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Jahn–Teller distortions, cation ordering and octahedral tilting in perovskites

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In transition metal oxides, preferential occupation of specific $d$ orbitals on the transition metal ion can lead to the development of a long-range ordered pattern of occupied orbitals. This phenomenon, referred to as orbital ordering, is usually observed indirectly from the cooperative Jahn–Teller distortions (CJTDs) that result as a consequence of the orbital ordering. This paper examines the interplay between orbital ordering, octahedral tilting and cation ordering in perovskites.

Both ternary $AMX_3$ perovskites containing an active Jahn–Teller (J–T) ion on the octahedral site and quaternary $A_2MM'X_6$ perovskites containing a J–T ion on one-half of the octahedral sites have been examined. In $AMX_3$ perovskites, the tendency is for the occupied $3d_{3z^2-r^2}$ and $3d_{3x^2-r^2}$ orbitals to order in the $ac$ plane, as exemplified by the crystal structures of LaMnO$_3$ and KCuF$_3$. This arrangement maintains a favorable coordination environment for the anion sites.

In $AMX_3$ perovskites, octahedral tilting tends to enhance the magnitude of the J–T distortions. In $A_2MM'X_6$ perovskites, the tendency is for the occupied $3d_{3z^2-r^2}$ orbitals to align parallel to the $c$ axis. This pattern maintains a favorable coordination environment about the symmetric $M'$-cation site.

The orbital ordering found in rock-salt ordered $A_2MM'X_6$ perovskites is compatible with octahedral rotations about the $c$ axis (Glazer tilt system $a^0b^0c^0$) but appears to be incompatible with GdFeO$_3$-type octahedral tilting (tilt system $-b^+a^-$).

1. Introduction

Perovskites containing Jahn–Teller ions (i.e. Cu$^{2+}$ and Mn$^{3+}$) on the octahedral site exhibit interesting physical properties, including charge ordering, spin ordering and cooperative Jahn–Teller distortions. In octahedral coordination, the first-row transition-metal cations Mn$^{3+}$ (high-spin) and Cu$^{2+}$ have electron configurations $(t_{2g})^3(eg)^1$ and $(t_{2g})^6(eg)^3$, respectively. The Jahn–Teller (J–T) theorem predicts that a distortion of the ideal octahedral geometry will occur, thus providing an energetic stabilization by removing the electronic degeneracy of the highest occupied molecular orbital (Kanamori, 1960). It has been shown that a larger energetic stabilization is realized when the primary distortion mechanism is elongation of two bonds $trans$ to each other and contraction of the remaining bonds, as opposed to the inverse distortion, i.e. contraction of two $trans$ bonds and elongation of the remaining four (Burdett, 1981). In extended solids, ionic effects and lattice strains can stabilize less symmetric distortions. For example, a distortion where two $M$–$X$ bonds shorten and two $M$–$X$ bonds lengthen, denoted as $Q2$, is typically observed in ternary perovskites such as LaMnO$_3$. Changing the symmetry and/or the identity and arrangement of the surrounding...
Throughout this manuscript, tolerance factors are calculated to compare the sizes of the ions on the structural features of perovskites. The tolerance factor, \( \tau \), is defined as:

\[
\tau = d( A - X ) / [2^{1/2} d( B - X )],
\]

where \( d( A - X ) \) is the ideal \( A - X \) distance and \( d( B - X ) \) is the weighted average of the ideal \( M - X \) and \( M' - X \) distances. Throughout this manuscript, tolerance factors are calculated with the \textit{SPuDS} software package (Lufaso & Woodward, 2001). \textit{SPuDS} uses the bond-valence model to calculate the ideal \( A - X, M - X \) and \( M' - X \) distances, assuming 12 equidistant \( A - X \) bonds and six equidistant \( M - X \) and \( M' - X \) bonds. Perovskites with a tolerance factor equal to or greater than unity often exhibit no octahedral tilting. More commonly, the \( A \) cation is too small for the corner-sharing octahedral network, and an octahedral-tilting distortion takes place (Woodward, 1997b). Cooperative tilting of the undistorted octahedra occurs to shorten the \( A - X \) bonds and thereby improve the coordination environment and bonding of the \( A \)-site cation. The various combinations of octahedral tilting and the resulting space-group symmetries have been described previously (Glazer, 1972, 1975; Woodward, 1997). In fact, at room temperature, the aristotype cubic perovskite structure is realized in only a small percentage of perovskites. The most commonly observed octahedral tilt system, reported for more than half of the ternary perovskites at room temperature, lowers the symmetry from \( P m 3 m \) to \( P n m a \) (Lufaso & Woodward, 2001). This type of tilting, described as \( a '' b ' a ' \) in Glazer’s (1972) notation, is now associated with GdFeO\(_3\) and/or the mineral perovskite, CaTiO\(_3\). Octahedral-site cation ordering also modifies the space-group symmetry. The space-group symmetries that result from the combination of rock-salt ordering and octahedral tilting have been reported on several occasions (Aleksandrov & Misjul, 1981; Woodward, 1997a; Gateshki et al., 2003; Howard et al., 2003). Large differences in size (greater than 0.1 \( \AA \)) and/or oxidation state (greater than two) are two factors that favor cation ordering on the octahedral site (Anderson et al., 1993).

