

## *Chapter 1*

### *Brief Review and Objective of the Thesis*

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IIT Kharagpur

# Chapter 1

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### **1.1 Introduction**

Physics, material science and engineering have been at the frontier of technological development since the historical era. The industrial revolution was heavily supported by the improvement of better, smaller and smarter materials for memories, data storage, signal processing, probing and new generation electronics. Materials can be divided into numerous categories, depending on their origin, use or morphology.

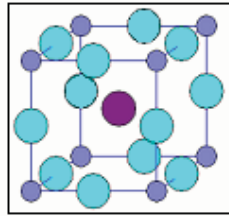
One prime example of small but diverse group of materials is 'Perovskite Family'. Physicists, chemists and material scientists have shown a wide interest in these materials because of their varieties of properties like high temperature superconductivity, colossal magnetoresistance (CMR), ferroelectricity, magnetocaloric effect etc. Still new and unexplored possibilities of perovskites may yet to appear. Therefore, these complex oxides are strategically important and expected to have widespread applications including magnetic sensor, electronic device, microwave component, data storage and magnetic recording device, chemical and gas sensor, catalysts, spin devices, electrode in fuel cells etc.

#### **1.1.1 Perovskite Compounds**

Perovskites are the most abundant material on earth constituting about 70-80% of the upper mantle and above 90% of the lower one. The parent compound, Barium/ Calcium titanate, is a crystalline ceramics derived its name in 1830's by the geologists Gustov Rose, who named it after the famous Russian mineralogist 'Aleksievich von Perovski'. The prototype perovskites with general formula,  $ABO_3$  (Hasen, 1988), are isotropic and have cubic symmetry. The structure is shown in figure 1.1.

Ideal perovskites are electrical insulators with all the atomic sites filled and strong ionic bonds keep the atoms and their electrons in place making it difficult

for electrons to move through the crystal. Most interesting physics arise when there is some slight distortion in perovskites structure. It is known that perovskites structure will be stable only if the Goldschmidt tolerance factor  $t$ , defined as  $t = (r_A + r_O) / \sqrt{2}(r_B + r_O)$  ( $r$  is the radii of the corresponding ions) approximately equal to 1 (Goldschmidt, 1927). Then if, for example,  $A$  cation is too small compared to  $B$  cation, the perovskites structure will get distorted and symmetry will be lowered, altering the electrical, magnetic, elastic, optical and other physical properties. The results can be the materials that are semiconducting, conducting or superconducting. The change in position of  $B$  cation in the structure can also create electric polarity in the crystal making ferroelectricity possible to execute.



**Figure 1.1** The perovskite structure with  $A$ -ion at the center of cube,  $B$ -ions at the corners and Oxygen ions is between them.

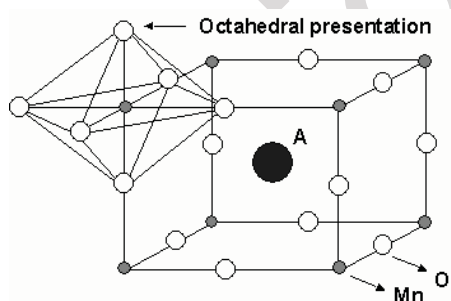
## 1.2 Mixed valence Manganite perovskites

The manganites, i.e.  $AMnO_3$  compounds, where  $A$  is the large lanthanide and/or alkaline earth ions such as  $La^{3+}$ ,  $Sr^{2+}$ ,  $Ca^{2+}$ ,  $Pb^{2+}$ ,  $K^{+1}$ ,  $Na^{+1}$  etc, follow the crystal structure of perovskites and belong to the large family of 'transition metal oxides'. The partial replacement of lanthanide  $La^{3+}$  by divalent/monovalent alkaline earth ions mentioned above will induce mixed valence of  $Mn$  ions (due to existence of both  $Mn^{3+}$  and  $Mn^{4+}$  in corresponding proportions) in the structure. One of the most interesting property of this mixed valence manganites is the influence of magnetic transition on the electronic conduction. In this section, we will describe some of the physics and basic properties of the mixed valence manganites.

