Chapter 1

Introduction

1.1 Transition metal oxides

Transition metal oxides form a series of compounds with a uniquely wide range of electronic properties from insulator (e.g. Cr_2O_3) to metallic (e.g. TiO). Some of these properties have been known since antiquity. Other properties, especially the "high-temperature" superconductivity of mixed oxides containing copper have been discovered only recently. Serious attempts to characterize and understand the electronic structure of transition metal oxides began in the late 1930's, but as the discovery of high-temperature superconductors and magnetoresistive materials illustrate, these compounds continue to surprise us in many ways.

The chemistry and thus the electronic and physical properties of transition metal oxides can be understood only when we have a sound knowledge of their crystal chemistry. Crystal chemistry represents not only the crystal structures of the oxides, but also the nature of bonding in them. Crystal chemistry is indeed a crucial constituent of solid state chemistry and provides the basis for designing and synthesizing new materials. Transition metal oxides are by far the most fascinating class of materials when it comes to crystal chemistry. Associated with the changes in bonding, transition metal oxides show also a gamut of fascinating properties. In recent years, it has been possible to determine the structures of complex transition metal oxides by employing some of the new techniques of crystallography. Today, we can obtain detailed structures not only of oxides in single-crystal form, but also of powders employing methods of X-ray and neutron diffraction. These two techniques have become really powerful because of the availability of synchrotron X-rays and intense pulsed neutron sources [1]. The phase diagram upon doping of $La_{1-x}Sr_xMnO_3$ is a good illustration of the rich variety of properties that one can encounter while studying transition metal oxides (see figure 1.1).

We used diffraction technique through out this thesis. Synchrotron and neutron radiations were specifically of use in our study of the hexagonal rare-earth manganates and rare-earth titanates. One of the long term interest in the field of transition metal oxides has been dedicated to the study of orbital ordering (see below section 1.2 and chapter 3) in relationship or not with the presence of the colossal magnetoresistance [1, 1]. In this thesis, we bring our contribution to the study of orbital ordering in the rare-earth titanates family (see chapter 3). A very recent or rather a revival in the field of transition metal oxides has been the study of the interplay between dielectric properties and magnetic properties. This interplay has been mostly investigated in recent years in spinels [3], orthorhombic and hexagonal related perovskites [4, 5]. The study of the interplay between dielectric and magnetic properties in transition metal oxides concerns the main core of this thesis both experimentally (see chapters 4 and 5) and theoretically (see chapter 6). We describe in section 1.3 in more details the notions associated with this interplay.
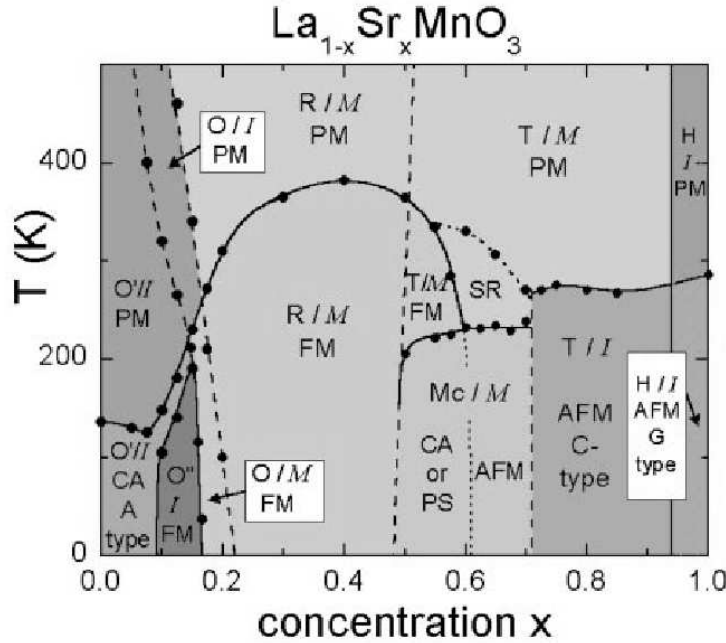

Figure 1.1: *Phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ for the complete concentration regime. The crystal structures (Jahn-Teller distorted orthorhombic: O$'$, orthorhombic O; orbital-ordered orthorhombic: O$''$, rhombohedral: R, tetragonal: T, monoclinic: Mc, and hexagonal: H) are indicated as well as the magnetic structures [paramagnetic: PM, short-range order (SR), canted (CA), A-type antiferromagnetic structure: AFM, ferromagnetic: (FM), phase separated (PS), and AFM C-type structure] and the electronic state [insulating: I, metallic: M]. The phase diagram is reproduced from [6].*

1.2 Orbital Ordering: Cooperative versus dynamical Jahn-Teller effect

The theorem by Jahn-Teller was originally formulated to describe the instability of symmetric molecules in the presence of orbital electronic degeneracy [7]. They enumerated all the possible ionic (or molecular) symmetries and showed that in all cases there is at least one vibrational mode for which a splitting is allowed by symmetry. The only exception they found was the linear molecule.