Cooperative Jahn–Teller distortions describe the orbital-ordering arrangement and occur to minimize the elastic energy (Goodenough, 1998). The CJTD in KCuF\(_3\) is complex because of the numerous ways in which the crystals may form stacking errors. The type and concentration of these stacking faults can influence the space-group determination, thus making assignment of a space group difficult. Consequently, the structure of KCuF\(_3\) has been reported with space-group symmetries \( I4/mcm \) (Hutchings et al., 1969; Buttner et al., 1990), \( P4/mbm \) (Hutchings et al., 1969) and \( P2_12_12_1 \) (Hidaka et al., 1998). Crystallization of KCuF\(_3\) in space group \( I4/mcm \), with three distinct Cu–F bond lengths and a CJTD with long and short Cu–F bonds alternating in the \( ab \) plane, was reported by Buttner et al. (1990). Viewed perpendicular to the \( ab \) plane, there are two possible orientations of the CuF\(_2\) layers. The structure is said to be \( d \)-type (\( P4/mbm \)) when the pattern of long and short Cu–F bonds is the same from one layer to the next (layers separated by a mirror plane), whereas when the orientations of the long and short Cu–F bonds are rotated by 90° from one layer to the next, the structure is designated as \( a \)-type (\( I4/mcm \)) (Hutchings et al., 1969). The KCuF\(_3\) structure exists in both forms (even in the same crystal), with the \( a \)-type favored. The \( a \)-type arrangement is illustrated in Fig. 1.

In \( A_2M'M'X_6 \) perovskites, the octahedral cations can order in one of three ways, viz. (a) in a three-dimensional rock-salt...
chains of Mn$^{3+}$O$_6$ and Mn$^{4+}$O$_6$ (Woodward et al., 1999). In these compounds, all of the long Cu–O bonds orient parallel to the $c$ axis. La$_2$CuSnO$_6$ possesses an unusual layered arrangement of Sn$^{4+}$ and Cu$^{2+}$ ions, with a large J–T distortion about the latter ion (Anderson & Poeppelmeier, 1991), but retains a CJTD in which the long Cu–O bonds align in a direction that is nearly parallel to the $c$ axis (the long Cu–O bonds are not strictly parallel to the $c$ axis because of octahedral tilting). Charge ordering occurs near 160 K for NdSrMn$_2$O$_6$, resulting in a structure with chains of Mn$^{3+}$O$_6$ and Mn$^{4+}$O$_6$ (Woodward et al., 1999). Another compound that has been reported with this type of ordering is LaCaMn$_2$O$_6$ (Radaelli et al., 1997). In compounds with this type of charge ordering, the long Mn$^{3+}$–O bonds lie in the ac plane, in a fairly complex arrangement that is compatible with the charge and magnetic ordering. The most common CJTDs for each type of cation ordering discussed above are shown in Fig. 1. Recent results suggest the possibility that electron localization in compounds belonging to the AlMn$_2$O$_4$ family may actually involve dimerization of two Mn atoms into a Zener polaron, rather than ordering of distinct Mn$^{3+}$ and Mn$^{4+}$ ions (Daoud-Aladine et al., 2002). Regardless of how this controversy is settled, there is no a priori reason why the topology of the chain-ordered structure could not be realized when the charge difference between different cation sites is small.

The bond-valence concept (Brown, 1978, 2003; Brese & O’Keeffe, 1991) has been used to understand and predict the structures of oxides in general and perovskites in particular (Lufaso & Woodward, 2001). The valence of each bond is calculated on the basis of the ions involved and the bond distance. By summing the individual bond valences, a bond-valence sum (BVS) is obtained for each ion. Normally, this sum should be near the oxidation state of the ion. The need to maintain a reasonable bond-valence sum at the anion sites plays an important role in determining the most favorable orbital-ordering arrangement. A large J–T distortion at the octahedral-site cation causes a loss of bonding to the anion involved in the resulting long $M$–X bond. However, this anion typically forms a short bond to the octahedral-site cation on its opposite side, in order to maintain a reasonable bond-valence sum. For example, consider the crystal structure of KCuF$_3$ (Buttnner et al., 1990). Two crystallographically and chemically distinct F-atom sites are present. The fluoride ion that resides on the 8h site has one short and one long Cu–F bond, while the fluoride ion that sits on the 4b site forms two intermediate-length bonds to the Cu atom. Each environment provides a satisfactory bonding arrangement for fluorine, as shown by the bond-valence sums. Bond-valence calculations show that the short Cu–F(8h) bond [1.8888 (4) Å] contributes 0.45 v.u. (valence units), the long Cu–F(8h) bond [2.2527 (4) Å] contributes 0.17 v.u. and four K–F bonds [2.8585 (3) Å] contribute a total of 0.38 v.u., for a BVS of 1.00 v.u. at the F(8h) site. A similar analysis of the F atom on the 4b site reveals two medium-length Cu–F(4b) bonds [1.9622 (2) Å], each of which contributes 0.37 v.u., and four K–F bonds [2.9285 (3) Å] that contribute a total of 0.32 v.u., for a BVS of 1.06 v.u. at the F(4b) site. This arrangement is much more favorable than a CJTD where all of the long Cu–F bonds are oriented parallel to each other. In that case, one F-atom site would have two long bonds to the Cu atom, while another anion site would have two short bonds to the Cu atom and the third site would have two intermediate-length Cu–F bonds. Clearly, the first two F-atom sites would have BVSs that deviate significantly from 1.00 v.u., barring radical changes in the K–F bond distances.

