From manganites to ferrites: a study on the structural, polar, magnetic and magnetoelectric properties

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Abstract

Rare-earth manganites form an interesting set of materials, known for their complex physics, that results from the interplay of spin, charge, orbital and lattice degrees of freedom. In 2003, an investigation by Kimura et al., led to the discovery of ferroelectricity driven by spiral magnetism in TbMnO$_3$ and DyMnO$_3$ [1, 2]. This new phenomena was uncovered in these manganites and has since been found in several other compounds[3]. These manganites show impressive magnetoelectric effects, due to the magnetic origin of the ferroelectricity. Noteworthy, this discovery was made while exploring the magnetic phase diagram of the rare-earth manganites.

In the interest of exploring the phase diagram in a new direction, we here discuss the structural, polar, magnetic and magnetoelectric properties of the solid solutions TbMn$_{1-x}$Fe$_x$O$_3$ and DyMn$_{1-x}$Fe$_x$O$_3$, which take us from the manganites to the ferrites.

We provide a description of the structure of manganites and ferrites and their differences. The lattice degree freedom is of central importance in understanding the magnetic phase diagram, so we report on X-ray diffraction and Raman spectroscopy results for TbMn$_{1-x}$Fe$_x$O$_3$, for the full range.

For low concentrations of Fe$^{3+}$, $x \leq 0.1$, the impact of the substitution on the ferroelectricity and the magnetoelectric properties is investigated. Measurements of the magnetization, polarization, electric permittivity, specific heat and magnetoelectric response are reported. Using these results a phase diagram for the low substitution range is proposed.
Resumo

As manganitas de terras raras constituem um família de materiais de grande interesse, conhecida pela sua física complexa, resultante da interacção de diferentes factores como a rede cristalina, carga, orbital e spin. Em 2003, uma investigação por parte de Kimura et al. conduziu à descoberta de ferroelecricidade induzida por ordem magnética espiral nas manganitas TbMnO$_3$ e DyMnO$_3$. Este novo fenómeno foi descoberto nas manganitas e, entretanto, estendido para vários outros materiais. Estas manganitas demonstram efeitos magnetoelétricos impressionantes, devido à origem magnética da ferroelecricidade. Note-se que esta descoberta foi feita enquanto se explorava o diagrama de fases magnético das manganitas de terras raras.

No interesse de explorar o diagrama de fases numa nova direcção, nós analisámos as propriedades estruturais, polares, magnéticas e magnetoelétricas das soluções sólidas TbMn$_{1-x}$Fe$_x$O$_3$, que nos levam das manganitas às ferrites.

Neste texto, é dada uma descrição completa da estrutura das manganitas e das ferrites e das suas diferenças. A estrutura cristalina têm grande relevância na compreensão do diagrama de fases. Por isso, nós reportamos medições de difração de raios-X e de espectroscopia Raman para a solução sólida TbMn$_{1-x}$Fe$_x$O$_3$.

Para baixas concentrações de Fe$^{3+}$, $x \leq 0.1$, o impacto da substituição de Mn$^{3+}$ por Fe$^{3+}$ na ferroelectricidade e nas propriedades magnetoelétricas foi investigado. Medidas de magnetização, polarização elétrica, permittividade, calor específico e da resposta magnetoelétrica são apresentados. Usando estes resultados, um diagrama de fases é proposto para a região de baixas concentrações de Fe$^{3+}$. 
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Chapter 1

Introduction

This thesis is devoted to the study of solid solutions RMn$_{1-x}$Fe$_x$O$_3$ for R=Tb,Dy. Their structure, lattice dynamics, polar, magnetic and magneto-electric properties were investigated in an attempt to explore the interesting physics of manganites in a new direction, opening up new phase diagrams and phenomena.

This introductory chapter has two purposes. One is to provide some context and situate this thesis in the field of transition metal oxides. A lot of interest and multiple theoretical and experimental investigations have been devoted to rare-earth manganites, both doped and undoped, and this study should be seen as integrated in this effort. The second goal is to review previously reported work in these matters. Many of the key concepts mentioned here in passing are more carefully defined in subsequent chapters. The point is to provide some motivation and perspective on the subject at hand.

1.1 Phase diagram of rare-earth manganites

Rare-earth manganites, with general formula RMnO$_3$ (R=La,...,Lu), are known for their complex physics, resulting from the interplay of charge, spin, lattice and orbital degrees of freedom. In particular, doped LaMnO$_3$ has generated an explosion of interest since the discovery of colossal magnetoresistance in these compounds [11]. But even the simpler, undoped, rare-earth manganites have a very rich phase diagram [12]. We will here describe some of its main features.

We will focus on the magnetic ordering of the Mn$^{3+}$ spins and mainly neglect the role of the R$^{3+}$ spins, since they order at lower temperatures. The Mn$^{3+}$ spins interact with each other via superexchange interactions, mediated by the oxygen ions (Figure 1.2).

A brief note on the structure is here required. These manganites have an orthorhombically distorted perovskite structure (space group $Pbnm$). A detailed description of this structure and its main distortions is of great relevance to the physics and is provided in Chapter 2. For now, we note only that the
smaller the R cations the more distorted these perovskites are and the more the Mn-O-Mn bond angles, represented in Figures 1.2 and 1.3, deviate away from 180 degrees. This bond angle variation leads to changes in the balance of the different magnetic interactions and to the appearance of different magnetic phases (see Figure 1.2). Hence, the phase diagram of the various rare-earth manganites is traced in Figure 1.1 as a function of the size (ionic radius) of the rare-earth cations.

For the larger R-cations (R=La to Sm) we have a single magnetic phase transition from paramagnetic to A-type antiferromagnetic (AFM). In this magnetic ordering, the Mn$^{3+}$ spins couple ferromagnetically in the $ab$ plane and antiferromagnetically along the $c$-axis. The spins lie mainly along the $b$-axis but a slight canting gives rise to a weak ferromagnetic component (WFM) along the $c$-axis (Figure 1.2). For R=Eu and Gd, this phase is still present at low temperatures but through a collinear incommensurate sinusoidal magnetic ordering. For the smaller cations (R=Ho to Lu), the first transition is again to the incommensurate collinear ordering but the second transition is into the so-called "up-up-down-down" magnetic ordering or E-type antiferromagnetic ordering.
All these phases are paraelectric (PE).

For intermediate sized rare-earth cations (R=Tb,Dy), something different happens. First, a phase transition to the incommensurate phase at 41K for TbMnO$_3$ and 39K for DyMnO$_3$. Second, at 27K for TbMnO$_3$ and 19K for DyMnO$_3$, the system transitions to commensurate cycloidal ordering (see Figures 1.2 and 1.3). At this magnetic transition, the system becomes ferroelectric (FE), with an electric polarization along the c axis.

This discovery was made by Kimura et al. in 2003 [1] and it was really new. It ultimately led to the current revival in the field of multiferroics [13]. Noteworthy, the discovery was made while exploring the phase diagram of rare-earth manganites [1, 14].

Multiferroics are materials in which more than one ferroic order parameter exist (ferroelasticity, ferromagnetism, ferroelectricity, ferrotoroidicity). A particular case is the one of magnetoelectrics, materials with coupled (anti)ferromagnetic and ferroelectric orders. This coupling is not only interesting from the physics standpoint but very desired for applications since it might allow for an electric field control of the magnetization and magnetic field control of the polarization. This is usually termed the magnetoelectric effect.

Magnetoelectrics are not a new subject but interest in them faded when it was found that magnetic and ferroelectric orders were practically exclusive in transition metal oxides, for fundamental reasons [15]. Even when these orders were found to coexist, there was very weak coupling between them. The reason being that the ferroelectric and magnetic ordering had different physical origins (and frequently corresponded to different ions), with ferroelectric phase transitions happening at much higher temperatures than magnetic transitions. The two phenomena were essentially independent [16].

In TbMnO$_3$ and DyMnO$_3$ the ferroelectricity emerges at the magnetic phase transition [1, 2] moreover it is now known to be a consequence of the cycloidal spin ordering. This crucial finding of magnetically driven ferroelectrics opened the door for multiferroics once again and there have since been found many more examples of materials were the ferroelectricity is driven by spiral magnetism [3].

Due to their magnetic origin, the ferroelectricity responds to magnetic fields and often displays considerable magnetoelectric effects [1, 13]. In both TbMnO$_3$ and DyMnO$_3$ a polarization flop from the c-axis to the a-axis has been observed when a magnetic field greater than 5T is applied along the b-axis [1, 2]. Additionally, a giant magnetodielectric effect is observed in DyMnO$_3$ [2].

Numerous experimental studies have been performed in TbMnO$_3$ and DyMnO$_3$ by means of neutron diffraction [17, 18, 19], x-ray diffraction [14, 1, 20], raman [21, 22, 23, 24] and terahertz [25] spectroscopy, dielectric constant and polarization measurements [1, 2, 26] and others techniques. A plethora of different topics arose from these studies as, for example, the behaviour of magnetoelectric domain walls and the existence of electric field controllable excitations termed electromagnons.

Theoretical modelling on these materials has also been actively pursued. Indeed, it began as soon as the experimental finding itself. Kimura et al. [14] applied the two dimensional $J_1 - J_2$ Ising model to qualitatively describe the
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phase diagram of rare-earth manganites. Although they predicted long wavelength magnetic structures between AFM(A) and AFM(E) phases, they inevitably failed to reproduce the cycloidal phase since Mn spins were considered as Ising spins.

More accurate models followed with an emphasis on explaining the origin of the electric polarization. Mostovoy developed a phenomenological theory based on the Ginzburg-Landau approach [27]. A microscopic model was proposed by Katsura, Nagaosa and Balatsky (KNB model) based on the spin supercurrent scenario [28]. Another proponent for a microscopic explanation was the one of Sergienko and Dagotto, who used the inverse Dzyaloshinskii-Moriya effect to explain the polarization [29]. In all these theories, the following expression follows:

\[ \mathbf{P} = \lambda \mathbf{e}_{i,i+1} \times (\mathbf{S}_i \times \mathbf{S}_{i+1}) \]  

(1.1)

where \( \mathbf{e}_{i,i+1} \) is the versor connecting two neighboring spin sites and the constant \( \lambda \) is dictated by the exchange and spin-orbit interactions.

In TbMnO\(_3\) and DyMnO\(_3\), the cycloidal forms in the \( bc \) plane and the spin modulation is along the \( b \)-axis (see Figure 1.3). The polarization emerges in the \( c \) direction in agreement with the theoretical prediction.

Despite the two previous microscopic theories having similar predictions the origin of the polarization is distinct. In the KNB model the polarization is purely electronic, while in the inverse Dzyaloshinskii-Moriya effect, the polarization is ionic. These ionic displacements are very small and hard to measure. So \textit{ab initio} calculations were performed to test the models. Density functional theory calculations done by Xiang et al. [30] and also by Malashevich and Vanderbilt [31] favored ionic displacements over electronic origin. Conclusive evidence in favor of ionic displacements came in 2011 with high precision measurements of the extended x-ray absorption fine structure of TbMnO\(_3\) by Walker et al [32].