The understanding of many properties of solids is based on the assumption that the motion of electrons localized in unfilled shells of ions is independent of the motion of the atomic nuclei. This is known as the Born-Oppenheimer approximation and it may be expressed algebraically as:

$$\Psi(\mathbf{q}, \mathbf{Q}) = \phi_{\mathbf{Q}}(\mathbf{q})\chi(\mathbf{Q}) \tag{1.1}$$

Here $\Psi(\mathbf{q}, \mathbf{Q})$ is the exact coupled wavefunction which is a function of the electronic coordinates $\mathbf{q}$ and the nuclear coordinates $\mathbf{Q}$. It is expressed approximately as the product of the nuclear wavefunction $\chi(\mathbf{Q})$ and the electronic wavefunction $\phi_{\mathbf{Q}}(\mathbf{q})$ which depends parametrically on $\mathbf{Q}$. $\phi_{\mathbf{Q}}(\mathbf{q})$ is an eigenfunction of the electronic hamiltonian which includes a potential energy term $V_{\mathbf{Q}}(\mathbf{q})$ [8]. The Born-Oppenheimer approximation amounts to assuming that the electronic motion is so rapid compared with the nuclear motion that this potential $V_{\mathbf{Q}}(\mathbf{q})$ is a function of $\mathbf{q}$ only and is almost independent of $\mathbf{Q}$. If there is an orbital degeneracy of the electronic states then this approximation is no longer valid. This is why the statement is often made that Jahn-Teller effects are corrections to the Born-Oppenheimer approximation. Under these circumstances it is not strictly correct to refer to the modes as electronic or lattices modes. We will use the term vibronic coupling to describe that mode which is mostly electronic in character but has some vibrational character too. In other words vibronic coupling describes the bridge between electronic and nuclear motions. The consequences of the corrections to the Born-Oppenheimer approximation can be expressed by a Jahn-Teller contribution to the hamiltonian in the form:

$$H_{JT} = A\mathbf{Q}S^z \tag{1.2}$$

where S^z is some electronic operator, which, in the case of an electronic doublet, can have the eigenvalues ± 1. The constant A measures the strength of the coupling [8].

If a crystal is formed from molecules that interact by stericlike forces, the energy of their interaction in the lattice U depends on the mutual orientation of these molecules. In such cases the minimum of the free energy F = U- TS (S is the entropy) requires at T = 0 an ordering of the interacting

molecules in which their mutual orientations make U minimal. At higher temperatures the entropy term TS becomes large, and at a certain temperature a phase transition to the disordered state for which the entropy is a maximum takes place (*order-disorder transitions*). In inorganic and coordination compounds, in addition to such order-disorder transitions, *displacive phase transitions* may take place. In them, as distinct from order-disorder transitions, the atomic arrangement in the coordination center center itself changes. Displacive transitions are related directly to the electronic structure, demonstrating the fact that in crystal stereochemistry of transition metal coordination compounds, the electronic structure of the coordination center plays a key role and cannot be ignored [9]. Thus if the different Jahn-Teller centers can interact, we will have an ordering of the local distortions which will lead to a macro-deformation of the crystal as a whole. New properties of the crystal arising from the correlation (ordering) of the Jahn-Teller center distortions, including the formation of new crystal structures and structural phase transitions, are called the *cooperative Jahn-Teller effect*. One important point is that the structural phase transition resulting from a cooperative Jahn-Teller effect is one of the most important features of the cooperative vibronic effects [9]. Many structural phase transitions in many classes of materials have been attributed to cooperative vibronic effects. In particular, in a series of tetragonal rare-earth zircons of general formula RXO_4, where R is a rare-earth (R=Tm, Dy and Tb) and X = V, As, P, a direct correspondence between electronic structure parameters of the Jahn-Teller rare-earth ion and the temperatures of structural phase transitions in the cooperative Jahn-Teller approach was established. Other crystals, such as spinel (e.g., $NiCr_2O_4$, $FeCr_2O_4$, $CuCr_2O_4$, FeV_2O_4, $FeCr_2S_4$), perovskites ($KCuF_3$, $KMnF_3$), and other structures ($CsCuCl_3$, K_2CuF_4) were also studied using the vibronic approach (see [8, 10] and references therein).

