EPR and Magnetic Properties on LaCaMnO manganites

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Abstract

Electron paramagnetic resonance (EPR) and AC Susceptibility measurements were carried out as a function of temperature on $La_{0,7}Ca_{0,3}MnO_3$ polycrystalline samples. The samples displayed a transition from paramagnetic-insulator to ferromagnetic-metal at T_c around 261K. T_c was determined from the inverse of the real part of a.c. susceptibility $(1/\chi')$ vs temperature, which follows a simple Curie-Weiss behavior. The inverse of the EPR intensity also follows a Curie-Weiss type behavior down to $T_{EPR} = 253$K. The structure of the samples as determined by X-Ray diffraction (XRD) corresponds to a single perovskite phase with orthorhombic unit cell.

Keywords: LaCaMnO manganites, EPR, a.c. susceptibility

1. Introduction

The phenomenon called anisotropic magneto-resistance (AMR) is the change of resistance of a conductor when it is placed in an external magnetic field. The maximum AMR effect is defined as

$$\Delta R/R = R(j//M) - R(j \perp M)/R(j \perp M) \tag{1}$$

The main mechanism behind AMR is spin-orbit scattering of the spin polarized charge carriers, which results in an anisotropic angular dependence of the current density j relative to the magnetization M. However, compared with exchange interaction, spin-orbit coupling is relative weak, which produces small AMR effect of a few percent in some Ni-based alloys.

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This phenomenon was observed at the first time (1858) by W. Thompson (later Lord Kelvin) in iron and nickel in the presence of a magnetic field. The phenomenon magnetoresistance caused the electrical conductivity of a ferromagnetic material depend of the orientation of the remanent magnetization with respect to the direction of the flowing current. A first microscopic explanation of the ordinary magnetoresitance was given by Mott in 1936. He uses a two -current model (spin up and spin down) consist in two different contribution to the electrical current, which are scattered different. In this way Mott pointed out the strong connection between electrical phenomena and magnetism. It was a great surprise when in 1988 two research groups independently discovered materials with a very large magnetoresistance, now know as Giant magnetoresitance (GMR). These materials (Multilayers) consist of nanometric layers of ferromagnetic and non-magnetic metals stacked on each other.In the original experiments the Peter Gruemberg group used a trylayer system Fe/Cr/Fe, while the other one led by Albert Fert used multilayers of the form $(Fe/Cr)n$ with n as high as 60.

In the past years, was discovered giant and colossal magnetoresistance (CMR) in doped perovskite-type manganites $Ln_{1-x}A_xMn_{1-y}$ B_yO_3 with Ln = lanthanide, $A = Ba, Sr, Ca$ and $B = Cr, Ni, Co$. These materials appear as an interesting class of compounds which, show both metal-insulator and ferromagnetic (FM) / antiferromagnetic (AFM)-paramagnetic (PM) transitions at the same temperature. Since the discovery a lot of experimental and theoretical studies were carried out. Among the potential applications like magnetic sensors and in magnetic memories (RAMS), these perovskite oxides display other interesting catalytic properties, which, are attractive for environmental issues as cathode materials in solid oxide fuel cells. On the other hand it is know that the magnetic behavior and transport properties of these compounds are determined by different factors like: the structure, the percentage of divalent ions, the ionic radius of the A-site and the preparation methods. This results in some kind of rotations and deformations of the MnO_6 octahedra which weaken the double-exchange coupling between Mn^{3+} and Mn^{4+} ions, causing a decrease of the Curie temperature. [1][5]. In this work we present the correlation observed between EPR and a.c. magnetic susceptibility measurements carried out in $La_{0,7}Ca_{0,3}MnO_3$ polycrystalline samples produced by solid state methods.

2. Experimental

Polycrystalline samples of $La_{0,7}Ca_{0,3}MnO_3$ were prepared by the solid state reaction method using high purity powders of La_2O_3, CaO and Mn_2O_3. The raw materials were well mixed and heated at 800°C in air for 16 hours. After that the powder were reground and annealed during 16 h at two different temperatures: 850°C and 900°C. Finally were reground again pressed into pellets and sintered at 1200°C for 32 h. The crystalline structure was determined by XRD techniques. EPR measurements were carried out using a Brucker spectrometer (ESP-300) in X-band at a fixed frecuency of 9.5 Ghz from 200 to 300K. The EPR spectra were obtained by using tiny samples in quartz tubes.