The anion environment changes in the ordered $A_2MM'O_6$ perovskite structure, and this change impacts the orbital ordering. In general, the $M'$ cation is not a J–T ion and will...
prefer a fairly symmetric coordination environment. This conformation disrupts the simultaneous formation of both long and short bonds at a given anion site, thereby reducing the stabilization of the ab-plane ordering seen in KCuF₃. As an illustration, consider the crystal structure (space group I4/m) of Ba₂CuWO₆ (Iwanaga et al., 1999). In Ba₂CuWO₆, and in A₂CuMO₆ compositions in general (A = Ba and Sr, and M = W and Te), all of the long Cu−O bonds are directed parallel to the c axis. A bond-valence analysis of the Ba₂CuWO₆ structure shows that the O atom that resides on the 4c site forms a long bond [2.41 (2) Å, 0.14 v.u.] to the Cu atom, a relatively short bond to the W atom [1.90 (2) Å, 1.05 v.u.] and four bonds to Ba atoms [2.79 (2) Å, 4 × 0.25 v.u.]. The O atom on the 8d site forms a much shorter bond to the Cu atom [2.01 (2) Å, 0.41 v.u.], but the structure compensates for this bond form by forming a slightly longer bond to the W atom [1.93 (2) Å, 0.96 v.u.] and noticeably longer bonds to the Ba atoms [2 × 2.83 (3) Å, 2 × 0.23 v.u.; 2 × 3.01 (3) Å, 2 × 0.14 v.u.]. The anion BVSs are 2.19 v.u. for the O atom on the 4c site and 2.11 v.u. for the O atom on the 8d site. In La₂CuSnO₆, the O atom involved in the long Cu−O bonds compensates by forming shorter Sn−O bonds. The charge-ordered structure of NdSrMn₂O₆ has three distinct Mn sites and a more complicated orbital-ordering scheme, but once again consideration of the bonding at the O atoms is a very useful way to understand the structure. Bond-valence sums for each of the ions in the four structures are listed in Table 1.

It is interesting to consider how the presence of octahedral tilting influences the orbital ordering in both ternary AMX₃ and ordered quaternary A₃MM’X₆ perovskites, and this question is the focus of the next two sections of this paper. The M−X bond lengths, octahedral distortion parameters, space-group symmetries and octahedral tilt systems for a representative cross-section of perovskites exhibiting a CJTD, namely LaMnO₃ (Rodríguez-Carvajal et al., 1998), KCuF₃ (Buttner et al., 1990), Sr₂CuWO₆ (Iwanaga et al., 1999), and La₂CuTiO₆ (Palacin et al., 1993), are shown in Table 2.

### Table 1

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<tr>
<th>Structure</th>
<th>A site</th>
<th>Oct. site (I−T)</th>
<th>Oct. site (Sym.)</th>
<th>X (long M−X')</th>
<th>X</th>
<th>Bond lengths (Å)</th>
<th>Octahedral distortion (°)</th>
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<td>1.98</td>
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<td>3.98, 3.98</td>
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<td>2.10</td>
<td>2.04, 2.05, 2.20</td>
<td>2.14, 2.14</td>
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<tr>
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<td>4.05</td>
<td>1.93, 1.95, 1.96</td>
<td>1.92, 2.04, 2.18</td>
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<tr>
<td>NdSrMn₂O₆</td>
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<td>1.90, 1.94</td>
<td>1.92, 1.95</td>
<td>2.00, 2.05, 2.20</td>
<td>2.15, 2.18, 2.18</td>
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### Table 2

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<th>Sr₂CuWO₆</th>
<th>KCuF₃</th>
<th>Ba₂CuTiO₆</th>
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<td>2.022(4)</td>
<td>2.0072(14)</td>
<td>2.03(3)</td>
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<td>Pnma</td>
<td>Pnma</td>
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<td>a’a’b’a’</td>
<td>a’b’c’</td>
<td>a’b’c’</td>
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<td>NaCuF₃</td>
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### 3. Octahedral tilting and CJTDs in AMX₃ systems

Compounds with the composition ACuF₃ (A = Na, K and Rb) prefer to adopt an a-type CJTD (space group I4/mcm). No octahedral tilting occurs for ACuF₃ (A = K and Rb) and the structure retains F−Cu−F bond angles of 90° (A = K: Buttner et al., 1990; A = Rb: Kaiser et al., 1990), whereas NaCuF₃ (τ = 0.918) exhibits significant octahedral tilting. NaCuF₃ has four similar coordination environments for the Cu atom, with strongly distorted average F−Cu−F angles (91, 94 and 105°; Kaiser et al., 1990). Three distinct Cu−F bond distances (average Cu−F bond distances presented for NaCuF₃) are shown for ACuF₃ (A = Na, K and Rb) in Fig. 2. The three distinct Cu−F bond distances are similar for A = Na and K; however, the larger size of the Rb atom (r = 1.089) causes a stretching of the octahedron, with the longest (weakest) bond undergoing the largest expansion.

The rare-earth manganates RMnO₃ (R = La, Pr, Nd, Dy, Tb and Ho) have been studied extensively. They crystallize in tilt system a’b’a’− with Pnma symmetry, and accurate structures have been obtained from neutron powder diffraction studies (Rodríguez-Carvajal et al., 1998; Alonso et al., 2000). The CJTD in these compounds, indicative of orbital ordering, is the d-type arrangement seen sometimes in KCuF₃, with an a’b’a’− octahedral-tilting distortion superimposed. The ordered arrangement of the long bonds is shown looking down the b axis of LaMnO₃ in Fig. 3.

