be described by rotations such that a one-to-one correspondence exists between values of tilt parameters and crystal structure.

(ii) Parameters for tilt and deformations should be defined in the same way for all structures, so that it will be possible to compare structures of different symmetries and different tilt systems in terms of these parameters.

The main problem is that a given crystal structure cannot uniquely be separated into parameters for tilt and parameters for deformations of the BX_6 octahedral group. Some, initially arbitrary, definitions need to be introduced. One such choice – restricted to structures with a $2^{1/2}a_c \times 2^{1/2}a_c \times 2a_c$ unit cell and space group *Pbnm* – has been given by Thomas (1996). Here we present a more general definition of tilt and deformation parameters that can be applied to all tilt systems and symmetries, and that satisfies the requirements above.

The ideal ABX_3 structure of highest symmetry (space group $Pm\bar{3}m$) is the natural choice for the structure of zero tilt that corresponds to any compound composed of regular BX_6 octahedra. The tilted structure is then characterized by non-zero values for tilt parameters (defined below) and zero values for parameters describing the deformations of BX_6 groups. The zero-tilt structure of regular octahedra can be characterized and defined as that structure for which all $B-X$ bonds are parallel to one out of three directions: the three basis vectors of the primitive cubic lattice. Alternatively, the zero-tilt structure of regular octahedra can be defined through the bisectors of $X-B-X$ angles of 90° forming an F-centered cubic lattice. In particular, the zero-tilt structure possesses a plane containing the B atom and four X atoms of each octahedron on which the bisectors of $X-B-X$ angles define a rectangular grid (Fig. 1*a*). The latter property is retained in compounds with deformed octahedra if BX_6 groups obey the point symmetry $\bar{1}$.

Hence, for compounds composed of distorted octahedra we propose the zero-tilt structure be defined as the structure in which one plane of bisectors of $X-B-X$ bond angles forms a rectangular grid (Figs. 1*b* and *c*). Notice that this structure can and should always be constructed by pure rotations of the deformed octahedral groups as they are present in the real crystal structure. In this way a unique separation is obtained between tilt and deformation of the BX_6 octahedral groups. A single type of deformed octahedral group may form zero-tilt structures of different symmetry (Fig. 1).

A distorted octahedron of point symmetry $\bar{1}$ can be described by three vectors, $\mathbf{r}_1, \mathbf{r}_2$ and $\mathbf{r}_3$, that define the directions and lengths of the $B-X$ bonds (Fig. 2). Denote the angle between $\mathbf{r}_i$ and $\mathbf{r}_j$ by ψ_{ij}, for $i, j = 1, 2, 3$ (Fig. 2). A Cartesian coordinate system (XYZ) is defined with the X axis parallel to the bisector of $\mathbf{r}_1$ and $\mathbf{r}_2$, with the Y axis parallel to the bisector of $-\mathbf{r}_1$ and $\mathbf{r}_2$, and with Z perpendicular to XY (Fig. 2). Unit vectors along X, Y and Z are denoted by $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{e}_3$, respectively. As noted in the discussion above, this definition of X and Y leads to perpendicular vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ for any set of $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$, while the latter are not necessarily perpendicular to each other. The vectors $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$ may be expressed in terms of the Cartesian basis vectors as

$$\mathbf{r}_1 = r_1\left(\cos\frac{\psi_{12}}{2}\mathbf{e}_1 - \sin\frac{\psi_{12}}{2}\mathbf{e}_2\right)$$

$$\mathbf{r}_2 = r_2\left(\cos\frac{\psi_{12}}{2}\mathbf{e}_1 + \sin\frac{\psi_{12}}{2}\mathbf{e}_2\right)$$

$$\begin{aligned}\mathbf{r}_3 = r_3\Bigg\{&\frac{\cos\psi_{13}+\cos\psi_{23}}{2\cos(\psi_{12}/2)}\mathbf{e}_1 + \frac{\cos\psi_{23}-\cos\psi_{13}}{2\sin(\psi_{12}/2)}\mathbf{e}_2 + \\ &[(1-\cos^2\psi_{12}-\cos^2\psi_{13}-\cos^2\psi_{23} \\ &+2\cos\psi_{12}\cos\psi_{13}\cos\psi_{23})^{1/2}]/\sin\psi_{12}\mathbf{e}_3\Bigg\} \\ = r_3&[\sin\tau_1\cos\tau_2\mathbf{e}_1 + \sin\tau_1\sin\tau_2\mathbf{e}_2 + \cos\tau_1\mathbf{e}_3]. \qquad (1)\end{aligned}$$

Angles τ_1 and τ_2 are polar coordinates for the vector $\mathbf{r}_3$, with τ_1 the angle between $\mathbf{r}_3$ and $\mathbf{e}_3$, and with τ_2 the angle between the projection of $\mathbf{r}_3$ onto the XY plane and $\mathbf{e}_1$. The angles τ_1 and τ_2 are related to the bond angles ψ_{ij} as

$$\tan\tau_2 = \frac{\cos\psi_{23}-\cos\psi_{13}}{\cos\psi_{23}+\cos\psi_{13}}\cot\frac{\psi_{12}}{2}$$

$$\sin\tau_1 = \frac{\cos\psi_{23}}{\cos[(\psi_{12}/2)-\tau_2]}. \qquad (2)$$

The octahedral angles ψ_{12}, ψ_{13} and ψ_{23} take only positive values near 90° by definition, hence the angles τ_1 and τ_2 will take values between −90 and 90°.

The orientation of a distorted octahedron is completely defined by three parameters. These parameters can be chosen in three different ways:

(i) one angle, χ, describing the rotation of the octahedron about an axis R, the direction of which is defined by two independent parameters *via* direction cosines with respect to the Cartesian coordinate system;

(ii) two angles, ϕ and θ, describing rotations about a pair of perpendicular axes, *e.g.* the **Z** axis and an axis **R** lying in the XY plane in a direction defined by one angle, δ;

(iii) three angles, α_1, α_2 and α_3, describing the rotations of an octahedron about the X, Y and Z axes, respectively.

In description (i) the orientation of the octahedron is described by a single rotation. This description has been used for analyzing the octahedral tilt in one-tilted ABX_3 structures with symmetries $R\bar{3}c$, $I4/mcm$ and $Im\bar{3}$ (Megaw & Darlington, 1975; O'Keeffe & Hyde, 1977; Thomas & Beitollahi, 1994). However, if the orientation of the rotation axis is not fixed by symmetry this method becomes complicated because of the arbitrary orientation of the rotation axis. Description (iii) has been used by Glazer (1975). In contrast to description (i) the rotation axes are fixed in space, but difficulties in interpretation arise because of noncommutative rotations (for the same set of angles α_1, α_2 and α_3 describing rotations of octahedra about three orthogonal axes the orientation of the octahedron depends on the sequence of rotations). Description (iii) is not

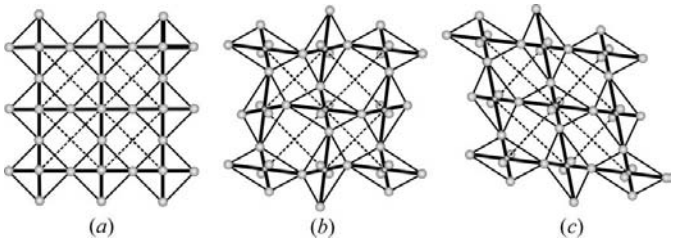

Figure 1
Schematic representations of the (XY) layer of zero-tilt ABX_3 structures. (*a*) Structure with regular octahedra; (*b*) structure with tetragonal arrangement of distorted octahedra; (*c*) structure with orthorhombic arrangement of distorted octahedra. Large circles correspond to X atoms, small circles to B atoms. Thick lines correspond to $B-X$ bonds, thin lines to octahedral edges and dashed lines to bisectors of $X-B-X$ angles.