### 1.2.1 Crystal structure

In the crystal structure of manganites, the rare-earth atom (e.g.  $La$ ) lies at the center, eight  $Mn$  atoms at the corners and oxygen will be at the midway between each  $Mn$  pairs (figure 1.2). In other way, the perovskite crystal structure of manganites can be regarded as a three dimensional network of corner sharing  $MnO_6$  octahedra with rare-earth atoms at the interstitial positions.

In the literatures, manganites have been described in cubic, rhombohedral, hexagonal, orthorhombic and monoclinic unit cells. All these descriptions however can be seen as distortion of the basic perovskites unit cell with lattice site  $a = 3.9 \text{ \AA}$ . If there is a deviation from the ideal value of Goldschmidt tolerance factor ( $t=1$ ), the crystal will lower its symmetry by the rotation of the oxygen octahedra and a new unit of some other type will be formed. For small deviation from ideal structure, there will be a slight rhombohedral distortion. With larger misfit of ionic sizes, there will be a buckling of  $MnO_6$  octahedra leading to orthorhombic structure.



**Figure 1.2** Crystal structure of rare-earth manganite perovskites ( $AMnO_3$ :  $A$  is the rare earth ion as  $La$ ,  $Pr$ ,  $Nd$  etc.)

### 1.2.2 Double exchange

The theory of 'Double-Exchange (DE)' was introduced by Zener in 1951 and was used to explain the correlation between the electrical conductivity and ferromagnetism (Zener, 1951a) found by Jonker and Van Santen (1950, 1950a). The basic idea is that the two configurations  $Mn^{3+} - O - Mn^{4+}$  and  $Mn^{4+} - O - Mn^{3+}$  are degenerate that lead to a delocalization of the electrons on  $Mn^{4+}$  sites. DE depends

on the transfer integrals between the  $Mn$  and  $O$  orbitals. This delocalization lowers the energy of the system and therefore there will be a gain in energy by aligning the  $t_{2g}$  spins of  $Mn$  ions. For doping level, where there is a large number of  $Mn^{3+} - Mn^{4+}$  pairs, this will lead to ferromagnetism. The relation between the electrical conductivity  $\sigma$ , the temperature  $T$ , the Curie temperature  $T_C$  and the fraction of  $Mn^{4+}$ ,  $x$  as given by Zener (1951), can be written as:

$$\sigma \cong \left( \frac{xe^2}{ah} \right) \left( \frac{T_C}{T} \right) \quad (1.1)$$

where  $a$  is the lattice parameter,  $h$  is Planck's constant and  $e$  is the electron charge.

A more extensive treatment of double-exchange has been given by Anderson and Hasegawa (1955), where the  $t_{2g}$  spins are treated classically and the  $e_g$  electron quantum mechanically. The effective transfer integral can then be found as:

$$t = b \cdot \cos(\theta/2) \quad (1.2)$$

where  $b$  is the transfer integral depending on spatial wave functions, cosine term is due to spin wave function and  $\theta$  is the angle between the  $t_{2g}$  spins of the neighboring ions. Generally, the perovskite structure is not perfect i.e. the bond angle  $\angle Mn-O-Mn \neq 180^\circ$ . This imperfect structure can also affect the ferromagnetic transition and the conductivity of the system. A detailed study by Hwang et al (1995) proved that effective transfer integral  $b$ , which gives the overlap of the manganese  $d$  orbital and oxygen  $p$  orbital, is the deciding factor that dominates the ferromagnetic transition and the conductivity of the system. The overlap integral will be maximum for a bond angle of  $180^\circ$ . For any imperfect manganite structure, Goldschmidt tolerance factor is less than 1 and hence the oxygen octahedra rotate. By increasing  $A$ -site radius, the rotation of octahedral becomes smaller and the  $Mn-O-Mn$  bond angle  $\theta$  comes closer to  $180^\circ$ .

Undoped  $LaMnO_3$  is an insulator because here due to strong Hund's coupling, electron from lower  $e_g$  state cannot move to higher  $e_g$  state. A fully doped manganite, say  $CaMnO_3$ , is also insulator because of absence of any carriers in  $e_g$  level.