To separate the effects of the J−T distortion and the octahedral-tilting distortion it is insightful to compare RMnO₃
perovskites with $R\text{FeO}_3$ perovskites. The $\text{Fe}^{3+}$ and $\text{Mn}^{3+}$ ions have identical crystal radii (0.785 Å; Shannon, 1976). Consequently, for the same rare-earth cation, $R\text{FeO}_3$ and $R\text{MnO}_3$ perovskites will have the same tolerance factor. Thus the approximate crystal structure in the absence of a J–T distortion can be obtained by replacing $\text{Mn}^{3+}$ with the octahedrally symmetric $\text{Fe}^{3+}$ ion. Examination of the $R\text{FeO}_3$ ($R = \text{La, Pr, Nd, Sm, Eu, Gd, Tb, Er, Dy, Y, Tm, Yb and Lu}$; Marezio et al., 1970) and $R\text{MnO}_3$ ($R = \text{La, Pr, Nd, Dy, Tb and Ho}$) series confirms that both sets of compounds crystallize with the same tilt system and space group. A plot of the $\text{Mn-O}$ bond distances versus the tolerance factor is shown in Fig. 4, while the $\text{O-Mn-O}$ bond angles versus the tolerance factor are shown in Fig. 5. The distortion of the $\text{Mn-O}$ bond distances and the $\text{O-Mn-O}$ bond angles increases as the tolerance factor decreases (larger octahedral-tilt angle). The tendency for the individual $\text{O-Mn-O}$ angles to deviate from 90° increases as the length of the long $\text{Mn-O}$ bonds increase. This behavior is quite reasonable, as these bonds are weaker and more susceptible to distortion, not to mention the fact that the $\text{O-O}$ repulsions are lessened by elongation of the $\text{Mn-O}$ bonds. The bond-angle distortion parameter is defined as

$$\Delta \theta_{\text{XXX}} = \frac{1}{3} \left\{ \sum_{\theta_{\text{XXX}}(n)} \left[ \theta_{\text{XXX}}(n) - \langle \theta_{\text{XXX}} \rangle \right] / \langle \theta_{\text{XXX}} \rangle \right\}^2,$$

where $\theta_{\text{XXX}}$ represents the individual $\text{cis O-Mn-O}$ bond angles and $\langle \theta_{\text{XXX}} \rangle$ is the mean of all $\text{cis O-Mn-O}$ bond angles greater than 90° (an equivalent set of bond angles equally displaced in the opposite direction from 90° is also present). Fig. 5 shows that the bond-angle distortion is enhanced in the $R\text{MnO}_3$ series for the smaller rare-earth ions (Dy, Tb and Ho), whereas the distortions are similar to those in the $R\text{FeO}_3$ series for the larger rare-earth ions.

A comparison of lattice parameters for $A\text{MnO}_3$ and $A\text{FeO}_3$ is shown in Fig. 6. Since both $A\text{MnO}_3$ and $A\text{FeO}_3$ have approximately the same degree of tilting (for the same $A$-site cation), a comparison of the two reveals the influence of the CJTD on the lattice parameters. Replacing $\text{Mn}^{3+}$ with $\text{Fe}^{3+}$ leads, on average, to a 4.1% decrease in $a$ [$a(\text{Fe}) < a(\text{Mn})$], a 2.8% increase in $b$ [$b(\text{Fe}) > b(\text{Mn})$] and a 0.4% increase in $c$ [$c(\text{Fe}) > c(\text{Mn})$]. The $A\text{MnO}_3$ compounds have, on average, a 0.7% larger unit-cell volume than the corresponding members of the $A\text{FeO}_3$ series. In the absence of tilting, the CJTD causes the $a$ and $c$ axes to expand equally, while the $b$ axis contracts. However, in the presence of Gd$\text{FeO}_3$-type tilting, we see a relatively large expansion of the $a$ axis and relatively little change in the length of the $c$ axis. The inequality in the expansion of the $a$ and $c$ axes originates from the in-phase tilting about the $b$ axis. The octahedral rotations cause the long $\text{Mn-O}$ bonds to align more closely with the $a$ axis than with the $c$ axis, as shown in Fig. 3. If we limit the tilting to rotations about the $b$ axis (tilt systems $a^0b^+a^0$ or $a^0b^+a^0$), we

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**Figure 3**
View down the $b$ axis ($Pnma$) of the crystal structure of $\text{LaMnO}_3$, showing the $ac$-plane orbital ordering. Long $\text{Mn-O}$ bonds are depicted as thick black bonds, whereas thinner lines are used for the short and medium-length $\text{Mn-O}$ bonds.

**Figure 4**
M–O distances versus tolerance factor for $A\text{MnO}_3$ and $A\text{FeO}_3$ series. Filled symbols represent $M = \text{Mn}$ and open symbols represent $M = \text{Fe}$.