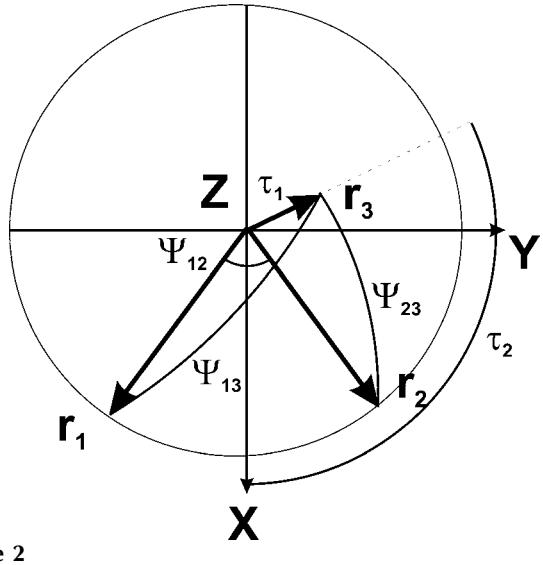

Figure 2
The stereographic projection of basic vectors $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$ of distorted BX_6 octahedra. The X, Y and Z axes of the Cartesian coordinate system XYZ are indicated (the Z axis is perpendicular to the plane of the figure). ψ_{12}, ψ_{13}, ψ_{23} indicate the angles between the corresponding basic vectors, τ_1 is the angle between $\mathbf{r}_3$ and the Z axis, and τ_2 is the angle between the projection of $\mathbf{r}_3$ on the XY plane and X axis.

easily generalized towards a full characterization of structures with deformed octahedra. Therefore, we propose a set of parameters on the basis of description (ii), that provides a unique characterization of tilt in ABX_3 structures. The direction of the rotation axis **R** is defined by the angle δ between **R** and the Y axis. Then the rotations $\mathbf{Z}(\varphi)$ and $\mathbf{R}_\delta(\theta)$ may be defined on the basis of the Cartesian coordinates as

$$\mathbf{R}_\delta(\theta) = \begin{pmatrix} \cos\theta + \sin^2\delta(1-\cos\theta) & -\sin\delta\cos\delta(1-\cos\theta) & \cos\delta\sin\theta \\ -\sin\delta\cos\delta(1-\cos\theta) & \cos\theta + \cos^2\delta(1-\cos\theta) & \sin\delta\sin\theta \\ -\cos\delta\sin\theta & -\sin\delta\sin\theta & \cos\theta \end{pmatrix} \tag{3}$$

$$\mathbf{Z}(\phi) = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{4}$$

The rotations are not commutative, but they obey the simple relation

$$\mathbf{Z}(\varphi)\mathbf{R}_\delta(\theta) = \mathbf{R}_{\delta+\varphi}(\theta)\mathbf{Z}(\varphi). \tag{5}$$

Inspection of Fig. 3 shows that $\mathbf{R}_\delta$ in the zero-tilt structure and $\mathbf{R}_{\delta+\phi}$ in the $\mathbf{Z}(\phi)$-rotated structure have identical orientations with respect to the octahedron. In this way, the parameters δ, ϕ and θ uniquely correspond to a particular tilt in ABX_3 structures. Using the transformation matrices (3) and (4), the basis vectors $\mathbf{r}'_i$ of the $\mathbf{Z}(\varphi)\mathbf{R}_\delta(\theta)$-rotated octahedron may be expressed as follows [see (1)]

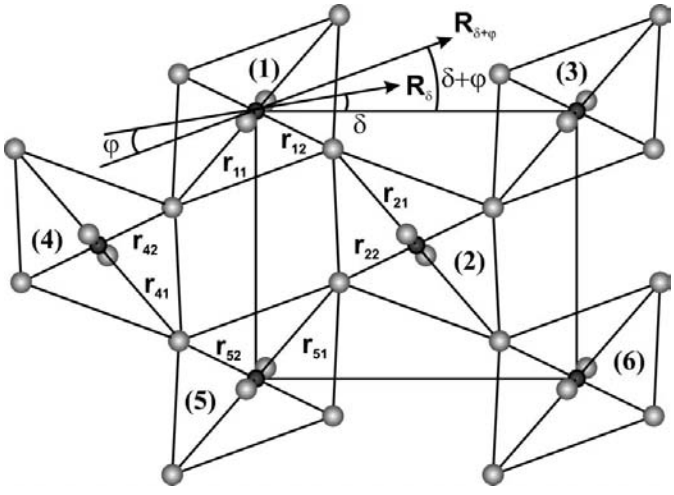

Figure 3
The schematic representation of the (XY) layer of the $\mathbf{R}(\theta)$ and $\mathbf{Z}(\varphi)$ tilted ABX_3 structure. The θ tilting axis $\mathbf{R}_\delta$ is indicated, the φ tilting axis is perpendicular to the figure.

$$\begin{aligned}
\mathbf{r}'_1 &= r_1[\cos(\tfrac{\psi_{12}}{2}-\varphi) - \cos(\tfrac{\psi_{12}}{2}+\delta)\cos(\delta+\varphi)(1-\cos\theta)]\mathbf{e}_1 \\
&\quad + r_1[-\sin(\tfrac{\psi_{12}}{2}-\varphi) - \cos(\tfrac{\psi_{12}}{2}+\delta) \\
&\quad \times \sin(\delta+\varphi)(1-\cos\theta)]\mathbf{e}_2 \\
&\quad - r_1\cos(\tfrac{\psi_{12}}{2}+\delta)\sin\theta\mathbf{e}_3 \\
\mathbf{r}'_2 &= r_2[\cos(\tfrac{\psi_{12}}{2}+\varphi) - \cos(\tfrac{\psi_{12}}{2}-\delta)\cos(\delta+\varphi)(1-\cos\theta)]\mathbf{e}_1 \\
&\quad + r_2[\sin(\tfrac{\psi_{12}}{2}+\varphi) - \cos(\tfrac{\psi_{12}}{2}-\delta)\sin(\delta+\varphi)(1-\cos\theta)]\mathbf{e}_2 \\
&\quad - r_2\cos(\tfrac{\psi_{12}}{2}-\delta)\sin\theta\mathbf{e}_3 \\
\mathbf{r}'_3 &= r_3[\sin\tau_1\cos(\varphi+\tau_2) - \sin\tau_1\cos(\delta-\tau_2)\cos(\delta+\varphi) \\
&\quad \times (1-\cos\theta) + \cos\tau_1\cos(\delta+\varphi)\sin\theta]\mathbf{e}_1 \\
&\quad + r_3[\sin\tau_1\sin(\varphi+\tau_2) - \sin\tau_1\cos(\delta-\tau_2)\sin(\delta+\varphi) \\
&\quad \times (1-\cos\theta) + \cos\tau_1\sin(\delta+\varphi)\sin\theta]\mathbf{e}_2 \\
&\quad + r_3[\cos\tau_1\cos\theta - \sin\tau_1\cos(\delta-\tau_2)\sin\theta]\mathbf{e}_3.
\end{aligned} \tag{6}$$

Equation (6) describes the basis vectors of the tilted octahedron in terms of octahedral parameters r_1, r_2, r_3, ψ_{12}, τ_1, τ_2 and and tilt parameters δ, ϕ and θ. Alternatively, the vectors $\mathbf{r}'_i$ can be obtained directly from the atomic coordinates and lattice parameters of a structure model. Equation (6) can thus be used for the construction and analysis of crystal structures of perovskite-related ABX_3 structures.

The deformation state of an octahedron can be characterized by the local strain tensor e_{ij} ($i, j = 1, 2, 3$), defined as (Zhao *et al.*, 1993)

$$e_{ij} = \begin{cases} \frac{r_i}{\langle r_i\rangle} & i = j \\ \frac{\pi}{2} - \psi_{ij} & i \neq j \end{cases}, \tag{7}$$

where $\langle r_i\rangle = (r_1 + r_2 + r_3)/3$ is the average B—X bond length. The local strain tensor is completely determined by the octahedral parameters r_i and ψ_{ij} ($i, j = 1, 2, 3$), while the latter can be obtained from the combination of local strain tensor and average bond length. In this way, deformed perovskite structures are completely characterized by nine parameters: the average B—X bond length, five independent local strain parameters and three tilt parameters. Octahedron point symmetries higher than $\bar{1}$ and translational symmetries of up to fourfold superstructures are reflected by relations between, and restrictions on, these parameters, as they will be discussed for selected cases in §3.

