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Chap. 5 : Structural distortions of orthorhombic $R\text{FeO}_3$ and RMnO_3

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Abstract : We will address in detail the structural distortions responsible for the symmetry lowering of the ideal cubic $Pm\bar{3}m$ perovskite to the orthorhombic $Pnma$ structure of $R\text{FeO}_3$ and RMnO_3 (R = trivalent rare-earth cation), important to the stabilization of the different magnetic and multiferroic phases in these materials. We will also show how the *Amplimodes* tool of *Bilbao Crystallographic Server* is useful in quantifying these distortions and establish which phonons can be used as probes of both the octahedra tilting and deformation.

Keywords : PEROVSKITES, ORTHOFERRITES, ORTHOMANGANITES, STRUCTURAL DISTORTIONS, RAMAN SCATTERING, STRONGLY CORRELATED ELECTRON SYSTEM, MULTIFERROICS

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I. Introduction

The demand for new functional materials with higher performance and versatility has been focused on those exhibiting coupling between elementary excitations ^[1,2]. The transition metal oxides, with perovskite structure, have been largely studied because these materials exhibit strong coupling between orbital, electronic, spin and lattice degrees of freedom ^[1,3]. This is because the transition metal *s*-electrons are transferred to the oxygen ions, and the remaining strongly correlated *d*-electrons determine their physical properties such as charge and spin transport, magnetism, optical response, thermal conductivity and superconductivity ^[4]. The electron correlations constrain the number of electrons at a given lattice site and induce a local entanglement of the charge, spin and orbital degrees of freedom, giving rise to a variety of phenomena, for example, Mott insulators, various charge, spin and orbital orderings, metal to insulator transitions, multiferroicity and superconductivity ^[4]. The interplay among the electronic degrees of freedom produces various forms of symmetry-breaking patterns, leading to novel emergent phenomena that appear only through the collective behavior of electrons, and thus cannot be expected from individual electrons^[4]. In recent years, there has been a burst of activity to manipulate these phenomena, as well as to create new ones ^[4].

In this scope, an interesting material class are the multiferroics, which present co-existence of more than one primary ferroic order parameter in a single-phase material ^[1]. The coexistence of several order parameters brings about novel physical phenomena and offers possibilities for new device functions. These ferroic orders can be associated with ferromagnetism, ferroelectricity, ferroelasticity and ferrotoroidicity. Figure 1(a) shows the required coexistence for multiferroic materials presenting ferroelectric and ferromagnetic phases ^[2]. However, it has been later extended to those displaying other orderings, namely the coexistence of ferroelectricity and antiferromagnetism ^[5].

Figure 1: Relationship between multiferroic and magnetoelectric materials and (b) schematic illustrating different types of coupling between magnetization (M), electric polarization (P) and elasticity (ϵ), via magnetic field (H), electric field (E) and strain (σ).

Towards a complete knowledge of the physics encompassing multiferroics, the deep understanding of its driving mechanisms, as it is the case of an existent cross-coupling among the magnetic, electric and elastic orders, is of far great interest (see Figure 1(b)). This is due to the emergent functionalities which are promising for innovative technology, and the quest for multifunctional devices. For instance, magnetoelectric coupling can be exploited in novel types of memory elements. As ferroelectric polarization and magnetization are used to encode binary information in FeRAMs (ferroelectric random-access memories) and MRAMs (magnetic random access memories), respectively, the coexistence of coupled magnetization and polarization in a multiferroic material allows for processing four-state logic states in a single device ^[3]. More complex schemes have even been proposed in order to store up to eight logic states ^[3]. The exciting new development is the discovery that even a weak magnetoelectric interaction can lead to spectacular cross-coupling effects when it induces electric polarization in a magnetically ordered state ^[6]. Such ferroelectricity, showing an unprecedented sensitivity to applied magnetic fields, occurs in frustrated magnets with competing interactions between spins that originate complex magnetic structures ^[6,7].

Multiferroic and magnetoelectric materials are rare, as ferroelectricity and magnetism tend to be mutually exclusive and interact weakly with each other when they coexist ^[8]. This is because the transition metal *d*-electrons, which are essential for magnetism, reduce the tendency for off-center ferroelectric distortion. Consequently, an additional electronic or structural driving force must be present for ferromagnetism and ferroelectricity to be both present. One scenario for multiferroicity is when a material

