

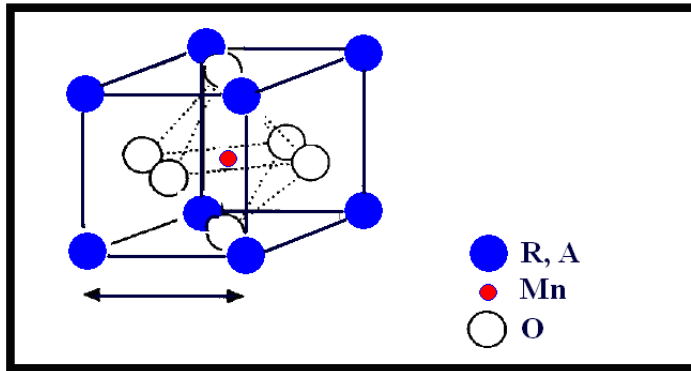
# 1

## Introduction



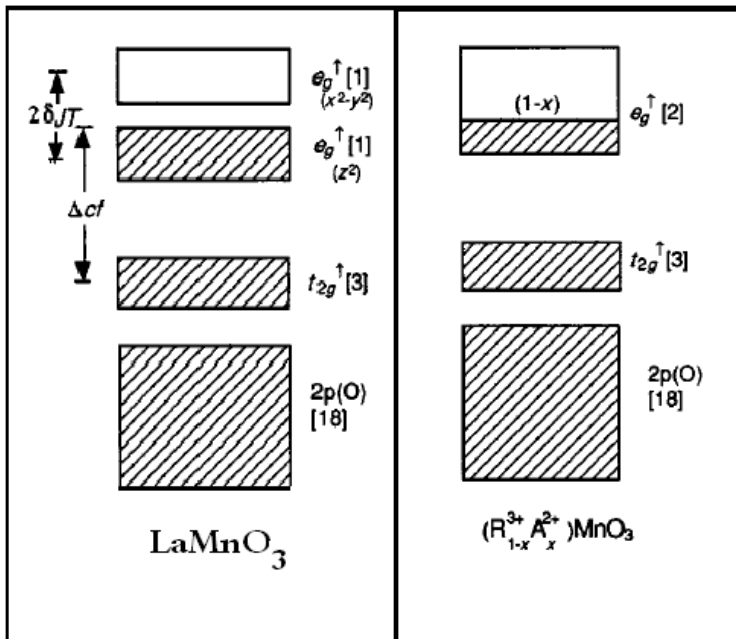
Manganites, Ferrites and coblates are the materials which composed of manganese, iron and cobalt respectively so any material in its content manganese is so called manganites. There are many types of compounds in their content exists manganese, for example manganese oxides. In the recent years, a lot of interest has been devoted to research on rare earth manganese oxides, within perovskites-like structure. These rare earth manganese oxides have exciting properties such as the colossal magnetoresistance (CMR) [1] and multiferroic effects [2]. These compounds could be used as a magnetic storage media and magnetic sensors [3-4]. The great attention increased due to the potential applications in spintronics [5-6] and in ferroelectromagnets [7-8].

Perovskites have the general formula  $ABO_3$  where A and B are metallic cations and O is a nonmetallic anion [9]. A is a large cation, similar in size to  $O^{2-}$ ; B is a small cation such as  $Mn^{3+}$  or  $Mn^{4+}$ , octahedrally-coordinated by oxygen. In the present case A is rare earth element (Nd, Eu, Sm, ...), B is 3d transition metal element (Mn, Fe, Co, ...) and O is oxygen. The ideal cubic structure is shown in Fig. 1.1 One can say that the ideal perovskite structure is considered as a cubic close-packed array formed of  $O^{2-}$  anions and  $A^{+3}$  cations with small  $B^{+3}$  cations in octahedral interstitial sites. Partially replacement of rare earth element by divalent element in this compound (a divalent element like Ca, Sr, Ba, ...) has been extensively investigated [9]. The ideal, cubic perovskite structure is distorted by cation size mismatch and the *Jahn & Teller effect*, whereby a distortion of the oxygen octahedron surrounding the B site cation splits the energy levels of a 3d ion such as  $Mn^{3+}$ , thus lowering the energy. The distorted structures are frequently orthorhombic. So one can say crystal structure of these materials not only has cubic structure but also is found to be in the orthorhombic, rhombohedral, hexagonal.



**Fig. 1.1** The ideal, cubic perovskite structure.

Mixed-valence manganites are solid solutions based on  $\text{AMnO}_3$  where A is a rare earth ion. [10] In the  $\text{ABO}_3$  perovskite structure, Mn is on the B site in octahedral oxygen coordination, with crystal field splitting  $\Delta_{cf}$  between the  $t_{2g}$  and  $e_g$  orbitals.



