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Group-Theoretical Analysis of Octahedral Tilting in Perovskites

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Abstract

A group-theoretical analysis is made of the structures derived from the aristotype cubic perovskite ($Pm\bar{3}m$) by the simple tilting of rigid octahedral units. The tilting is mediated by the irreducible representations R_4^+ and M_3^+ or the two in combination. These result in 15 possible structures, compared with the 23 possibilities suggested previously by Glazer [*Acta Cryst.* (1972), B**28**, 3384–3392]. The analysis makes the group–subgroup relationships apparent.

1. Introduction

Structures in the perovskite family ABX_3 have held the interest of crystallographers over many years (Kay & Bailey, 1957; Glazer, 1972, 1975; Megaw, 1973; Thomas, 1989, 1996; Burns & Glazer, 1990; Woodward, 1997*a*,*b*) and continue to attract a wider interest on account of their fascinating electrical and magnetic properties. Perovskite compounds exhibit ferroelectricity, piezoelectricity and non-linear optical behaviour (Newnham & Ruschau, 1991), and certain closely related compounds are famous as high-temperature cuprate superconductors (Cava *et al.*, 1987; Capponi *et al.*, 1987). The majority of materials displaying giant magnetoresistive effects are compounds with the perovskite structure (Gong *et al.*, 1995).

The ideal perovskite, being cubic, in space group $Pm\bar{3}m$, is a particularly simple structure, but it is also a demanding one, because, aside from the lattice parameter, there are no variable parameters in the structure. Consequently, the majority of perovskites are in fact distorted perovskites (hettotypes). Three different types of distortions have been identified (Megaw, 1973): distortions of the BX_6 octahedral units, B-cation displacements within the octahedra, and the tilting of the BX_6 octahedra relative to one another as practically rigid corner-linked units. The third type of distortion, octahedral tilting, is the most common type of distortion and forms the subject of this paper.

The most promising approach to the classification of perovskites with octahedral tilting is to consider first the possible tilting patterns and then to find the corresponding subgroups. This approach has been used by Glazer (1972), who developed a description of the different tilting patterns and then obtained space groups by inspection. We review Glazer's work, briefly, in the next section, because we shall make use of his notation in this paper. The group-theoretical analysis adopted in this paper and described in the third section is developed along similar lines. The different possible tilting patterns are first described by different vectors in a representation space and then for each tilting pattern (vector) the required space group is the *isotropy subgroup*, comprising the operations which leave that vector invariant.

The analysis yields a list of 15 possible space groups for perovskites derived through octahedral tilting. A connection is made to the (23) tilt systems given previously by Glazer (1972, 1975). The group–subgroup relationships are derived and displayed. It is interesting to note that all known perovskites based on octahedral tilting conform with the 15 space groups on our list, with the exception of one high-temperature structure which seems poorly determined.

2. Octahedral tilting

The ideal cubic perovskite is commonly visualized as a three-dimensional network of regular corner-linked BX_6 octahedra, the B cations being at the centres of these octahedra and the A cations being centrally located in the spaces between them. The tetrad axes of the octahedra coincide with the crystallographic cubic axes.

The majority of distorted perovskites are derived from the cubic aristotype by the practically rigid tilting of the octahedral units. By this we mean the tilting of octahedra around one or more of their symmetry axes, maintaining both the regularity of the octahedra (any distortions at most second order in the tilt angle) and their corner connectivity (strictly). Such tilting allows greater flexibility in the coordination of the A cation, while leaving the environment of the B cation essentially unchanged.

Glazer (1972) found it convenient to describe octahedral tilting in terms of component tilts around 'pseudo-cubic' axes, that is, the cubic axes of the aristotype. It becomes apparent that a tilt around one of

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these axes determines (*via* the corner connections) the tilts in directions perpendicular to this axis, but that successive octahedra along this axis can be tilted in either the same or opposite sense. Glazer describes the tilting using symbols of the type $a^{\#}b^{\#}c^{\#}$, in which the literals refer (in turn) to tilts around the [100], [010] and [001] directions of the aristotype, and the superscript # takes the value 0, + or − to indicate no tilt around an axis or tilts of successive octahedra in the same or opposite sense. Letters are repeated to indicate equal tilts around the different pseudo-cubic axes. Glazer's notation, which we use in this paper, is described at greater length in the original paper by Glazer (1972) and in the recent work by Woodward (1997*a*). Glazer drew out the different possible schemes for octahedral tilting and examined his results for lattice centring, and for other symmetry elements such as mirror planes and rotation axes. The subgroups were accordingly determined by inspection. 23 tilt systems were identified and classified in this way. We shall return to Glazer's (1972) results later.

3. Group-theoretical analysis

In line with Glazer (1972), we consider those simple tilt systems that can be described in terms of certain basic component tilts around the pseudo-cubic axes. These component tilts are each tilts around one axis only and repeat periods of more than two octahedra are specifically excluded. Allowing for tilting of successive octahedra along this axis in the same or opposite sense, and for tilting around any of the three pseudo-cubic axes, there are six basic component tilt systems. The tilt systems of interest then can be expressed to first order as linear combinations of these six component tilts. We recognize that the coefficients in this expression span a six-dimensional reducible representation of the parent space group $Pm\bar{3}m$, in fact, $M_3^+ \oplus R_4^+$. Finally, we use well established group-theoretical methods to identify, for each pattern of tilting, the isotropy subgroup, comprising those operations of the parent group that leave this pattern of tilts invariant. A similar approach has been used to obtain possible tilt systems in perovskite-like structures (Hatch & Stokes, 1987, 1988; Hatch *et al.*, 1989), but it has not hitherto been applied to the perovskites themselves.† The various steps are explained more fully in the paragraphs that follow.