**Figure 5**
O–M–O bond angles versus tolerance factor for $A\text{MO}_3$ ($M = \text{Fe}$ and Mn). Filled symbols represent $M = \text{Mn}$ and open symbols represent $M = \text{Fe}$. The inset shows $\Delta \theta_{O-M-O} \times 10^4$ versus tolerance factor for $A\text{MO}_3$ ($M = \text{Fe}$ and Mn).
can express mathematically the effect of rotations on the response of the $a$ and $c$ axes to the development of a J-T distortion at the octahedral site. These relationships are

$$a = 2[d_{\text{long}} \cos(45 - \varphi) + d_{\text{short}} \sin(45 - \varphi)],$$

$$c = 2[d_{\text{long}} \sin(45 - \varphi) + d_{\text{short}} \cos(45 - \varphi)],$$

(4)

where $d_{\text{long}}$ and $d_{\text{short}}$ are the longest and shortest Mn–O bonds, respectively, and $\varphi$ is the rotation angle of the octahedra about the $b$ axis. When $\varphi$ is zero, the two cell edges are equal, but as $\varphi$ increases, the cosine terms get larger while the sine terms get smaller, which necessarily leads to the condition that $a$ will expand in response to the CJTD, while the impact on $c$ will be smaller. In practice, this effect is quite pronounced.

The lattice distortion index ($D$) is a measure of the distortion of the lattice from pseudocubic symmetry and is defined as

$$D = (1/3) \sum_{n=1,3} 100[(a_n - \langle a \rangle)/\langle a \rangle],$$

(5)

where $a_n$ is the individual lattice parameter converted to the length of the equivalent primitive unit cell ($a_n \approx 4 \, \text{Å}$) ($a/2^{1/2}$, $c/2^{1/2}$ and $b/2$) and $\langle a \rangle$ is the mean of the converted lattice parameters. The effect of the CJTD on the lattice parameters is illustrated in the plot of $D$ versus tolerance factor shown in Fig. 7. The trends show that, as expected, both octahedral tilting and the CJTD cause the lattice metrics to distort from cubic, but the effect is more pronounced for a CJTD.

The $A$-site cation displacement from the high-symmetry position (at the center of the eight surrounding octahedra) is significantly larger for the $RMnO_3$ series than it is for the $RFeO_3$ series, particularly in the $x$ direction, as evidenced in the $x$ coordinate of the $A$-site cation. This displacement occurs because the combination of octahedral tilting and the CJTD creates a cavity into which the $A$-site cation can shift. The $A$-site displacement from the high-symmetry position for $RMO_3$ ($R = Fe$ and Mn) compositions versus tolerance factor is shown in Fig. 8. The $R$–O bond lengths are surprisingly similar for the six closest distances, despite the distortion of the MnO$_6$ octahedra. The majority of the $R$–O bonding is contained in the first six bonds, e.g. 80.4 and 82.0% of the Nd bond-valence sums of 2.96 v.u. (NdMnO$_3$) and 2.93 v.u. (NdFeO$_3$) can be attributed to the first six Nd–O bonds. All

Figure 6
Filled symbol represent lattice parameters for $AMnO_3$ compounds at room temperature. Open symbol represent lattice parameters for the corresponding $AFeO_3$ compositions. Lattice parameters are represented by squares ($a$), circles ($b/2^{1/2}$) and triangles ($c$).

Figure 7
Lattice distortion, $D$, for $AMnO_3$ (filled diamonds), $AFeO_3$ (open diamonds), $Ca_2MnMO_6$ ($M = Sb, Ta, Nb and Ru$) (open triangles) and $A_2MnGaO_6$ ($A = Nd and La$) (filled squares).

Figure 8
The $A$-site fractional displacement from the high-symmetry position in $Pnma$ versus tolerance factor for $AMO_3$, $AFeO_3$, $Ca_2MnMO_6$ ($M = Sb, Ta, Nb and Ru$) and $A_2MnGaO_6$ ($A = Nd and La$). The symbol description order is the same as that used in Fig. 7.
twelve Nd—O bond distances for NdMnO3 and NdFeO3 are shown in Table 3, illustrating the similarity in coordination environments for the A-site cations, even in the presence of the J—T distortion. The R—O distances for several members of the RMO3 (M = Fe and Mn) series are shown in Fig. 9. The distribution of R—O distances shows very little perturbation in response to the CJTD.

In both series, the decreasing tolerance factor (increased tilting) leads to a larger distortion of the O—M—O angles. However, this trend is much more pronounced in the AMnO3 series, as a result of the J—T distortion. The Pnma perovskite structure becomes increasingly unstable as the octahedral tilting increases (τ < 0.88), a trend that is exacerbated by the presence of a J—T cation on the octahedral site. Soft chemistry synthesis and/or high-pressure synthesis is required to stabilize the perovskite phase for manganites with an A-site ion smaller than Tb3+ (Alonso et al., 2000). A hexagonal structure type (space group P63/mcm) with manganese in a trigonal-bipyramidal coordination is observed for AMnO3 compounds when the ionic radius of the A-site cation becomes too small (τ < 0.88). Interestingly, for the same set of small rare-earth cations, the orthorhombic perovskite structure remains stable when the octahedral cation is Fe3+. As the tolerance factor continues to decrease, eventually a hexagonal structure (space group P63/mmc), with trigonal-bipyramidal coordination about Fe, is observed, as exemplified by InFeO3 (τ = 0.85; Giaquinta et al., 1994). The destabilization of the perovskite structure when the J—T Mn3+ ion is present is likely to be at least partially related to the fact that trigonal-bipyramidal coordination does not produce an electronic degeneracy of the highest occupied molecular orbital (HOMO).