In each ABX_3 structure there are octahedra of various orientations defined by the point symmetry of the structure. The number of distinguishable orientations is equal to the ratio of point symmetry of the structure and the point symmetry of the octahedron. For example, in orthorhombic structures containing octahedra of the point symmetry $\bar{1}$ there are four distinguishable orientations of octahedra, but only two distinguishable orientations are found for octahedra of point symmetry $2/m$. Possible arrangements of octahedra are defined by the space group, but for a given space group the possible tilts and deformations are restricted by the condition

that the sum of bond vectors along any closed path should be identical to zero. For example, in the layer defined by $\mathbf{r}_1$ and $\mathbf{r}_2$ bonds, the octahedra numbered (1), (2), (5) and (4) form a closed loop (Fig. 3). The following connectivity condition should then be satisfied

$$\mathbf{r}_{12} - \mathbf{r}_{21} + \mathbf{r}_{22} - \mathbf{r}_{51} + \mathbf{r}_{52} - \mathbf{r}_{41} + \mathbf{r}_{42} - \mathbf{r}_{11} = 0. \qquad (8)$$

Equation (8) is a connectivity condition for one layer. For the three-dimensional network of BX_6 octahedra similar conditions should be satisfied for the layers $\mathbf{r}_1\mathbf{r}_3$ and $\mathbf{r}_2\mathbf{r}_3$. Since the symmetry relations between octahedra (1), (2), (5) and (4) also need to be satisfied, the connectivity conditions will lead to relations between octahedral parameters (r_1, r_2, r_3, ψ_{12}, ψ_{13}, ψ_{23}) and tilt parameters (δ, ϕ, θ). In §3, these relations will be presented for structures with various tilt patterns of regular and distorted octahedra.

3. Applications

3.1. Orthorhombic symmetry *Pbnm*

Many compounds have been found to crystalize in the distorted perovskite-type structure of symmetry *Pbnm* on a $2^{1/2}a_c \times 2^{1/2}a_c \times 2a_c$ supercell of the primitive cubic unit cell. Tilt systems that lead to this structure are $a^-a^-c^+$ and $a^-a^-a^+$. The point symmetry of *Pbnm* is the orthorhombic subgroup $m_{a+b}m_{b-a}m_c$ of cubic $m\bar{3}m$. Orientations of these mirror planes can also be given as the point group $m_xm_ym_z$ with respect to the Cartesian coordinates (*XYZ*) (see §2). Hereafter, the subscripts a, b, c will be used to indicate quantities defined with respect to the pseudo-cubic unit cell, and subscripts x, y, z will indicate quantities defined on the Cartesian coordinates (*XYZ*). The *Pbnm* structure contains a single crystallographically independent octahedron. Within a single (*XY*) layer, two orientations are found that are related by the mirror $\mathbf{S}(\mathbf{m}_x)$. That is, octahedra (1), (3), (5) and (6) in Fig. 3 have the same orientation, while the orientations of (2) and (4) are obtained from (1) by the operator $\mathbf{S}(\mathbf{m}_x)$. Orientations of octahedra consecutive along *Z* are related by the mirror $\mathbf{S}(\mathbf{m}_z)$. Employing these symmetries, two independent connectivity conditions are obtained, that can be written as

$$\begin{aligned}
&\mathbf{r}'_2 - \mathbf{S}(\mathbf{m}_x)\mathbf{r}'_1 + \mathbf{S}(\mathbf{m}_x)\mathbf{r}'_3 - \mathbf{S}(2_y)\mathbf{r}'_3 + \mathbf{S}(2_y)\mathbf{r}'_1 - \mathbf{S}(\mathbf{m}_z)\mathbf{r}'_2 \\
&+ \mathbf{S}(\mathbf{m}_z)\mathbf{r}'_3 - \mathbf{r}'_3 = 0 \\
&\mathbf{r}'_2 - \mathbf{S}(\mathbf{m}_x)\mathbf{r}'_1 - \mathbf{S}(\mathbf{m}_x)\mathbf{r}'_2 + \mathbf{r}'_1 - \mathbf{r}'_2 + \mathbf{S}(\mathbf{m}_x)\mathbf{r}'_1 \\
&+ \mathbf{S}(\mathbf{m}_x)\mathbf{r}'_2 - \mathbf{r}'_1 = 0, \qquad (9)
\end{aligned}$$

where $\mathbf{S}(2_y) = \mathbf{S}(\mathbf{m}_z)\mathbf{S}(\mathbf{m}_x)$. These conditions are satisfied if $(\mathbf{r}'_1)_z = (\mathbf{r}'_2)_z$, leading to [see (6)]

$$r_1 \cos\left(\frac{\psi_{12}}{2} + \delta\right) = r_2 \cos\left(\frac{\psi_{12}}{2} - \delta\right). \qquad (10)$$

It follows that the direction of the tilt axis $\mathbf{R}_\delta$ is completely defined by the octahedral parameters. For a regular octahedron $\delta = 0^\circ$ and $\mathbf{R}_\delta$ is parallel to *Y*, *i.e.* to **b**. Basis vectors of the orthorhombic lattice can be expressed in terms of octahedral and tilt parameters as (Fig. 4)

$$\begin{aligned}
\mathbf{a} &= 2[r_1 \cos\left(\frac{\psi_{12}}{2} - \varphi\right) + r_2 \cos\left(\frac{\psi_{12}}{2} + \varphi\right) \\
&\quad - 2r_1 \cos\left(\frac{\psi_{12}}{2} + \delta\right)\cos(\varphi + \delta)(1 - \cos\theta)]\mathbf{e}_1 \\
\mathbf{b} &= 2[r_1 \sin\left(\frac{\psi_{12}}{2} - \varphi\right) + r_2 \sin\left(\frac{\psi_{12}}{2} + \varphi\right)]\mathbf{e}_2 \\
\mathbf{c} &= 4r_3[\cos\tau_1 \cos\theta - \sin\tau_1 \cos(\delta - \tau_2)\sin\theta]\mathbf{e}_3. \qquad (11)
\end{aligned}$$

It follows that **b** does not depend on θ tilting, while **c** does not depend on ϕ tilting. Tilt parameters can be expressed in the structural parameters as [see (6) and (10)]

$$\begin{aligned}
\tan\delta &= \frac{r_1 - r_2}{r_1 + r_2}\cot\frac{\psi_{12}}{2} \\
\sin\theta &= -\frac{(\mathbf{r}'_2)_z}{r_2\cos(\psi_{12}/2 - \delta)} = -\frac{(\mathbf{r}'_1)_z}{r_1\cos(\psi_{12}/2 + \delta)} \\
\tan(\varphi + \delta) &= 2\frac{(\mathbf{r}'_1)_x - (\mathbf{r}'_2)_x}{b}. \qquad (12)
\end{aligned}$$

As an example, consider the structure of $La_{0.82}Ca_{0.18}MnO_3$. At room temperature the lattice parameters are a = 5.5126 (3), b = 5.5125 (2) and c = 7.7741 (3) Å. At room temperature the lattice parameters are a = 5.5126 (3), b = 5.5125 (2), c = 7.7741 (3) Å (unpublished). Structural parameters of the MnO_6 octahedron are r_1 = 2.0064, r_2 = 1.9577, r_3 = 1.9785 Å, ψ_{12} = 88.72, ψ_{13} = 89.99, ψ_{23} = 90.64°, leading to tilt parameters of δ = 0.72, φ = −6.63 and θ = 11.05°. The tetragonal feature of the lattice depends on a certain relation between tilting angles and octahedral parameters. From (11) this relation is obtained as

$$\begin{aligned}
&\frac{r_1\cos(\psi_{12}/2 - \varphi + \pi/4) + r_2\cos(\psi_{12}/2 + \varphi + \pi/4)}{2^{1/2}r_1\cos(\psi_{12}/2 + \delta)\cos(\varphi + \delta)} \\
&= (1 - \cos\theta). \qquad (13)
\end{aligned}$$

The tilt parameters satisfy this condition with accuracy better than 4%.