Each of the tilt systems we wish to consider can be written as a superposition of the six component tilt systems just described. We write these component tilt systems as: $a^+b^0b^0$, $b^0a^+b^0$, $b^0b^0a^+$, $a^-b^0b^0$, $b^0a^-b^0$ and $b^0b^0a^-$. The notation owes much to Glazer, but for the moment we take all the tilts to be of the same (say 'unit') angle. We shall introduce different tilt angles later. The six basic component tilt systems form a set of basis functions $\{\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_6\}$. When an element g of the parent space group $G_0 = Pm\bar{3}m$ operates on any one of these basis functions, the result is some linear combination of these six basis functions (basic tilts)

$$g\varphi_i = \sum_{j=1}^{6} \varphi_j D(g)_{ji}.$$

For example, a 90° rotation about the z axis (denoted by $g = C_{4z}^+$) takes $a^{\pm}b^0b^0$ into $b^0a^{\pm}b^0$ and takes $b^0a^{\pm}b^0$ into $-a^{\pm}b^0b^0$ (clockwise tilt around the y axis becomes an anticlockwise tilt around the x axis), while leaving $b^0b^0a^{\pm}$ unchanged, so that

$$D(C_{4z}^+) = \begin{pmatrix} 0 & -1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}.$$

As another example, the translation by a distance a along the x axis (denoted by $g = \mathbf{a}_1$) takes $a^+b^0b^0$ into itself, but carries every other basis function into its own negative, the sign of the tilt around the y or z axis being reversed because of the corner-connectivity constraint. The matrix in this case is

$$D(\mathbf{a}_1) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}.$$

In this way every element $g \in G_0$ is mapped onto a matrix $D(g)$ and the set of matrices $D(g)$ form a representation of G_0.

The representation presented in the previous paragraph is reducible, since no element of g mixes the first three basis functions (corresponding to + tilt systems) with the last three (− tilt systems). In fact, this six-dimensional representation can be decomposed into two three-dimensional irreducible representations (irreps). With the aid of the computer program *ISOTROPY* (see Appendix *A*) and using the notation of Miller & Love (1967), we identify these two irreps as M_3^+ (carried by the basic + tilt systems) and R_4^+ (carried by the − tilt systems), and denote the six-dimensional reducible representation by the direct sum $M_3^+ \oplus R_4^+$. The distortions associated with irreps M_3^+ and R_4^+ correspond to the freezing of vibrations (phonons) with **k** vectors at high-symmetry points on the surface of the first Brillouin zone.

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† *Note added in proof:* The authors have recently become aware of an analysis of perovskites by Aleksandrov (1976) by methods somewhat similar to those described here. The results are similar but not identical to those given here.

Let us now define an 'order parameter' $\boldsymbol{\eta} = (\eta_1, \eta_2, \eta_3, \eta_4, \eta_5, \eta_6)$, where the component η_i is proportional to the tilt angle associated with the basis function φ_i. The order parameter specifies the linear combination of basis functions, which defines a particular tilt system. For example, the tilt system $a^0b^+c^-$ (Glazer's notation) is denoted by $\boldsymbol{\eta} = (0b000c)$. A tilt system φ can thus be written in the form

$$\varphi = \sum_i \eta_i \varphi_i.$$

An operation on φ by an element $g \in G_0$ results in

$$g\varphi = \sum_i \eta_i g\varphi_i = \sum_i \eta_i \sum_j \varphi_j D(g)_{ji}$$

$$= \sum_j \left[\sum_i D(g)_{ji} \eta_i \right] \varphi_j.$$

It now becomes possible to take the basis functions φ_i as fixed and consider the operation g to act on the order parameter $\boldsymbol{\eta}$ rather than on the basis functions φ_i. The equation for such an operation reads

$$g\eta_j = \sum_i D(g)_{ji} \eta_i$$

and it can be seen that the six-dimensional order-parameter space carries the representation $M_3^+ \oplus R_4^+$ of interest.

We are now in a position to obtain subgroups of G_0. Given a particular order parameter $\boldsymbol{\eta}$, the space group G of the corresponding tilt system comprises those elements $g \in G_0$ which keep $\boldsymbol{\eta}$ invariant, that is for which

$$g\boldsymbol{\eta} = \boldsymbol{\eta}.$$

Such a space group G is termed an isotropy subgroup of G_0. Group-theoretical methods for enumerating isotropy subgroups have been developed by Hatch and Stokes (Hatch, 1984; Stokes & Hatch, 1984, 1988; Hatch & Stokes, 1985, 1986, 1987, 1988), and have been implemented in *ISOTROPY*. The complete list of isotropy subgroups of $Pm\bar{3}m$ for the representation $M_3^+ \oplus R_4^+$ contains every possible tilt system that can be obtained from linear combinations of the six basis functions φ. This list, generated using *ISOTROPY*, consists of 25 distinct isotropy subgroups[†] in the present case. By distinct we mean subgroups which are not equivalent to each other. For example, the tilt systems $a^+b^0b^0$ and $b^0a^+b^0$ are equivalent since a 90° rotation about the z axis brings one into the other; they are merely different domains. The 25 distinct isotropy subgroups can be culled to 15 by considering only 'simple' tilt systems, in which the tilts around a particular axis have the same magnitude and either the same sign (the + pattern) or alternating signs (the − pattern). This restriction excludes, for example, the tilt system corresponding to $\boldsymbol{\eta} = (a00b00)$, for this would be superposition of the basic tilts $a^+b^0b^0$ and $a^-b^0b^0$, constituting a system in which the tilts around the x axis would differ in magnitude in addition to any difference of sign. In Table 1 we present the 15 possible space groups[†] obtained in our analysis.