presenting a ferroelectric order below the Curie temperature T_C , contains magnetic ions that order antiferromagnetically at the Néel temperature $T_N \ll T_C$, such as in YMnO_3 ($T_C = 913 \text{ K}$, $T_N = 70 \text{ K}$), BiFeO_3 ($T_C = 1100 \text{ K}$, $T_N = 640 \text{ K}$) and BiMnO_3 ($T_C = 450 \text{ K}$, $T_N = 105 \text{ K}$)^[9–11]. In YMnO_3 , ferroelectricity is stabilized through a double potential well, emerging from the fivefold oxygen coordination^[12], while in BiFeO_3 and BiMnO_3 , the charge asymmetry is created by the Bi-O hybridization^[13,14]. Though YMnO_3 and BiFeO_3 present rather larger electric polarizations (6 and $100 \mu\text{C}\cdot\text{cm}^{-2}$, respectively), the magnetic transition is only slightly sensed by the polar properties, mirroring a weak magnetoelectric coupling. Such feebleness happens because the order parameter associated with the ferroelectric transition is already saturated when the magnetic order parameter emerges. Thus, those materials are not the most suitable for magnetoelectric applications as standalone materials. Despite this handicap, BiFeO_3 has been used to fabricate multifunctional devices operating at room temperatures^[3]. Nevertheless, the better solution to improve devices is to increase magnetoelectric coupling by bringing T_C and T_N closer together.

Another scenario is observed when ferroelectricity emerges simultaneously from the magnetic order parameter, such as in the case of complex modulated spin structures that break the spatial inversion symmetry^[15]. This is the example of the cycloidal spin structure stabilized below 28 and 20 K in TbMnO_3 and DyMnO_3 , respectively, which gives rise to a ferroelectricity of improper nature (i.e. the electric polarization is a second-order parameter), both presenting an electric polarization of $0.06 \mu\text{C}\cdot\text{cm}^{-2}$ at 2 K^[15]. Moreover, as the electric polarization is intrinsically connected with the spin structure, there is a strong magnetoelectric coupling, allowing a magnetic-field control of the ferroelectricity^[16].¹

At this point, it is crucial to highlight that their spin structure has been proved to be highly dependent on the elementary structural distortions, which is mediated by a driving force based on the subtle balance between competitive ferro- and antiferromagnetic super-exchanges. In this regard, these materials have been at the focus of intense research, because of their outstanding structurally distortion-controlled phase transitions sequences, accompanied by changes on the magnetic,

¹ However, to the best of our knowledge, the reverse effect, wherein the magnetization is controlled by an applied electric field, has not yet been enough studied in these materials^[68]. This matter can be attributed to the fact that in TbMnO_3 and DyMnO_3 , the linear magnetoelectric coupling (P.M) is in fact forbidden by symmetry, and only biquadratic ($P^2.M^2$) or linear in the gradient of the inhomogeneous magnetization ($P.M.\text{grad}(M)$) couplings are allowed^[69,70].

electronic transport and ferroelectric properties. The RFeO₃ and RMnO₃ families comprise a noteworthy number of that kind of materials, presenting definite couplings among those degrees of freedom.

II. Structural Distortions of Orthorhombic *Pnma* Perovskites

Most of the known multiferroics present a crystallographic structure that emerges from the ideal cubic perovskite with *Pm-3m* symmetry, shown in Figure 2(a). It is one of the most known structure for solid materials, and its general formula is given by ABX₃. Typically, the A-cation is a rare-earth (La to Lu), a post-transition metal (Pb or Bi) or an alkali-metal (Sr, Ca, Na), being the B-cation a transition metal and the X-anion is nitrogen, oxygen or fluorine ^[17]. The simple ideal perovskite structure consists in corner shared BX₆ octahedra, where the B-cation occupies the octahedra centers. The BX₆ octahedra then form chains along the cubic axis, and the A-cation occupying the center of the dodecahedron cavity created by the BX₆ network. However, to preserve the cubic symmetry, the ionic diameter of the A-cation must match the cavity between the BX₆ octahedra chains. This matching can be calculated by the ionic radii (12th coordination for the A- and 6th for the B-cation), resulting in the Goldschmidt tolerance factor, expressed as ^[18]:

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)} \quad (1)$$

Actually, the situation of $t = 1$ of the ideal perovskites structure is rarely observed, being SrTiO₃ the most notable case ($t = 1.002$) ^[19]. Yet, in most perovskite-like structures this is not the case. If X is an oxygen and A a rare-earth ion, its ionic radius is typically smaller than the formed cavity between the BX₆ octahedra chains ($t < 1$). To compensate this and improve cationic coordination, there is a short-period cooperative rotation of the BO₆ octahedra. This lowers the cubic symmetry, often to a tetragonal (e.g. SrTiO₃ below 105 K), hexagonal (e.g. YMnO₃ and HoMnO₃) or orthorhombic symmetry (e.g. TbMnO₃ and DyMnO₃). Here we will focus solely on the orthorhombic *Pnma* symmetry, shown in Figure 2(b), found in most the perovskite oxides, namely on the rare-earth orthomanganites (RMnO₃) and orthoferrites (RFeO₃), and their solid solutions, which will be hereafter designated simply as rare-earth manganites and ferrites, respectively ^[20]. Yet, before further advancing, it is worth to understand how this orthorhombic *Pnma* structure is obtained from the cubic *Pm-3m* structure.