Explained how spiral magnetism generates an electric polarization, still remains the problem of why this phase is stabilized in these manganites and the explanation for the polarization flop. As expected by the previous theories the magnetic phase in which the polarization is along the \( a \)-axis, is a cycloidal in the \( ab \) plane (Figure 1.3). By taking a classical Heisenberg \( S=2 \) model and extending it by including magnetic anisotropies and interactions, Mochizuki and Furukawa [4] developed a model that properly reproduces the phase diagram of the rare-earth manganites, and the solid solutions mentioned in the following, predicts the polarization flop and has since been applied to describe many other phenomena involving these manganites [33, 34].

Returning to the phase diagram of Figure 1.1, the rare-earth manganites can provide us only with a series of discrete values of the ionic radius. The phase diagram between them, can, however, be explored by means of solid solutions. In solid solutions, where one species of atom is randomly replaced by another, in a well defined proportion, a description of the structure as possessing an "average atom" is often possible [35]. This is a commonly used method of obtaining a continuous variation of physical parameters.
1.2 Exploring the solid solutions RMn$_{1-x}$Fe$_x$O$_3$

The solid solutions discussed in the previous section referred only to substitution of the rare-earth cations (A-site cations, see section 2.1). In an attempt to explore the phase diagram in a new direction, we focused on substitution on the Mn site (B-site) by Fe.

Fe$^{3+}$ and Mn$^{3+}$ have the same ionic radius of 0.645 angstroms, for six-fold coordination and a high spin configuration, allowing for a stable solid solution for...
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Figure 1.4: Phase diagram of Eu$_{1-x}$Y$_x$MnO$_3$. Adapted from [4]

the full range, from $x=0$ (manganites) to $x=1$ (ferrites), in TbMn$_{1-x}$Fe$_x$O$_3$ and DyMn$_{1-x}$Fe$_x$O$_3$. We chose $R=$Tb,Dy, due to the interesting magnetoelectric effects mentioned in the previous section.

Ferrites are by themselves systems of considerable interest, known to possess various spin reorientation transitions and magnetoelectric effects at low temperatures and applied magnetic fields [38].

We already pointed out that behind the appearance of ferroelectricity in these manganites lies the Dzyaloshinskii-Moriya interaction, the antisymmetric part of the exchange interactions. In DyFeO$_3$, however, considerable magnetoelectric effects were observed, but at its roots lies the coupling of the Mn and R spins by a symmetric exchange interaction. In a transition from manganites to ferrites, we are therefore changing the predominance of different magnetic interactions.

Some work has already been done in this kind of approach. Huang et al. [39] investigated the solid solution YbMn$_{1-x}$Fe$_x$O$_3$ and Nagata et al. [40] investigated the magnetic properties of RMn$_{1-x}$Fe$_x$O$_3$ for $R=$Pr,Gd,Dy. Magnetizations curves and mossbauer spectroscopy has been measured for crystals of TbMn$_{1-x}$Fe$_x$O$_3$ with $x \leq 0.3$ [41].

Investigations of the structure and magnetic properties of the solid solution DyMn$_{1-x}$Fe$_x$O$_3$ were also performed [42, 43, 40], the most detailed being the one by Chiang et al [5]. The obtained phase diagram is in Figure 1.5. Some preliminary results of ours on TbMn$_{1-x}$Fe$_x$O$_3$ are also shown, which, despite the need for further analysis, suggest these systems present similar physics.
1.3 Differences in structure and lattice dynamics

There is another reason for the inclusion of Fe. An essential part of the physics of manganites is the establishment of the cooperative Jahn-Teller distortion and consequent orbital ordering (section 2.3). Fe ions, unlike Mn, are not Jahn-Teller active. So, by Fe substitution, we are effectively removing Jahn-Teller distortions from the picture. Other lattice distortions, such as octahedral tilting (section 2.2), which is at the basis of the phase diagram of the manganites, remain unchanged, due to the equal ionic radius of the two ions.

The reduction of Jahn-Teller distortions is, together with the different magnetic interactions brought by the Fe$^{3+}$ ions, the sense in which we claim to be exploring the phase diagram in a new direction.

The structural changes are, by themselves, of interest and have, as seen already, great relevance to the physics. The impact of the Fe-substitution on the structure is investigated in this thesis by X-ray diffraction and Raman spectroscopy.

Rare-earth ferrites have already been carefully studied in the literature [44], by x-ray diffraction. Data is also available for the manganites and it comes mainly from neutron diffraction [45]. A detailed description of the structure of manganites and ferrites is provided in this thesis (sections 2.1-2.3).

Raman scattering is the inelastic scattering of light [46]. In the case of interest, light is scattered from the vibrational modes of a lattice (phonons). Raman spectroscopy is a means not only to study the lattice dynamics and structure of our samples, but also a probe of disorder, local deformations [47] and even magnetism, via the spin-phonon coupling [23].
The space group symmetry of manganites and ferrites allows for 24 Raman active modes. The assignment of the modes in the observed Raman spectra of rare-earth manganites to their respective symmetries and atomic dislocations has been established, after some discussion, in the literature [48, 49, 47]. The assignment was made by comparison of the spectra of LaMnO$_3$ and YMnO$_3$ with the results of lattice dynamical calculations [48], and by correlating the changes in the frequency of the several stretching, bending and rotational modes to the changes in the relevant crystallographic parameters [49, 47].

The melting of the Jahn-Teller distortion with temperature has been studied with Raman spectroscopy, in LaMnO$_3$ [50]. The authors used the deviations in the temperature dependence of the linewidths from the expected due to the three phonon anharmonic effects. The Raman spectra of the solid solution La$_{1-x}$Ca$_x$MnO$_3$, where there is the loss of Jahn-Teller distortions, has also been analyzed in the literature [47].

The Raman spectra of the ferrites has been less actively researched. The main reported works focus on magnons and devote only a small fraction of the text to the phonon spectra [51, 52, 53, 54]. A short range force constant model has been applied to calculate the frequencies of the modes, with good agreement to available data [55]. The Raman spectra of the solid solutions La$_{1-x}$Sm$_x$FeO$_3$ [56] and Yb$_{1-x}$Pr$_x$FeO$_3$ [57] has been reported. Overall, a full vibrational analysis of the orthoferrite family is still missing.

The studies of the structure and lattice dynamics are an essential part of the phase diagram exploration, since the lattice degree of freedom is of first importance in understanding the magnetism.

1.4 Outline of the thesis

The phase diagram of the solid solutions RMn$_{1-x}$Fe$_x$O$_3$, R=Tb,Dy, is still being explored and in this thesis we will only treat two features: The structural changes for the full solid solution in Chapter 2 and the impact of Fe-substitution on the ferroelectricity and the magnetoelectric effect, for the low substitution range, in Chapter 3. In an attempt to make the thesis as self-contained as possible, the exposition of the experimental results is often preceded with an exposition of the fundamental concepts necessary for a full understanding of the experiments.

The detailed structure of the thesis is as follows:

In Chapter 2, a detailed description is made of the structure of the manganites, ferrites and solid solutions between them, beginning with the ideal perovskite (section 2.1) to then describe its two main distortions: octahedral tilting (section 2.2) and cooperative Jahn-Teller distortion (section 2.3). These sections are pedagogical, with an intent of providing a concise exposition of the complex and subtle structure of these materials. The structure of manganites and ferrites are compared and x-ray diffraction (section 2.4) and Raman spectroscopy (section 2.5) results on the solid solutions between them are presented and discussed.
In Chapter 3, the solid solutions for low concentrations of Fe, $x \leq 0.1$, are characterized. The ZFC and FC magnetization curves (section 3.1) and the polarization measurements (section 3.3) are exposed and discussed, tracing the parallels between the two solid solutions (R=Tb and Dy). Anomalies in dielectric constant (section 3.2) and specific heat (section 3.4) are pointed out and used to trace out the phase diagrams in this low substitution range. Finally, the impact on the magnetoelastic effect is analyzed (section 3.5).

Some conclusions and comments on future work are given in Chapter 4.
CHAPTER 1. INTRODUCTION
Chapter 2

Structure and lattice dynamics

In this chapter, we discuss the structure and lattice dynamics of the rare-earth manganites, ferrites and solid solutions between these end-members.

We will begin by introducing the structure, starting from the ideal perovskite structure and then discussing the distortions. A rather complete discussion of the problem of octahedral tilting is given, beginning with the basic definitions and arriving at the relationship between the lattice parameters and tilt angles. This kind of rigorous and explicit derivation is not easily found in the literature. The Jahn-Teller distortion is also introduced, together with its relations to orbital ordering. This sets the background for a structural and lattice dynamical study of our solid solution TbMn$_{1-x}$Fe$_x$O$_3$, using X-ray diffraction and Raman spectroscopy.

2.1 Ideal perovskite structure

Perovskite structures are extremely common [6]. They can be formed by many different combinations of cations and anions, though most frequent examples are oxides and fluorides [7, 58]. Most of the metallic ions in the periodic table can be incorporated into the perovskite structure. From this wide range of compounds, comes also a wide variety of physical properties.

Many of the latest great discoveries made in condensed matter physics regarded materials with variants of the perovskite structure: the colossal magnetoresistance of mixed-valence manganites [11], high temperature superconducting cuprates [59], magnetic ferroelectrics [1]...

This variety is due to the great flexibility of this structure to distort and accommodate different size ions. The vast majority of these compounds follow complex distorted variants of the ideal perovskite (SrTiO$_3$ is perhaps the most notable case of an ideal perovskite [35]). Despite this, a knowledge of the ideal perovskite structure is required before we analyse more complex structures.
CHAPTER 2. STRUCTURE AND LATTICE DYNAMICS

Figure 2.1: Ideal perovskite structure ABX$_3$: in red, the A-site cation; in blue, B-site cations; in yellow, X anions. Adapted from [6]

The ideal ternary perovskite ABX$_3$ has a cubic symmetry (space group Pm$ar{3}$m) and is composed of A-site cations at the corners of the conventional unit cell, B-site cations at the body center and anions at the face centers (see Figure 2.1).

There are various ways of viewing this structure. It can be regarded as derived from a cubic close-packed structure of oxygen atoms by replacing one quarter of the atoms by A-site cations. A quarter of the octahedral interstices is then filled with the B-site cations [6].

The most useful way to look at this structure is perhaps as a framework of corner-sharing octahedra [6, 35] (see Figure 2.2). These are the coordination polyhedra of the B-site cations which are at their centers. The A-site cations fill the space between these octahedra. The A-site and B-site cations have coordination numbers 12 and 8, respectively.

This ideal perovskite structure will form only if the sizes of the cations match perfectly. Goldshmidt introduced a tolerance factor $t$ to quantify the size misfit [6, 35] (for SrTiO$_3$ $t = 1.02$):

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$  \hspace{1cm} (2.1)

When the A-site cation has too small or too large a radius, a distorted perovskite forms.