Table 1 gives pertinent information on the perovskite structures resulting from octahedral tilting. In addition, group–subgroup relations can be obtained from it. These are of particular interest in the study of perovskites adopting different structures (for example, at different temperatures) and in the analysis of the phase transitions then occurring. The group–subgroup relations can be found from an examination of the order parameter $\boldsymbol{\eta}$. The order parameter in the different isotropy subgroups can be seen to span subspaces of the six-dimensional order-parameter space, for example, ($00c000$), ($0bb000$) and ($aaa000$) span one-dimensional subspaces, and ($abc000$) a three-dimensional subspace. An isotropy subgroup corresponding to order parameter $\boldsymbol{\eta}'$ will be a subgroup of that corresponding to order parameter $\boldsymbol{\eta}$ if (a) the dimension of the subspace spanned by $\boldsymbol{\eta}'$ is larger than that spanned by $\boldsymbol{\eta}$ and (b) $\boldsymbol{\eta}$ can be changed into $\boldsymbol{\eta}'$ by an infinitesimal change in its components. Referring to the four subspaces mentioned above, the three-dimensional subspace ($abc000$) contains each of the three one-dimensional subspaces ($00c000$), ($0bb000$) and ($aaa000$). It follows that $Immm$ is a subgroup of each of $P4/mbm$, $I4/mmm$ and $Im\bar{3}$. The group–subgroup relations for the tilt systems in Table 1 are shown schematically in Fig. 1. Note that in some cases the group–subgroup relation does not actually apply to the particular domains shown in the figure. For example, $a^0b^+c^-$ is not a subgroup of $a^0a^0c^+$; it is a subgroup of $a^0b^+a^0$, which is another domain of $a^0a^0c^+$. Fig. 1 also shows which phase transitions between group–subgroup pairs are required to be first order by

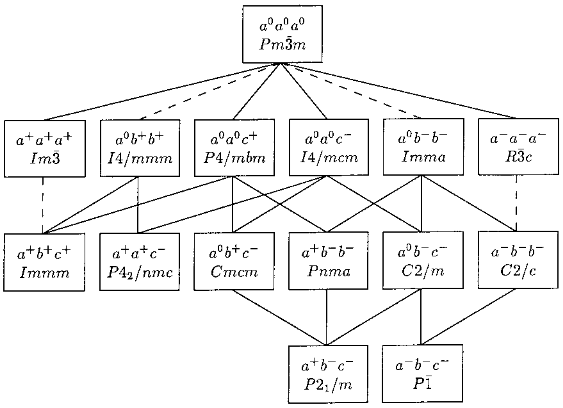

Fig. 1. A schematic diagram indicating the group–subgroup relationships among the 15 space groups of Table 1. A dashed line joining a group with its subgroup indicates that the corresponding phase transition is required by Landau theory to be first order.

[†] Including the space group $Pm\bar{3}m$ of the aristotype itself.

Table 1. *Isotropy subgroups of* $Pm\bar{3}m$ *for the representation* $M_3^+ \oplus R_4^+$

For each subgroup we give the order parameter $\boldsymbol{\eta}$, the tilt system using the notation of Glazer (1972, 1975; and Glazer's sequence number) and the space-group symmetry (and number), along with its lattice vectors (in terms of the lattice vectors of $Pm\bar{3}m$) and its origin (in terms of the lattice vectors of $Pm\bar{3}m$ with respect to the origin of $Pm\bar{3}m$). The lattice vectors and origins are given for the conventional settings of space groups in *International Tables for Crystallography* (Hahn, 1983). The hexagonal setting is used for $R\bar{3}c$. The second origin choice is used for $P4_2/nmc$. The setting with unique axis *b*, cell choice 1, is used for the monoclinic space groups.

$\boldsymbol{\eta}$	Tilts	Space group	Lattice vectors	Origin
(000000)	$a^0a^0a^0$ (#23)	$Pm\bar{3}m$ (#221)	(100), (010), (001)	(000)
(00*c*000)	$a^0a^0c^+$ (#21)	$P4/mbm$ (#127)	(110), $(\bar{1}10)$, (001)	(000)
(0*bb*000)	$a^0b^+b^+$ (#16)	$I4/mmm$ (#139)	(020), (002), (200)	$(\frac{1}{2}\frac{1}{2}\frac{3}{2})$
(*aaa*000)	$a^+a^+a^+$ (#3)	$Im\bar{3}$ (#204)	(200), (020), (002)	$(\frac{1}{2}\frac{1}{2}\frac{1}{2})$
(*abc*000)	$a^+b^+c^+$ (#1)	$Immm$ (#71)	(200), (020), (002)	$(\frac{1}{2}\frac{1}{2}\frac{1}{2})$
(00000*c*)	$a^0a^0c^-$ (#22)	$I4/mcm$ (#140)	(110), $(\bar{1}10)$, (002)	(000)
(0000*bb*)	$a^0b^-b^-$ (#20)	$Imma$ (#74)	(011), (200), $(01\bar{1})$	(000)
(000*aaa*)	$a^-a^-a^-$ (#14)	$R\bar{3}c$ (#167)	$(\bar{1}10)$, $(0\bar{1}1)$, (222)	(000)
(0000*bc*)	$a^0b^-c^-$ (#19)	$C2/m$ (#12)	$(0\bar{2}0)$, (200), (011)	$(\frac{1}{2}\frac{1}{2}0)$
(000*abb*)	$a^-b^-b^-$ (#13)	$C2/c$ (#15)	$(2\bar{1}\bar{1})$, $(01\bar{1})$, (011)	$(\frac{1}{2}\frac{1}{2}0)$
(000*abc*)	$a^-b^-c^-$ (#12)	$P\bar{1}$ (#2)	(011), (101), (110)	(000)
(0*b*000*c*)	$a^0b^+c^-$ (#17)	$Cmcm$ (#63)	(200), $(00\bar{2})$, (020)	$(\frac{1}{2}0\frac{1}{2})$
(*a*000*bb*)	$a^+b^-b^-$ (#10)	$Pnma$ (#62)	(011), (200), $(01\bar{1})$	(000)
(*a*000*bc*)	$a^+b^-c^-$ (#8)	$P2_1/m$ (#11)	$(0\bar{1}1)$, (200), (011)	(000)
(*aa*000*c*)	$a^+a^+c^-$ (#5)	$P4_2/nmc$ (#137)	(200), (020), (002)	$(00\bar{1})$

the Landau theory of phase transitions (Landau & Lifshitz, 1980). We obtained this information for each of the group–subgroup pairs using *ISOTROPY*.