4. Cation ordering, octahedral tilting and CJTDs in A2MM’X6 systems

Compounds with the composition A2CuM06 (A = Ba and Sr, and M = W and Te) have a strong driving force for rock-salt cation ordering as a result of the oxidation-state difference of four between the Cu2+ and W6+/Te4+ ions. Additionally, these compounds exhibit out-of-phase tilting about the c axis (a’ a c”). The long Cu—O bonds, oriented parallel to the c axis, induce a large tetragonal distortion. Lattice parameter ratios c/(21/2a) for Ba2CuMO6 (τ = 1.042) are 1.098 (M = W) and 1.092 (M = Te), and for Sr2CuMO6 (τ = 0.983) are 1.096 (M = W) and 1.102 (M = Te). Octahedral distortion parameters Δdca = 70.8 × 10−4 (M = W) and 85.0 × 10−4 (M = Te) are observed for A = Sr, whereas Δdca = 79.9 × 10−4 (M = W) and 84.8 × 10−4 (M = Te) when A = Ba. It is interesting to note that octahedral tilting occurs even in Ba2CuWO6 and Ba2CuTeO6, for which the tolerance factor is larger than unity. The tilt angle is somewhat larger in the Sr analogues, as the smaller tolerance factor would lead us to expect. A recent study has shown that in Sr2CuWO6 the octahedral tilting decreases upon heating, tending towards zero at a temperature of ~783 K (Gateski & Irgartua, 2003). It seems likely that similar transitions occur in the other three compounds at varying temperatures.

<table>
<thead>
<tr>
<th>Table 3</th>
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<td>Nd—O bond distances and valence for experimental crystal structures of NdFeO3 (BVS = 293 v.u.) and NdMnO3 (BVS = 296 v.u.).</td>
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<tr>
<th>Nd—O distance number</th>
<th>NdFeO3 (Å)</th>
<th>NdFeO3 BVS (%)</th>
<th>NdMnO3 (Å)</th>
<th>NdMnO3 BVS (%)</th>
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In La2CuSnO6, the charge difference of two, combined with a large J—T distortion about the Cu2+ ion, and a significant octahedral-tilting distortion (τ = 0.917), stabilizes a layered ordering of octahedral-site cations. Layered octahedral-site ordering is very unusual. Its stability appears to be closely coupled with the size of the octahedral-tilting distortion. In this structure, the long Cu—O bonds are all aligned effectively in a single direction (along the a axis of P21/m), similar to the Ba2CuWO6 structure. Additional layered compounds of composition A2CuSnO6 (A = Pr and Nd) and La2CuZrO6 have been synthesized under high-pressure high-temperature conditions (Azuma et al., 1998).

On going from La2CuSnO6 (τ = 0.917) to La2CuTiO6 (τ = 0.945) (Palacin et al., 1993), the difference in the radii of the octahedral cations actually increases (rTi = 0.75 Å, rSn = 0.83 Å and rCa = 0.87 Å), yet the long-range cation ordering disappears, as does the CJTD. The octahedral site contains a

![Figure 9](image)

R—O bond distances (eight shortest) for RMnO3 (filled) and RFeO3 (open) as a function of tolerance factor. Triangles indicate a multiplicity of one, squares a multiplicity of two (see Table 3).
random mixture of Cu$^{2+}$ and Ti$^{4+}$ with a symmetric distribution of $M-O$ bond distances $[2 \times 2.033 (4), 2 \times 2.022 (4) \text{ and } 2 \times 2.007 (1) \text{ Å}; \Delta d_{Ca} = 0.27 \times 10^{-4}]$. This example illustrates the sensitivity of both the orbital and the cation ordering to changes in octahedral tilting.

The crystal structures of $A_2MnGaO_6 (A = \text{La and Nd})$ were determined from Rietveld refinement of high-resolution neutron powder diffraction data (Cussen et al., 2001). Octahedrally symmetric Ga$^{3+}$ and the J–T active Mn$^{3+}$ ions are disordered over a single crystallographic site (as in $La_2CuTiO_6$). Surprisingly, the refinements show that the coordination of the disordered octahedral site in the two compounds is quite different. Nd$_2$MnGaO$_6$ has a considerable orbital ordering and a CJTD in Nd$_2$GaMnO$_6$ but O and La$-$O bonding are expected to be similar. Thus the extent of octahedral tilting induced by the smaller Nd$^{3+}$ is not in La$_2$MnGaO$_6$; rather, it is more likely that J–T distortions along a single axis is a ferrodistortive orbital ordering seen in LaMnO$_3$ and KCuF$_3$ (Battle et al., 2002). Previous work of Woodward (1997) investi-
gated the structures of Sr$_2$MnTaO$_6$ and Sr$_2$MnNbO$_6$. Replacing Sr$^{2+}$ with the smaller Ca$^{2+}$ decreases the tolerance factor and increases the tilting, so that the Ca$_2$MnMO$_6$ compounds undergo tilting analogous to that seen in AMnO$_3$ and AFeO$_3 (a-b^t a^-)$ octahedral tilting and crystallize with $Pnma$ space-group symmetry. The increased octahedral tilting appears to destabilize the orbital ordering and CJTD seen for Sr$_2$MnRuO$_6$ and Sr$_2$MnSbO$_6$. Tolerance factors, $M-O$ bond lengths, distortion parameters, lattice parameters and orientations of the long $M-O$ bonds are given in Tables 4 and 5. Note that in all of the $A_2MnM^{2+}O_6 (A = \text{Ca and Sr})$ compounds studied the octahedral cations are disordered.