3.2. Tetragonal substructures of *Pbnm*

The question arises, which values of octahedral and tilt parameters define a tetragonal structure in contrast to an

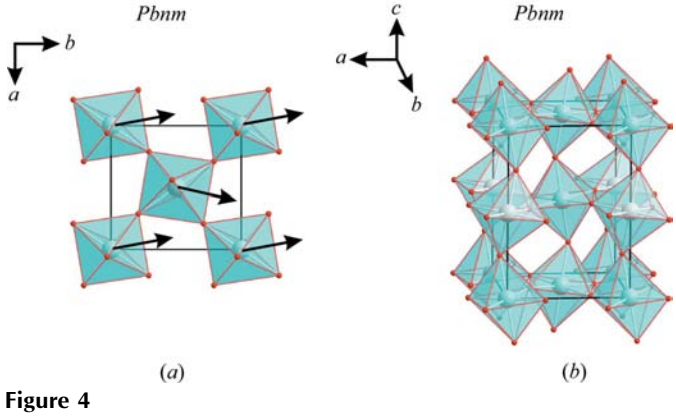

Figure 4
Perspective views of the *Pbnm* structure: (*a*) along **Z** (the arrows indicate the orientations of the $\mathbf{R}_\delta$ tilting axis for each octahedron); (*b*) along $\mathbf{R}_\delta$.

orthorhombic structure with a pseudo-tetragonal lattice, as was found for $La_{0.82}Ca_{0.18}MnO_3$. Equation (11) demonstrates that the lattice constant a depends on both tilt angles, while the lattice constant b depends only on φ tilting. In tetragonal structures the a and b lattice constants are equal and it follows that $\theta = 0^\circ$, leading to the condition [see (13)]

$$r_1 \cos\left(\frac{\psi_{12}}{2} - \varphi + \frac{\pi}{4}\right) + r_2 \cos\left(\frac{\psi_{12}}{2} + \varphi + \frac{\pi}{4}\right) = 0. \qquad (14)$$

This equation has the solutions:

(i) $\psi_{12} = \pi/2$, with $r_1 = r_2$ and

(ii) $\psi_{12} = \pi/2$, with $\varphi = 0$.

Solution (i) together with the additional condition $\tau_1 = 0$ determines that the point symmetry of the octahedron is $4_z/m_z$, thus the consecutive octahedra along Z become translationally equivalent. The n glide of the space group $Pbnm$ transforms into an a glide, determining the space group of this structure as $P4/mbm$ (Fig. 5*a*). The tilt system is $a^o a^o c^+$ (Glazer, 1975). The basis vectors of the lattice are

$$\begin{aligned}\mathbf{a} &= 2(2)^{1/2} r_1 \cos\varphi \mathbf{e}_1\\ \mathbf{b} &= 2(2)^{1/2} r_1 \cos\varphi \mathbf{e}_2\\ \mathbf{c} &= 2r_3 \mathbf{e}_3.\end{aligned} \qquad (15)$$

In the structure corresponding to solution (ii) consecutive octahedra along Z are translationally equivalent, but the symmetry of an octahedron is $m_{x+y} m_{x-y} m_z$. The space group of this structure is $P4/mbm$ (Fig. 5*b*) with basis vectors of the lattice given by

$$\begin{aligned}\mathbf{a} &= 2^{1/2}(r_1 + r_2)\mathbf{e}_1\\ \mathbf{b} &= 2^{1/2}(r_1 + r_2)\mathbf{e}_2\\ \mathbf{c} &= 2r_3 \mathbf{e}_3.\end{aligned} \qquad (16)$$

This perovskite-derived structure is obtained from the ideal cubic perovskite structure by distortions of octahedra and zero tilt. The tilt system is $a^o a^o a^o$, and this structure does not appear in the classification of Glazer (1975). It is one of ten additional structures derived by Bock & Müller (2002).

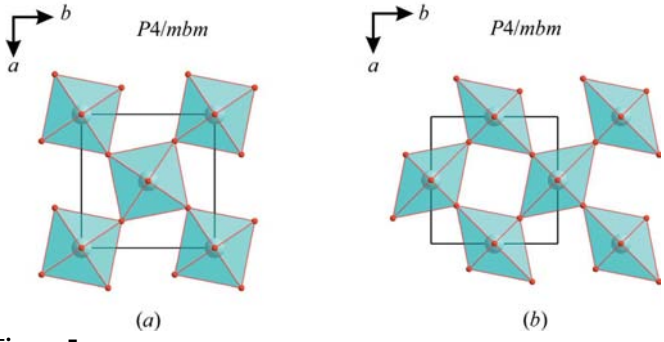

Figure 5
The projections of tetragonal $P4/mbm$ structures on the ab plane. (*a*) Structure corresponding to the ($\psi_{12} = \pi/2$, $r_1 = r_2$, $\tau_1 = 0$) solution of equation (14), BX_6 octahedra are on the fourfold axes. (*b*) Structure corresponding to the ($\psi_{12} = \pi 2$, $\varphi = 0$, $\tau_1 = 0$) solution of equation (14), BX_6 octahedra are on twofold axes.

3.3. *I*2*c* Monoclinic symmetry *I*2/*c*

The tilt system $a^- a^- c^-$ describes the monoclinic $I2/c$ structure. This structure and the orthorhombic $Pbnm$ structure display identical arrangements of octahedra within a single (XY) layer, but the orientations of consecutive octahedra along the Z direction are related by the symmetry operator $\mathbf{S}(\mathbf{m}_x)$ rather than $\mathbf{S}(\mathbf{m}_z)$ for $Pbnm$. Connectivity conditions (8) are always fulfilled and they do not lead to constraints on the octahedral and tilt parameters. Basis vectors of the monoclinic $2^{1/2}a_c \times 2^{1/2}a_c \times 2a_c$ lattice can be expressed *via* basis vectors $\mathbf{r}'_1$, $\mathbf{r}'_2$ and $\mathbf{r}'_3$ of the tilted BX_6 octahedron as

$$\begin{aligned}\mathbf{a} &= -2[(\mathbf{r}'_2)_y - (\mathbf{r}'_1)_y]\mathbf{e}_2 + 2[(\mathbf{r}'_2)_z - (\mathbf{r}'_1)_z]\mathbf{e}_3\\ \mathbf{b} &= 2[(\mathbf{r}'_2)_x + (\mathbf{r}'_1)_x]\mathbf{e}_1\\ \mathbf{c} &= 4[(\mathbf{r}'_3)_y \mathbf{e}_2 + (\mathbf{r}'_3)_z \mathbf{e}_3].\end{aligned} \qquad (17)$$

In the monoclinic structures there is no symmetry element restricting the rotation of the whole structure about the unique axis. Hence, the octahedral rotations about $\mathbf{Z}$ and $\mathbf{R}_\delta$ axes describe not only the tilting of octahedra, but also the rotation of the whole structure about X (twofold axis). Keeping the ab layers of the structure parallel to the XY plane of the Cartesian coordinate system then gives the same condition, $(\mathbf{r}'_1)_z = (\mathbf{r}'_2)_z$, as was obtained from connectivity conditions in the case of orthorhombic $Pbnm$ symmetry [see (10)]. Basis vectors of the monoclinic lattice can then be expressed in octahedral and tilt parameters [see (6), (10) and (17)]

$$\begin{aligned}\mathbf{a} &= 2[-r_1 \sin(\frac{\psi_{12}}{2} - \varphi) - r_2 \sin(\frac{\psi_{12}}{2} + \varphi)]\mathbf{e}_2\\ \mathbf{b} &= 2[r_1 \cos(\frac{\psi_{12}}{2} - \varphi) + r_2 \cos(\frac{\psi_{12}}{2} + \varphi)\\ &\quad - 2r_1 \cos(\frac{\psi_{12}}{2} + \delta)\cos(\varphi + \delta)(1 - \cos\theta)]\mathbf{e}_1\\ \mathbf{c} &= 4r_3[\sin\tau_1 \sin(\varphi + \tau_2) - \sin\tau_1 \cos(\delta - \tau_2)\sin(\delta + \varphi)\\ &\quad \times (1 - \cos\theta) + \cos\tau_1 \sin(\delta + \varphi)\sin\theta]\mathbf{e}_2 + 4r_3[\cos\tau_1 \cos\theta\\ &\quad - \sin\tau_1 \cos(\delta - \tau_2)\sin\theta]\mathbf{e}_3.\end{aligned} \qquad (18)$$