Another way that leads to derivatives of the perovskite structure is the introduction of a Jahn-Teller active ion. Ordered perovskites, where more than one type of B-site cation is present, also lead to many complex and diverse (and wonderful) perovskites [6, 60], but those will not be addressed here.

Overall, the following main distortions might be present in a perovskite structure [7]: cation displacements (closely related to ferroelectricity), tilting of
2.2 Octahedral tilting

Octahedral tilting occurs due to a size misfit between the cations ($t < 1$) and consists of a cooperative rotation of the octahedra and a shift of the A-cations from the high symmetry positions. In this section, we will focus mainly on the octahedral framework.

The problem of octahedral tilting in perovskites was addressed by various authors, the most influential work arguably being Glazer 1972 paper [61] on the classification of all the tilts systems and the establishment of the notation that is currently used. In this paper, as in most of the literature, small tilt angles are assumed.

We begin with the ideal perovskite structure as before and then rotate one octahedron about one of its 4-fold axes (tetrad axes) maintaining the topology of the octahedral framework. If one octahedron rotates in one direction, the neighbouring octahedra in a plane orthogonal to the rotation axis must also

---

1 The corners of the cube in Figure 2.1
2 Say $\phi < 15^\circ$. The small angle approximation is used throughout this section and it is at the basis of all the reasoning, since the rotation group is treated as if it were an abelian group. In the calculations this effectively translates into ignoring terms of the order $\alpha^3$, where $\alpha$ is any angle addressed here.
CHAPTER 2. STRUCTURE AND LATTICE DYNAMICS

Figure 2.3: View along the [001] direction of two adjacent layers of octahedra for (a) the \( a^0a^0c^+ \) tilt system and (b) the \( a^0a^0c^- \) tilt system. Adapted from [7].

rotate, but in the opposite sense. We can follow the necessary implications on the framework of rotating one octahedron and we will find there are actually several possibilities.

From a structural point of view, it is clear that if in one plane an octahedron rotates by a certain angle, due to the size of the A-cation, in the following planes along the rotation axis, we must have the same rotation angle. However, the rotation might be in the same (in-phase) or in the opposite (anti-phase) sense than the previous plane.

Glazer notation allows us to specify a particular structure (tilt system) by indicating whether the rotations are in-phase \( a^+ \) or out of phase \( a^- \) or whether there is no rotation at all \( a^0 \). One symbol for each tetrad axis is sufficient to fully determine the structure.

Examples of a one-tilt system are given in Figure 2.3. \( a^0a^0c^+ \) means no tilting along the [100] \( p \) and [010] \( p \) axes and in-phase tilts about the [001] \( p \) axis\(^3\). \( a^0a^0c^- \) is similar but has anti-phase tilts along the [001] \( p \) axis.

An useful way to visualize the consequences of the rotations of one octahedron in the framework is presented in Figure 2.4. The tilt systems are the same than before. The +, −, 0 indicate now the positive, negative or absent rotations\(^4\) of a single octahedron along its three tetrad axis. If we start with +

\(^3\)[\( p \) stands for pseudocubic axis. These axes always go through the octahedra centers and, prior to rotation, through the vertices of the octahedra. After the tilting, these vertices move off the pseudocubic axes and the convencional unit cell might be considerably different. The subscript \( p \) is then used to distinguish between the pseudocubic and the unit cell axes.

\(^4\)Which sense of rotation about an axis is considered positive is of course a matter of convention. What matters is the sense of rotation of one octahedron relative to its neighbours.
2.2. OCTAHEDRAL TILTING

on one octahedron, the Glazer notation for that tilt system tell us how to fill in for the rest.

The first two indices of each octahedron are 0 since there are no rotations relative to those axes. The third indice refers to the tilt axis and the pattern of + and - on each layer follows the rule that each octahedron rotates in a opposite sense than its neighbours. This is similar for both mentioned tilt systems. The distinction exists in the transition from one layer to the next. In $a^0a^0c^+$ we have in-phase tilts and therefore the same rotations for both (actually all) layers. The $a^0a^0c^-$ reverses the sense of rotation from one plane to the next.

![Figure 2.4: Schematic representation of the tilted octahedra in (a) the $a^0a^0c^+$ and (b) the $a^0a^0c^-$ tilt systems. Two adjacent layers are shown, projected in the (001)$_p$ plane. +, − and 0 represent positive, negative and no rotations, respectively, of each octahedron along one of its three tetrad axes.]

This scheme is also very useful to identify the conventional unit cell of the distorted structure. In the one-tilt system $a^0a^0c^+$, we have a change of basis that leads to the lattice parameters $a = \sqrt{2}a_p$, $b = \sqrt{2}a_p$ and $c = a_p$, where $a_p$ is the pseudocubic lattice parameter. Hence, by tilting, the symmetry reduces from cubic to tetragonal. The system new axes and symmetry could be ascertained from Figure 2.4.

It should be noted that whenever an $a^0$ or $a^+$ symbol appears a mirror symmetry plane must exist orthogonal to that direction. So for $a^0a^0c^+$ we have a mirror plane at $z = 1$ (relative position). In the case of $a^0a^0c^-$ this mirror plane is absent and the c-axis doubles to $c = 2a_p$.

When tilt angles are equal in two directions the same letter is used. So $a^+b^+c^+$ implies three different angles of rotation along the three axis while $a^+a^-c^+$ means no rotation about [001]$_p$ and rotations about the [100]$_p$ and [010]$_p$ directions by the same angle. When this happens the rotation can be regarded to be along the [110]$_p$ direction.

The distances between octahedral centers are of course affected by the presence of rotations. If we call these distances $a_p$, $b_p$, $c_p$ along the pseudocubic

---

5 The $a$ and $b$ axes of the unit cell now follow the diagonals in Figure 2.4, connecting octahedra with the same rotated configuration.

6 $R_x(\alpha)R_y(\alpha) = e^{iL_x\alpha}e^{iL_y\alpha} = e^{i(L_x+L_y)\alpha}e^{-[L_x,L_y]\alpha^2}$ where $L_x$ and $L_y$ are generators of the rotation group. If we approximate the group as abelian, $R_x(\alpha)R_y(\alpha) = e^{i(L_x+L_y)\alpha} = e^{i\vec{n}(\sqrt{2}\alpha)}$ with $\vec{n}$ being the versor in the [110]$_p$ direction.
axis, \( a_0 \) the distance prior to rotations and \( \alpha, \beta, \gamma \) the rotation angles about the same axes we have [61]:

\[
\begin{align*}
a_p &= a_0 \cos(\beta) \cos(\gamma) \quad (2.2a) \\
b_p &= a_0 \cos(\alpha) \cos(\gamma) \quad (2.2b) \\
c_p &= a_0 \cos(\alpha) \cos(\beta) \quad (2.2c)
\end{align*}
\]

These equations, as all the analysis in this section, assume that the rotation angles are small.

We can see from here that the number of different angles of rotation is equal to the number of differing pseudocubic lattice parameters. If we go back to the tilt system \( a^+a^+c^0 \), we have three orthogonal mirror planes and therefore three orthogonal symmetry axes. Applying the previous equations,

\[
\begin{align*}
a_p &= b_p = a_0 \cos(\alpha) \quad (2.3) \\
c_p &= a_0 \cos(\alpha) \cos(\alpha) = a_0 \cos(\sqrt{2}\alpha) = a_0 \cos(\theta) \quad (2.4)
\end{align*}
\]

where \( \alpha \) and \( \theta \) regard rotations along the \([100]_p\) and \([110]_p\) directions, respectively.

After a change of basis to the conventional unit cell, we have

\[
\begin{align*}
a &= b = \sqrt{2}a_p = \sqrt{2}a_0 \cos(\alpha) \quad (2.5) \\
c &= c_p = a_0 \cos(\theta) \quad (2.6)
\end{align*}
\]

Therefore, the lattice system is again tetragonal.

Complications arise when we move to tilt systems in which more than one direction possesses anti-phase tilts, e.g. \( a^-a^-c^0 \). These systems are incompatible with orthogonal pseudocubic axes. Glazer provides an excellent graphic proof of this fact.

In Figure 2.5, his argument is recreated. A diagram is drawn on the assumption of orthogonal pseudocubic axes and one arrives at a conclusion that two adjacent octahedra layers cannot be connected. For us to maintain the topology of the framework, the octahedron in the upper layer must be displaced by a distance \( d \) along \( a_p \) relative to the bottom layer. This implies that the \( b_p \) axis is inclined towards the \( a_p \) axis.

There are in total 23 different tilt systems [61]. They have all been ascribed their space groups. It has been noted, however, that some are incompatible with the condition of regular octahedra [7].

A group theoretical study of the relations between different tilt systems and the group-subgroup relationships has been done and summarized in a diagram [62]. This analysis indicates the theoretical possible sequence of phase transitions associated with octahedral tilting due to changing pressure, temperature and composition.
2.2. OCTAHEDRAL TILTING

Figure 2.5: Projection in the (010)_p plane between two octahedra layers, drawn on the assumption of orthogonal pseudocubic axes. The open circle stands for the bottom anion of the octahedron on the upper layer and the filled circle stands for the upper anion in bottom layer. For the octahedra to be connected this must be the same anion. The situation is represented (a) before any rotation, (b) after tilt about a_p and (c) after a second tilt about b_p. After the second tilt, the octahedra are no longer connected.

Rare-earth manganites and ferrites possess the GdFeO_3-type structure, a^-a^-c^+ in Glazer notation (Figure 2.8). Their space group is Pbnm.

We will for the remaining of this section focus on deriving the unit cell and lattice parameters for this structure for given tilt angles $\theta$ and $\phi$ along the [110]_p and [001]_p directions, respectively. This configuration is harder to visualize than the previous.

Figure 2.6: Schematic representation of the tilted octahedra in the $a^-a^-c^+$ tilt system. Two adjacent layers are shown, projected in the (001)_p plane. + and − represent positive and negative rotations, respectively, of each octahedron along one of the its three tetrad axes.

If we once again use a pictorial representation for the impact of one rotated octahedron on the framework (Figure 2.6) we find that $a \simeq \sqrt{2}a_0$, $b \simeq \sqrt{2}a_0$, $c \simeq 2a_0$. These are approximate relations since we know that the pseudocubic lattice parameters change with rotations:
\[ a_p = b_p = a_0 \cos(\alpha) \cos(\phi) \]  
\[ c_p = a_0 \cos^2(\alpha) = a_0 \cos(\theta) \] 

in which \( \alpha = \theta / \sqrt{2} \).

The complication considering the two anti-phase tilting directions must still be considered. By the argument pointed out before, the \( a_p \) and \( b_p \) axes must be inclined towards each other, in a plane orthogonal to the \( c_p \) axis.

![Diagram](image)

Figure 2.7: Illustration of the relation between pseudocubic and real lattice parameters in the \( a^-a^-c^+ \) tilt system. Black dots stand for the B-cations at the center of the octahedra. The octahedron sharing corners are not shown but go approximately along the pseudocubic axes.