However, one question may arise from the discussion above concerning the degeneracy of the electronic states. Are the corrections to the Born-Oppenheimer approximation and the Jahn-Teller effect related to the exact degeneracy of the electronic states, or may the latter be just close in energy? In short, the answer is that electronic states with sufficiently close energy levels are similar in behavior to exact degenerate states. The case of sufficiently close energy states is called the *pseudo Jahn-Teller effect* [9]. We will not discuss further this point. We refer the reader to the literature for further details [11]. The most recent example of cooperative pseudo Jahn-Teller effect is probably the case of $LaMnO_3$ which experiences an isostructural phase transition around $T_{PJT} \simeq 750K$ [12]. In recent years, the term of orbital ordering has been preferred to the denomination of cooperative Jahn-Teller effect.

In opposition to the static pseudo Jahn-Teller and cooperative Jahn-

Teller effects, averaged effects can be observed and are called dynamic Jahn-Teller effects. Typically, a Jahn-Teller systems will exhibit at least 2 possible states below T_{JT}. However due to dynamic effects, these two states or more may be very difficult to probe. In such cases, we will observe an average. Dynamic Jahn-Teller effects can arise for a number of different reasons. The rather trivial one is thermal fluctuations. If $kT \gtrsim E_{JT}$ where E_{JT} is the energy gained by the system due to the distortion, there will be rapid, thermally induced fluctuations between the 2 states. Thus no static distortion will be observed. For other possible reasons, we refer the reader to the literature [8, 13]. These dynamical effects may bring serious difficulties in deciding whether a system is orbital ordered (static or dynamic) or not.

1.3   Multiferroic materials

Multiferroic materials can be considered as being materials presenting at least two ferroic states. These ferroic states are ferroelasticity, ferroelectricity and ferromagnetism. Thus, as a logical definition to the term multiferroic, we could use the term multiferroic to any material presenting two of these three properties. However, the most interesting combination was thought to be materials presenting ferroelectricity and ferromagnetism. Hill discussed the conditions required for ferroelectricity and ferromagnetism to be compatible in transition metal oxides, and declared them to be rarely met [14]. Thus, the current trend is that any material presenting simultaneously a polar state and a long range magnetic order is considered as a multiferroic. A recent resurgence of interested has been observed in the recent years which is driven by long-term technological applications [15].

In parallel to the work on multiferroics, a significant work has been done especially in the 1950's and 1960's on the magnetoelectric effect [16]. The magnetoelectric effect is the possibility to induce a polarization by application of a magnetic field (linear effect) or by application simultaneously of an electric and a magnetic field, for instance (non-linear effect) (see ref. [12] and chapter 2). The reverse effect is that a magnetization can be induced by an electric field (linear effect) or by application simultaneously, for instance, of an electric and a magnetic field (non-linear effect). While the non-linear effect is allowed in most of the multiferroic compounds, the ones presenting a linear effect are rather rare (see figure 1.2). Consequently, the strong interplay between dielectric and magnetic properties (linear magnetoelectric effect) is rare. For more details on the magnetoelectric effect, we refer to the recent review of Fiebig [18]. The linear magnetoelectric effect in multiferroics is important since it enhances the interplay between dielectric and magnetic properties. This interplay is of prime importance for technological applications.
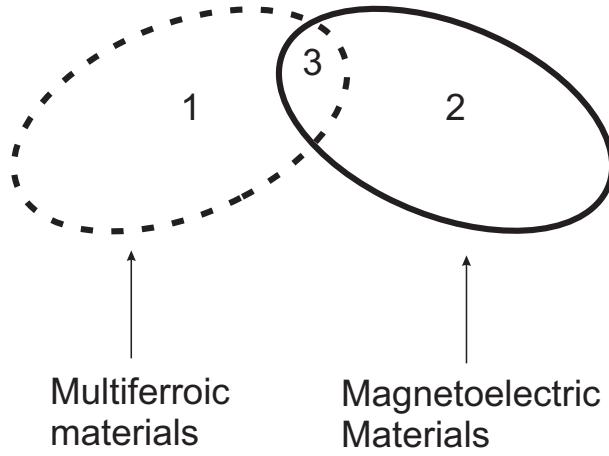
Figure 1.2: *Relationship between multiferroic and linear magnetoelectric mate-rials. Multiferroic materials (area 1) and linear magnetoelectric materials (area 2) may overlap giving rise to an enhancement of the interplay between dielectric and magnetic properties (area 3).*

In chapter 5 of this thesis, we study the linear and non-linear magneto-electric effects in a multiferroic and non-multiferroic materials illustrating the cases of areas 2 and 3 (see figure 1.2). We show that the magnetoelectric coupling is significantly stronger in the case of area 2 than in area 1 for our studied material. In addition, we predict based on symmetry arguments the existence of new multiferroic and/or magnetoelectric materials in chapter 6.

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