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Recent trends in the Exploration of Colossal Magneto Resistance Manganites

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Abstract. The recent developments of the colossal magnetoresistance (CMR) properties of the manganites $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) are presented herein. Two types of oxides must be distinguished : type I oxides that display a FMM-PMI transition obtained for $0.2 < x < 0.5$ and type II oxides $x = 0.50$ that exhibit an AFMI-FMM transition. Two key factors govern the CMR properties of these materials : the average size of the interpolated cations and the hole carrier density [Mn(III)Mn(IV) mixed valence]. The doping of the Mn sites by various cations $\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Sn}, \text{Ti}, \text{Mg}, \text{Fe}$ is also studied showing spectacular results for magnesium and iron. The role of the structure is also discussed.

Layered magnetic metals were investigated several years ago for their giant magnetoresistance (GMR) properties that are of the highest interest for device applications in the field of magnetic recording. Recent observations of very large GMR effects in $\text{Nd}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$ [1] have attracted attention on ferromagnetic oxides, and especially on manganite perovskites $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ with $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$. The important characteristic of these materials deals with their resistance ratio, $\text{RR} = R_0/R_B$, where R_0 is the resistance in a zero magnetic field and R_B is the resistance in a magnetic field B . These new manganites exhibit RR values of several orders of magnitude by applying a field of several teslas, so that they have been called colossal magneto resistance (CMR) manganites.

The two types of CMR manganites.

Very recently, extremely high resistance ratios were found in thin films [2-3], single crystals [4] and ceramics [5-8] of perovskite type manganites $\text{Ln}_{0.7}\text{A}_{0.3}\text{MnO}_3$, with $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$. Figure 1 shows the resistivity curves of these phases, $\text{Pr}_{0.7}\text{Sr}_{0.05}\text{Ca}_{0.25}\text{MnO}_3$ [6], that exhibit a spectacular CMR effect with a RR ratio of $2.5 \cdot 10^5$ at 85 K in a magnetic field of 5 T. In these materials, named type I, one generally observes a resistivity peak whose temperature T_{max} , coincides with the Curie temperature T_C as shown from the corresponding magnetization curve (Fig. 2). Thus, the type I CMR perovskites are characterized by a transition from a ferromagnetic metallic (FMM) to a paramagnetic insulating (PMI) state with increasing the temperature, the transition temperature corresponding to T_C .

Fig. 1. Temperature dependence of R_0 ($H=0$), R_H ($\mu_0 H = 5 \text{ T}$) and R_0/R_H for $\text{Pr}_{0.7}\text{Sr}_{0.05}\text{Ca}_{0.25}\text{MnO}_3$: R_0 (○), R_H (□) and R_0/R_H (▲).

Fig. 2. $M(T)$ of $\text{Pr}_{0.7}\text{Sr}_{0.05}\text{Ca}_{0.25}\text{MnO}_3$ (1.4 T).

The type II - CMR manganites, exhibit the formulation $\text{Ln}_{0.5}\text{A}_{0.5}\text{MnO}_3$ [9-11] and are characterized by a transition from an antiferromagnetic insulating (AFMI) to a ferromagnetic metallic state (FMM) at low temperature, followed by a transition to the PMI state at higher temperature. Such a behaviour is illustrated on figure 3 for the oxide $\text{Pr}_{0.5}\text{Sr}_{0.41}\text{Ca}_{0.09}\text{MnO}_3$, which is the type II CMR manganite that exhibits the highest T_N of 190 K to date [11]. Note that the magneto resistance effect is much smaller for the type II manganites than for the type I. One indeed observes that the RR ratio reaches a maximum value of 3.10^3 at 150 K in a magnetic field of 7 T for the phase $x = 0.09$ (Fig. 3) [11].

Fig.3. T dependence of ρ at 0T and 7T for $\text{Pr}_{0.5}\text{Sr}_{0.41}\text{Ca}_{0.09}\text{MnO}_3$ (solid lines, left y-axis). The ratio $R_0/R_{H=7T}$ is also shown (dashed lines, right y-axis).