In this case, however, \( a_p = b_p \) and this allows for a change to an orthogonal basis (Figure 2.7):

\[ \vec{a} = \vec{b}_p - \vec{a}_p = a_p(\sin(\psi) - 1, \cos(\psi), 0) \]  
\[ \vec{b} = \vec{b}_p + \vec{a}_p = a_p(\sin(\psi) + 1, \cos(\psi), 0) \]

This leads to the lattice parameters,

\[ a = \sqrt{2} a_p (1 - \sin(\psi))^{1/2} \]  
\[ b = \sqrt{2} a_p (1 + \sin(\psi))^{1/2} \]  
\[ c = 2c_p \]

The structure has then three orthogonal symmetry axes and three distinct lattice parameters. Hence, it is an orthorhombic structure.

We are now left to calculate \( \psi \), knowing \( \tan(\psi) = d/a_p \), where \( d \) is the distance marked in Figure 2.5. By applying rotation matrices \( R_x(\alpha) \), \( R_y(\alpha) \) and \( R_z(\phi)^7 \) to the vector \((0,a_0/2,0)\) marking the original position of X anion, we can find this distance:

\[ ^7 \text{In this order.} \]
2.2. OCTAHEDRAL TILTING

\[ d = a_0 \sin^2(\alpha) \cos \phi \]  
(2.11)

This gives us \( \psi \),

\[ \tan(\psi) = \frac{d}{a_p} = \frac{a_0 \sin(\alpha)^2 \cos(\phi)}{a_0 \cos(\alpha) \cos(\phi)} = \sin(\alpha) \tan(\alpha) \]  
(2.12)

Remembering that we are ignoring terms of the order \( \alpha^3 \), we have the following relations

\[
\sin \psi = \tan \psi = \sin \alpha \tan \alpha = \alpha^2
\]  
(2.13)

\[
(1 - \sin(\psi))^{1/2} = \cos(\alpha)
\]  
(2.14)

\[
(1 + \sin(\psi))^{1/2} = \frac{1}{\cos(\alpha)}
\]  
(2.15)

Substituting these relations and the equations (2.7) in equations (2.10) we have

\[
a = \sqrt{2}a_0 \cos(\theta) \cos(\phi)
\]  
(2.16a)

\[
b = \sqrt{2}a_0 \cos(\phi)
\]  
(2.16b)

\[
c = 2a_0 \cos(\theta)
\]  
(2.16c)

Note that we always have \( a < b \) and \( a < c/\sqrt{2} \).

This ends our discussion of the problem of octahedral tilting. Next, we address octahedral distortions and their relation with the Jahn-Teller effect.

Figure 2.8: \( a^- a^- c^+ \) tilt system (A) clinographic projection and (B) (001)\(_p\) projection. Adapted from [6].
2.3 Jahn-Teller Effect and Orbital Order

The idea behind the Jahn-Teller theorem was first formulated by Lev Landau [63], in a discussion with Edward Teller, about the work of his student. The theorem was later more rigorously stated and proved by Teller and Hermann Jahn, for which it is now named. It states: A molecule with an orbitally degenerate electronic state is unstable with respect to spontaneous distortion of the nuclear configuration that removes the degeneracy [63].

The orbital degeneracy of interest in manganites involves the 3d orbitals of the Mn$^{3+}$ ion (Figure 2.9). For the free ions, all spatial directions are equivalent and the 3d orbitals are all degenerate. When a Mn$^{3+}$ ion is placed inside an octahedron of negatively charged oxygen ions, the electrostatic field of this charges leads to a splitting of the energy levels. The calculation of the value of the splitting might be a complicated problem, to be solved by perturbation theory, but which degeneracy remains after the splitting is a standard textbook application of group theory to quantum mechanical problems.

![Figure 2.9: (a) 3d orbitals, grouped according to the doublet $e_g$ or triplet $t_{2g}$ to which they belong (b) Splitting of the energy levels of the 3d orbitals with the crystal field of cubic symmetry. The tetragonal distortion of the octahedron leads to additional splittings. Adapted from [8, 9].](image)

This splitting is represented in Figure 2.9. The result is a doublet, $e_g$, and a triplet, $t_{2g}$. For Mn$^{3+}$, in a high spin configuration, three electrons occupy the $t_{2g}$ states and one occupies an $e_g$ state.

This situation brings us back to the Jahn-Teller theorem. The orbitally degenerate $e_g$ state is unstable under a distortion of the octahedron which raises that degeneracy (see Figure 2.9). The energy cost of the distortion of the lattice is compensated by a reduction in the electronic energy.

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*Bruno Renner*
2.3. JAHN-TELLER EFFECT AND ORBITAL ORDER

A distinction might here be traced with the Fe$^{3+}$ ion in the ferrites. In this case, the electronic configuration is t$_{2g}^3e_g^2$. Due to the existence of two electrons in the e$_g$ states, there is no reduction in electronic energy upon distortion, since the increase in energy in one electron is cancelled by a decrease in energy of the other. As such, there is no spontaneous distortion in the ferrites and the Fe$^{3+}$ ion is said not be Jahn-Teller active.

The Jahn-Teller theorem gives no information on the direction of the distortion. Indeed, in manganites at high temperatures the octahedron resonates between different directions of distortion (dynamic Jahn-Teller effect). As the temperature is lowered, a cooperative Jahn-Teller distortion sets in. In it, the octahedra distort according to a static and regular pattern.

The pattern in manganites is represented in Figure 2.10. In the distortion of each octahedron there is two long and two short Mn-O bond distances, alternating in the ab plane. Two medium bonds align approximately along the c axis. The Jahn-Teller distortion forms the only structural difference between ferrites and manganites.

This cooperative Jahn-Teller distortion has further implications. The direction of the distortion indicates the orbital the electron will occupy. As the distortion form a regular pattern in space so do the occupied orbitals (Figure 2.10). This phenomena is called orbital ordering and is a key feature of the physics of manganites.

The exchange interactions, referred to in the section 1.1, are determined by this ordering. The parallel alignment of the orbitals along the c axis leads to an antiferromagnetic coupling, while the ninety degree angle between neighbouring orbitals, in the ab plane, causes a ferromagnetic coupling.

Orbital ordering is hard to observe directly. Most commonly it is deduced from...\[9\]Well above 700K.
from the presence of cooperative Jahn-Teller distortions. And these can be seen by x-ray and neutron diffraction.

2.4 X-ray diffraction

After having introduced the general description of the structural distortions present in the rare-earth manganites and rare-earth ferrites, we now go through X-ray diffraction results on the solid solution TbMn$_{1-x}$Fe$_x$O$_3$.

A series of polycrystalline samples of TbMn$_{1-x}$Fe$_x$O$_3$ was obtained by the sol-gel method, with $x$=0, 0.01, 0.025, 0.04, 0.05, 0.075, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1. Powder x-ray diffraction was performed, at room temperature. Some representative results are presented in Figure 2.11.

The x-ray diffraction spectra exhibits the typical spectral profile observed for orthorhombic rare-earth manganites, described by the $Pbnm$ space group. The lattice parameters calculated from these spectra are shown in Figure 2.12.

As shown in section 2.2, for a perovskite with GdFeO$_3$-type distortion only, we always have $a < b$ and $a < c/\sqrt{2}$. Usually, the tilt angles over the three tetrad axes are not too different and we have also $a < c/\sqrt{2} < b$. For the case of RFeO$_3$, these inequalities are indeed satisfied, but in RMnO$_3$ the presence of Jahn-Teller distortions leads to an inversion of the lattice parameters to $c/\sqrt{2} < a < b$.

In the solid solution, we see this inversion. In Figure 2.12, we can see that indeed for $x$=0 (TbMnO$_3$), we have $c/\sqrt{2} < a < b$, and at $x$=1 (TbFeO$_3$), we have $a < c/\sqrt{2} < b$. The numerical values of lattice parameters for these end-members agree with literature [45, 44]. Throughout the solid solution, we can see a smooth, linear behavior with Fe concentration, with the crossing of the $a$ and $c/\sqrt{2}$ parameters at $x$=0.4. The expected gradual reduction in the volume as the Jahn-Teller distortion is removed is seen. From manganites to ferrites, we have a reduction of 0.6% in volume.

The lattice parameters variation agrees with the expected from the imposition of cooperative Jahn-Teller distortions [60]: increase of the $c$-axis, nearly constant $a$-axis, considerable contraction of the $b$-axis, moving from the manganites to the ferrites. This gradual change from a structure dominated by octahedral tilting and octahedral distortions to one determined only from the tilting, has been observed for similar solid solutions DyMn$_{1-x}$Fe$_x$O$_3$ [5, 42] and YbMn$_{1-x}$Fe$_x$O$_3$ [39], in which cases the crossing happened at $x$=0.3.

The nearly constant $a$ axis and the expansion of the $b$ axis are a consequence of the superposition of cooperative Jahn-Teller distortion to octahedral tilting. In the absence of tilting, the gradual substitution by an Jahn-Teller active ion would lead to an equal expansion of the $a$ and $b$ axes.

As an example we have the case of KMg$_{1-x}$Cu$_x$F$_3$ [64]. For small concentrations of the Jahn-Teller active Cu$^{2+}$ ion, we have local distortion centers associated with these ion but the observed overall symmetry remains cubic, as in KMgF$_3$. At $x=0.4$, interactions between these distortions leads to a first order phase transition from cubic to tetragonal symmetry ($a=b\neq c$). After this point, the aforementioned gradual and equal expansion of the $a$ and $b$ axes takes
Figure 2.11: X-ray diffraction spectra for the solid solution TbMn$_{1-x}$Fe$_x$O$_3$, with $x=0, 0.1, 0.3, 0.5, 0.9, 1$, recorded at room temperature.
CHAPTER 2. STRUCTURE AND LATTICE DYNAMICS

Figure 2.12: (a) Lattice parameters and (b) unit cell volume for TbMn$_{1-x}$Fe$_x$O$_3$. Blue: $a$, Black: $b$, Red: $c/\sqrt{2}$.

place. In the case of TbMn$_{1-x}$Fe$_x$O$_3$, since there is no change in symmetry, the lattice parameters have no abrupt change.

To better understand these structural changes we have done a Rietveld refinement on the spectra of Figure 2.11. The obtained bond distances are displayed in Figure 2.13.

The bond distances start ($x = 0$) with three distinct bond lengths as expected for TbMnO$_3$, due to Jahn-Teller distortions. With Fe substitution, the bond lengths approach each other and, at around $x=0.5$, the Mn-O(1) bond length becomes equal to one of the two Mn-O(2) bond lengths. The difference with the other Mn-O(2) bond length that prevails at $x = 1$ is due to tilting. For the smaller rare-earth cations like Tb$^{3+}$, the perovskites are more heavily distorted and the octahedral tilting itself forces a small octahedral distortion. This distortion is much smaller than the one associated to Jahn-Teller distortions [60].