4. Discussion

4.1. *Comparison with previous results*

In comparing our results in Table 1 with those from Glazer (1972, 1975), the first point to note is that our group-theoretical analysis gives only 15 tilt systems compared with Glazer's 23. Woodward (1997*a*) lists the same 23 tilt systems as Glazer. The reason that the eight extra tilt systems are not on our list is that each of them has higher symmetry than required by the corresponding space group. Of course, in listing only 15 distinct space groups in his tables, Glazer was fully aware of this fact.

For example, tilt system $a^0b^+b^-$ (#18), with equal tilts around *y* and *z* axes, has space-group symmetry *Cmcm*. This is the same space-group symmetry as tilt system $a^0b^+c^-$ (#17), in which the tilt angles around the *y* and *z* axes are not equal. However, there is no operation in this space group which changes tilts around the *y* axis into tilts around the *z* axis, so the space-group symmetry does *not* require the tilt angles around the *y* and *z* axes to be equal. Furthermore, the tilt patterns that dictate the orthorhombic symmetry will also result in interatomic forces which produce *different* tilt angles around the *y* and *z* axes. A real crystal may actually exhibit an $a^0b^+c^-$ tilt pattern where the two tilt angles denoted by *b* and *c* are almost equal, but they cannot be *exactly* equal. Therefore, the tilt system $a^0b^+b^-$ will never be observed in any real crystal and should not appear in a list of possible tilt systems of the perovskite structure. The same consideration applies to tilt systems $a^+b^+b^+$ (#2) and $a^0b^+c^+$ (#15), which have the same symmetry as $a^+b^+c^+$ (#1), tilt system $a^+a^-c^-$ (#9), which has the same symmetry as $a^+b^-c^-$ (#8), and tilt system $a^+a^-a^-$ (#11), which has the same symmetry as $a^+b^-b^-$(#10). It is interesting to note that in a detailed analysis of tilt systems $a^+a^+a^+$, $a^-a^-a^-$, $a^+a^+a^-$ and $a^+a^-a^-$, O'Keeffe & Hyde (1977) ruled out $a^+a^+a^-$ and $a^+a^-a^-$ on geometrical grounds.

A different problem arises with tilt system $a^+b^+c^-$ (#4), along with tilt systems $a^+b^+b^-$ (#6) and $a^+a^+a^-$ (#7), which are shown with space-group symmetry *Pmmn*. This space group does not appear in the list of Table 1. However, we do find this space group on our *complete* list of isotropy subgroups. The order parameter for *Pmmn* is $\boldsymbol{\eta} = (abc00d)$. We culled this subgroup from our list because of the presence of both + and − tilt patterns around the *z* axis. In other words, the space-group symmetry of $a^+b^+c^-$ also allows a + tilt pattern along the *z* axis. This means that the tilt patterns that dictate the *Pmmn* symmetry will also result in interatomic forces which produce tilt angles around the *z* axis, which *may* alternate in sign but *must* differ in magnitude. A real crystal could only approximately exhibit the $a^+b^+c^-$ tilt pattern. Neither could the tilt systems with equal angles, $a^+b^+b^-$ and $a^+a^+a^-$, be physically realized. As we are only considering crystal structures which exhibit *exact* + or − tilt patterns, $a^+b^+c^-$ and the other tilt systems in *Pmmn* have been omitted from our list.

There are two more differences between our results and those of Glazer (1972). First, we find the space group for tilt system $a^0b^+b^+$ (#16) to be *I*4/*mmm*, in agreement with the space group as corrected by Glazer

(1975). Secondly, we find the space group for tilt system $a^+a^+c^-$ (#5) to be $P4_2/nmc$ rather than *Pmmn*. Leinenweber & Parise (1995) also concluded that this system is correctly described in $P4_2/nmc$. They do not give their argument in full, but the space group is presumably assigned by inspection of the symmetry elements, in the manner of Glazer's original work. Woodward (1997*a*) asserts that the $a^+a^+c^-$ tilt system cannot be produced by rigid rotations of the octahedra (see §4.3). The corner-linking requires distortion of the octahedra. The space-group symmetry depends on how the octahedra are distorted. He concludes that actual compounds probably crystallize in $P4_2/nmc$, the more symmetric of the available space groups. In addition, we note that Glazer's space-group symmetry *Pmmn* does not require the tilt angles around the *x* and *y* axes to be equal and also, as discussed above, allows a + tilt pattern around the *z* axis to be superimposed on the − tilt pattern around the same axis.

4.2. *The known perovskite structures*

In this section we consider the extent to which the experimentally determined structures of perovskites with octahedral tilting are in accord with the scheme given in Table 1. Fortunately, for this purpose, the perovskite literature has been reviewed recently by Woodward (1997*b*) and we base our comments entirely on the results of his review. Woodward focused on finding perovskites in the less common tilt systems and his literature search for examples of these was very thorough.