Figure 2: (a) Structure of the ideal cubic perovskite with $Pm-3m$ symmetry and general formula AXO_3 . (b) Distorted perovskite structure with $Pnma$ symmetry resulting from the octahedra rotation due to the small A-cation size.

The symmetry-lowering distortions to the $Pnma$ structure consist of both the BO_6 octahedra in-phase and anti-phase tilts, yielding a fourfold increase of the primitive unit cell ($Z = 4$) [19,21,22]. The in-phase tilt occurs around the $[010]_{pc}$, and the anti-phase tilt around the $[101]_{pc}$ pseudocubic axes, with respect to the ideal $Pm-3m$ perovskite structure [21]. The tilt system of this kind of materials is usually described using the Glazer notation [21]. In this notation, the $a^0a^0a^0$ designates an untitled system [21]. When tilts are present around a given axis, a^+ is introduced on the index of that respective axis if the tilt is in-phase, and a^- if the tilt is anti-phase along that same axis. Figure 3(a) and (b) show a view along the tilt axis for a single in-phase and anti-phase tilt, respectively. When more than one tilt is present with different values, then different letters are used [21].

Figure 3: View along the $[010]_{pc}$ direction of two adjacent layers of octahedra for (a) the $a^0b^+a^0$ tilt system, (b) the $a^0b^-a^0$ tilt system and (c) the $a^-b^+a^-$ tilt system. + and - represent positive and negative rotations, respectively, along each axis. Projection in the $[100]_{pc}$ plane between two octahedra layers. The white and black circles stand for the same shared anion of adjacent octahedra (d) before any rotation, (e) after the first anti-phase tilt about $[100]_{pc}$ axis and (f) after the second anti-phase tilt about the $[001]_{pc}$ axis. Adapted from [22].

In the $Pnma$ perovskites, there is the coexistence of an in-phase tilt, represented as $a^0b^+a^0$, with two anti-phase tilts, represented as $a^-b^+a^-$ [21]. Thus, the three tilts in the $Pnma$ structure results in the $a^-b^+a^-$ notation. Since both the anti-phase tilts around the $[100]_{pc}$ and $[001]_{pc}$ axes have the same angle, Megaw has shown that they can be described as a single tilt around the $[101]_{pc}$ axis, therefore being sufficient to consider

only the two independent tilts ($[010]_{pc}$ in-phase and $[101]_{pc}$ anti-phase tilts) to describe the octahedral rotations underlying the $Pnma$ phase^[23]. Figure 3(c) shows the positive and negative rotations of the octahedra in adjacent layers of the $Pnma$ structure. It is still worth to stress that the coexistence of the two anti-phase tilts imposes a deformation of the otherwise regular BO_6 octahedra. The reason for the octahedra deformation is schematically shown in Figure 3(d) to (f) and is as follows. In the untilted structure (Figure 3(d)), the adjacent octahedra are able to share the O2 oxygens between them. Also, when the first anti-phase tilt along the $[100]_{pc}$ axis ($a^-b^0b^0$) is considered, this sharing is still possible as both octahedra equally displace the shared oxygen (Figure 3(e)). However, when the second anti-phase tilt along the $[001]_{pc}$ axis ($a^0a^0c^-$) is included, these octahedra displace the shared oxygen into opposite directions (Figure 3(f)). This is only possible to accommodate by deforming the otherwise regular octahedra. Yet, this deformation is rather small, as we will discuss in the next section for the $RFeO_3$.

The structural distortions driving the symmetry reduction affect the symmetry constraints on the position of each atom in the primitive cell, as summarized in Table 1. In the $Pm-3m$ phase, both the A and B -cations occupy symmetry inversion sites, while the oxygens are at the center of the cube faces (cf. Figure 2(a)). The coordinates of each atom are totally fixed by symmetry.

Table 1: Wyckoff positions of $Pm-3m$ and $Pnma$ phases for ABO_3 perovskite structure.