As mentioned in the Chapter 1, the ionic radius of the Mn$^{3+}$ and Fe$^{3+}$ cations is the same, for a coordination number 8 and a high-spin configuration. This means the tolerance factor (section 2.1) is the same and the mismatch between the rare-earth (A-site) cation and the Mn or Fe (B-site) cation is the same. We therefore expect the tilt angles to be the same.

We have tried to take the tilt angles from the obtained atomic coordinates to confirm that there were no appreciable variations, but the error was too high with the tilt angle varying in the range $14^\circ - 18^\circ$. This is due to the inherent difficulty of doing the refinement on a solid solution. A similar error was found when we used data from [5]. Additional caution is therefore required in interpreting the bond distances in Figure 2.13.

The distortions of the octahedra are more carefully analysed using $\Delta d$ (Fig-
2.4. X-RAY DIFFRACTION

Figure 2.13: (a) Bond lengths for TbMn$_{1-x}$Fe$_x$O$_3$. Black: Mn-O(1) Red, Blue: Mn-O(2) Green: Tb-O(1) Pink: Tb-O(2). (b) Average B-O bond distance (black squares) and average octahedral distortion (blue triangles).

This is the parameter usually taken to quantify the octahedral distortions:

$$\Delta d = \frac{1}{6} \sum_{i=1}^{6} \left( \frac{d_i - \langle d \rangle}{\langle d \rangle} \right)^2$$

(2.17)

in which $d_i$ are the individual B-O bond distances (B=Mn,Fe) and $\langle d \rangle$ is the average of the six B-O bond distances. The variation of the octahedral distortion $\Delta d$ with Fe-substitution is represented in Figure 2.13. Here is much more clear that the distortion begins to increase considerably below $x = 0.5$.

The average Mn-O bond length is also included in Figure 2.13 (b), and shows little variation with Fe-substitution, maintaining a value of approximately 2 angstroms. This means that despite the different Mn-O bond distances being changed considerably by Jahn-Teller distortions, they maintain the average distance.

One may suggest that the disappearance of the cooperative Jahn-Teller distortion takes place at the point indicated by the inversion of the lattice parameters ($x = 0.4$). There is, however, no clear indication that this should be the case. Comparing the phase diagrams of DyMn$_{1-x}$Fe$_x$O$_3$ [5] and YbMn$_{1-x}$Fe$_x$O$_3$ [39] with our preliminary measurements mentioned in section 1.2, and together with the previous analysis of octahedral distortion, it seems likely that the change from cooperative to dynamic Jahn-Teller distortions takes place at $x \simeq 0.5$. 
2.5 Raman spectroscopy

In this section, we discuss the results of Raman spectroscopy for the solid solution TbMn$_{1-x}$Fe$_x$O$_3$. These spectra allow us to make a bridge between the well known modes of the rare-earth manganites and the still largely uninvestigated modes of the orthoferrites.

Manganites and ferrites have the same set of symmetry allowed Raman modes: 7$A_g$+5$B_{1g}$+7$B_{2g}$+5$B_{3g}$. These modes are illustrated in Figure 2.14.

![Figure 2.14: The 24 symmetry allowed Raman active modes of the Pbnm structure. Adapted from [10].](image)

In the ideal cubic perovskite, there are no symmetry allowed Raman modes. The various distortions such as Jahn-Teller, tilt about [110]$_{p}$, tilt about [001]$_{p}$ and R-shifts are in the origin of the various Raman active modes. Moreover, the activation of a given Raman mode can be assigned to one or two lattice distortions.

There are various kinds of modes: stretching (and antistretching) modes, with a frequency roughly proportional to $\langle Mn - O \rangle^{-3/2}$; bending modes, dependent on the rare-earth ion displacements; rotational modes, roughly proportional to the tilt angle in question. In this last regard, it has been shown that the proportionality constant is closely the same for all ABO$_3$ perovskites.

In Figure 2.15, we have a Raman spectrum for TbMnO$_3$. The three lower frequency peaks, at 112 cm$^{-1}$, 141 cm$^{-1}$ and 163 cm$^{-1}$, are R-shifts. The mode at $\sim$380 cm$^{-1}$, signaled with a T, is the tilt mode $A_g$(4). It is sensitive to changes in the tilt angle $\theta$ about [110]$_{p}$. The most intense peak is at $\sim$ 310 cm$^{-1}$ and is a symmetric stretching mode (SS), of symmetry $B_{2g}$(1). It is activated uniquely by the Jahn-Teller distortion. Another intense peak is the antisymmetric stretching mode (AS) at $\sim$490 cm$^{-1}$, of symmetry $A_g$(1). This one is activated by Jahn-Teller and tilting about [001]$_{p}$. At $\sim$510 cm$^{-1}$, we have a bending mode (B), of symmetry $A_g$(3). These last two modes have the same symmetry and lie very close to each other.

$^{10}$Displacements of the rare-earth cations from the high symmetry positions.
close to each other in frequency. It has been shown by following their frequencies through the rare-earth manganite series, that these modes are mixed. This was inferred from the mode repulsion and spectral weight transfer between the two modes [24].

There are two smaller modes superimposed on these two. One is below the AS mode, at $\sim 475$ cm$^{-1}$, and has the symmetry $B_{2g}(3)$ mode, another bending mode. At $\sim 530$ cm$^{-1}$, there is the $B_{2g}(2)$ mode, which involves a "scissor-like" movement of the equatorial oxygens.

Very low intensity modes exist at 280 cm$^{-1}$, 310 cm$^{-1}$ and 330 cm$^{-1}$ and correspond to the $A_g(7)$, $A_g(2)$ and $B_{2g}(7)$ modes, respectively. The $A_g(7)$ mode responds to the tilt angle about [001].

The broad feature observed at $\sim 645$ cm$^{-1}$ is not considered to be a proper Raman mode [48, 66]. This feature is also present in the ferrites.

The spectra in the Figure 2.15 correspond to one of our samples. Since these samples are polycrystalline, we see all the modes of different symmetries superimposed.

Figure 2.16 shows the Raman spectra for the full solid solution $TbMn_{1-x}Fe_xO_3$.

For $x=0$ to $x=0.4$, the spectra retains the same form as in $TbMnO_3$, although with a gradual broadening and lost of intensity, due to disorder. Interestingly, the symmetrical stretching mode disappears at $x=0.5$, in agreement with the supposition that the cooperative Jahn-Teller vanishes at this concentration, made in the previous section. Above $x=0.7$, other modes start to emerge. At $x=1$, the more complex spectra of $TbFeO_3$ is observed.

Below 200 cm$^{-1}$, the R-shift modes maintain their frequency as expected.
Figure 2.16: Raman spectra for the solid solution TbMn$_{1-x}$Fe$_x$O$_3$. The various concentrations are laid out in sequence: $x = 0, 0.01, 0.025, 0.04, 0.05, 0.075, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, 1$
The frequency of these modes goes with $m_R^{-1/2}$. Since the rare-earth ion is the same throughout this solid solution, there is no appreciable change in frequency for these modes. There is however a very significant increase in intensity. This increase cannot be associated with the differences in R-O bond distances, they are essentially unchanged from manganites to ferrites [60].

![Figure 2.17: Phonon frequencies as a function of x in TbMn$_{1-x}$Fe$_x$O$_3$, for (a) the tilt mode and (b) the symmetrical stretching mode.](image)

In Figure 2.17 we see the changes in the phonon frequency along the solid solution for two of the main Raman modes: tilt and symmetrical stretching. The modes are followed up to $x=0.6$. For the tilt mode, a linear dependence with $x$ was observed. The tilt mode, as mentioned before, is sensitive to the tilt angle $\theta$. Iliev et al. [24] showed that a linear relation exists between phonon frequency and tilt angle, with slope $23.5\text{ cm}^{-1}/\text{deg}$. We can use this to estimate the changes in the tilt angle with Fe-substitution: $\Delta \theta = \Delta \omega / 23.5 \approx 0.5\text{ deg}$, for a frequency change of $12\text{ cm}^{-1}$. We can see that even with the Fe substitution at 60%, the change in the tilt angle is negligible. For the symmetrical stretching mode, a non-linear increase with Fe concentration is observed. The relevant crystallographic parameter in this case is the average Mn-O distance. The change in frequency is again small, expected from the fact that the average bond distance changes little across the solid solution. However, there seems to be no correlation between these results for the phonon frequency of the SS mode and the ones from the x-ray data in Figure 2.13 (b).

The large number of modes in the spectra of the TbFeO$_3$ and the lack of a mode assignment for the ferrites makes this study very challenging. We have therefore initiated measurements on the Raman spectra of various ferrites, including as a function of temperature, in collaboration with Luxembourg Institute for Science and Technology (LIST). The goal is to provide a vibrational analysis for the full orthoferrite family. Mode assignment, by comparison with *ab initio* calculations, is underway. We show in Figure 2.18 some of our first results in these studies.
Figure 2.18: Raman spectra of RFeO$_3$ with R=Eu,Tb,Dy.
Chapter 3

Magnetoelastic effect at low Fe$^{3+}$ concentrations

TbMnO$_3$ and DyMnO$_3$ are well known magnetoelastics. They display very interesting and complex phenomena and serve as the prototype of ferroelectrics driven by spiral magnetism. In this chapter, we will explore the impact that Fe-substitution has on the magnetic, ferroelectric and magnetoelastic properties of these manganites.

Since TbFeO$_3$ and DyFeO$_3$ are not ferroelectric (in zero magnetic field), at some point ferroelectricity must be lost. As we will see, that will happen still within the low substitution range. Here, we will therefore focus on the characterization of the solid solutions TbMn$_{1-x}$Fe$_x$O$_3$ and DyMn$_{1-x}$Fe$_x$O$_3$ for low substitution, $x < 0.1$.

Polycrystalline samples of TbMn$_{1-x}$Fe$_x$O$_3$, with $x=0$, 0.01, 0.025, 0.04, 0.05, 0.075, and DyMn$_{1-x}$Fe$_x$O$_3$, with $x=0$, 0.01, 0.02, 0.03, 0.04, 0.05, 0.075, were prepared by the sol-gel method. Additionally, a crystal of TbMn$_{1-x}$Fe$_x$O$_3$ for $x=0.02$ was grown by the floating zone method.

In this chapter, we present a characterization of the magnetic, polar, dielectric, thermodynamic and magnetoelastic properties. A phase diagram for the low substitution range is proposed.

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These samples were provided by Pedro Tavares from Centro de Química at Universidade de Trás-os-Montes a Alto Douro. The quality of the samples was checked by XRD, SEM-EDS, XPS and FTIR. See appendix A for more details on the sample characterization.
3.1 Magnetic properties

The substitution of Mn$^{3+}$ by Fe$^{3+}$ in RMnO$_3$ has not only an impact in the structure, by leading to the gradual disappearance of the cooperative Jahn-Teller distortion, but also on the magnetism. As mentioned in section 2.3, the electronic distribution of the Mn$^{3+}$ and the Fe$^{3+}$ ions is $t_{2g}^3e_g^1$ and $t_{2g}^3e_g^2$, respectively. The different electronic distributions lead to a different balance of the ferromagnetic and antiferromagnetic interactions.