Woodward (1997*b*) records the results of his literature survey in the form of a tabulation (Tables 2 and 3 in his paper) of known examples of the different tilt systems. A number of interesting observations can be made by examining Woodward's tables, for example, the preponderance of perovskites in space group *Pnma* (tilt system $a^+b^-b^-$), which is the structure adopted by the mineral perovskite, $CaTiO_3$, itself. It is of greater interest in the context of this work to note which tilt systems are observed and which are not. An examination of Woodward's tables reveals that examples in 12 of our 15 space groups have been reported to date – only for I4/*mmm, Immm* and *C2/c* are examples yet to be found.

The only structure which appears not to fit our scheme is that reported for $NaNbO_3$, in the temperature range 753–793 K. This structure has been given as $a^+b^+c^-$, space group *Pmmn*, by Ahtee *et al.* (1972), largely on the evidence of the X-ray lattice parameters. The structure was taken to be orthorhombic, with unequal pseudo-cubic subcell parameters, and the structure was assigned on this basis, even though the intensities (specifically the absences) were *not* accounted for by this assignment. We speculate that the structure might be monoclinically distorted and more accurately described in space group $P2_1/m$.

We emphasize that, except for the one possibly dubious exception noted just above, every experimentally determined tilt system found by Woodward's (1997*b*) literature search is on our list of isotropy subgroups in Table 1. The tilt systems of Glazer which have been omitted from Table 1 have not been experimentally observed.

4.3. *Octahedral distortions*

The tilting of octahedra might be accompanied by slight distortions, although we have already decreed that the differences from regular octahedra should be at most second order in the tilt angle. Woodward (1997*a*) has discussed these distortions at some length, on the basis of computer calculation of coordinates, and has concluded that distortions of BX_6 octahedra are geometrically necessary in tilt systems $a^0b^+c^-$ (#17) in *Cmcm*, $a^+a^+c^-$ (#5) in $P4_2/nmc$ and in certain other tilt systems which appear in Glazer's work, but not in ours. The question of small distortions of the octahedra is not central to this work. However, since there appears to be some problem with Woodward's analysis, we take the opportunity to address it here.

In the aristotype perovskite, in $Pm\bar{3}m$, the octahedra are necessarily regular. All the hettotypes allow distortions and, in general, we expect them, although the geometry may not require them. The simple tilt system $a^0a^0c^+$ (#21) in *P*4/*mbm* is an example of a system which permits octahedral distortions, but does not necessitate them. If we suppose the octahedra are rotated by the angle φ around the *z* axis [refer to Fig. 1*b* in Woodward's (1997*a*) paper], then it can be seen that the octahedra will be regular provided $a/c = \cos\varphi(2^{1/2})$. If the ratio *a*/*c* differs from this (and it cannot be expected to have exactly this value), then the octahedra will be either axially elongated or compressed. This result, obtained here by inspection, can be confirmed by the methods to be outlined below. The tilt system $a^0a^0c^-$ (#22) in *I*4/*mcm* can be considered in a similar way.

We have systematically examined all the 15 tilt systems in Table 1. For each system we have first written down the coordinates of the *B* cation and of three neighbouring *X* anions which define the octahedron about *B*. (In every case the *B* cation is at a centre of inversion.) From these coordinates, we write down in fractional crystallographic coordinates the three (at least notionally) orthogonal *BX* vectors which define the octahedron. Taking account of the lattice parameters, these three vectors can be written in terms of rectangular Cartesian coordinates. We then consider whether and under what conditions the three vectors defining the octahedron can be orthogonal and of equal length. In some cases the solution has been assisted by examining whether the three vectors can be expressed in the form

$$\begin{aligned}\boldsymbol{v}_1 &= (D\cos\psi\cos\varphi - D\cos\theta\sin\varphi\sin\psi,\\ &\quad -D\sin\psi\cos\varphi - D\cos\theta\sin\varphi\cos\psi,\\ &\quad D\sin\theta\sin\varphi)\\ \boldsymbol{v}_2 &= (D\cos\psi\sin\varphi + D\cos\theta\cos\varphi\sin\psi,\\ &\quad -D\sin\psi\sin\varphi + D\cos\theta\cos\varphi\cos\psi,\\ &\quad -D\sin\theta\cos\varphi)\\ \boldsymbol{v}_3 &= (D\sin\psi\sin\theta, D\cos\psi\sin\theta, D\cos\theta)\end{aligned}$$

obtained by rigid rotation, through the Euler angles φ, θ and ψ (Goldstein, 1965), of the vectors (D,0,0), (0,D,0) and (0,0,D). Since the vectors (D,0,0), (0,D,0), (0,0,D) define a regular octahedron, with $B{-}X$ separation D, so do the vectors $\boldsymbol{v}_1$, $\boldsymbol{v}_2$ and $\boldsymbol{v}_3$. We give two examples of our analysis below.