$Pm-3m$				$Pnma$			
Atom	Multiplicity	Wyckoff	Symmetry	Atom	Multiplicity	Wyckoff	Symmetry
A	1	a	$m-3m$	A	4	c	$.m.$
B	1	b	$m-3m$	B	4	b	-1
O	3	c	$4/mm.m$	O1	4	c	$.m.$
				O2	8	d	1

In the $Pnma$ phase, the B -cation remains at the inversion center, while the A -cation now occupies a site with a mirror plane symmetry, with two unconstrained coordinates (x and z). The oxygens are now divided into two different sets according the respective site symmetry. The two O1 (the apical oxygens of the octahedron) have the same symmetry as the A -cation, occupying the same ac -plane. The four O2 (the equatorial

oxygens of the octahedron) are in general positions, without any constraints on their coordinates (cf. Figure 2(b)). It is worth to mention that due to the oxygen tilting, the A-cation now forms 8 shorter bonds and 4 longer bonds with the oxygens. Thus, its coordination is reduced from 12 to 8, which must be considered when calculating the tolerance factor.

Figure 4: (a) The fivefold degeneracy of the d-orbitals is lifted by the cubic crystal field into two e_g -orbitals [(x^2-y^2) , $(3z^2-r^2)$] and three t_{2g} -orbitals [(xy) , (yz) , (zx)], whose degeneracy is then lifted by the Jahn-Teller effect. (b) Effect of the $Pnma$ tilt system and of the Jahn-Teller effect on the B-O bond lengths of the BO_6 octahedra.

In some special cases, the deformation of the octahedra is greatly increased due to the cooperative Jahn-Teller distortion, which does not further lower the $Pnma$ symmetry^[24]. It follows from the Jahn-Teller theorem that any nonlinear molecule, with a spatially degenerate electronic ground state, will undergo a distortion to remove that degeneracy and lower the overall energy. Figure 4(a) schematically shows the atomic energy levels splitting of the Mn^{3+} ion d^4 -configuration on the $RMnO_3$ $Pnma$ structure. Firstly, the fivefold degeneracy of the is partially lifted by the crystal field of the cubic

array of the MnO_6 octahedra into three half-filled degenerate t_{2g} -orbitals and two degenerate e_g -orbitals sharing one electron. Then, the Jahn-Teller effect lifts the degeneracy on the e_g -orbitals, causing the $d(x^2-y^2)$ to be half-filled and the $d(3z^2-r^2)$ empty. This effect yields an additional distortion of the already tilted distorted BO_6 octahedra, with a gain in electronic energy that is larger than the elastic energy paid for the distortions of the octahedron and the lattice ^[25]. The local distortions from the Jahn-Teller effect present a staggered long-range order due to the also staggered orbital ordering on the ac -plane ^[24,26,27]. The Jahn-Teller distortion is then called cooperative ^[24,26,27]. Figure 4(b) shows the effect of the tilts and Jahn-Teller effect on distorting the BO_6 octahedra, by the distance between the center B -cation and each pair of oxygens along each of three octahedron axes. The tilts cause a slight elongation of one pair of the $B\text{-O}2$ bond lengths, which is further elongated by the Jahn-Teller distortion, while the other pair of $B\text{-O}2$ bond lengths and the pair of $B\text{-O}1$ bond lengths both decrease.

The octahedra tilts are key elements for understanding the elastic, magnetic and electronic properties of the perovskites, and can be tuned by the size of the rare-earth ion ^[28]. The tilt angles φ are given by the angle between neighbors octahedra, which can be expressed as a function of the angle between the neighbors $B\text{-O-B}$ atoms ^[21]:

$$\varphi = \frac{(180 - (B - O - B))}{2} \quad (3)$$

For the following considerations regarding the structural distortions of RMnO_3 and RFeO_3 , bear in mind that a direct comparison between the two systems can be drawn for the same R -cation as the same tolerance factor is obtained. This particularity occurs for the reason that the Mn^{3+} and the Fe^{3+} cations share the same ionic radius of 0.645 Å, whilst considering the high spin configuration and the 6th coordination of the BO_6 environment.

The magnitude of the tilt angles around the $[101]_{\text{pc}}$ and $[010]_{\text{pc}}$ directions increase as the tolerance factor decreases for the RMnO_3 and RFeO_3 , as shown in Figure 5. Compounds with smaller tolerance factor present greater tilt angles, and thus greater tilt distortions. Moreover, the magnitude of the anti-phase tilt angle around the $[101]_{\text{pc}}$ direction is always larger than the value of the in-phase tilt angle around the $[010]_{\text{pc}}$ direction. For the same R -cation, both RMnO_3 and RFeO_3 systems have similar values for the tilt angle around the $[101]_{\text{pc}}$ direction, while the RMnO_3 present slightly larger values for the tilt angle around the $[010]_{\text{pc}}$ direction than the RFeO_3 .