Octahedral tilt parameters can be obtained from the structural parameters by

$$\begin{aligned}\tan\delta &= \frac{r_1 - r_2}{r_1 + r_2}\cot\frac{\psi_{12}}{2}\\ \sin\theta &= -\frac{(\mathbf{r}'_2)_c \sin\beta}{r_2 \cos(\psi_{12}/2 - \delta)} = -\frac{(\mathbf{r}'_1)_c \sin\beta}{r_1 \cos(\psi_{12}/2 + \delta)}\\ \tan(\varphi + \delta) &= 2\frac{(\mathbf{r}'_1)_b - (\mathbf{r}'_2)_b}{a},\end{aligned} \qquad (19)$$

where $(\mathbf{r}')_c$ is the component of the $\mathbf{r}'$ parallel to the monoclinic $\mathbf{c}$ axis and $(\mathbf{r}')_b$ is the component of the $\mathbf{r}'$ parallel to $\mathbf{b}$ (Fig. 6).

3.4. Substructures of *I*2/*c*

As for $Pbnm$ symmetry (§3.1), structures for which the space group is a supergroup of $I2/c$ are of most interest. First, consider the transformation of the monoclinic $I2/c$ structure

into orthorhombic structures. An orthogonal lattice is obtained, if the $\mathbf{e}_2$ component of $\mathbf{c}$ is zero [see (18)]

$$\sin\tau_1[\sin(\varphi+\tau_2)-\cos(\delta-\tau_2)\sin(\delta+\varphi)(1-\cos\theta)] + \cos\tau_1\sin(\delta+\varphi)\sin\theta=0. \quad (20)$$

However, the fulfillment of this condition is not sufficient to obtain an orthorhombic structure as it is demonstrated by the monoclinic low-temperature structure of $La_{0.815}Ba_{0.185}MnO_3$ (Rotiroti *et al.*, 2005). Initially, X-ray powder diffraction indicated an orthorhombic lattice for this compound (Arkhipov *et al.*, 2000). Structure refinements against single crystal diffraction data showed, however, that the structure is monoclinic (Rotiroti *et al.*, 2005). The octahedral parameters are r_1 = 1.975 (3), r_2 = 1.968 (3), r_3 = 1.976 (1) Å, ψ_{12} = 89.75, ψ_{13} = 90.46, ψ_{23} = 90.19, τ_1 = −0.50, τ_2 = −22.65°, leading to tilt angles θ = 9.62, φ = −0.22, δ = 0.10°. Parameters τ_1, φ and δ are close to zero, and it is easily verified that zero values of τ_1 and $\phi+\delta$ are a solution to equation (20), making the lattice orthogonal, but retaining the monoclinic symmetry of the structure. A structure with orthorhombic symmetry is obtained by the solution $\tau_1=\theta=0$ of (20), then defining a structure with space group *Ibam* and lattice constants (Fig. 7)

$$\begin{aligned}\mathbf{a}&=2\left[-r_1\sin\left(\frac{\psi_{12}}{2}-\varphi\right)-r_2\sin\left(\frac{\psi_{12}}{2}+\varphi\right)\right]\mathbf{e}_2\\ \mathbf{b}&=2\left[r_1\cos\left(\frac{\psi_{12}}{2}-\varphi\right)+r_2\cos\left(\frac{\psi_{12}}{2}+\varphi\right)\right]\mathbf{e}_1\\ \mathbf{c}&=4r_3\mathbf{e}_3. \end{aligned} \quad (21)$$

This structure corresponds to the tilt system $a^oa^oc^-$.

The solution $\delta=\varphi=\tau_2=0$ of (20) defines the orthorhombic structure with space group *Ibmm*, tilt system $a^-a^-c^o$ and lattice parameters (Fig. 8)

$$\begin{aligned}\mathbf{a}&=4r_1\cos\frac{\psi_{12}}{2}\cos\theta\mathbf{e}_1\\ \mathbf{b}&=4r_1\sin\frac{\psi_{12}}{2}\mathbf{e}_2\\ \mathbf{c}&=4r_3\cos(\theta+\tau_1)\mathbf{e}_3. \end{aligned} \quad (22)$$

Notice that *Ibmm* is a supergroup structure of *Pbnm* with the same octahedral and tilt parameters.

Further restrictions on the octahedral parameters of the *Ibam* structure, *viz.* $r_1=r_2$ and $\psi_{12}=\pi/2$, in addition to $\tau_1=\theta=0$, define a tetragonal structure with the space group $I4/mcm$, while the tilt system remains that of *Ibam*.

The space group $I2/c$ is a subgroup of the space group $R\bar{3}c$ (tilt system $a^-a^-a^-$). The phase transition observed for $La_{0.815}Ba_{0.185}MnO_3$ at T_s = 187 K (Rotiroti *et al.*, 2005) is a group–subgroup phase transition. As shown above, octahedral tilting in the $I2/c$ structure is described by two independent rotations, while octahedral tilting in the $R\bar{3}c$ structure has traditionally been described by a single rotation about [111] of the pseudo-cubic unit cell (Megaw & Darlington, 1975). This makes analysis of this phase transition in terms of octahedral tilting and deformations difficult. Obviously, the tilting in $R\bar{3}c$ should also be described by φ and θ rotations.

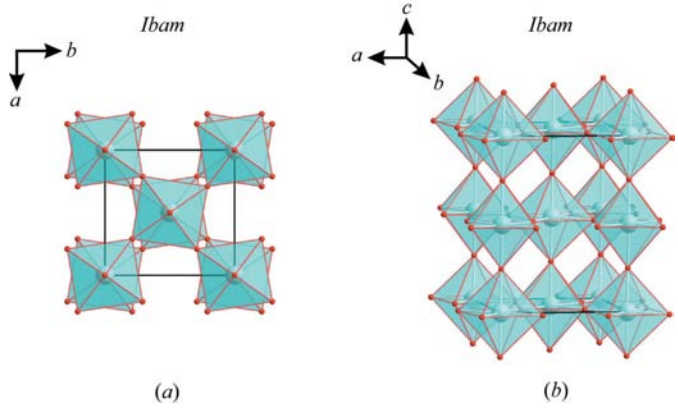

Figure 7
Perspective views of the *Ibam* structure: (*a*) along **Z**; (*b*) along $\mathbf{R}_\delta$.

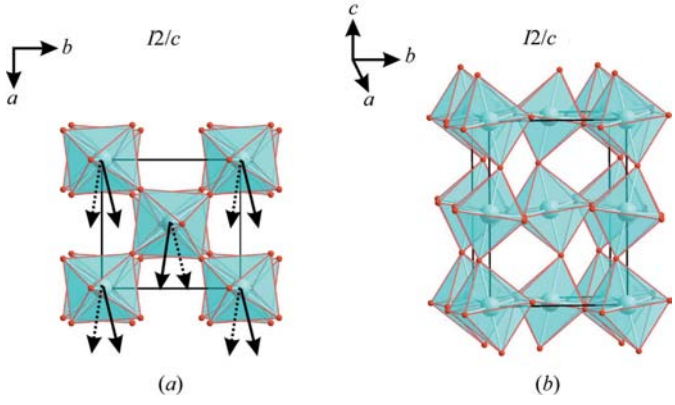

Figure 6
Perspective views of the $I2/c$ structure: (*a*) along **Z** (the orientations of $\mathbf{R}_\delta$ tilting axes are indicated, the dashed arrows relate to the lower layer and the solid arrows relate to the upper layer); (*b*) along $\mathbf{R}_\delta$.