For the case of tilt system $a^0b^+c^-$ (#17) in *Cmcm*, we consider the cation B at $(\frac{1}{4},\frac{1}{4},0)$ and the neighbouring X anions at $(\frac{1}{2}-x,\frac{1}{2},0)$ with $x \simeq \frac{1}{4}$, at $(\frac{1}{2},\frac{1}{2}-y,z)$ with $y \simeq \frac{1}{4}$ and $z \simeq 0$, and $(x,y,\frac{1}{4})$ with $x \simeq \frac{1}{4}$ and $y \simeq \frac{1}{4}$. The three $B{-}X$ vectors, in fractional coordinates, are $(\frac{1}{4}-x,\frac{1}{4},0)$ with $x \simeq \frac{1}{4}$, $(\frac{1}{4},\frac{1}{4}-y,z)$ with $y \simeq \frac{1}{4}$ and $z \simeq 0$, and $(x-\frac{1}{4},y-\frac{1}{4},\frac{1}{4})$ with $x \simeq \frac{1}{4}$ and $y \simeq \frac{1}{4}$. Multiplying the fractional coordinates by the relevant lattice parameters transforms these fractional coordinates to Cartesian coordinates. With obvious abbreviations, then the three $B{-}X$ vectors are $(a/4,\varepsilon_1,\varepsilon_2)$, $(\varepsilon_3,b/4,0)$, $(\varepsilon_4,\varepsilon_5,c/4)$. The variables ε_i are defined so that they are zero when the tilt angles are zero. The symmetry of *Cmcm* allows each of the variables ε_i to take on any value. The problem now is to determine values of a, b, c, ε_1, ε_2, ε_3, ε_4 and ε_5 which make these vectors orthogonal and of equal length. This is equivalent to identifying these vectors with $\boldsymbol{v}_1$, $\boldsymbol{v}_2$ and $\boldsymbol{v}_3$. A solution is found by setting $\varphi = -\pi/2$. We obtain $a = 4D\cos\theta\sin\psi$, $b = 4D\sin\psi$, $c = 4D\cos\theta$, $\varepsilon_1 = D\cos\theta\cos\psi$, *etc.* By these means we find a regular octahedron in tilt system $a^0b^+c^-$, a system in which, according to Woodward (1997*a*), the octahedra are necessarily distorted.[†]

In the case of tilt system $a^+a^+c^-$ (#5) in $P4_2/nmc$, we consider the cation B at (0,0,0) and the neighbouring anions X at $(\frac{1}{4},y,z)$ with $y \simeq 0$ and $z \simeq 0$, at $(\frac{1}{2}-y,\frac{1}{4},z-\frac{1}{2})$ with $y \simeq \frac{1}{2}$ and $z \simeq \frac{1}{2}$, and at $(\frac{1}{2}-x,x-\frac{1}{2},\frac{1}{4})$ with $x \simeq \frac{1}{2}$. Since the B atom is at the origin, the anion positions also represent the $B{-}X$ vectors in the octahedron. Multiplying fractional coordinates by the relevant lattice parameters, and abbreviating as above, gives for the three $B{-}X$ vectors $(a/4,\varepsilon_1,\varepsilon_2)$, $(\varepsilon_3,a/4,\varepsilon_4)$ and $(\varepsilon_5,-\varepsilon_5,c/4)$. The question again is whether we can find values for a, b, c, ε_1, ε_2, ε_3, ε_4 and ε_5 which make these vectors orthogonal and of equal length. We attempt to identify these vectors with $\boldsymbol{v}_1$, $\boldsymbol{v}_2$ and $\boldsymbol{v}_3$. Identifying the third of our vectors here with $\boldsymbol{v}_3$ implies $\cos\psi = -\sin\psi$, that is $\psi = -\pi/4$. It is then necessary to equate the components with values $a/4$, leading to $\cos\varphi + \cos\theta\sin\varphi = \sin\varphi + \cos\theta\cos\varphi$, implying either $\cos\varphi = \sin\varphi$, $\varphi = \pi/4$ or $\cos\theta = 1$, $\theta = 0$. Both these solutions are valid, but neither represents the tilt system we have assumed. The first, corresponding to Euler rotations $\varphi = \pi/4$, θ, $\psi = -\pi/4$, represents a rotation of the octahedron around [110], and the second, corresponding to the rotations φ, $\theta = 0$, $\psi = -\pi/4$, represents a simple rotation about the z axis. We conclude that the tilt system $a^+a^+c^-$ (#5), in $P4_2/nmc$ and requiring two independent tilt angles, cannot be realized without octahedral distortion.

As already mentioned, the octahedra in the aristotype perovskite are necessarily regular. We find that the only tilt system in which the octahedra are necessarily distorted, on geometrical grounds, is the system $a^+a^+c^-$ (#5), for which two independent tilts must be accommodated in the tetragonal symmetry of $P4_2/nmc$. Departures from regularity are not necessary in the other tilt systems, but are allowed by the space-group symmetry and certainly expected.

5. Summary

Group-theoretical methods have been applied to the classification of perovskites with octahedral tilting. The analysis leads to 15 simple, distinct, tilt patterns. The space groups and other pertinent data have been recorded in Table 1. The group–subgroup relationships have been derived and are shown in Fig. 1.

In previous studies, Glazer (1972, 1975) and, more recently, Woodward (1997*a*) have given 23 possible tilt systems. The eight tilt systems missing from our list have higher symmetry than the corresponding space groups. Corrections to space groups proposed by Glazer (1975) and Leinenweber & Parise (1995) have been confirmed.

The known perovskites based on octahedral tilting conform with the 15 patterns on our list, with the exception of one high-temperature structure which may warrant further investigation.

The question as to whether octahedral distortion is associated with octahedral tilting has been considered. In the ideal perovskite the octahedra are required to be regular. Among the perovskites with tilted octahedra we find only one system in which the octahedra are necessarily distorted. Departures from regularity are possible and indeed expected in the other systems, but not required by the geometry.

We are hopeful that the data on tilt systems presented in Table 1, and the group–subgroup relationships shown schematically in Fig. 1, will prove to be of assistance to those studying perovskite structures and the transformations between them.

APPENDIX *A*

ISOTROPY is a computer program which applies group-theoretical methods to the analysis of crystal

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[†] Woodward (private communication) now agrees with our analysis of distortions in this tilt system.

Table 2. *Modes of the irrep M_3^+: rotations centred on the B atoms*

In the first column are the coordinates of the positions of the *B* atoms inside a cell, $2a \times 2a \times 2a$. Coordinates are given in terms of the lattice vectors of the cubic parent space group. For each mode, the relative coordinates of the rotation vector for each position are given.