5. Orbital ordering and cation ordering

The orbital-ordering schemes observed in ACuF$_3$ ($a$- and $d$-type) and AMnO$_3$ ($d$-type) perovskites are shown in Figs 10(a) and 10(b) (neglecting octahedral-tilting distortions). On going from a ternary to an ordered $A_2MM'X_6$ perovskite, several arrangements are possible. The simplest pattern is to replace every other J–T active cation with a symmetric cation in a 1:1 rock-salt ordered pattern, as shown in Fig. 10(c). This is the orbital-ordering scheme adopted by $A_2CuM^{4+}O_6$ compounds. Note that all of the long $M-X$ bonds are oriented in the same direction. This cooperative pattern of J–T distortions along a single axis is a ferrodistortive orbital ordering, as opposed to the $ac$-plane antiferrodistortive orbital ordering seen in LaMnO$_3$ and KCuF$_3$ (Battle et al., 2002).

![Figure 10](image)

**Figure 10** Orbital-ordering schemes in (a)–(b) ternary $AMX_3$ perovskites and (c)–(f) quaternary ordered $A_2MM'X_6$ perovskites. The solid lines indicate the simple cubic perovskite unit cell, while the dotted line shows the $a$ and $c$ axes of the $Pnma$ unit cell. For clarity, only the octahedral ions are shown.
Why does the introduction of cation order lead to a re-orientation of the orbital ordering? To understand the link between cation ordering and orbital ordering, consider the hypothetical structure that would result if ac-plane orbital ordering and rock-salt cation ordering were superimposed. The result is shown in Fig. 10(d). We can immediately see that this arrangement is unfavorable because, in order to maintain connectivity, the $M-X$ bonds are compressed at one-half of the symmetric $M$'s and elongated at the remaining $M$'s. Thus there are two crystallographically and chemically distinct sites for the $M$'s, violating Pauling’s (1929) rule of parsimony. A search of the literature revealed no compounds that adopt such an arrangement. This unfavorable arrangement can be avoided if one reverses the orientation of the occupied $e_g$ orbitals in every other row, as shown in Fig. 10(e). In this arrangement, the long $M-X$ bonds are stabilized by a shift of the symmetric $M'X_6$ octahedra, as indicated by the arrows in Fig. 10(e). However, notice that $M'X_6$ octahedra in neighboring layers shift in opposite directions, thus creating a lattice strain that is energetically unfavorable. On the other hand, if the cation ordering is modified to the chain type (see Fig. 1), the symmetric $M_X'X_6$ octahedra in the neighboring layers can shift in the same direction, as shown in Fig. 10(f). This is the CJTD and orbital-ordering scheme reported for $RMn^3\text{III}Mn^2\text{II}_6$ compounds, such as NdSrMn$_4$O$_6$ (Woodward et al., 1999). Clearly, the cation- and orbital-ordering possibilities are diverse but closely linked.

6. Discussion

The J–T theorem states that a distortion of the octahedra should occur when there is a partially occupied degenerate set
of HOMOs. However, the theorem specifies neither the magnitude of the distortion, \( \Delta d_M \), nor the long-range pattern of distortions in an extended solid. Ternary perovskites containing a J-T ion exhibit a large CJTD, with \( \text{Cu}^{2+} \) octahedra exhibiting a much larger distortion than \( \text{Mn}^{3+} \) octahedra. In \( \text{RbCuF}_3 \), the presence of the Rb cation causes a lengthening of the longest and weakest Cu-F bonds, which results in a larger distortion of the octahedra than is observed in \( \text{KCuF}_3 \). Ordered perovskites containing \( \text{Cu}^{2+} \), i.e. \( \text{A}_2\text{CuM}_6\text{O}_{6} \) (A = Ba and Sr, and M = W and Te), contain distorted \( \text{CuO}_6 \) octahedra with sizes and shapes similar to those observed for \( \text{RbCuF}_3 \). Fig. 10(c) shows that the CJTD and orbital ordering in these quaternary ordered perovskites can be obtained from the ternary \( \text{KCuF}_3 \) perovskite by replacing 50% of the \( \text{Cu}^{2+} \) centered octahedra with symmetric \( \text{M}^{3+} \)-centered octahedra.

In the \( \text{RMnO}_3 \) series, increased octahedral tilting leads to an increase in the magnitude of the CJTD. This effect can be seen from the increase in \( \Delta d_M \) that occurs as the tolerance factor decreases across the \( \text{RMnO}_3 \) series. Increased octahedral bond-angle distortion of the \( X-M-X \) bond angles also occurs in the \( \text{RMnO}_3 \) series for the smaller rare-earth cations.

In contrast, no increase in \( \Delta \theta_{\text{MAX}} \) is observed with increased tilting in the corresponding \( \text{AFeO}_3 \) series. Octahedral tilting in \( \text{NaCuF}_3 \) is also accompanied by a strong distortion of the F- - Cu- - F bond angles, with an average \( \Delta \theta_{\text{MAX}} \) of 36.6 ° .