Zero field cooled (ZFC) and field cooled (FC) magnetization curves$^2$, as a function of temperature, were obtained for all the samples, with the use of a Quantum Design superconducting quantum interference device (SQUID). The resolution in the magnetization measurements is better than $5 \times 10^{-7}$ emu.

All magnetization curves show a rather smooth behaviour with temperature and have a gradual change with composition. In all cases, a paramagnetic tail is observed, raising up to a transition temperature, below which there is a decrease in the magnetization. This temperature is around 10 K for DyMnO$_3$ and gradually decreases with $x$ to around 6 K for DyMn$_{0.95}$Fe$_{0.05}$O$_3$. For DyMn$_{0.925}$Fe$_{0.075}$O$_3$, the downturn is at too low a temperature to be observed. Similar description applies to the TbMn$_{1-x}$Fe$_x$O$_3$ system.

The paramagnetic behaviour is easily understood from a simple look at the magnetic moments of the magnetic ions involved. This involves some straightforward calculations. We have

$$
\mu = g_J \mu_B \sqrt{J(J+1)}
$$

(3.1)

where $\mu$ is the magnetic moment, $\mu_B$ the bohr magneton, $J$ is total angular momentum quantum number and $g_J$ is the Landé factor

$$
g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}
$$

(3.2)

with $L$ and $S$ the orbital and spin quantum numbers.

Considering the electronic distribution and Hund rule, we can take as an input $L = 3$, $S = 3$, $J = 6$ for the Tb$^{3+}$ ion and $L = 5$, $S = 5/2$, $J = 15/2$ for the Dy$^{3+}$ ion. Due to orbital quenching and assuming a high spin configuration, we have $L = 0$, $S = 5/2$, $J = 5/2$ for Fe$^{3+}$ and $L = 0$, $S = 2$, $J = 2$ for Mn$^{3+}$. This gives magnetic moments of $9.7\mu_B$, $10.7\mu_B$, $4.9\mu_B$ and $5.9\mu_B$, for the Tb$^{3+}$, Dy$^{3+}$, Mn$^{3+}$ and Fe$^{3+}$ ions, respectively.

We can see that the magnetic moments of the rare-earth spins, Tb and Dy, double the ones from the transition metals, Fe and Mn. This leads to strong paramagnetic curves from the rare-earth spins, which dominate over

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$^2$Zero field cooled measurements are those in which no magnetic field is applied in cooling. Field cooled measurements involve an applied field, in this case of 40 Oe, while cooling. In both cases, the measurement of the magnetization temperature dependence is then done in heating, with an applied field.
3.1. MAGNETIC PROPERTIES

Figure 3.1: Zero field cooled (ZFC) and field cooled (FC) magnetization curves for DyMn$_{1-x}$Fe$_x$O$_3$, with (a) $x=0$, (b) $x=0.03$, (c) $x=0.05$ and (d) $x=0.075$.

The magnetic contributions of the latter spins. The aforementioned transition temperatures, observed in Figure 3.1, are the transition temperatures $T_N(Dy)$ of Dy$^{3+}$ spins.

Below $T_N(Dy)$, the decrease of the magnetic moment reflects the typical behaviour for an antiferromagnetic polycrystalline sample.

Above 100K, the magnetization curves were fitted to a Curie-Weiss law,

$$M = \frac{C}{T - T_C}H$$  \hspace{1cm} (3.3)

with the $C$ the Curie-Weiss constant, from which the effective magnetic moment follows,

$$\mu_{eff} = \sqrt{3k_B C} \mu_B$$  \hspace{1cm} (3.4)

if $C$ is first converted to the appropriate units.
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Figure 3.2: Illustrative example of a Curie-Weiss law fit (red line), for DyMn$_3$O$_7$.
The fit was done for $T > 100K$ and extrapolated to lower temperatures.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_C$ (K)</th>
<th>$\mu_{eff}/\mu_B$</th>
<th>$\mu_{theor}/\mu_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>26±1</td>
<td>11.2±0.5</td>
<td>11.7</td>
</tr>
<tr>
<td>0.01</td>
<td>24±1</td>
<td>11.0±0.5</td>
<td>11.7</td>
</tr>
<tr>
<td>0.02</td>
<td>25±1</td>
<td>11.5±0.5</td>
<td>11.7</td>
</tr>
<tr>
<td>0.03</td>
<td>25±1</td>
<td>11.0±0.5</td>
<td>11.7</td>
</tr>
<tr>
<td>0.04</td>
<td>25±1</td>
<td>11.7±0.5</td>
<td>11.7</td>
</tr>
<tr>
<td>0.05</td>
<td>25±1</td>
<td>10.9±0.5</td>
<td>11.7</td>
</tr>
<tr>
<td>0.075</td>
<td>25±1</td>
<td>11.0±0.5</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Table 3.1: Effective paramagnetic moments obtained by a Curie-Weiss law fit, for DyMn$_{1-x}$Fe$_x$O$_3$

All magnetization curves display a good fit to the Curie-Weiss law. An example is presented in Figure 3.2 and the effective paramagnetic moments are contained in Table 3.1. The theoretical values of paramagnetic moment are also shown and were calculated by summing the contributions of all magnetic ions, according to

$$\mu_{eff}^2 = \mu_R^2 + \mu_{Mn/Fe}^2$$  \hspace{1cm} (3.5)

A good agreement between expected and measured values was found.

Returning to Figure 3.1, there is still an interesting feature worth discussing. The ZFC and FC curves start identical for $x=0$ and gradually separate, the distinction being clearly visible for $x=0.75$. The opening of the ZFC and FC curves is suggestive of a new magnetic phase. Considering the analysis of Chiang et al. [5], a field-induced weak ferromagnetic phase is likely for $x=0.075$. Due to the gradual separation, it is not clear at which concentration is this magnetic phase installed.

The magnetization curves for the policrystalline samples of TbMn$_{1-x}$Fe$_x$O$_3$, shown in Figure 3.3 for the case $x=0$ and $x=0.01$, have presented an unexpected and dubious character. These ZFC and FC curve separations is set already at
3.1. MAGNETIC PROPERTIES

Figure 3.3: Zero field cooled (ZFC) and field cooled (FC) magnetization curves for TbMn$_{1-x}$Fe$_x$O$_3$, with (a) $x=0$ and (b) $x=0.01$

$x=0.01$, and varies considerably afterwards, in disagreement with literature [41] and with what one would expect from the analysis of the following sections. The effective magnetic moment also varies wildly. Moreover, the magnetization of a crystal sample of $x=0.02$ was measured and displays different behaviour (Figure 3.4). This led us to believe that the discrepancies might be caused by some contamination of the polycrystalline samples.

Figure 3.4: Zero field cooled (ZFC) and field cooled (FC) magnetization curves for a crystal of TbMn$_{0.98}$Fe$_{0.02}$O$_3$.

For the crystal sample, there is no appreciable distinction between ZFC and FC curves. More interestingly, it has marked features showing the transition temperatures at which the Mn/Fe spins order, 23 K and 39K. These marked
features were not observed in any policrystalline sample. In the literature, some similar peaks are also observed when measured in crystals leading to the conclusion that they are required, if one intends to retrieve transition temperatures from magnetization measurements.

### 3.2 Electric permittivity and relaxations

In the interest of studying the impact of Fe-substitution on the ferroelectric phase, an investigation of the dielectric properties was made.

The measurements of the electric permittivity were performed using an LCR meter, in the electric field frequency range 1kHz-1MHz. Gold electrodes were deposited on the ceramic pellets by sputtering, for application of the electric field. Measurements were made in both heating and cooling runs, at fixed temperature rate of about 0.6K/min.

For TbMnO$_3$ and DyMnO$_3$, there are reported anomalies in the electric permittivity, marking the ferroelectric transition [1, 2, 26]. We observed these anomalies, at the expected transition temperatures. By continuity, we assume that the anomalies observed in the solid solutions, for low Fe substitution, also mark the transition to a polar phase.

![Figure 3.5: Temperature dependence of the (a) real and (b) imaginary parts of the dielectric constant of TbMn$_{1-x}$Fe$_x$O$_3$, for low temperatures and concentrations. Electric field frequency was 1 MHz. Data was vertically offsetted to be included all in the same graph. For absolute values, consult appendix B.](image)

In Figure 3.5, we see the temperature dependence of the real and imaginary parts of the dielectric constant of TbMn$_{1-x}$Fe$_x$O$_3$ on the narrow temperature range of interest. A set of sharp peaks marks the ferroelectric transition. For x=0, the peak is at 24K, in agreement with literature [3]. The critical temperature signaled by that peak raises slightly to 25K for x=0.01, with a considerable
3.2. ELECTRIC PERMITTIVITY AND RELAXATIONS

drop in magnitude. For $x=0.025$, the transition temperature decreases to 21K and, at $x=0.04$, no anomaly is observed.

Figure 3.6 shows similar results for the temperature dependence of the electric permittivity of DyMn$_{1-x}$Fe$_x$O$_3$. At $x=0$, there are clear anomalies at about 19K, in agreement with literature [3]. At $x=0.01$, the anomaly is better seen in the imaginary part, at 14K. At $x=0.02$, there is no observed anomaly.

The magnitude of the anomalies in the dielectric constant are very small, less than 0.3, indicating an improper ferroelectric transition. The anomaly at 21K in TbMn$_{0.975}$Fe$_{0.025}$O$_3$ agrees well with the magnetic transition observed in the crystal of TbMn$_{0.998}$Fe$_{0.002}$O$_3$, at 29K, providing evidence for magnetoelectric effects. It seems clear that the transitions observed in the solid solutions should be of the same nature than the ones in TbMnO$_3$ and DyMnO$_3$, namely, to a ferroelectric phase derived from a cycloidal spin ordering. The observed disappearance of the anomalies, for $x \geq 0.05$ in TbMn$_{1-x}$Fe$_x$O$_3$ and $x \geq 0.02$ in DyMn$_{1-x}$Fe$_x$O$_3$, is suggestive of the suppression the cycloidal magnetic phase and the ferroelectricity.

Some caution should be taken in defining the ferroelectric transition temperatures from the electric permittivity, since there are other features present. It can bee seen clearly in Figures 3.5 and 3.6, that there is an continuous increase in the permitivitty, towards lower temperatures. This increase is part of a broad step-like feature, shown in Figure 3.7, which is independent of the ferroelectricity.

Other features include a relaxation at slighty higher temperatures. As a representative example, we show in Figure 3.7 the temperature dependence of the real and imaginary part of the electric permittivity, in the temperature range 10-135K. Both heating and cooling runs are represented, though no thermal hys-
teresis was found in the low temperature range. At even higher temperatures, much more significant features dominate the dielectric properties\(^3\). These properties are common to the various manganites and of unclear origin [67]. They will not be studied here.