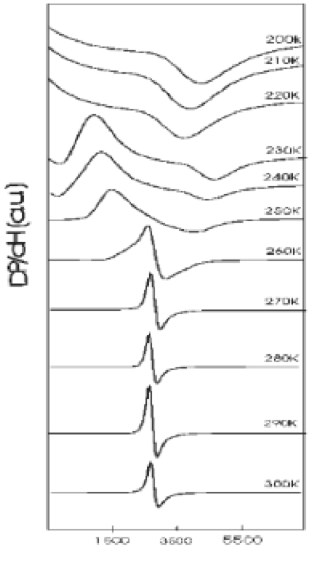

FIGURA 1. EPR spectra for the sample $La_{2/3}Ca_{1/3}MnO_3$ at different temperatures

From a.c Susceptibility measurements carried out at different frequencies in the temperature range from 80 to $300K$, values of the transition temperature (T_c) around $261K$ were found out. Resistivity measurements using the electrical four probe method showed an insulator to metal transition at T_t around $232K$.

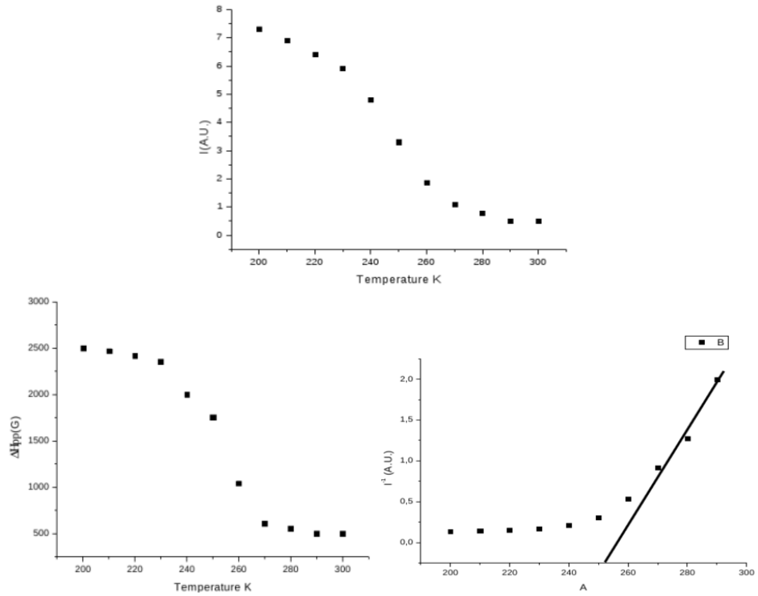

FIGURA 2. (a)EPR - Line intensity I vs. T. (b) Linewidth (ΔHpp) vs. T. (c)Inverse of EPR intensity vs. Temperature. The solid line is the best fit of experimental data to a Curie-Weiss type behavior.

3. Results and Discussion

The EPR spectra as a function of temperature are shown in Figure 1. The amplitude of the EPR signal decreases with increasing temperature. Below T_c, the signal became irregular, which has been attributed to local inhomogeneity effects in the ferromagnetic (FM) region. The line shape goes to a narrower and more symmetric signals at $T > T_c$ in the paramagnetic (PM) region. No secondary signal at lower fields, which, have been associated to magnetic inhomogeneities in the system, were observed.

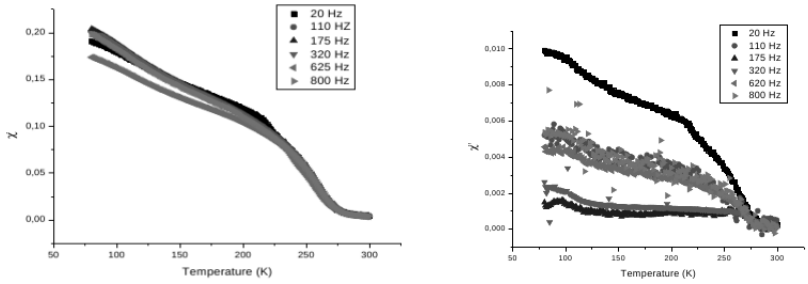

FIGURA 3. (a)Real part of a.c - susceptibility vs. T at different frequencies. (b)Imaginary part of a.c-susceptibility vs. T at different frequencies.

Figures 2a and 2b display the EPR intensity I and linewidth ΔHpp respectively. The EPR intensity defined as $A\Delta Hpp$ decreases at the temperature increases (A is the amplitude and ΔHpp the width of the main signal). As expected in PM systems the linewidth also decreases by increasing temperature until it reaches a minimum at temperature of aprox. $260K$. With further Temperature increase ΔHpp remains approximately constant. The inverse of EPR intensity, fig.2c, follows a Curie-Weiss behavior down to aprox. $253K$. This temperature is close to that obtained from the deviation of Curie-Weiss law ($T_c = 261K$) of inverse a.c susceptibility χ' vs tempertaure data . See inset fig.5). It is worth to note that all the EPR parameters displayed a slopes change around T_c.

