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Octahedral tilting in the tungsten bronzes. Addendum.

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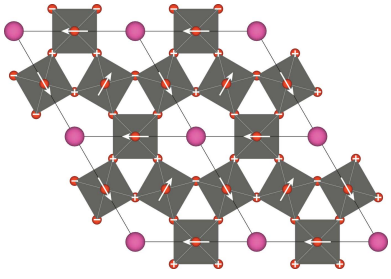
The studies of octahedral tilting in the tungsten bronzes [Whittle *et al.* (2015). *Acta Cryst.* B**71**, 342–348] were continued in the context of a more general approach to cooperative rotations of interconnected rigid units [Campbell *et al.* (2018). *Acta Cryst.* A**74**, 408–424]. That more general approach has detailed possible structures not identified in our 2015 paper. A brief comment on the implications of finite tilts for octahedral distortion is included.

In a recent paper on the tungsten bronzes (Whittle *et al.*, 2015) we attempted to enumerate the possibilities for tilting of the WO_6 octahedra in the hexagonal and tetragonal tungsten bronzes. There is no reason to doubt the structures we presented there. It soon became apparent, however, that at least in the case of tetragonal tungsten bronze (TTB) we had missed a number of acceptable tilt structures. Recall that TTB has a starting structure in space group *P*4/*mbm*, and that from searches at all the special points of the Brillouin zone we reported finding only one acceptable tilt system, at the *A*-point ($\boldsymbol{k} = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). Through a subsequent analysis of TTB using the computer program *CRUSH* (Giddy *et al.*, 1993), and from a paper (Smirnov & Saint-Grégoire, 2014) of which regrettably we were unaware until our work was in print, we realized that we should have found tilt systems at the *Z*- and *R*-points ($\boldsymbol{k} = 0, 0, \frac{1}{2}$ and $\boldsymbol{k} = 0, \frac{1}{2}, \frac{1}{2}$) as well.

Many of the arguments presented in our previous paper were sound. For example we argued that tilting around the unique (z) axis was not possible for three octahedra corner-linked around a triangular channel. It followed that the only possible tilting would be around axes in the horizontal (x–y) planes. Any tilting around axes in a horizontal layer implied tilting in the reverse sense around layers above and below. This meant there must be a doubling of the c parameter and so we needed to consider only those (special) points of the Brillouin zone with $k_z = \frac{1}{2}$. For HTB, with parent symmetry *P*6/*mmm*, these are the *A*-, *H*- and *L*-points ($\boldsymbol{k} = 0, 0, \frac{1}{2}$, $\boldsymbol{k} = \frac{1}{3}, \frac{1}{3}, \frac{1}{2}$ and $\boldsymbol{k} = \frac{1}{2}, 0, \frac{1}{2}$) while for TTB they are the *Z*-, *A*- and *R*-points already mentioned. The *ISOTROPY* computer program (Stokes *et al.*, 2014) was used to list the irreducible representations (irreps[1]) at each of those points leading to tilting of the octahedra centred on the W atoms, these atoms being on Wyckoff 3*f* in HTB or on 2*d* and 8*i* in TTB. Irreps implying tilting of the octahedra around the z axis were immediately eliminated, which in the case of TTB for example left for consideration only Z_5^+, A_5^- and R_1. But the examination of



[1] The notation of Miller & Love (1967) is employed here.

tilting possibilities corresponding to multidimensional irreps was far from straightforward: our somewhat *ad hoc* searches, involving the choice of amplitudes of perhaps six or more modes of distortion,[2] proved to be wanting. It is for this reason that acceptable structures were missed.

At this point we began collaboration with a team at Brigham Young University to devise a systematic approach to the tilting problem, the result of which has just been published (Campbell *et al.*, 2018). In this approach we calculated the effects of tilting around any 'pivot' atom on the atoms influenced (displaced) by this tilting, these atoms being called 'passenger' atoms. An atom influenced by tilting around more than one pivot atom was a shared atom, and the sharing of this atom defined a set of constraints. By restricting to infinitesimal tilting angles we linearized the equations of constraint, reducing the tilting problem to a problem in linear algebra. We used group-theoretical techniques to represent the problem in terms of symmetry-mode amplitudes rather than individual rotation angles.