There is, however, a point worth noting. The relaxation in Figure 3.7, so clearly seen in DyMnO\(_3\), vanishes completely with \(x=0.03\). In fact, it gradually decreases up to that concentration and disappears only when the ferroelectricity is lost. This shows that there is some relationship between this feature and the ferroelectricity.

\[\text{(a)}\] \[\text{(b)}\] \[\text{(c)}\] \[\text{(d)}\]

Figure 3.7: Temperature dependence of the real and imaginary part of the dielectric constant of DyMn\(_{1-x}\)Fe\(_x\)O\(_3\), for (a),(c) \(x=0\) and (b),(d) \(x=0.03\), as a function of temperature, at different electric field frequencies. The higher frequency curves have the lower values of permittivity. Black curves were measured in cooling, red curves in heating. Arrow indicates the anomaly marking the ferroelectric transition.

\(^3\text{See appendix B}\)
3.3 Polar properties

In the previous section, it was observed that polar phases are present in the solid solutions, but it was suggested that they are suppressed with an increase of the Fe substitution. In this section, we describe how the Fe substitution impacts the ferroelectricity, by measuring the electric polarization.

The polarization was measured by the thermally stimulated depolarizing currents method. In this method, what is obtained is the depolarization current, which is integrated in time to obtain the polarization. To measure the polarization as a function of temperature, we must first cool the sample to the lowest temperature, while applying an electric field to direct the polarization in the appropriate sense for measurement. The measurement is then made in heating, without field, at 5K/min.

The values of the electric polarization are not unique, but depend on the magnitude of the poling electric field. Larger applied fields give larger polarizations, usually with a linear dependence. The example of DyMnO$_3$ is given in Figure 3.14.

However, the electric polarization always emerges at the same transition temperature, regardless of the temperature rate and poling electric field. This is indicative of a transition to a ferroelectric phase. The frequency independent anomalies in the electric permittivity, seen in the previous section, also confirm the existence of a ferroelectric phase.

To provide a meaningful comparison, the same poling electric fields were applied to all samples. The switching of the electric polarization with the sign of the electric field was checked. The temperature dependence of the electric polarization for the TbMn$_{1-x}$Fe$_x$O$_3$ and DyMn$_{1-x}$Fe$_x$O$_3$ systems is presented in Figure 3.9.

Polarizations of the order of 100 $pC/cm^2$ were obtained for $x=0$, in both R=Tb and Dy. The ferroelectric transition temperatures were 25K and 19K, in
CHAPTER 3. MAGNETOELECTRIC EFFECT AT LOW FE$^{3+}$ CONCENTRATIONS

Figure 3.8: (a) Temperature dependence of the electric polarization of DyMnO$_3$ for different poling electric fields. (b) Electric polarization at 10K as a function of the poling electric field. A linear dependence is observed.

Figure 3.9: Temperature dependence of the polarization of (a) TbMn$_{1-x}$Fe$_x$O$_3$ and (b) DyMn$_{1-x}$Fe$_x$O$_3$.

agreement with literature$^4$ [3].

After Fe substitution, the transition temperature decreases and the polarization suffers an abrupt drop. In R=Tb, it drops already by an order of magnitude for $x=0.01$. By $x=0.04$, it is two orders of magnitude below. In R=Dy, it falls off even faster. With $x=0.01$, a polarization of less than 50 $pC/cm^2$ was obtained. With $x=0.02$, it is negligible.

For concentrations above or equal to $x=0.05$ in R=Tb and $x=0.03$ in R=Dy, no ferroelectricity was measured, with applied poling electric fields up to 90 V/mm. The inevitable conclusion is that Fe substitution suppresses the ferro-

$^4$In literature, it is reported 27K and 19K for R=Tb and Dy, respectively, in single crystals.
3.4 SPECIFIC HEAT AND TRANSITION TEMPERATURES

Electricity, even in low concentrations.

It is clear that R=Tb and Dy share the same physics, but in the case R=Dy the loss of the ferroelectricity happens at lower concentrations.

The ferroelectricity in these systems is, as described in Chapter 1, driven by spiral magnetism. The disappearance of the ferroelectricity implies a change in the magnetic phase, as suggested by the magnetization measurements.

Further investigations are required to elucidate the magnetic phase that emerges right after the disappearance of the ferroelectricity and to understand how is the Fe substitution destabilizing the magnetic phase. Both theoretical modelling and neutron diffraction could provide a better understanding of these systems.

In the absence of such tools, different experimental techniques are of use in identifying the transition temperatures and providing hints on the phase diagram. In the following section, we will look into the associated anomalies in the specific heat.

3.4 Specific heat and transition temperatures

Specific heat provides one of the clearest ways to measure the transition temperatures. It is not affected by the predominance of the rare-earth magnetic moment, nor by the dynamics of dielectric relaxations.

The temperature dependence of the specific heat of all samples of the TbMn$_{1-x}$Fe$_x$O$_3$ system, with $x \leq 0.1$, and the DyMn$_{1-x}$Fe$_x$O$_3$ system, with $x=0, 0.05, 0.1$ was measured, using a Quantum Design PPMS (Physical Property Measurement System). The results are displayed in Figure 3.10.

![Figure 3.10](image)

Figure 3.10: Temperature dependence of the heat capacity of the solid solutions RMn$_{1-x}$Fe$_x$O$_3$ for (a) R=Tb and (b) R=Dy, within the low substitution range $x \leq 0.1$
Three sharp peaks are seen for TbMnO$_3$ and DyMnO$_3$. The lower temperature corresponds to the ordering of the rare-earth spins and takes place at around 6K, close to reported values in the literature [3]. The highest temperature peaks consist in the first magnetic transition of the Mn spins to the incommensurate collinear spin ordering [14]. The peak in the middle, at 26K for R=Tb and 18K for R=Dy, signals the ferroelectric transition.

As Fe substitution takes place, all transition temperatures decrease. In R=Tb, the ordering temperature of the Tb spins is the least affected. For the transition to incommensurate ordering, the transition temperature decreases and the peak becomes broader and less discernible. Similar features are observed for R=Dy.

For the peak marking the ferroelectric transition, it moves to lower temperature and broadens as well, but at x=0.05 no peaks are seen at all, for both R=Tb and Dy. The disappearance of the peaks is suggestive of the lost of ferroelectricity.

For R=Tb, this happens at exactly the expected concentration, x=0.05. For R=Dy, presumably a peak would be seen for $x < 0.03$ if such samples were measured. An additional measurement, not shown, of the sample with x=0.02, by a different method, provided indications that the ferroelectric transition is still manifest in the specific heat, at this concentration.

So far, all the discussions were made with regard to the magnetic contributions to the specific heat. Superimposed on these is the contribution from the lattice. These contributions can be removed by a fit to the Debye model, which leave us only with the magnetic features.

Such fits were made and, in Figure 3.11, the magnetic contribution to the specific heat is isolated and its changes with applied magnetic field measured for TbMn$_{0.975}$Fe$_{0.025}$O$_3$.

Figure 3.11: Temperature dependence of the magnetic contribution to the heat capacity for different values of the applied magnetic field, for TbMn$_{1-x}$Fe$_x$O$_3$, $x=0.025$. 
3.4. SPECIFIC HEAT AND TRANSITION TEMPERATURES

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_N(Tb)$</th>
<th>$T_{FE}$</th>
<th>$T_N(Mn)$</th>
<th>$T_{FE}$</th>
<th>$T_{FE}$</th>
<th>$T_{FE}$</th>
<th>$T_N(Mn)$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>6.5</td>
<td>26</td>
<td>41</td>
<td>24</td>
<td>24</td>
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<tr>
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<td>39</td>
<td>25</td>
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<td>23</td>
<td>23</td>
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<tr>
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<td>6</td>
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<td>38.5</td>
<td>23</td>
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</tr>
<tr>
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<td>6</td>
<td>20.5</td>
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<tr>
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<td>16</td>
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<tr>
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</tr>
</tbody>
</table>

Table 3.2: Transition temperatures, obtained by different experimental techniques, for TbMn$_{1-x}$Fe$_x$O$_3$.

Again we have the same three peaks for zero magnetic field. Upon the application of a magnetic field, the peak marking the ordering of the Tb spins broadens and is gradually suppressed. At 7T, it is no longer noticeable. A slight increase in the magnitude of the specific heat with the magnetic field is observed. This sample is illustrative of the remaining samples of R=Tb. This behaviour is suggestive of a suppression of the ordering of the Tb spins. No measurements of this sort were done on R=Dy.

We have now a set of transition temperatures, obtained by different means. These results were all gathered in Tables 3.2 and 3.3, for comparison.

As it seen, the results are consistent. The derived picture is that transition temperatures in general decrease and, in the case of the ferroelectric transition, are eventually suppressed. Taking into account the considerations made in the previous sections, namely section 3.1, a phase diagram is proposed for R=Tb and Dy, in Figure 3.12.

At high temperatures, the system is paramagnetic and paraelectric. For those concentrations and temperatures in which there is still ferroelectricity, the system should maintain its cycloidal magnetic phase, since it lies at the origin of the electric polarization. Above this phase, it is expected that the incommensurate phase remains, since there were no new features observed and there is no reason to believe otherwise. For $x > 0.05$, the magnetization measurements and comparison with the literature suggest a field-induced weak ferromagnetic
CHAPTER 3. MAGNETOELECTRIC EFFECT AT LOW Fe\textsuperscript{3+} CONCENTRATIONS

3.5 Magnetoelectric properties

We end this chapter with the analysis of the impact of Fe substitution on the magnetoelectric effect. The magnetoelectric properties are one of the most interesting aspects of these manganites and provided the original motivation for the work on this low substitution range.

Electric polarization was measured by the thermally stimulated depolarizing currents method, now with an external applied magnetic field. To apply a magnetic field and reach low temperatures, the SQUID magnetometer was used. Poling electric fields of around 50 V/mm were applied perpendicularly to the magnetic field, in cooling. Measurements of the depolarization currents were made in heating, with no applied electric field. Integration of these currents, yield the electric polarizations in Figures 3.13 and 3.15, for R=Tb and Dy, respectively.

We take the case of R=Tb first. For TbMnO\textsubscript{3}, x=0, the electric polarization component in a antiferromagnetic spin ordering. At what concentration the magnetic phase changes from incommensurate to FI weak ferromagnetic is unclear.

Some further measurements on the magnetic phases are therefore required to see the variations in the incommensurate phase, to confirm to field-induce phase and more precisely describe the cycloidal phase, by identifying the wavevector and cycloidal plane.