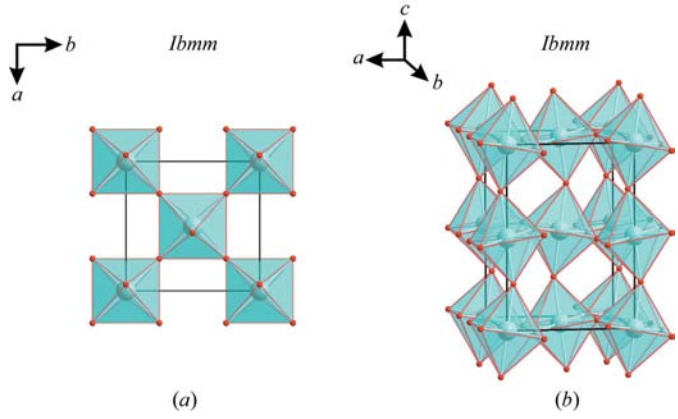

Figure 8
Perspective views of the *Ibmm* structure: (*a*) along **Z**; (*b*) along $\mathbf{R}_\delta$.

In the rhombohedral structure the B atoms occupy positions on the threefold axes and the point symmetry of the BX_6 octahedron is $\bar{3}m$ ($r_1 = r_2 = r_3 = r$, $\psi_{12} = \psi_{13} = \psi_{23} = \psi$). These octahedral parameters determine the orientation of the $\mathbf{R}_\delta$ tilt axis by $\delta = 0$. The twofold axis of $I2/c$ coincides with a twofold axis of $R\bar{3}c$. Applying the restraints on the octahedral parameters to the lattice translation vectors of $I2/c$ [see (18)], and to the basis vectors of the octahedron [see (6)], the following relation between φ and θ tilt parameter angles can be derived; it must be fulfilled for the structure to become rhombohedral

$$\sin\theta = -\tan\varphi\cot\frac{\psi}{2}\left(3-\tan^2\frac{\psi}{2}\right)^{1/2}. \qquad (23)$$

The lattice constants of this structure in a hexagonal setting can be expressed in octahedral and tilt parameters as (Fig. 9)

$$\begin{aligned} a_h &= 4r\sin\frac{\psi}{2}\cos\phi\cos\theta \\ c_h &= 12r\cos\frac{\psi}{2}\left(1-\frac{1}{3}\tan^2\frac{\psi}{2}\right)^{1/2}. \end{aligned} \qquad (24)$$

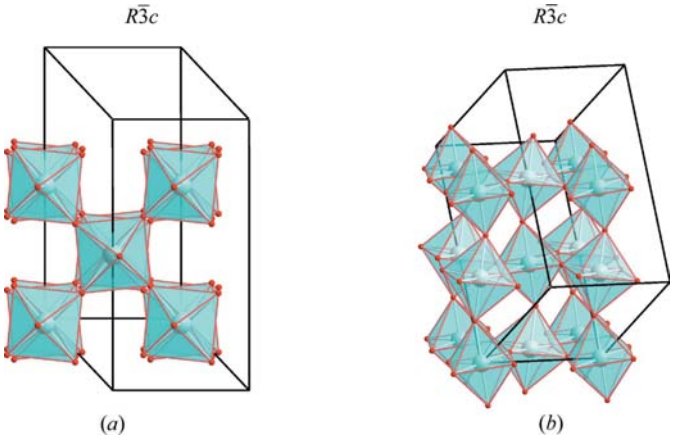

Figure 9
Perspective views of the $R\bar{3}c$ structure: (*a*) along $\mathbf{Z}$; (*b*) along $\mathbf{R}_\delta$. The hexagonal unit cell is indicated.

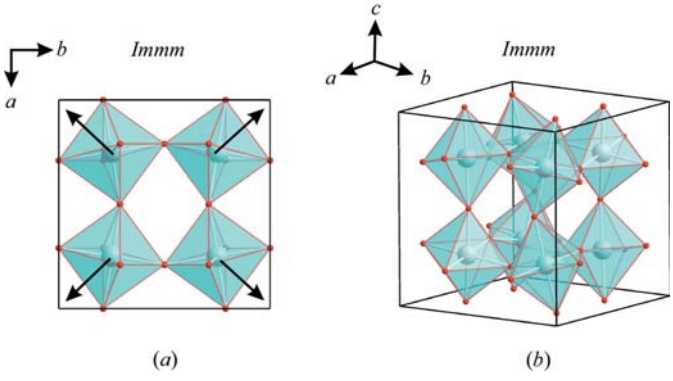

Figure 10
Perspective views of the *Immm* structure: (*a*) along $\mathbf{Z}$ (the arrows indicate the orientations of $\mathbf{R}_\delta$ tilt axes); (*b*) along $\mathbf{R}_\delta$.

If the tilting angle of octahedra about [111] of the pseudo-cubic lattice is ν, then the relations between ν, θ and φ angles may be written as

$$\begin{aligned} \cos\nu &= \cos\varphi\cos\theta \\ \tan\varphi &= -\sin\nu\frac{\tan(\psi/2)}{[3-\tan^2(\psi/2)\sin^2\nu]^{1/2}} \\ \tan\theta &= \tan\nu\left(1-\frac{1}{3}\tan^2\frac{\psi}{2}\right)^{1/2}. \end{aligned} \qquad (25)$$

The transition of the rhombohedral $R\bar{3}c$ structure into the monoclinic $I2/c$ structures may arise due to two independent processes:

(i) by the symmetry reduction of the BX_6 octahedron and

(ii) by the violation of the coupling between ϕ and θ [see (23)].

At room temperature in the high-symmetry $R\bar{3}c$ structure of $La_{0.815}Ba_{0.185}MnO_3$ the octahedral parameters are r = 1.975 Å and $\psi = 90.95^\circ$, and the octahedra are tilted about [111] of the pseudo-cubic lattice by $\nu = 9.32^\circ$. The latter is equivalent to $\mathbf{Z}(\varphi)$ tilting and $\mathbf{R}_\delta(\theta)$ tilting about [110] by $\varphi = -5.46$ and $\theta = 7.57^\circ$, respectively. Comparing the values of octahedral and tilt parameters at temperatures above and below the phase transition, the latter could be described in terms of octahedral deformations and tilting (Rotiroti *et al.*, 2005). Three equal Mn—O bond lengths and $\psi \neq 90^\circ$ of the rhombohedral $R\bar{3}c$ structure are replaced by unequal bond lengths and angles ψ_{ij} close to 90° in the monoclinic phase, thus reducing the shear distortion of the MnO_6 octahedron at the expense of introducing a Jahn–Teller-type distortion. Also, the tilting changes with $\theta_{\rm monoclinic}$ close to $\nu_{\rm rhombohedral}$ and $\varphi_{\rm monoclinic}$ close to zero replacing $\phi_{\rm rhombohedral} = -5.46^\circ$. Such a change in tilting angles might also be interpreted as a change in the direction of the ν tilt axis from [111] in the rhombohedral structure toward [110] in the monoclinic phase.

3.5. Orthorhombic symmetry *Immm*

The $a^+b^+c^+$ tilt system creates the orthorhombic *Immm* structure. In this structure octahedra linked *via* $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$ have orientations related by the symmetry operators $\mathbf{S}(\mathbf{m}_{x+y})$, $\mathbf{S}(\mathbf{m}_{x-y})$ and $\mathbf{S}(\mathbf{m}_z)$, respectively. Connectivity conditions are identically fulfilled and they do not produce restrictions on octahedral and tilt parameters. Basis vectors of the $2a_c \times 2a_c \times 2a_c$ superlattice can be expressed in octahedral and tilt parameters as (Fig. 10)

$$\begin{aligned}
\mathbf{a} &= 2[\mathbf{r}'_1 - \mathbf{S}(\mathbf{m}_{x+y})\mathbf{r}'_1] = 2r_1\Big\{\sin\Big(\frac{\psi_{12}}{2}+\delta\Big)[\cos(\varphi+\delta)\\
&\quad + \sin(\varphi+\delta)] + \cos\theta\cos\Big(\frac{\psi_{12}}{2}+\delta\Big)[\cos(\varphi+\delta)\\
&\quad - \sin(\varphi+\delta)]\Big\}(\mathbf{e}_1 - \mathbf{e}_2)\\
\mathbf{b} &= 2[\mathbf{r}'_2 - \mathbf{S}(\mathbf{m}_{x-y})\mathbf{r}'_2] = 2r_2\Big\{\sin\Big(\frac{\psi_{12}}{2}-\delta\Big)[\cos(\varphi+\delta)\\
&\quad - \sin(\varphi+\delta)] + \cos\theta\cos\Big(\frac{\psi_{12}}{2}-\delta\Big)[\cos(\varphi+\delta)\\
&\quad + \sin(\varphi+\delta)]\Big\}(\mathbf{e}_1 + \mathbf{e}_2)\\
\mathbf{c} &= 2[\mathbf{r}'_3 - \mathbf{S}(\mathbf{m}_z)\mathbf{r}'_3] = 4r_3[\cos\tau_1\cos\theta\\
&\quad - \sin\tau_1\cos(\delta-\tau_2)\sin\theta]\mathbf{e}_3. \qquad (26)
\end{aligned}$$