Figure 5: Tilt angles about the $[101]_{pc}$ (black) and $[010]_{pc}$ (blue) axes as a function of tolerance factor for $R\text{MnO}_3$ (squares) and $R\text{FeO}_3$ (triangles). Values taken from [29–31].

Figure 6: (a) B-O distances as a function of the tolerance factor for the $R\text{FeO}_3$ (open symbols) and $R\text{MnO}_3$ (closed symbols). Reproduced with permission of the [International Union of Crystallography](#) [32]. (b) c -axis view of a $R\text{MnO}_3$ structure ($R = \text{Tb}$). s , m and l stand for the short, medium, and long $B\text{-O}$ bonds, whereas ϕ_1 and ϕ_2 correspond to the $[101]_{pc}$ and $[010]_{pc}$ tilt angles, respectively. Reprinted figure with permission from R. Vilarinho et al., [Phys. Rev. B 97, 144110 \(2018\)](#). Copyright 2019 by the American Physical Society [33].

This difference is apparently associated with the Jahn-Teller distortion, as the $[010]_{pc}$ tilt angle involves the O2 oxygens on the ac -plane affected by this distortion.

Figure 6(a) shows the B -O (i.e. Fe-O and Mn-O) bond lengths along the 3 different octahedron axes, as a function of the tolerance factor, for the $RFeO_3$ and $RMnO_3$ [32]. It is readily seen that for the $RFeO_3$ (open symbols) the three Fe-O bond lengths take very similar values. Only for the compounds with the smallest tolerance factors, one of the Fe-O2 is elongated. This is due to the increase of the strain imposed by the two co-existing tilts that increase as the tolerance factor decreases. In the case of $RMnO_3$, three very distinct Mn-O distances are found, due to the Jahn-Teller effect. Figure 6(b) presents a schematic c -axis view of these bonds and tilt angles of the $RMnO_3$ structure [33]. The Mn-O medium bond length is always along the b -direction, while the short and long bond lengths are staggered on the ac -plane.

Figure 7: Lattice parameters of the $Pnma$ structures of $RMnO_3$ (squares) and $RFeO_3$ (triangles), as a function of the tolerance factor. Values taken from [29–31].

The lattice parameters of the primitive cell of the $Pnma$ structures of RMnO_3 and RFeO_3 , as a function of the tolerance factor, are shown in Figure 7. As the tolerance factor increases, the b and c lattice parameters also increase. Yet, the lattice parameter a is only slightly dependent on the tolerance factor, presenting a maximum between the Gd and Eu rare-earth ions. Comparing the RMnO_3 and RFeO_3 , there is a substantial difference of the values of the a and b lattice parameters, which further mirrors the key role played by the Jahn-Teller distortion.

The tilt and Jahn-Teller distortions can be tuned by chemical substitution and various external parameters, such as temperature, stress, electric-field and hydrostatic pressure [34–38]. The chemical substitution is an easy way to tune the effective A-cation size, by controlled substitution of the rare-earth cation by another different ion.

III. Following distortions with Amplitudes tool and Raman scattering

The low-symmetry crystallographic structure can be described as the high-symmetry crystalline structure plus a static symmetry-adapted structural distortion modes. A quantitative way of expressing the crystallographic distortions is by calculating the distortion modes amplitudes by the corresponding atomic displacements with respect to the high-symmetry phase. Figure 8 schematically shows these symmetry-adapted distortion modes for the $Pnma$ phase, with respect to the $Pm\text{-}3m$ phase. The two octahedra tilts are the two primary order parameters, with symmetries given by the irreducible representations (irreps) $R4+$ and $M3+$, respectively, of the high symmetry cubic space group [24,26]. That symmetry lowering allows for the displacements of the A-cations in the ac -plane that were otherwise forbidden by symmetry constraints. Thus, two anti-polar displacements of the rare-earths cations emerge, with $X5+$ and $R5+$ symmetries, which act as secondary order parameters [24]. The A-cation displacement with $X5+$ symmetry is larger, and couples with the two primary order parameters. This feature was recently referred to be crucial in further decreasing the energy, making the $Pnma$ symmetry so widely stable in these perovskites [20,39]. Finally, the BO_6 octahedra slightly deform with $M2+$ symmetry, due to the strain imposed by the inclusion of the two tilts [19,22,24].

Figure 8: Symmetry-adapted distortion modes of the orthorhombic $Pnma$ structure with respect to the cubic $Pm-3m$ perovskite structure, along with their respected symmetries. The atomic movements are described in the text. Reprinted figure with permission from J. Varignon et al., [Phys. Rev. B 96, 235106 \(2017\)](#) [40]. Copyright 2019 by the American Physical Society.