Position	Mode 1	Mode 2	Mode 3
(0,0,0)	(0,0,1)	(1,0,0)	(0,1,0)
(0,0,1)	(0,0,1)	(−1,0,0)	(0,−1,0)
(0,1,0)	(0,0,−1)	(−1,0,0)	(0,1,0)
(0,1,1)	(0,0,−1)	(1,0,0)	(0,−1,0)
(1,0,0)	(0,0,−1)	(1,0,0)	(0,−1,0)
(1,0,1)	(0,0,−1)	(−1,0,0)	(0,1,0)
(1,1,0)	(0,0,1)	(−1,0,0)	(0,−1,0)
(1,1,1)	(0,0,1)	(1,0,0)	(0,1,0)

symmetry, particularly the changes in symmetry that may occur in a phase transition.† We indicate here how the results presented in this paper are obtained using *ISOTROPY*.

First, *ISOTROPY* can calculate crystalline distortions that have the symmetry of a given irrep. These distortions can be macroscopic, such as strains, or microscopic, such as atomic displacements or molecular rotations. The group-theoretical methods for calculating microscopic distortions have been explained by Stokes *et al.* (1991). In this case we are looking for irreps which produce tilt patterns which are rotations about the *B* atoms. We specify the parent space group #221 and the Wyckoff position (*a*). We also specify that we only want to consider the irreps for **k** vectors at the points of symmetry, Γ, *R*, *X* and *M* for this space group. For each irrep, *ISOTROPY* displays all the modes involving rotations about the *B* atoms. *ISOTROPY* finds 24 modes, three from each of the three-dimensional irreps, Γ_4^+, R_4^+, X_3^+, M_3^+, and six from each of the six-dimensional irreps, X_5^+, M_5^+.

Shown in Table 2, as an example of the information displayed by *ISOTROPY*, are the three modes associated with M_3^+. Mode 1 consists of rotations about the *z* axis. From the table we see that the octahedron at (0,0,0) is tilted in the $+z$ direction. The octahedron at (0,0,1) is tilted in the same direction, whereas the octahedra at (1,0,0) and (0,1,0) are tilted in the opposite direction. Evidently, this is the $b^0b^0a^+$ tilt pattern.

From a similar inspection of the other modes in this table, and of modes associated with other irreps, we identify the three M_3^+ modes to be the $b^0b^0a^+$, $a^+b^0b^0$, $b^0a^+b^0$ tilt patterns and the three R_4^+ modes to be the $b^0b^0a^-$, $a^-b^0b^0$, $b^0a^-b^0$ tilt patterns. The other 18 modes found by *ISOTROPY* are rejected because they do not maintain corner connectivity.

Once the irreps are known, we can obtain a list of isotropy subgroups from *ISOTROPY*. This is how we obtained the information presented in Table 1. The group-theoretical methods for obtaining the isotropy subgroups have been explained in greater detail by Hatch & Stokes (1986). The algorithm for identifying the space-group symmetry of each isotropy subgroup has been discussed by Hatch & Stokes (1985). A complete list of isotropy subgroups for irreps at **k** points of symmetry for each of the 230 space groups has been given by Stokes & Hatch (1988). The first 11 isotropy subgroups in Table 1 can be found in this reference. The remaining four isotropy subgroups in Table 1 involve more than one irrep at the same time and must be calculated using *ISOTROPY*.

In addition, *ISOTROPY* can also calculate the Wyckoff positions of the atoms in each isotropy subgroup (given their Wyckoff positions in the parent group). This information for the current case has been tabulated by Woodward (1997*a*) in his Table 5.

Each of the group–subgroup relations shown in Fig. 1 represents a possible phase transition involving a single irrep, which can be found in the work of Stokes & Hatch (1988), or more easily by using *ISOTROPY*. For example, the transition from *I*4/*mmm* to $P4_2/nmc$ involves a distortion which has the symmetry of the irrep M_4^- of *I*4/*mmm*. This is a one-dimensional irrep with matrices (1) and (−1). The Landau theory of phase transitions (Landau & Lifshitz, 1980) allows this transition to be continuous (second order). We have identified the irrep associated with each group–subgroup relation in Fig. 1 and have determined whether the Landau theory allows the transition to be continuous. (This information is included in the tables of isotropy subgroups presented by Stokes & Hatch, 1988, and can also be obtained using *ISOTROPY*.) We found that four of the transitions (those indicated by dashed lines in Fig. 1) are not allowed to be continuous.

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References

Ahtee, M., Glazer, A. M. & Megaw, H. D. (1972). *Philos. Mag.* **26**, 995–1014.

Aleksandrov, K. S. (1976). *Ferroelectrics*, **14**, 801–805.

Burns, G. & Glazer, A. M. (1990). *Space Groups for Solid State Scientists*, 2nd ed. Boston: Academic Press.

Capponi, J. J., Chaillout, C., Hewat, A. W., Lejay, P., Marezio, M., Nguyen, N., Raveau, B., Soubeyroux, J. L., Tholence, J. L. & Tournien, R. (1987). *Europhys. Lett.* **3**, 1301–1307.

Cava, R. J., van Dover, R. B., Batlogg, B. & Rietman, E. A. (1987). *Phys. Rev. Lett.* **58**, 408–410.

Glazer, A. M. (1972). *Acta Cryst.* B**28**, 3384–3392.

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† *ISOTROPY* is a software package developed by Stokes and Hatch at Brigham Young University. *ISOTROPY* is available at www.physics.byu.edu/~stokesh/isotropy.html.

Glazer, A. M. (1975). *Acta Cryst.* A**31**, 756–762.

Goldstein, H. (1965). *Classical Mechanics*, pp. 107–109. Reading: Addison-Wesley.

Gong, G.-Q., Canedy, C., Xiao, G., Sun, J. Z., Gupta, A. & Gallagher, W. J. (1995). *Appl. Phys. Lett.* **67**, 1783–1785.