Tilt angles are related to the structural parameters through

$$\begin{aligned}
\tan\delta &= -\frac{r_2(\mathbf{r}'_1)_z - r_1(\mathbf{r}'_2)_z}{r_2(\mathbf{r}'_1)_z + r_1(\mathbf{r}'_2)_z}\cot\frac{\psi_{12}}{2}\\
\sin\theta &= \frac{(\mathbf{r}'_1)_z}{r_1\cos(\psi_{12}/2+\delta)} = \frac{(\mathbf{r}'_2)_z}{r_2\cos(\psi_{12}/2-\delta)}\\
\tan(\phi+\delta) &= \frac{r_2(\mathbf{r}'_1)_x\cos(\psi_{12}/2-\delta) - r_1(\mathbf{r}'_2)_x\cos(\psi_{12}/2+\delta)}{r_2(\mathbf{r}'_1)_x\cos(\psi_{12}/2-\delta) + r_1(\mathbf{r}'_2)_x\cos(\psi_{12}/2+\delta)}.
\end{aligned} \qquad (27)$$

Notice that $(\mathbf{r}')_x$, $(\mathbf{r}')_y$ and $(\mathbf{r}')_z$ are components of the octahedral basis vectors in the *XYZ* Cartesian coordinate system, which is oriented differently than the crystallographic coordinate system.

3.6. Substructures of *Immm*

The *Immm* structure with a $2a_c \times 2a_c \times 2a_c$ lattice (see §3.5) is characterized by tilted octahedra of point symmetry $\bar{1}$. Structures of higher symmetry, of which *Immm* is a subgroup, can be defined by restrictions on the octahedral and tilt parameters with the *Immm* type of connectivity (Fig. 10).

First consider structure with $\mathbf{r}'_3$ parallel to $\mathbf{c}$ and $\mathbf{r}'_1$ and $\mathbf{r}'_2$ in the (*XY*) plane. Consecutive octahedra along *Z* then become translationally equivalent and the structure of higher symmetry is described by *Cmmm* on a $2a_c \times 2b_c \times c_c$ superlattice. This structure is obtained by the restriction $\tau_1 = \theta = 0$ and it corresponds to the $a^o b^o c^+$ tilt system. Different settings of this structure follow as *Ammm* (tilt system $a^+ b^o c^o$) for $\varphi = 0$ and $\tau_2 = -\delta = -\pi/4$, and as *Bmmm* (tilt system $a^o b^+ c^o$) for $\varphi = 0$ and $\tau_2 = -\delta = \pi/4$. Restrictions $\tau_1 = \varphi = \theta = 0$ and $\psi_{12} = \pi/2$ lead to a structure of zero tilt ($a^o b^o c^o$) with space group *Pmmm* on the $a_c \times a_c \times a_c$ lattice.

If the point symmetry of an octahedron is increased from $\bar{1}$ toward $2_x/m_x$ ($r_1 = r_2, \tau_2 = \pi/2$), $2_y/m_y$ ($r_1 = r_2$, $\tau_2 = 0$), $m_x m_y m_z$ ($r_1 = r_2, \tau_1 = 0$) or $4/m_z$ ($r_1 = r_2, \tau_1 = 0, \psi_{12} = \pi/2$), then restrictions on tilt parameters exist that result in a tetragonal structure. These special values of tilt parameters are found by the condition $a = b$ [see (27)]. Employing $r_1 = r_2$ this leads to

$$\begin{aligned}
\sin\phi\Big(\sin\frac{\psi_{12}}{2} - \cos\frac{\psi_{12}}{2}\Big) &= (\cos\theta - 1)[\sin(\varphi+\delta)\cos\delta\cos\frac{\psi_{12}}{2}\\
&\quad + \cos(\varphi+\delta)\sin\delta\sin\frac{\psi_{12}}{2}]. \qquad (28)
\end{aligned}$$

An infinite number of solutions to (28) exist, but tetragonal structures will only arise for those solutions for which the octahedral point symmetry given above becomes the symmetry of the crystal structure. The solution $\theta = 0$, $\psi_{12} = \pi/2$ (28) leads to $P4/mbm$ (tilt system $a^o a^o c^+$) on a $2^{1/2}a_c \times 2^{1/2}a_c \times a_c$ supercell, that already has appeared as the supergroup of *Pbnm* (see §3.2). Solutions ($\varphi = 0, \delta = 0$) and ($\varphi = 0, \delta = \pi/2$) lead to the space group $I4/mmm$ (tilt system $a^+ a^+ c^o$) on the $2a_c \times 2a_c \times 2a_c$ superlattice (Fig. 11). Basis vectors of this lattice can be expressed in octahedral and tilt parameters as

$$\begin{aligned}
\mathbf{a} &= 2r_1\Big(\sin\frac{\psi_{12}}{2} + \cos\theta\cos\frac{\psi_{12}}{2}\Big)(\mathbf{e}_1 - \mathbf{e}_2)\\
\mathbf{b} &= 2r_1\Big(\sin\frac{\psi_{12}}{2} + \cos\theta\cos\frac{\psi_{12}}{2}\Big)(\mathbf{e}_1 + \mathbf{e}_2)\\
\mathbf{c} &= 4r_3\cos\tau_1\cos\theta\mathbf{e}_3. \qquad (29)
\end{aligned}$$

Additional restrictions on the octahedral deformation ($\tau_1 = 0$) and tilt ($\theta = 0$) results in a structure in which consecutive octahedra along *Z* are translationally equivalent. The symmetry is $C4/mmm$ (tilt system $a^o a^o a^o$) on the

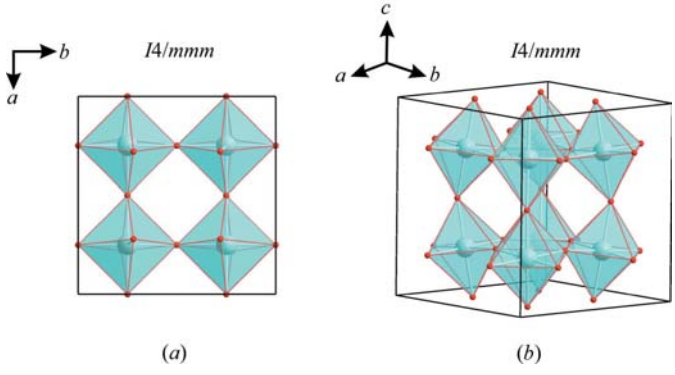

Figure 11
Perspective views of the $I4/mmm$ structure: (*a*) along **Z**; (*b*) along $\mathbf{R}_\delta$.

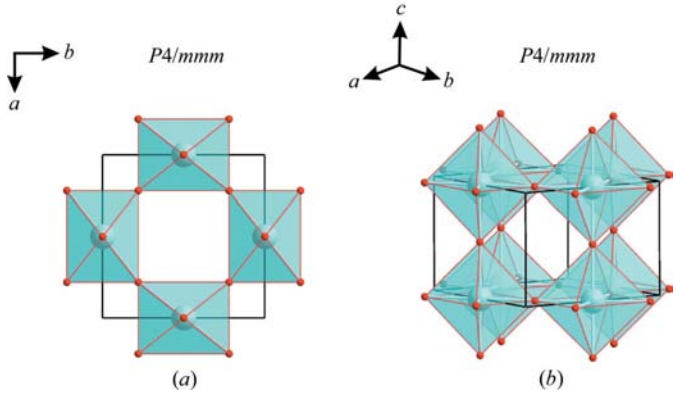

Figure 12
Perspective views of the $P4/mmm$ structure: (*a*) along **Z**; (*b*) along the $\mathbf{R}_\delta$.