In the $RFeO_3$ and $RMnO_3$ series, the size of the rare-earth cation acts on the amplitude of the structural distortions of the structure, as measured for example by the tilt angles or the strains, which can thus be tuned by R -cation substitution. Figure 9(a) and (b) present the amplitudes of the symmetry-adapted mode distortions for $RFeO_3$ and $RMnO_3$, respectively, as a function of the tolerance factor. The amplitude of the distortions was calculated from the atomic positions already available in the literature, using the Amplimodes tool of the Bilbao Crystallographic Server ^[24,41]. This is a more practical alternative to view the structural distortions evolution with the rare-earth cation size. The $R4+$ and $M3+$ distortions, associated with the tilts, show the larger amplitudes. The $X5+$ and $R5+$ distortions, associated with the rare-earth shifts, are

also significant. The $\text{M}2+$ distortion is associated with the BO_6 octahedra deformation. For the $R\text{FeO}_3$, the octahedra distortion has the smallest amplitude, originating from the coexistence of the anti-phase tilts, while for the RMnO_3 it also arises from the Jahn-Teller effect and presents much larger values. All these distortions increase linearly as the tolerance factor decreases, with the exception of the $\text{M}2+$ distortion for the RMnO_3 , which slightly increases.

Figure 9: Amplitude of the symmetry-adapted distortion modes as a function of the tolerance factor for (a) $R\text{FeO}_3$ and (b) RMnO_3 .

Another way to follow the structural distortions is through Raman scattering. Some specific phonons are excellent probes of some distinctive distortions, namely the Raman-active octahedra rotation modes that have been associated with the octahedra tilting distortions, schematically shown in the insets of Figure 10(a). Birman^[42] and Shigenari^[43] demonstrated, by means of Landau theory, that one A_g Raman-active mode of the $Pnma$ phase is assigned to one of the soft modes associated with a tilt distortion. The first realization of the A_g -symmetry modes displaying “soft mode” behavior was carried out by Iliev *et al.* for the RMnO_3 ^[44]. In their work, they report a linear scaling of the Raman octahedra rotation mode wavenumbers with the octahedra tilt angles, as shown in Figure 10(a). The proportionality constant was determined as $23.5 \text{ cm}^{-1}/\text{deg}$, for both the octahedra tilts around the $[101]_{\text{pc}}$ and $[010]_{\text{pc}}$ pseudocubic axes.

Figure 10: Frequency of the Raman octahedra rotation modes as a function of tilt angle for (a) $RMnO_3$ and (b) for RBO_3 , with $B = Al, Co, Ni, Cr, Fe, V, Ga, Mn, Ti$ and Sc . (a) Reprinted figure with permission from J. Varignon et al., [Phys. Rev. B 73, 064302 \(2006\)](#). Copyright 2019 by the American Physical Society [44]. (b) Values taken from [29].

Later, Todorov *et al.* have extended this result to a different number of rare-earth orthorhombic perovskites RBO_3 , with $B = Al, Co, Ni, Cr, Fe, V, Ga, Mn, Ti$ and Sc), having found a linear relation for each RBO_3 family, though with a different proportionality constant for each B -cation [29]. Figure 10(b) presents the wavenumber of the Raman octahedra rotation mode as a function of the octahedra tilt angle for these systems, along with the linear scaling and its slope. Through the analysis a wide variety of systems, they were able to identify the dependence of this proportionality constant with the average distance between the B -cation and the surrounding oxygens, expressed by:

$$\omega = (\alpha_1 - \alpha_2 \cdot \langle B-O \rangle) \varphi, \quad (4)$$

where φ is the tilt angle amplitude, $\langle B-O \rangle$ is the mean B -O bond length, $\alpha_1 = 109.1 \text{ cm}^{-1}/\text{deg}$, and $\alpha_2 = 42.3 \text{ cm}^{-1}/(\text{\AA} \cdot \text{deg})$.

Figure 11: Raman octahedra rotation modes wavenumber as a function of tilt angle for $R\text{FeO}_3$. Reprinted figure with permission from M. Weber et al., *Phys. Rev. B* **94, 214103 (2016). Copyright 2019 by the American Physical Society [30].**

Recently, Weber *et al.* have focused on the $R\text{FeO}_3$, and they were able to distinguish the proportionality constant associated with the octahedra tilts around the $[101]_{\text{pc}}$ and $[010]_{\text{pc}}$ pseudocubic axes, obtaining values of 23.9 and 21.1 $\text{cm}^{-1}/\text{deg}$, respectively [30]. This result, plotted in Figure 11, calls for a more detailed study of the aforementioned systems, as it is expected that the same distinction can be obtained, even for the parameters of eq. (4).