**Fig. 1.2** Schematic band structure of  $\text{LaMnO}_3$  and  $\text{R}_{0.7}\text{A}_{0.3}\text{MnO}_3$ .

The simple cubic perovskite structure undergoes a double distortion in the end member, reducing the symmetry to orthorhombic ( $O'$  structure). There is a buckling of the  $MnO_6$  octahedral array to accommodate the size discrepancy between  $R^{3+}$  and  $O^{2-}$ , and a checkerboard distortion to the octahedral in the basal plane that is due to the Jahn-Teller effect for  $Mn^{3+}$ , which splits the  $e_g^{\uparrow}$  orbitals ( $dz^2$  and  $dx^2-y^2$ ). The Jahn-Teller splitting  $\delta_{JT}$  is slightly greater than the  $e_g$  bandwidth  $W$  [11].  $LaMnO_3$  is an insulator, with a small activation energy *ca.* 0.1 eV.  $LaMnO_3$  is A-type antiferromagnet with a Neel temperature of 130 K. [9]

In particular, the neutron data revealed a very rich magnetic phase diagram where, for different doping levels, antiferromagnetism can take different configurations (A, C, G types) and can even coexist with ferromagnetism (B type). The magnetic structures are indicated on Fig. 1.3. There are three main regions: for small amounts of  $Mn^{4+}$  the compounds have essentially antiferromagnetic properties. For  $x$  around 0.3, they become ferromagnetic but, for  $x > 0.5$ , they revert to antiferromagnetism up to the end-member  $CaMnO_3$ . From magnetization and susceptibility results, Jonker [9] concluded that the exchange is weakly positive (ferromagnetic) between two  $3d^4 Mn^{+3}$  ions, negative (antiferromagnetic) between two  $3d^3 Mn^{4+}$  ions and positive between a  $3d^4 Mn^{+3}$  and a  $3d^3 Mn^{+4}$  ion. These measurements provided the first clear evidence of a ferromagnetic exchange interaction in an oxide. Moreover, resistivity measurements revealed a strong correlation between electron transport and magnetic properties in these oxides. The resistivity is lowest for the  $x = 0.3$  composition corresponding to the best ferromagnetism, whereas high resistivities are associated with the antiferromagnetic compositions.

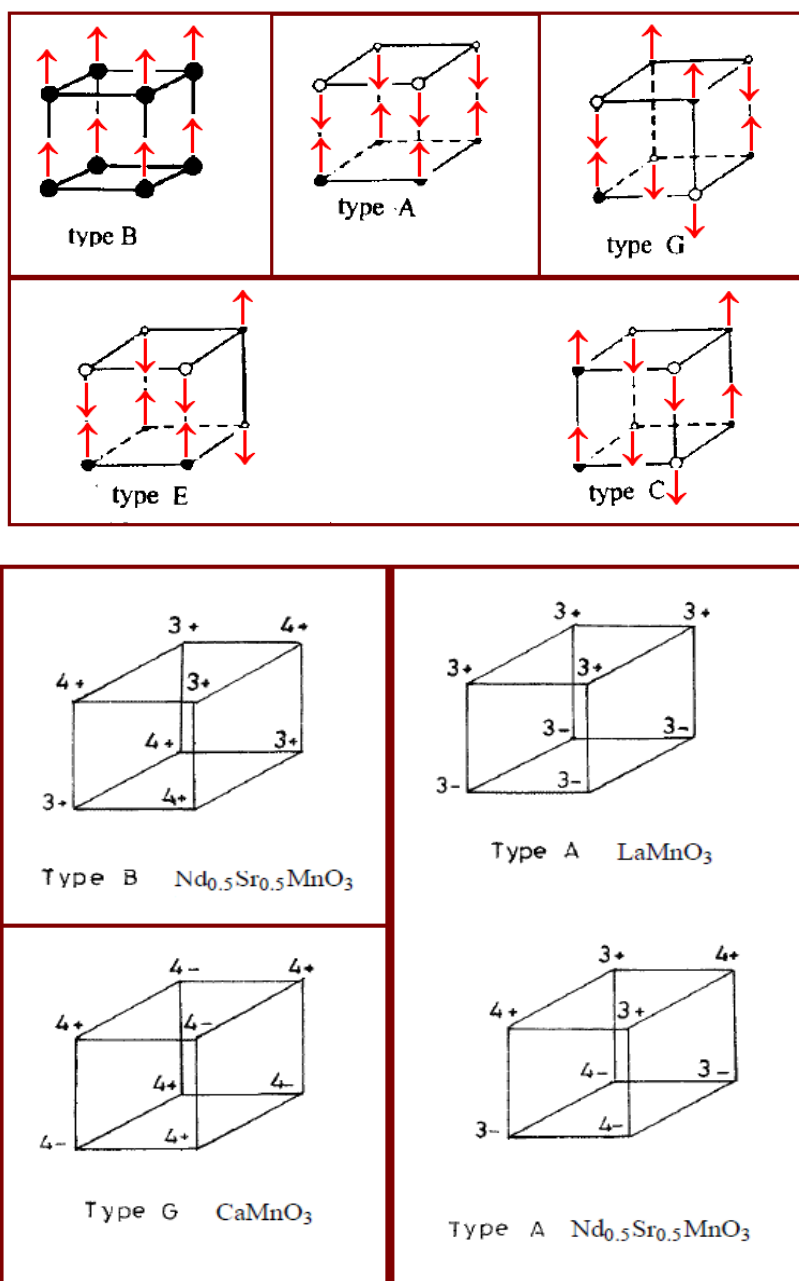
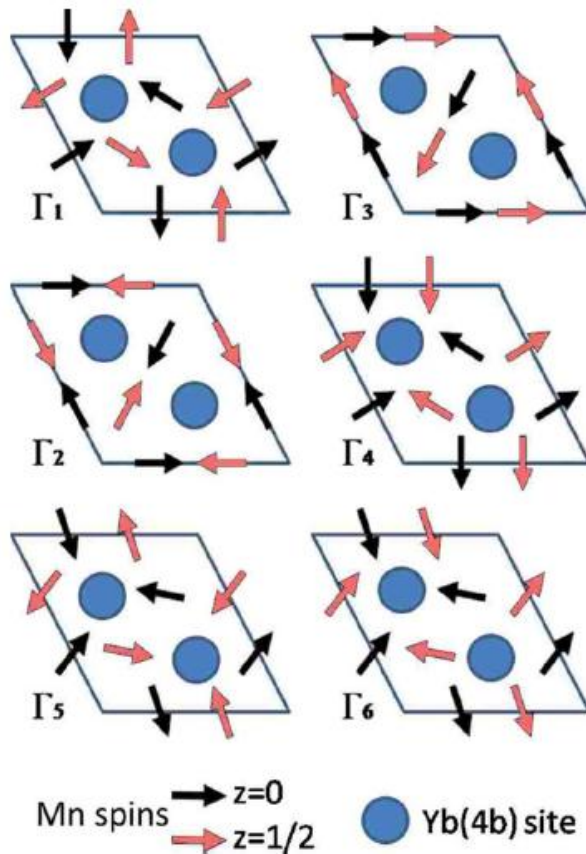