It has been shown by Millis et al (1995) that double-exchange alone cannot make correct quantitative prediction about ferromagnetic transition and CMR effect. It was proposed that electron-phonon coupling due to Jahn-Teller distortions must be taken into account. There will be a tendency of the conduction band electrons to be localized as small polarons above the Curie temperature. This is backed by several experimental supports reported by different authors (Snyder et al, 1996; Jaime et al, 1997; Wang et al, 1999; Adams et al, 2000).

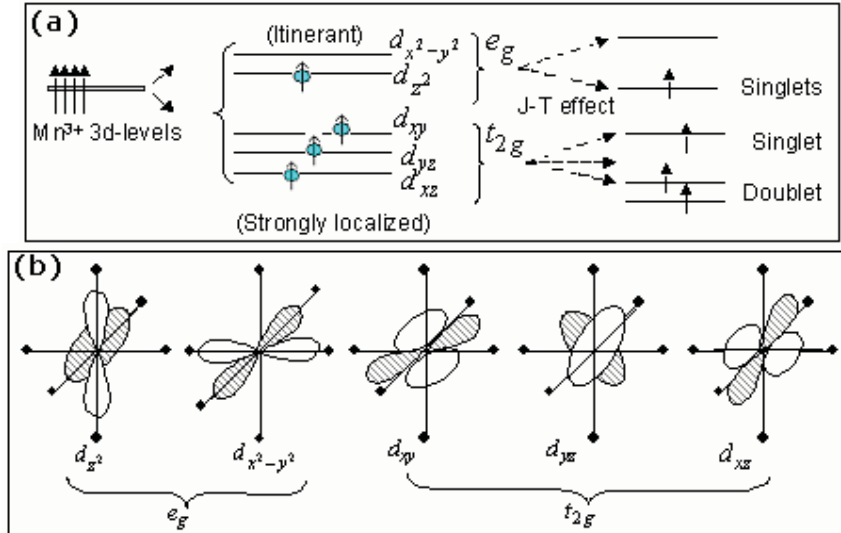
### 1.2.3 Electronic structure and Jahn-Teller distortion

The undoped lanthanum manganites have the chemical formula  $La^{3+}Mn^{3+}O_3^{2-}$ . Because of crystal field splitting, the five  $3d$  orbitals divide into two sets named  $t_{2g}$  and  $e_g$  orbitals (figure 1.3). The  $e_g$  orbitals are oriented towards the neighboring oxygen while the  $t_{2g}$  states have nodes in those directions, signifying that  $e_g$  orbital can intermix with oxygen  $p$  orbital.

There is a strong on-site Hund's coupling that requires all  $d$  electrons on a  $Mn$  ion should have the same spin as shown by upwards arrow in figure 1.3. Again certain electronic configurations have a tendency to distort their environment, with an elongated  $Mn-O-Mn$  bond. This is a consequence of Jahn-Teller theorem, which states that a magnetic ion in a crystal site (having high symmetry so that its degeneracy is not the minimum) will lower its energy by distorting the crystal in such a way so as to lower the symmetry enough to remove the degeneracy (Ashcroft and Mermin, 1976). This is shown schematically in figure 1.3. With an electron in the  $e_g$  state, this will lower the energy of the system.

In the mixed valence manganite of the type  $La_{1-x}A'_xMnO_3$  where  $A'$  is the divalent/monovalent alkaline earth ions, due to increase in concentration of  $Mn^{4+}$

ions,  $e_g$  state electron will no longer present. Then there will be no Jahn-Teller distortion as there is no gain in energy by distortion of the crystal.