IV. Continuously tuning the Jahn-Teller distortion

The possibility of performing a fine tuning of the structural distortions can be achieved through chemical substitution, towards the desired physical properties. We will only consider isovalent substitutions on oxide perovskites, where the valency $A^{3+}B^{3+}O_3^{2-}$ and the $Pnma$ phase are always maintained, in order to enable a continuous and controlled

change of the structural distortions. The obtained structure is considered $Pnma$ under the virtual crystal approximation, where average structure with average lattice parameters, tilts and deformations are considered, instead of the actual local values that differ around the substituted and the substitutional ions. Within these conditions, the chemical substitution can be divided into 2 groups: substitution of the A -site cation and substitution of the B -site cation. The first type of chemical substitution allows for the tuning of the tilt distortion ^[45], while the second one is associated with the octahedra distortion ^[33].

Figure 12: x -dependencies of the of the five symmetry-adapted distortion modes amplitude for $\text{TbMn}_{1-x}\text{Fe}_x\text{O}_3$ series. Open symbols are reference values of parent compounds. Reprinted figure with permission from R. Vilarinho et al., [Phys. Rev. B 97, 144110 \(2018\)](#). Copyright 2019 by the American Physical Society [33].

In the past, the effect of changing the tilt distortion was extensively studied by A -site substitution in rare-earth manganites ^[45–59]. In the rare-earth ferrites, the chemical

substitution is less studied, which may be due to the fact that the rare-earth sublattice can also couple with the iron sublattice, yielding a more intricate behavior of these compounds [60,61]. Thus, this substitution cannot be reduced to a simple tune of the structure, as the interplay between the R^{3+} and the Fe^{3+} spins is also being changed. The *B*-site substitution remains much more unexplored, though it must be noted that the substituted ion is the one whose spins are magnetically ordered (Mn^{3+} and Fe^{3+} spins in our case) [62–65]. Then, both the structure distortions and the magnetic properties are simultaneously changed. The chemical substitution on the *B*-site concerns another kind of distortions. In the special case where the *B*-site cation is Jahn-Teller active, as it is the case of $RMnO_3$, the chemical substitution by non-active Jahn-Teller cations tunes both the amplitude of the octahedra distortions and asymmetry. The *B*-site substitution in $RMnO_3$ can be achieved using different transition metal cations. In order to avoid changing other distortions, excluding the Jahn-Teller distortion, the most suitable choice is Fe^{3+} , since this cation has exactly the same ionic radius as Mn^{3+} , yielding the same BO_6 volume [66].

To study the effect of changing the Jahn-Teller distortion, we have followed the work of Vilarinho *et al.* on $TbMn_{1-x}Fe_xO_3$. Figure 12 presents the *x*-dependence of the five symmetry-adapted modes for this system [33]. We focus on the amplitude of the M2+ distortion, associated with the BO_6 octahedra deformation. For $x < 0.5$, it presents larger amplitudes, decreasing from 0.35 Å for $x = 0$ to below 0.10 Å for $x = 0.5$, evidencing large octahedra deformation that arises from the Jahn-Teller distortion. At $x = 0.5$ and above, it becomes constant, presenting small amplitudes that are of the order of the ones observed in non-Jahn-Teller systems, such as the $RFeO_3$, shown in Figure 9(b). The *x*-dependence of the amplitude of the M2+ symmetry-adapted mode associated with octahedra distortion allows the conclusion that the cooperative Jahn-Teller distortion in the solid solution decreases up to $x = 0.5$, above which its cooperativeness is suppressed. This critical *x*-value had been already found in previous studies of $DyMn_{1-x}Fe_xO_3$ and $LaMn_{1-x}Ga_xO_3$ [63,67], emerging as a universal rule for these solid solutions.

The wavenumber of the Raman modes associated with Tb^{3+} translations and rigid octahedra rotations were also studied as a function of *x*, as shown in Figure 13(a) [33]. The wavenumber of the Raman modes involving Tb^{3+} motion decreases linearly with *x*, evidencing a decrease of the AO_{12} dodecahedra deformation, also mirrored by the X5+ distortion amplitude behavior, associated with the average decrease of the BO_6 octahedra deformation. However, the Raman octahedra rotation modes wavenumbers exhibit two different linear relations with *x*, which change slopes at $x = 0.6$. The wavenumber of the Raman anti-phase $[101]_{pc}$ octahedra rotation mode increases with *x*, changing its linear relation slope at $x = 0.6$. Contrarily, the wavenumber of the Raman in-phase $[010]_{pc}$ octahedra rotation mode decreases linearly for $x < 0.6$ and

becomes constant for $x > 0.6$.