Hahn, Th. (1983). Editor. *International Tables for Crystallography*, Vol. A. Dordrecht: Reidel Publishing. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Hatch, D. M. (1984). *Lecture Notes in Physics*, edited by G. Denardo, G. Ghirardi & T. Weber, pp. 390–393. New York: Springer.

Hatch, D. M. & Stokes, H. T. (1985). *Phys. Rev. B*, **31**, 2908–2912.

Hatch, D. M. & Stokes, H. T. (1986). *Computer Modelling of Phase Diagrams*, edited by L. H. Bennett, pp. 145–162. Warrendale: Metallurgical Society.

Hatch, D. M. & Stokes, H. T. (1987). *Phys. Rev. B*, **35**, 8509–8516.

Hatch, D. M. & Stokes, H. T. (1988). *Phys. Rev. B*, **36**, 7185.

Hatch, D. M., Stokes, H. T., Aleksandrov, K. S. & Misyul, S. V. (1989). *Phys. Rev. B*, **39**, 9282–9288.

Kay, H. F. & Bailey, P. C. (1957). *Acta Cryst.* **10**, 219–226.

Landau, L. D. & Lifshitz, E. M. (1980). *Statistical Physics*, 3rd ed., ch. XIV. New York: Pergamon Press.

Leinenweber, K. & Parise, J. (1995). *J. Solid State Chem.* **114**, 277–281.

Miller, S. C. & Love, W. F. (1967). *Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups*. Boulder: Preutt.

Megaw, H. D. (1973). *Crystal Structures – A Working Approach*. Philadelphia: W. B. Saunders.

Newnham, R. E. & Ruschau, G. R. (1991). *J. Am. Ceram. Soc.* **74**, 463–480.

O'Keeffe, M. & Hyde, B. G. (1977). *Acta Cryst.* B**33**, 3802–3813.

Stokes, H. T. & Hatch, D. M. (1984). *Phys. Rev. B*, **30**, 4962–4967.

Stokes, H. T. & Hatch, D. M. (1988). *Isotropy Subgroups of the 230 Crystallographic Space Groups*. Singapore: World Scientific.

Stokes, H. T., Hatch, D. M. & Wells, J. D. (1991). *Phys. Rev. B*, **43**, 11010–11018.

Thomas, N. W. (1989). *Acta Cryst.* B**45**, 337–344.

Thomas, N. W. (1996). *Acta Cryst.* B**52**, 16–31.

Woodward, P. M. (1997*a*). *Acta Cryst.* B**53**, 32–43.

Woodward, P. M. (1997*b*). *Acta Cryst.* B**53**, 44–66.

Coupling of the lactone-ring conformation with crystal symmetry in 6-hydroxy-4,4,5,7,8-pentamethyl-3,4-dihydrocoumarin. Erratum

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In the paper by Budzianowski & Katrusiak (2002) *Acta Cryst.* (2002), B**58**, 125–133 Figs. 5 and 8 on pages 131 and 132 were transposed while adjusting colour details indicated by the authors in the proof. Revised PDF versions of these pages are available in the online version of this erratum, which is available through **Crystallography Journals Online**.

Two fluoradene derivatives: pseudosymmetry, eccentric ellipsoids and a phase transition. Erratum

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Numerous printing errors in the paper by Xia *et al.* [*Acta Cryst.* (2001), B**57**, 507–516] are corrected.

In the paper by Xia *et al.* (2001) a number of special characters (′, λ, Å, σ, Δ, ö) were omitted in the printed and PDF versions of the article; the HTML version, however, was correct. The corrected version of the paper is now available from **Crystallography Journals Online**.

References

Xia, A., Selegue, J. P., Carrillo, A., Patrick, B. O., Parkin, S. & Brock, C. P. (2001). *Acta Cryst.* B**57**, 507–516.

Group-Theoretical Analysis of Octahedral Tilting in Perovskites. Erratum

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An error has been noted within Fig. 1 of the paper by Howard & Stokes (1998). There is a group–subgroup relationship between $I4/mcm$ ($a^0a^0c^-$) and $C2/c$ ($a^-b^-b^-$), and this should be indicated on the figure by a continuous line joining the corresponding boxes. The corrected version of the figure is shown here.

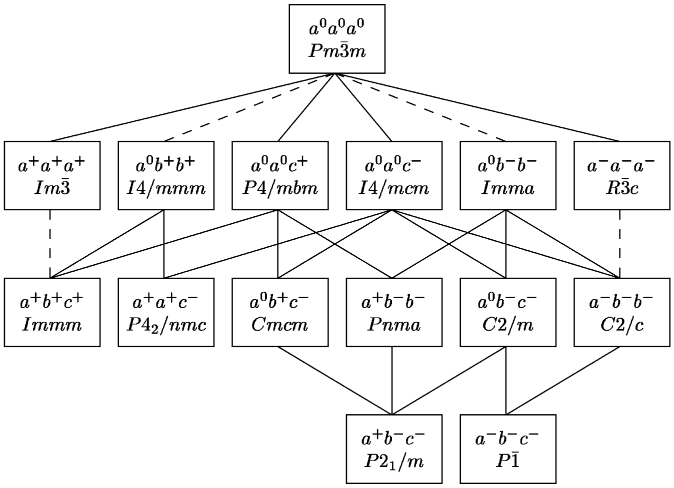

Figure 1
A schematic diagram indicating the group–subgroup relationships among the 15 space groups tabulated by Howard & Stokes (1998). A dashed line joining a group with its subgroup indicates that the corresponding phase transition is required by Landau theory to be first order.

References

Howard, C. J. & Stokes, H. T. (1998). *Acta Cryst.* B**54**, 782–789.