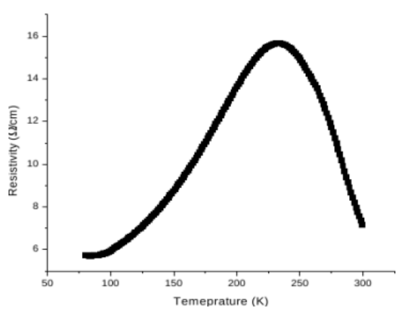

FIGURA 4. Resitivity vs. Temperature for $La_{2/3}Ca_{1/3}MnO_3$

Figures 3a and 3b show the real χ' and imaginary χ'' parts of the $a.c$ magnetic susceptibility respectively as a function of temperature for different frequencies and a.c field $H_{a.c} = 800A/m$. A broad jump is observed, which corresponds to the low temperature ferromagnetic (FM) to paramagnetic (PM) phase transition. The phase transition has been assigned to the increase of Mn^{4+} concentration that produces a decrease in the double exchange interactions. This behavior is correlated with the metallic to semiconducting transition observed at $T_t = 232K$, as determined from Resistance vs. Temperature measurements. Figure 4.

The reciprocal of real susceptibility part as a function of temperature for different frequencies (20, 320 and 800Hz) is displayed in Figure 5. The transition temperature T_c determined from the deviation of Curie-Weiss behavior and defined as the intersection point with the x axis, lies around 261K, independent of the frequency. Inset Fig. 5.

Deviations of Curie-Weiss law have been attributed to formation of FM clusters. Discrepancies between T_t and T_c (table 1) have been attributed to samples inhomogeneities[6].

T_c(K)	T_t(K)	T_{EPR} (K)
261	232	253

Table 1. Curie temperature (T_c), transition temperature (T_t) and EPR temperature (T_{EPR})

Latice parameter			Volume
$a(nm)$	$b(nm)$	$c(nm)$	$0,2309(nm)^3$
0,54621	0,54768	0,77193	

Table 2. Parameters of $La_{0,7}Ca_{0,3}MnO_3$ polycrystalline samples

X-ray diffraction patterns at room temperature (Figure 6) showed a single phase perovskite with an orthorhombic structure, indexed in the cell Pmma space group. The corresponding refined lattice parameters and volume can be seen in table 2.

Scanning electron microscopy showed a granular structure of the samples and EDX analysis displayed changes of the chemical composition $< 5\,\%$.

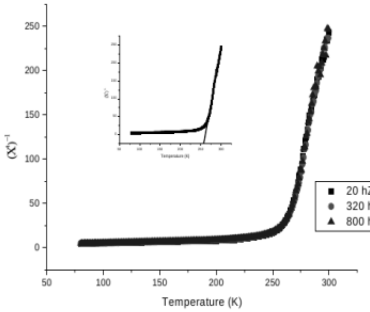

FIGURA 5. Reciprocal of real AC susceptibility part Vs T at different frequencies. Inset displays the Curie-Weiss behavior

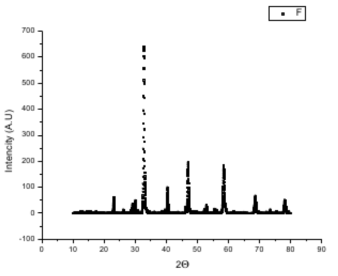

FIGURA 6. X Ray diffraction of $La_{2/3}Ca_{1/3}MnO_3$

4. Conclusions

Polycrystalline samples of $La_{0,7}Ca_{0,3}MnO_3$, prepared by the solid state reaction method displayed a Paramagnetic-Ferromagnetic transition at around $T_c = 261K$, The transition temperature T_c was determined from the deviation of experimental data from Curie-Weiss behavior. The inverse of EPR intensity followed a Curie-Weiss type behavior down to aprox. $253K$, which coincides with that obtained from a.c. susceptibility measurements. It is worth to note that EPR parameters like linewidth and intensity displayed slopes changes at temperatures close to T_c.

The transition temperature from metallic to semiconducting behavior at $T_t = 232K$, correlates with the paramagnetic-ferromagnetic phase transition. Discrepancies between T_t and T_c have been associated to samples inhomogeneities.

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