The \( \text{Sr}_2\text{MnMO}_6 \) (M = Ru and Sb) series have \( c/2(1/2-a) \) ratios of 1.028 and 1.025, respectively, and \( M-O \) bond distances as shown in Table 4. Their conformations imply that local J-T distortions are oriented along the c axis. The reduction (compared with those of \( \text{AMnO}_3 \)) in \( \Delta d_M \) values is due in part to dilution of the J-T ion with the symmetric ion. It seems likely that medium-range cation order, proposed as extended regions of cation ordering along the c axis, stabilizes the CJTD in \( \text{Sr}_2\text{MnMO}_6 \) (M = Ru and Sb). Local regions of cation order in \( \text{Sr}_2\text{MnRuO}_6 \) were reported from TEM studies (Goldberger et al., 2004). Although it is difficult to know the extent of cation order on the local scale in \( \text{Sr}_2\text{MnMO}_6 \) (M = Nb and Ta), we suspect that these compounds possess enough short-range cation order for the situation to be described as intermediate between a completely random distribution and the medium-range order suggested for \( \text{Sr}_2\text{MnMO}_6 \) (M = Ru and Sb). This distribution apparently destabilizes the CJTD, as no evidence for a CJTD can be found in \( \text{Sr}_2\text{MnMO}_6 \) (M = Nb and Ta). When the two octahedral-site cations have the same oxidation state and similar radii, as is the case for \( \text{La}_2\text{MnGaO}_6 \) and \( \text{Nd}_2\text{MnGaO}_6 \), it is likely that the cation distribution is nearly random. In this case, the magnitude of the CJTD appears to increase with increased octahedral tilting.

Replacing \( \text{Sr}^{2+} \) with \( \text{Ca}^{2+} \) clearly reduces the tolerance factor and increases the octahedral tilting. Within the \( \text{A}_2\text{MnMO}_6 \) (A = Sr and Ca, and M = Ru, Sb, Nb and Ta) series this process leads to a change of tilt type, from \( a^0d^0c^- \) to \( a^-b^-a^- \). Unlike the \( \text{A}_2\text{MnGaO}_6 \) and \( \text{RMnO}_3 \) compounds, where increased octahedral tilting stabilizes a larger CJTD, it appears that, in this case, the increased octahedral-tilting distortion actually destabilizes orbital ordering. This behavior can probably be seen most clearly from a comparison of the lattice parameters of \( \text{Sr}_2\text{MnMO}_6 \) and \( \text{Ca}_2\text{MnMO}_6 \) with those of \( \text{Sr}_2\text{FeMO}_6 \) and \( \text{Ca}_2\text{FeMO}_6 \). The lattice-distortion indices for the \( \text{Ca}_2\text{MnMO}_6 \) compounds are only slightly larger than those for \( \text{Sr}_2\text{FeMO}_6 \) (M = Ru, Sb, Nb and Ta), whereas the differences are much more pronounced for \( \text{Sr}_2\text{MRuO}_6 \) and \( \text{Sr}_2\text{M'SbO}_6 \). Another interesting observation is the fact that all of the \( \text{Sr}_2\text{MnMO}_6 \) compounds show octahedral rotations about the c axis (\( a^0d^0c^- \)), whereas each of the \( \text{Sr}_2\text{FeMO}_6 \) compounds undergoes a more complex form of octahedral tilting (either \( a^-b^-a^- \) or \( a^-b^-a^- \)). Finally, we note that perovskite oxides containing \( \text{Cu}^{2+} \) as the A-site cation and a 1:1 distribution of \( \text{Cu}^{2+} \) and \( \text{M}^{3+} \) on the octahedral sites (i.e. \( \text{Ca}_2\text{CuWO}_6 \) and \( \text{Ca}_2\text{CuTeO}_6 \) ) have not been reported in the literature. The combined implication of these observations is that, while \( a^0d^0c^- \) appears perfectly compatible with the development of a CJTD in ordered perovskites, further tilting (\( a^-b^-a^- \) in particular) seems to destabilize orbital ordering.

7. Conclusions

The crystal chemistry of perovskites containing an active J-T ion is diverse. The magnitude and orientation of the observed CJTD not only is dependent on the cation–anion pair but also exhibits sensitivity to local cation order and octahedral tilting. The coordination environment of \( \text{Mn}^{3+} \) appears to be more sensitive than that of \( \text{Cu}^{2+} \) to the transition from a ternary \( \text{AMX}_3 \) perovskite to an ordered quaternary \( \text{A}_2\text{MM'X}_6 \) perovskite. Octahedral-site cation ordering influences local ordering of the J-T distortions. A large difference in both charge and size is responsible for the observation that cation ordering is always present in \( \text{Cu}^{2+}-\text{M}^{3+} \) perovskites at room temperature. J-T distortions can be enhanced by chemical pressure induced by oversized A-site cations \((r > 1)\), as demonstrated by the behavior of \( \text{RbCuF}_3 \). In ternary \( \text{AMX}_3 \) perovskites, increased octahedral tilting enhances the size of the CJTD. Rock-salt ordering of the octahedral-site cations is incompatible with ac-plane ordering owing to the creation of two different sites for the octahedrally symmetric ion. Orbital ordering along a single axis is more stable for rock-salt ordered \( A_2\text{M'MX}_6 \) compositions with relatively small octahedral-tilting distortions \((r > 0.98)\). As the octahedral tilting increases in \( A_2\text{M'MX}_6 \) compositions, the orbital order and CJTD diminish, as observed in \( \text{La}_2\text{CuTiO}_6 \), \( \text{Ca}_2\text{MnSbO}_6 \) and \( \text{Ca}_2\text{MnRuO}_6 \). Thus it appears that the combination of rock-salt cation order, \( a^-b^-a^- \) octahedral tilting and orbital ordering are not mutually compatible.

References