Fig. 4. $T_{\max}$ corresponding to the $R(T)$ maximum value versus the ratios of the interpolated cation for the series $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_{3-\delta}$ a, $\text{Pr}_{0.66}\text{Ca}_{0.34-x}\text{Sr}_x\text{MnO}_{3-\delta}$ b, $\text{Pr}_{0.7-x}\text{La}_x\text{Ca}_{0.3}\text{MnO}_{3-\delta}$ c, and $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{Ba}_x\text{MnO}_{3-\delta}$ d.

Two key factors for the optimization of the CMR properties : size of the interpolated cation and hole carrier density.

Like for the superconducting cuprates, the transport and magnetic properties of the CMR manganites result from a super exchange mechanism, so that they should be greatly influenced by the overlapping of d orbitals of manganese and p orbitals of oxygen. Thus, two factors should be taken into consideration to optimize the CMR properties of these materials : the average size of the interpolated cation that governs the Mn-Mn distances and the Mn-O-Mn angles and the hole carrier density which can be modified by varying the Mn(III)/Mn(IV) ratio.

The relative influence of these two factors has been recently demonstrated with the study of the type I manganites $\text{Pr}_{0.7}\text{Ca}_{0.3-x}\text{A}_x\text{MnO}_3$ ($A = \text{Sr}, \text{Ba}$) and $\text{Pr}_{0.66}\text{Ca}_{0.34-x}\text{Sr}_x\text{MnO}_3$ [12], $\text{La}_{0.7-x}\text{Y}_x\text{Ca}_{0.3}\text{MnO}_3$ [13] and $\text{Nd}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ [14].

In all these materials, one observes that T_C decreases dramatically as the average size of the interpolated cation decreases for a fixed value of the Mn(III)/Mn(IV) ratio, whereas for a fixed value of the average cationic radius, T_C decreases dramatically as the Mn(III)/Mn(IV) ratio decreases, i.e. as the hole carrier density increases. Such a general behaviour is illustrated on figure 4 where a linear variation of T_C versus the average ionic radius cation (taken in six fold coordination) of several series of oxides can be seen.

The fact that the transition temperature T_C increases significantly as the applied magnetic field increases is also an interesting property of these compounds [14]. It is also remarkable that the value of the resistance ratio may depend upon the average size of the interpolated cation. For instance, for the latter oxides one observes (Fig. 5a and 5b) that RR goes through a maximum value for a particular value of the ionic radius of the interpolated cation corresponding to $x = 0.065$.

The role of the average size of the interpolated cation upon the CMR properties of the type II-manganites has also been clearly evidenced with the study of the oxides $\text{Pr}_{1/2}\text{Sr}_{1/2-x}\text{Ca}_x\text{MnO}_3$ [11] and $\text{Pr}_{1/2-x}\text{Y}_x\text{Sr}_{1/2}\text{MnO}_3$ [15]. As illustrated for the manganites $\text{Pr}_{1/2}\text{Y}_x\text{Sr}_{1/2}\text{MnO}_3$ (Fig. 6) which show slight increase of T_N and a large decrease of T_C as x increases i.e. as the average size of the interpolated cation decreases. This competition between the AFMI-FMM and the FMM-PMI transitions, which extends the AFMI and PMI states at the expense of the FMM, as the average size of the interpolated cation decreases seems to be a characteristic of these type-II manganites and may be due to the appearance of charge ordering (c.o.) in these materials.

From all these results, it appears clearly that magnetic phase diagrams in the plane (T, r_A) where T is the temperature and r_A the average ionic radius of the interpolated cation will have to be established for a given value of the applied magnetic field.

Fig. 5 a. $RR = R_{B=0}/R_{B=5T}$ versus T for the series $\text{Nd}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (from top to bottom : $x = 0.08$; $x = 0.09$; $x = 0.10$; $x = 0.12$; and $x = 0.14$).

Fig. 5 b. from top to bottom : $x = 0.065$, $x = 0.05$, $x = 0.04$, $x = 0.03$, $x = 0.02$ and $x = 0$

An example of such a diagram has been recently established for the manganites $(\text{Ln}, \text{Ln}')_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (Fig. 7) in a magnetic field of 100 G. It must also be emphasized that such a diagram will be strongly modified, increasing the extension of the FMM region by applying a larger magnetic field (dashed lines).