Having provided a picture of the magnetic, and ferroelectric, phases present in these solutions, with low substitution, we return to the electric polarization, now as a function of the applied magnetic field.
3.5. MAGNETOELECTRIC PROPERTIES

Figure 3.13: Temperature dependence of the electric polarization at several values of applied magnetic field, for TbMn$_{1-x}$Fe$_x$O$_3$, with (a) $x=0$, (b) $x=0.01$, (c) $x=0.025$ and (d) $x=0.04$

again sets in at 25K and grows to a value of the order of 300 $pC/cm^2$. Upon applied magnetic field, up to 5.5T, a reduction of $\sim 25\%$ on the polarization was observed. There is also a change in the ferroelectric transition temperature, but that is likely to be due to uncertainties in the measurement method.

Just as for the dielectric and magnetization measurements, limitations arise from the polycrystalline nature of our samples. Namely, we see an average of the contributions in different directions. This should be compared with the reported results on single crystals of TbMnO$_3$. In the case of a crystal, the electric polarization along the $a$ axis and the $c$ axis can be distinguished, which is of importance, since the interesting phenomena of polarization flop takes place in these manganites. Under an applied magnetic field of 5T along the $b$ axis, the polarization switches from the $c$ to the $a$ axis [1]. In our samples, we see the contributions from both the raising polarization along the $a$ axis and the falling polarization along the $c$ axis. The total variation is small.
For the solid solution in Figure 3.13, these variations increase with the Fe content. For \( x = 0.01 \) and \( x = 0.025 \), the total electric polarization is unaltered by the application of a magnetic field of 1T but is considerably reduced by a field of 5T. For \( x = 0.05 \), the suppression of the polarization begins already at 1T. As seen before, the values of the polarization and transition temperature decrease with \( x \).

Figure 3.14: Temperature dependence of the electric polarization at several magnetic fields, for TbMn\(_{1-x}\)Fe\(_x\)O\(_3\), with \( x \leq 0.05 \). The value of the electric polarization was normalized to the value in zero field.

Despite the negative impact of both a magnetic field and Fe substitution, it is interesting to note that the relative variations of the electric polarization with the magnetic field, and hence the magnetoelectric effect, increase with \( x \). Figure 3.14 makes this point clearer. At 1T, in \( x = 0 \), no change is seen. With the introduction of 4% of Fe, the relative polarization at 1T changes by almost 40%. The Fe substitution destabilizes the ferroelectricity, but also makes it more susceptible to the magnetic field.

Similar measurements were carried out for DyMn\(_{1-x}\)Fe\(_x\)O\(_3\). Here, there is a new difficulty. The ordering temperature of the Dy spins is closer to the ferroelectric transition temperature than in the previous case. As the Dy spins order, because of the coupling with Mn spins, they have an impact on the ferroelectricity. The consequence of this is that the value of the polarization depends strongly on the temperature to which we cooled the sample.

Due to this difficulty, the directly measured depolarization currents are also shown in Figure 3.15. Integration of these currents gives the polarizations. The results are of more difficult interpretation.

The impact of the applied magnetic field, however, is still to reduce the electric polarization. Variations in the transition temperature, seen on Figures 3.15 (a) and (b), should again not be taken too seriously. In these figures, there is two black curves for zero field. The lower one involved an cooling to 5K, while in the higher one, the sample was cooled to 7K. The inverted peak corresponds
to the ordering of the Dy spins. This dependence of the electric polarization on the lowest attained temperature for DyMnO$_3$ is in agreement with literature [2].

We have observed a similar response to the magnetic field in both of the previous solid solutions. In DyMnO$_3$ and TbMnO$_3$, the presence of a magnetic field above 5T stabilizes a cycloidal spin ordering in the $ab$ plane. With Fe-substitution, the disappearance of the electric polarization under an applied magnetic field indicates a gradual disappearance of the cycloidal phase altogether.

The stronger decrease of the electric polarization with the applied magnetic field for Fe-substituted manganites needs further investigations to be understood.
Figure 3.15: Temperature dependence of the depolarizing currents at several magnetic fields, for DyMn\(_{1-x}\)Fe\(_x\)O\(_3\), with (a) \(x=0\), (c) \(x=0.01\), (e) \(x=0.02\), and the obtained integrated electric polarization, for (b) \(x=0\), (d) \(x=0.01\) and (f) \(x=0.02\)
Chapter 4

Conclusions and Future work

We have studied the structure and lattice dynamics of the TbMn$_{1-x}$Fe$_x$O$_3$ solid solution, for the full range, at room temperature. Both the X-ray diffraction and Raman spectroscopy data indicate that the tilting of the octahedra is closely the same throughout the solid solution. Jahn-Teller distortions vanish, with gradual changes in the lattice parameters and the Raman modes. The passage from cooperative to dynamic Jahn-Teller is concluded to happen $x \sim 0.5$.

We have performed a characterization on the dielectric, thermodynamic, magnetic, polar and magnetoelectric properties for TbMn$_{1-x}$Fe$_x$O$_3$ and DyMn$_{1-x}$Fe$_x$O$_3$, with $x \leq 0.1$. A gradual opening of the ZFC and FC magnetization curves was observed with the introduction of Fe. This suggests the presence of a new magnetic phase, already at $x=0.075$ for DyMn$_{1-x}$Fe$_x$O$_3$. The ferroelectric phase is suppressed by Fe-substitution in both solid solutions, disappearing for $x=0.05$ in R=Tb and $x=0.03$ in R=Dy. With the use of the specific heat and dielectric constant measurements, a phase diagram was traced for these solid solutions in the low substitution range. The impact on the magnetoelectric effect was analyzed.

The precise determination of the magnetic phase brought by Fe-substitution is still lacking. In this direction, studies on neutron diffraction will be performed, to understand better, both the structure and the magnetism. A theoretical understanding of how Fe-substitution destabilizes the magnetic phase is also desirable. Further investigations of the response under an applied magnetic field are being pursued by Raman spectroscopy. As mentioned at the end of Chapter 2, the Raman spectra of the ferrites is complex and not properly understood. We are currently involved in a collaboration to do the mode assignment of the Raman spectra for the full orthoferrite family. This should allow for a better interpretation of the alterations in the Raman spectra, from manganites to ferrites.
Appendix A

Sample characterization

The samples used in this work were produced and characterized by Pedro B. Tavares and Eugénia Queirós, working in the Centro de Química at the Universidade de Trás-os-Montes e Alto Douro (UTAD). The results in this appendix were provided by them.

High quality ceramic pellets of TbMn$_{1-x}$Fe$_x$O$_3$, for the full range, and of DyMn$_{1-x}$Fe$_x$O$_3$, for $x < 0.1$, were produced by the sol-gel method. The resulting materials were characterized using different techniques such as x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS).

Powder XRD data were acquired by PANalytical XPert Pro diffractometer equipped with XCelearator detector. All the samples were analyzed at room temperature using a Cu K$_\alpha$ radiation and Bragg-Bentano geometry, 0.017/step and 100 s/step. The patterns were analyzed by Rietveld refinement. The results were discussed in section 2.4.

Images obtained with the Scanning Electron Microscope (FEI Quanta 400) are in Figure A.2. This device is attached with an Energy Dispersive X-ray Spectrometer (EDAX). Using the standardless EDAX ZAF quantification method it was possible to assess the composition of the samples (Figure A.1).
Figure A.1: EDS spectra of TbMn$_{0.1}$Fe$_{0.9}$O$_3$

Figure A.2: SEM images of TbMn$_{1-x}$Fe$_x$O$_3$, for (a) x=0, (b) x=0.1, (c) x=0.2, (d) x=0.4, (e) x=0.6, (f) x=0.8 and (g) x=1
Appendix B

Dielectric constant
This appendix contains the full characterization of the dielectric constant, as function of temperature and frequency, for the samples of DyMn$_{1-x}$Fe$_x$O$_3$, referred to in the text.

The black curves were measured in cooling, the red ones in heating. For the most part, a ramp of 0.5-0.6 K/min was applied. For convenience, the data is divided into high frequencies (HF) and low frequencies (LF).

**HF**: 1000, 900, 800, 700, 600, 500, 400, 300, 200, 100, 80, 70, 60 kHz

**LF**: 50, 40, 30, 20, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 kHz

Figure B.1: (a) Real and (b) imaginary parts of the dielectric constant for high frequencies. (c) Real and (d) imaginary part of the dielectric constant for low frequencies. The material is DyMn$_{1-x}$Fe$_x$O$_3$, x=0
Figure B.2: (a) Real and (b) imaginary parts of the dielectric constant for high frequencies. (c) Real and (d) imaginary part of the dielectric constant for low frequencies. The material is DyMn$_{1-x}$Fe$_x$O$_3$, $x=0.01$. 
Figure B.3: (a) Real and (b) imaginary parts of the dielectric constant for high frequencies. (c) Real and (d) imaginary part of the dielectric constant for low frequencies. The material is DyMn$_{1-x}$Fe$_x$O$_3$, x=0.02.
Figure B.4: (a) Real and (b) imaginary parts of the dielectric constant for high frequencies. (c) Real and (d) imaginary part of the dielectric constant for low frequencies. The material is DyMn$_{1-x}$Fe$_x$O$_3$, $x=0.03$. 
APPENDIX B. DIELECTRIC CONSTANT

Figure B.5: (a) Real and (b) imaginary parts of the dielectric constant for high frequencies. (c) Real and (d) imaginary part of the dielectric constant for low frequencies. The material is DyMn$_{1-x}$Fe$_x$O$_3$, $x=0.04$. 
Figure B.6: (a) Real and (b) imaginary parts of the dielectric constant for high frequencies. (c) Real and (d) imaginary part of the dielectric constant for low frequencies. The material is DyMn$_{1-x}$Fe$_x$O$_3$, $x=0.05$. 
Bibliography


tolectric phase diagrams of orthorhombic rmno$_3$ (r= gd, tb, and dy),” 


[28] H. Katsura, N. Nagaosa, and A. V. Balatsky, “Spin current and magneto-
lectric effect in noncollinear magnets,” Physical Review Letters, vol. 95, 

[29] I. A. Sergienko and E. Dagotto, “Role of the dzyaloshinskii-moriya inter-
action in multiferroic perovskites,” Physical Review B, vol. 73, p. 094434, 
2006.

coupling and ion displacements in multiferroic tbmno$_3$,” Physical Review 

[31] A. Malashevich and D. Vanderbilt, “First principles study of improper 
ferroelectricity in tbmno$_3$,” Physical Review Letters, vol. 101, p. 037210, 
2008.

[32] H. C. Walker, “Femtoscale magnetically induced lattice distortions in mul-

coupling in multiferroic manganese perovskites rmno$_3$,” Physical Review 

[34] M. Mochizuki and N. Furukawa, “Mechanism of lattice-distortion-induced 


correlation between ferromagnetism and ferroelectricity in perovskite man-

[37] J. Hemberger, “Multiferroic phases of en$_{1-x}$y$_x$no$_3$,” Physical Review B, 

[38] Y. Tokunaga, S. Iguchi, T. Arima, and Y. Tokura, “Magnetic-field-induced 
2008.

[39] Y. H. Huang, M. Karppinen, N. Imamura, H. Yamauchi, and J. B. 
Goodenough, “Structural transformation and magnetic competition in 