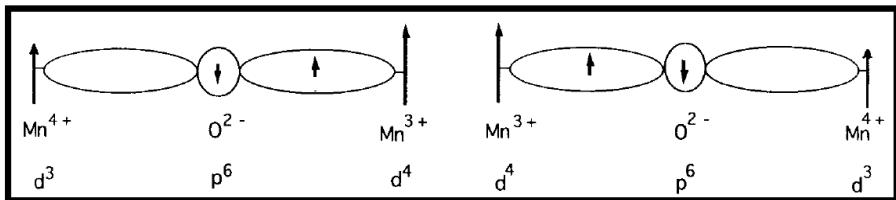
Fig. 1.3 Magnetic ordering in Perovskites.



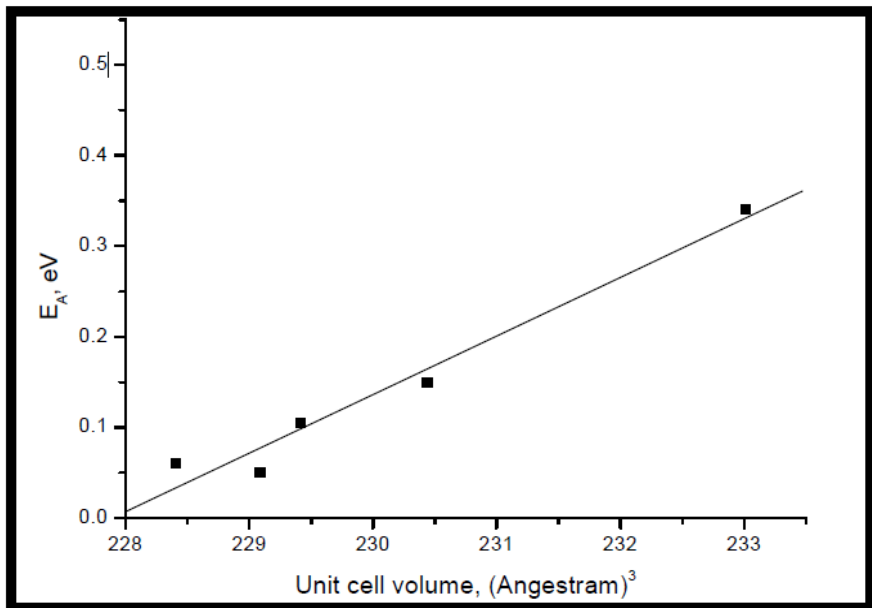
**Fig. 1.4** Symmetry allowed Mn spin orders in hexagonal  $\text{RMnO}_3$  [12].