We used this new approach to re-examine the possible tilting patterns in the tungsten bronzes (Campbell *et al.*, 2018). For HTB we found structures associated with irreps A_3^+, A_6^+ and L_2^- – for detail see Tables 3 and 4, Figs. 1, 2 and 3, and supporting information in Campbell *et al.* (2018). There were tilting patterns, particularly those associated with irrep A_6^+, that were missed in our earlier work (Whittle *et al.*, 2015). For TTB we found structures associated with all of the irreps Z_5^+, A_5^- and R_1 – see Tables 4 and 5, Figs. 4 and 5, and supporting information in Campbell *et al.* (2018) for detail. For TTB, we found all the structures reported by Smirnov & Saint-Grégoire (2014) plus one additional structure associated with irrep R_1, in space group $I4/m$, on a '$2a$ by $2a$ by $2c$' cell.

As explained by Campbell *et al.* (2018), and emphasized by Phillips (2018), our new analysis rests on a linearization of equations, valid for infinitesimal angles of tilt. What happens at finite angles of tilt? One possibility is that the tilt patterns obtained require octahedral distortion. In this addendum we do not offer any general analysis of which (finite) tilt patterns may necessitate octahedral distortion, but for the tungsten bronzes the situation is reasonably clear. Recall that the tilting is around axes in the horizontal plane, and for such tilting this reduces the height of the octahedron projected on to the unique (z) axis. Unless all octahedra tilt through the same (or for TTB very nearly the same) angles then the differences need to be accommodated by octahedral distortion. On the other hand, if all octahedra tilt through the same angle then finite tilts can be accommodated by a uniform contraction along the unique axis and, it would seem likely from inspection, uniform contraction in the horizontal plane as well.[3] We speculate, that of the various structures obtained in our recent analysis, those in which all octahedra tilt through the same angles are the most likely to occur. These have been identified from an inspection of the figures in Campbell *et al.* (2018) – including those in the supporting information – and are listed here in Tables 1 and 2.

Table 1
Selected subgroups of the parent space group $P6/mmm$ of HTB in which valid tilt patterns have been found.

The entries are extracted from Table 4 in Campbell *et al.* (2018) but the list is limited to those corresponding to structures in which all octahedra exhibit the same angle of tilt.

Irrep	Order parameter direction	Space group	Lattice vectors	Origin
A_3^+	$P1$ (a)	$P6_3/mmc$	(1,0,0),(0,1,0),(0,0,2)	(0,0,0)
A_6^+	$P1$ (a,0)	$Cmcm$	(1,0,0),(1,2,0),(0,0,2)	(0,0,0)†
L_2^-	$P3$ (a,a,a)	$P6/mmm$	(2,0,0),(0,2,0),(0,0,2)	(0,0,$\frac{1}{2}$)

† Tilts of equal magnitudes are achieved by including a suitable contribution from A_3^+, which appears as a secondary distortion.

Table 2
Selected subgroups of the parent space group $P4/mbm$ of TTB in which valid tilt patterns have been found.

The entries are extracted from Table 6 in Campbell *et al.* (2018) but the list includes only those corresponding to structures in which all octahedra exhibit nearly the same angle of tilt.

Irrep	Order parameter direction	Space group	Lattice vectors	Origin
Z_5^+	$P3$ (a,a)	$Pnma$	(1,0,0),(0,0,2),(0,$\bar{1}$,0)	(0,0,0)
A_5^-	$P1$ (a,0)	$I4/m$	(1,1,0),($\bar{1}$,1,0),(0,0,2)	(0,0,$\frac{1}{2}$)
R_1	$P4$ (0,0,a,0)	$Cmc2_1$	(0,0,2),(2,0,0),(0,1,0)	($\frac{3}{4}$,0,$\frac{1}{2}$)
R_1	$P5$ (a,a,$-a$,a)	$I4/m$	(2,0,0),(0,2,0),(0,0,2)	($\frac{1}{2}$,$\frac{3}{2}$,$\frac{1}{2}$)

Finally we remark that these group theoretical considerations were invoked in a recent study of $Sr_3TiNb_4O_{15}$ (Whittle *et al.*, 2018). In that it was concluded that the room-temperature structure was the *Pnma* structure recorded here in our Table 2, modified by cation displacement along the parent z axis, to give a ferroelectric structure in $Pna2_1$ on a cell defined by lattice vectors (1,0,0),(0,1,0),(0,0,2) and origin (0,0,0).

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[2] In the supporting infomation for Campbell *et al.* (2018), it can be seen that the tilt system for TTB, irrep Z_5^+ order parameter direction $P3$, requires 6 mode amplitudes for its specification.

[3] We have not carried out any comprehensive investigation on this point; we have however checked that for HTB the structure in $P6_3/mmc$, from irrep $A_3^+(P1)$, can accommodate regular octahedra at arbitrary angle of tilt.

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