Since the Raman octahedra rotation modes change their linear behavior with x for the same compositions where the cooperative Jahn-Teller distortion is suppressed, it was proposed that these Raman modes are also sensitive to the octahedra distortion. Note that the tilt angles behave linearly throughout this series, measured by the amplitudes of the associated M3+ and R4+ distortions (cf. Figure 12(b)). Thus, the behavior of these two Raman octahedra rotation modes wavenumbers with x cannot be understood by a linear scaling with the tilt angles. Moreover, in this series, the mean $B-O$ bond length is kept constant and still a single linear x -dependence of the Raman octahedra rotation modes wavenumber is not observed. In fact, a correlation between the Raman in-phase $[010]_{pc}$ octahedra rotation mode and M2+ distortion amplitude, which measures the octahedra deformation, is evident in Figure 13(b). This Raman mode is particularly sensitive to the octahedra deformations as it only involves the motions of the O2 oxygens that are associated with the Jahn-Teller distortion (cf. inset of Figure 13(b)).

Figure 13: (a) Wavenumber of the Raman R -shifts and octahedra rotation modes as a function of x . (b) Raman in-phase $[010]_{pc}$ octahedra rotation mode wavenumber (open symbols) and M2+ distortion amplitude (closed symbols) x -dependencies. Reprinted figure with permission from R. Vilarinho et al., [Phys. Rev. B 97, 144110 \(2018\)](#). Copyright 2019 by the American Physical Society [33].

The linear relation between the octahedra tilt angles and the wavenumbers of their corresponding Raman octahedra rotation modes referred to above, considers the basic relevant ingredients with primary order parameters associated with the octahedra tilts, but it does not comprise the role played by the cooperative Jahn-Teller distortion. As it was just demonstrated that the Raman octahedra rotation modes wavenumber correlates with the amplitude of Jahn-Teller distortion, then in eq. (4) the asymmetry between the distinct *B*-O distances should also be included. However, to achieve this, a study of a wide variety of systems would be needed. Nevertheless, for the case of RFeO₃ and RMnO₃, we are able to describe this correlation by:

$$\omega = (\beta_1 + \beta_2 \cdot \Delta d) \varphi, \quad (5)$$

where $\beta_1 = 21.1 \text{ cm}^{-1}/\text{deg}$, $\beta_2 = 410 \text{ cm}^{-1}/(\text{deg} \cdot \text{\AA})$, and $\Delta d = \sigma^2 / \langle B\text{-O} \rangle^2$ is the relative variance (σ) of the *B*-O distances. In summary, changes on the Raman rotation modes wavenumber only directly mirror changes on the corresponding tilt angle if the *BO*₆ octahedra size and deformation is kept constant. Although this is not strictly the case for a given *RBO*₃ series, the *BO*₆ deformation imposed by the increasing of the tilt angle within the series can be neglected, as it is too small to be experimentally relevant. However, when the *B*-cation is changed (such as *RB*_{1-x}*B'*_x*O*₃ solid solutions) both the contributions from *BO*₆ octahedra tilting and deformation must be considered. The fact that the Raman rotation modes wavenumber correlates with the octahedra deformation (i.e. M²⁺ distortion) amplitude, calls for some care in the interpretation of the octahedra tilt evolution on the Raman studies, namely for Jahn-Teller-distorted perovskites.

V. Conclusion

We have described the symmetry-lowering from the *Pm-3m* cubic to the *Pnma* orthorhombic perovskite structure and its structural distortions, namely on RFeO₃ and RMnO₃ materials. We have shown how these distortions can be expressed by symmetry-adapted distortion modes, through the Amplitudes tool of Bilbao Crystallographic Server. These are often better suited than atomic coordinates to follow distortions, as shown by our case-studies RFeO₃, RMnO₃ for the tilt distortion and their solid-solution RMn_{1-x}Fe_xO₃, with *R* = Tb, for the Jahn-Teller distortion. We also have shown how the *A*_g-symmetry Raman octahedra rotation modes can be used as probes for these structural distortions in many *RBO*₃ families. For the octahedra tilt a direct linear proportionality is found, however only if

the BO_6 octahedra remains unchanged. This is due to the fact that these modes also scale with the average $B-O$ bond length (i.e. different B -cations), as well as with the asymmetry between distinct $B-O$ bond lengths (i.e. Jahn-Teller active B -cations). This knowledge provides reference data for structural investigation of $Pnma$ orthorhombic RBO_3 series, helpful for studies of phenomena including structural instabilities, ferroelectricity and multiferroicity.

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