Double exchange concept for rare earth manganites doped with divalent element was developed and explained by Zener in 1951 in terms of his theory of indirect magnetic exchange between 3d atoms was discussed [9]. He considered that the intra-atomic Hund rule exchange was strong and that the carriers do not change their spin orientation when hopping from one ion to the next, so they can only free energy of the system, Zener found that ferromagnetic interactions are favored when the magnetic atoms are fairly well separated and conduction hop if electrons are present. The theory was applied to the manganese perovskites the spins of the two ions are parallel (see fig. 1.5). On minimizing

the total with the aim of explaining the strong correlation between conductivity and ferromagnetism, and the value of the zero-temperature saturation magnetization which corresponds to the sum of all the unpaired electron spins. Starting from the insulating antiferromagnetic  $\text{LaMnO}_3$  end member where electrons are localized on the atomic orbitals, Zener showed how the system should gradually become more ferromagnetic upon hole doping [9].

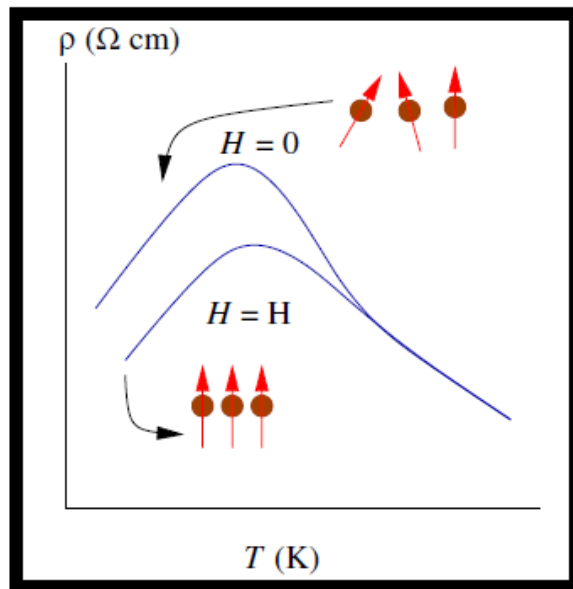


**Fig. 1.5** Schematic diagram of the double-exchange mechanism. The two states  $\text{Mn}^{3+}\text{-Mn}^{4+}$  and  $\text{Mn}^{4+}\text{-Mn}^{3+}$  are degenerate if the manganese spins are parallel [9].



**Fig. 1.6** The activation energy  $E_A$  as a function of unit cell volume of  $\text{Nd}_{0.65}\text{Sr}_{0.35}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ .





**Fig. 1.7** Effect of Magnetic field on resistivity (Magnetoresistance).

The correlation between crystal structure and its physical properties plays an important role in understanding and interpretation these interesting phenomena. An example for this correlation between crystal structure and electrical activation energy in  $\text{Nd}_{0.65}\text{Sr}_{0.35}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$  is represented in Fig. 1.6 which reported by *Abdel-latif et al.*, [3]. It is clear that the volume of unit cell is directly proportional to activation energy. Many ferromagnetic elements display an intrinsic negative magnetoresistance in the vicinity of their ferromagnetic transitions. This is because in the vicinity of the ferromagnetic transition, conduction electrons are scattered by magnetic fluctuations. Switching on a magnetic field suppresses such fluctuations and this results in a reduction of such scattering and consequently, a reduction in the electrical resistivity. Magnetoresistance MR is defined as the change in the electrical resistance produced by the application of an external magnetic field. It is usually given as a percentage [1].

$$MR = [(\rho_H - \rho_0) / \rho_0] \times 100\%$$

Where  $\rho_0$  is resistivity with no applied magnetic field and  $\rho_H$  is resistivity with o applied magnetic field. For rare-earth cations smaller than  $Tb^{3+}$  ( $R = Ho, Er, Tm, Yb, Lu$ ) as well as  $Y^{3+}$  and  $Sc^{3+}$ , in the rare earth manganites  $RMnO_3$  with perovskite structure becomes metastable and a new hexagonal polytype stabilizes (space group  $P6_3cm$ ). In the hexagonal phase, a ferroelectric behavior has been described to coexist with magnetic ordering at low temperature. The ferroelectricity in hexagonal  $RMnO_3$  was discovered by *Bertaut, Forrat*, and *Fang* in 1963 [12].

All these interests were the main goals to continue in research in this interesting field and the presented review deals mainly with studying different classes of the rare earth manganites; Orthorhombic distorted perovskites and hexagonal perovskites.