Fig. 6. Composition dependence (x) of the transition temperatures T_{co} and T_{max} (from the resistivity curves) and of T_N and T_C (from the magnetization curve) of the series $\text{Pr}_{0.5-x}\text{Y}_x\text{Sr}_{0.5}\text{MnO}_{3-\delta}$.

Fig. 7. Schematic phase diagram function of size and temperature of the manganites $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. (WFM : weak ferromagnetism metallic)

Doping the Mn sites : a promising route to optimize the CMR properties.

The substitution of foreign cations M for manganese is susceptible to modify dramatically the CMR properties of the manganites, interrupting the overlapping of the Mn-d orbitals and O-p orbitals. The results recently observed for the manganites $\text{Pr}_{0.7}(\text{Sr}, \text{Ca})_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ and $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ with $M = \text{Al}, \text{Ga}, \text{In}, \text{Ti}, \text{Sn}, \text{Mg}$ [16-18] show that in all cases T_C decreases as the M content increases in agreement with the fact that introduction of impurities prevents the overlapping of the Mn and O orbitals all over the crystal, and favours the insulating behaviour. Nevertheless, it is remarkable that for the type II phases, the decrease of T_C is similar for the trivalent M elements, ($M = \text{Al}, \text{Ga}, \text{In}$) and for tin of about 12 K per M %, whereas it is higher for titanium and can reach much higher values for magnesium of about 38 K per Mg %. In a similar way, the substitution of a foreign cation for manganese in the type-II manganites increases T_N and decreases T_C . This decrease of the FMM region at the benefit of the AFMI and PMI regions is also understandable on the basis of the rupture of "Mn-O-Mn" interactions. But the most interesting feature deals with the CMR properties of these Mn-site substituted manganites. For most of them, the resistance ratio is not strongly modified by the substitution, except for the magnesium phases. For the phase $\text{Pr}_{0.7}\text{Sr}_{0.1}\text{Ca}_{0.2}\text{Mn}_{1-x}\text{Mg}_x\text{O}_3$, a spectacular increase of the resistance ratio which can reach a value of 10^4 at 105 K in a magnetic field of 7 T is observed for $x = 0.01$.

The recent study of the iron doped manganites $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ [18] also shows a very spectacular increase of the CMR properties, with respect to the pristine phase $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_3$. One indeed observes a resistance ratio of 8.10^5 near $T_C = 55$ K in a magnetic field of 5T; moreover the latter phase shows an abrupt decrease of its resistance by more than one order of magnitude by applying a rather low magnetic field smaller than 0.2 T at 55 K.

Though they are not understood so far, these results show that the substitution on the manganese sites is susceptible to lead to CMR effects similar to those obtained by varying the average size of the A-site cations. Such a promising route will have to be investigated carefully, taking into consideration the role of the hole carrier density in the CMR properties.

Concluding remarks.

The investigations of the manganites with the perovskite structure performed these last two years open a route to the research and optimization of the CMR properties of these materials, the aim being to obtain large resistance ratios near room temperature and under low magnetic field.

These spectacular phenomena are far to be understood. One particular issue that has to be answered deals with the role of the structure and chemical bonding in these particular properties. There is no doubt that charge ordering, corresponding to a possible ordering of the Mn(III) and Mn(IV) species should play an important role in the transition. The first studies of the CMR manganites $\text{Pr}_{0.7}\text{Ca}_{0.25}\text{Sr}_{0.05}\text{MnO}_3$ and $\text{Ln}_{0.5}\text{A}_{0.5}\text{MnO}_3$ by electron diffraction and high resolution electron microscopy [19-20], as well as neutron diffraction studies of $\text{Pr}_{0.7}(\text{Ca},\text{Sr})_{0.3}\text{MnO}_3$ [21-23] support strongly this view point. The crystal chemistry of these phases is in fact very complex, showing clustering phenomena of Mn(IV) species with monoclinic domains for type I manganites and structural transitions leading to superstructures at low temperature for type II manganites. Another important issue deals with the role of the Jahn-Teller effect of manganese in these properties. Preliminary investigations suggest indeed that the Jahn-Teller distortion is correlated to the different magnetic transitions [21, 24-26]. A detailed structural study of these materials versus temperature in connection with their CMR properties will have to be performed in order to progress for their optimization.

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