$2a_c \times 2a_c \times a_c$ supercell. This is equivalent to the conventional setting $P4/mmm$ on the $2^{1/2}a_c \times 2^{1/2}a_c \times a_c$ lattice (Fig. 12). Basis vectors of this lattice are

$$\begin{aligned}\mathbf{a} &= 2r_1\left(\sin\frac{\psi_{12}}{2} + \cos\frac{\psi_{12}}{2}\right)\mathbf{e}_1\\ \mathbf{b} &= 2r_1\left(\sin\frac{\psi_{12}}{2} + \cos\frac{\psi_{12}}{2}\right)\mathbf{e}_2\\ \mathbf{c} &= 2r_3\cos\tau_1\cos\theta\mathbf{e}_3.\end{aligned} \tag{30}$$

Octahedral symmetry $\bar{3}m$ is obtained for the restrictions $r_1 = r_2 = r_3 = r$ and $\psi_{12} = \psi_{13} = \psi_{23} = \psi$. This local symmetry may become the point symmetry of the crystal structure for special values of the tilt parameters, then result in cubic supergroups of *Immm*. The threefold axis of the octahedron is parallel to the direction $[2^{1/2}, 0, 1]$ of the Cartesian coordinate system, if

$$\begin{aligned}&\sin\delta\left(3 - \tan^2\frac{\psi}{2}\right)^{1/2} = 2^{1/2}\sin(\varphi + \delta)\\ &\cos\theta\tan\frac{\psi}{2} - \sin\theta\cos\delta\left(3 - \tan^2\frac{\psi}{2}\right)^{1/2} = 1.\end{aligned} \tag{31}$$

All combinations of parameters φ, θ, δ and δ that satisfy (31) lead to cubic structures, with the space group $Im\bar{3}$ (tilt system $a^+a^+a^+$) on a $2a_c \times 2a_c \times 2a_c$ superlattice. The cubic lattice constant is

$$a = 4r\frac{\sin\psi\cos\theta + \cos\psi}{\cos\psi/2(3 - \tan^2\psi/2)^{1/2}}. \tag{32}$$

Introducing the additional constraint $\varphi = \delta = 0$ leads to $Im\bar{3}m$ (tilt system $a^+a^+c^o$) on the $2a_c \times 2a_c \times 2a_c$ lattice. Octahedral distortions are intrinsic to this structure, because (31) uniquely determines the magnitude of the distortion (value of ψ) for each tilt (value of θ). Regular octahedra ($\psi = \pi/2$) imply zero tilt ($\theta = 0$) and the aristotype structure is obtained with space group $Pm\bar{3}m$ on the $a_c \times a_c \times a_c$ lattice. The cubic lattice constant depends only on octahedral parameters ψ and r according to following expression

$$a = \frac{4}{3}r\left\{2(2)^{1/2}\sin\frac{\psi}{2} + \cos\frac{\psi}{2}\left(3 - \tan^2\frac{\psi}{2}\right)^{1/2}\right\}. \tag{33}$$

4. Discussions and conclusions

We have proposed a set of three parameters that describe the tilt of distorted octahedra in perovskite-related structures and that can be obtained from the atomic coordinates and lattice parameters in a unique way (see §2). This description applies to all ABX_3 structures containing one symmetry-independent octahedron. More than one independent octahedron allows B site ordering and for each independent octahedron the individual deformations and tilting should be derived. A single restriction of the method is the assumption that the BX_6 octahedron has inversion symmetry. This condition is fulfilled for most known compounds with distorted perovskite structures.

The advantage of the present set of parameters over previous treatments of perovskite structures is that the present analysis explicitly deals with distortions of BX_6 octahedra. Furthermore, the tilt parameters uniquely define the tilt as opposed to the tilt system introduced by Glazer (1972), where the magnitudes of the rotations depend on the order in which they are applied.

The method has been applied to transformations of *Pbnm*, *I*2/*c* and *Immm* structures corresponding to $a^-a^-c^+$, $a^-a^-c^-$ and $a^+b^+c^+$ tilting systems, respectively. Comparing the results of our analysis based on φ and θ tilting with Glazer's tilt systems allows the following relations to be obtained:

(i) Two equal rotations in Glazers notation (a^+a^+ or a^-a^-) correspond to the fixed direction of the tilt axis $\mathbf{R}_\delta$ (δ is fixed).

(ii) Three equal tilts in ($a^+a^+a^+$ and $a^-a^-a^-$) in $Im\bar{3}$ and $R\bar{3}c$ structures, respectively, can be interpreted as coupled φ and θ rotations.

(iii) Two in-phase a^+b^+ rotations correspond to the out-of-phase θ tilting of consecutive octahedra along [110] of the pseudo-cubic cell (Fig. 10), while two out-of-phase a^-b^- rotations correspond to in-phase θ tilting of consecutive octahedra along [110] of the pseudo-cubic cell (Figs. 4 and 6).

The proposed set of parameters allows analysis of structural transformations that arise from both octahedral tilt and octahedral deformations. As demonstrated for *Pbnm*, *I*2/*c* and *Immm* structures, the transformations between low- and high-symmetry structures correspond to tilt and octahedral parameters assuming special values in the high-symmetry phase. This allows the characterization of subgroup/supergroup relations in terms of the values of tilt and deformation parameters.

We suggest the following notation for structures with tilted and deformed octahedra: ($\theta^\pm$, $\varphi^\pm$, δ; G_O), where θ^+ or θ^- indicate a possible $\mathbf{R}_\delta(\theta)$ tilt of arbitrary magnitude θ and with in-phase (+) or out-of-phase (−) coupling in the direction of the X axis ([110] of the cubic perovskite lattice); φ^+ and φ^- are similarly defined for $\mathbf{Z}(\varphi)$ tilting. G_O is the point symmetry of the deformed BX_6 octahedral group with symmetry elements defined with respect to the Cartesian coordinates XYZ. A value of zero for θ, φ or δ is indicated by 0 in the corresponding place. Values of θ, φ and δ entirely determined by the octahedral parameters are indicated by $*$. Notice that this relation need not to be simple, for example, as in equation (3). In some cases θ and φ are related to each other [see (23) and (31)], which is indicated by $\theta{\sim}\varphi$. For example, *Pbnm* on a $2^{1/2}a_c \times 2^{1/2}a_c \times 2_c$ supercell (tilt system $a^-a^-c^+$) is denoted by (θ^+, φ^+, $*$; $\bar{1}$), $I4/mcm$ on a $2^{1/2}a_c \times 2^{1/2}a_c \times 2_c$ supercell (tilt system $a^oa^oc^-$) is denoted by (0, φ^-, 0; $4_z/m_z$) and $R\bar{3}c$ (tilt system $a^-a^-a^-$) is denoted by ($\theta^+{\sim}\varphi^-$, 0; $\bar{3}m$) in the new notation.

The tabulation of all ABX_3 structures is out of the scope of this paper, but the few examples in §3 already provide novel types of distorted ABX_3 structures. They include the structures with space group *Pmmm* on an $a_c \times a_c \times a_c$ lattice, and the structure with space group $P4/mmm$ on an

$2^{1/2}a_c \times 2^{1/2}a_c \times a_c$ lattice (§3.6), that both belong to the zero-tilt system, but that were not obtained from group–subgroup relations by Bock & Müller (2002).

The proposed method allows the possibility of a quantitative analysis of perovskite-related structures with distorted octahedra resulting from the octahedra tilting. The method will also be of interest in the study of the perovskites adopting different structures (for example, at different temperatures or with different compositions) and in the analysis of phase transitions.

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