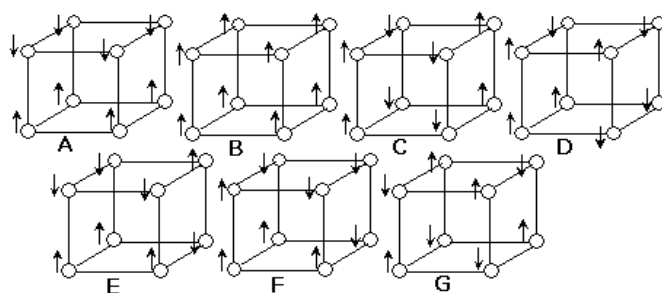
**Figure 1.3 (a)** Electronic energy levels of  $Mn^{3+}$  ion in manganite compound. In crystal field the  $Mn$   $3d$  level's degeneracy is lifted partially to form a doublet  $e_g$  state and a triplet  $t_{2g}$  state, **(b)** The  $3d$  orbital of  $Mn$  ion in the octahedral site showing the orientation of  $e_g$  and  $t_{2g}$  staets. Black dots represent the oxygen ions.

### 1.2.4 Magnetic structure

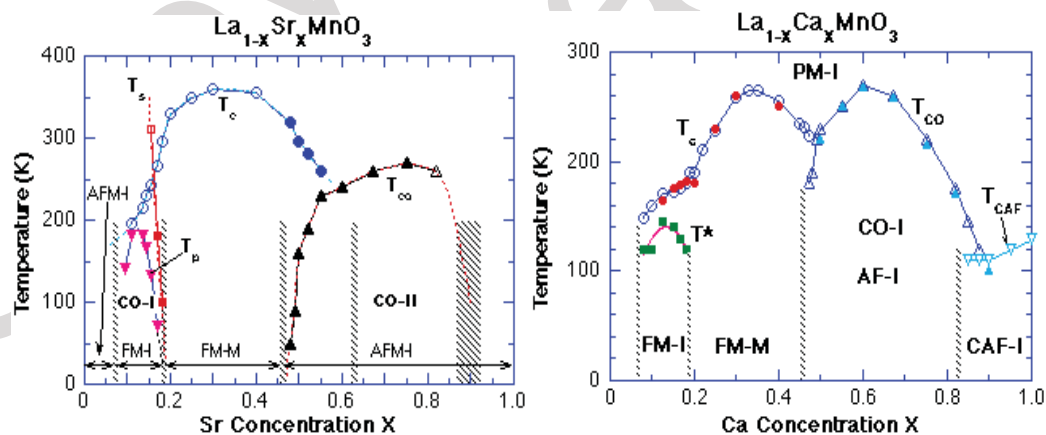
In 1995, Wollan and Koehler made a study on the magnetic behavior on a series of  $La_{1-x}Ca_xMnO_3$  samples, through Neutron diffraction measurements (Wollan and Koehler, 1955). Depending on the doping level, samples showed different kind of antiferromagnetic and ferromagnetic behavior. The different magnetic structures obtained by them are shown in figure 1.4. There can also be combinations of these structures. The end member  $LaMnO_3$  was found to be antiferromagnetic with ferromagnetic planes having alternating directions of magnetization, leveled 'A' in figure 1.4. The other end member  $CaMnO_3$  was also found to be antiferromagnetic with each  $Mn^{4+}$  ion surrounded by the six closest neighbors having opposite spins,

leveled 'G' in figure 1.4. The intermediate doping levels within  $x \approx 0.3$  gave other types of antiferromagnetic ordering.

Different groups have made measurements on the magnetic states of manganites as a function of temperature and doping (Shiffer et al, 1995; Urushibara et al, 1995). Typical phase diagrams are shown in figure 1.5. The CMR effect generally takes place at the ferromagnetic-paramagnetic transition with a doping level between  $\sim 20-50\%$ . The maximum Curie temperature is achieved with a doping level  $\sim 30\%$ . Goodenough (1955, 1961) has explained the magnetic structures for different doping levels in terms of different types of bonding, where some bonds are ferromagnetic and others are antiferromagnetic or paramagnetic. This is determined by the relative orientation of occupied and unoccupied orbitals of the  $Mn-O-Mn$  pairs.



**Figure 1.4** Possible magnetic structures of perovskite manganites. The circles represent manganese ions and the arrow indicates the direction of spin along z-axis.



**Figure 1.5** Typical phase diagrams of  $La_{1-x}Sr_xMnO_3$  and  $La_{1-x}Ca_xMnO_3$  respectively.