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Magnetic and intergranular transport properties in manganite/alumina composites

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Abstract

We report the magnetic and transport properties of $La_{2/3}Ca_{1/3}MnO_3/Al_2O_3$ crystal composites at low insulator component ratio. Phase purity and microstructure are guaranteed by X-ray and microanalysis studies. DC electric conduction is progressive blocked by scattering in alumina regions. With an insulator percentage around 10% in volume, percolation occurs. Merging the spin polarization of the manganite and the extra disorder contribution to electric transport induced by alumina we have been able to increase the low temperature magnetoresistance (MR) nearly three times with respect to the undoped manganese perovskite. Experimental results are analyzed on the basis of an earlier theory developed for a granular ferromagnetic material in an insulator matrix.

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1. Introduction

The development of magneto electronic devices, has created a great interest in the spin-polarized transport properties of ferromagnetic materials [1]. In a classical ferromagnetic metal (that is, Fe, Co, Ni), the exchange energy splits the conduction band into majority and minority carrier bands, resulting in a spin disproportionation at the Fermi level [1,2]. The spin polarization, P, is a measure of this imbalance, and it is between 30% and 50% for the ferromagnetic elements and their alloys [2]. By definition, the maximum spin polarization is unity, and in this special case, one electron spin has a band gap at the Fermi level, while the Fermi level intersects the band for the other electron spin [3]. The materials in which this property is present are called half-metallic, mainly because the conduction is metallic for one spin and insulator for the other one.

Half-metallic materials were first proposed in the so-called Heusler alloys (that is, NiMnSb or PtMnSb) after theoretical band calculations [4]. Since then, this property has been experimentally proved in a great variety of compounds [2,5]. The group to which interest has been directed is, with no doubt, manganese mixed-valence perovskites [6]. These oxides are all based in the parent compound $AMnO_3$, where A a trivalent rare-earth element (as La^{3+}, Pr^{+3} ...). When some proportion of A is substituted by a divalent alkali B (say Ca^{2+}, Sr^{2+} ...), the same amount of Mn^{3+} transforms to Mn^{4+} in order to maintain electrical neutrality.

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For intermediate doping levels $(0.2 < x < 0.5)$ in the combination $A_{1-x}B_xMnO_3$, the resulting material has a ground state which is ferromagnetic and metallic which becomes a paramagnetic insulator at a temperature in which magnetic and electrical transitions happen together [7]. The rediscovery of colossal magnetoresistance (CMR) attracted a great attention to these materials. The increased spin transport promoted by the almost complete spin polarization expects to left behind the original CMR [8–10]. In this way, spin-polarized transport properties in manganites has been employed in fine particle systems [10], tunnel junctions [11], artificial boundaries [12], spin injection devices [13] and composites [14].

Following this motivation, we merge two features: first, the intergranular magnetoresistance (MR) obtained in granular fine particle samples of manganites, and second, the theory and data of decades of studies of heterogeneous ferromagnetic-insulator (FI) microstructures for MR phenomena [15,16]. For this purpose, we have studied magnetic and transport properties of composites including grains with nanometric dimensions of the prototypical ferromagnetic $La_{2/3}Ca_{1/3}MnO_3$ [17] and of the well-known inert insulator Al_2O_3.

2. Experimental procedures

$La_{2/3}Ca_{1/3}MnO_3$ (LCMO) particles with nanometric dimensions were prepared by the sol–gel method as reported elsewhere [18]. The final sintering temperature was 900°C, and the samples had grains with mean grain size of 150 nm. Alumina commercial particles had a mean grain size of 100 nm (material and size analysis provided by Goodfellow Cambridge). The combinations $(1-x)La_{2/3}Ca_{1/3}MnO_3 + xAl_2O_3$ (with x: 0%, 5.5%, 8%, 15% and 25% in volume) were sintered in a fast heating process for 1 h at 1100°C. Resistivity was measured in bars with typical sizes of $10 \times 1 \times 1$ mm^3 by the four-probe method in the range 77–300 K and in fields up to 10 kOe. Magnetization was measured with a vibrating sample magnetometer in the same temperature and field range. The structure was examined by the X-ray diffraction and the particle size and shape were investigated by means of scanning electronic microscopy (SEM).

3. Results and discussion

The structural and morphological characterization of the samples by X-ray diffraction and electronic microscopy respectively, show that $La_{2/3}Ca_{1/3}MnO_3$ and Al_2O_3 phases are present and clean in the composite and we can observe manganite and alumina grains without mixture (see Fig. 1). Fig. 2 shows the effect of alumina substitution on the electrical resistivity. The metal–insulator transition temperature (T_{M-I}) decreases with increasing alumina presence and is not detected for Al_2O_3 percentage >8% in volume. Furthermore, the resistivity increases several orders of magnitude in the samples studied as alumina percentage increases. However, the Curie temperature (T_C) remains unchanged around 265 K in all samples, that is, T_C of the undoped compound (Fig. 3). Moreover, the low temperature magnetization is reduced in direct linear proportion to alumina presence, that does not contribute to magnetic moment. The disengagement between transport and magnetism is due to the interruption of electric conduction in alumina regions, as has been observed in similar systems [19]. This effect leads to an extended range of temperatures in which the composites are FI and can be explained in terms of the theory developed by Sheng et al. [20] for films containing Ni grains dispersed in SiO_2. That work suggests a functional dependence for resistivity in the FI range as

$$\rho(T) = a \exp\left\{2\sqrt{\frac{E}{\mathrm{kT}}}\right\},$$

where a is an appropriate factor and E represents the activation energy in the fitting range of temperatures. This equation provides satisfactory fits for our experimental data with activation energies increasing as alumina percentage does. This fact is another sign that conduction is reduced by alumina addition, because more energy is needed to overcome the extra barriers created by the insulator grains. Moreover, resistivity data in the whole

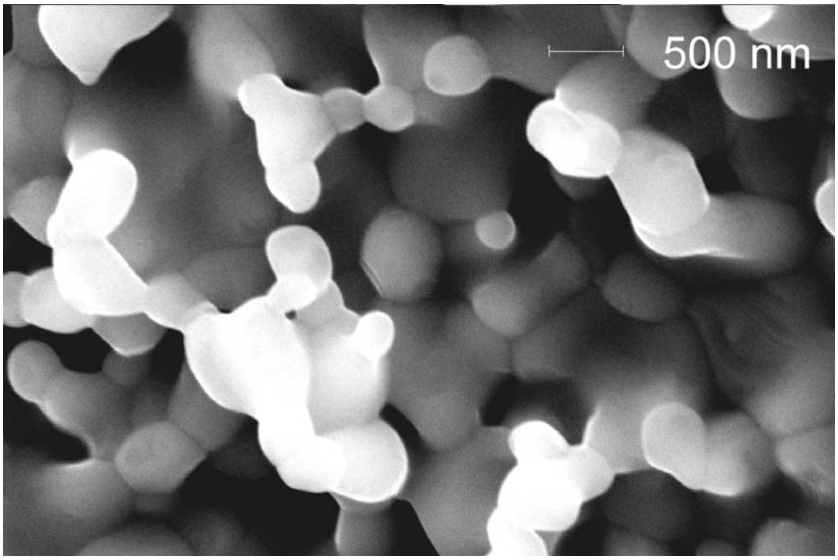

Fig. 1. SEM photograph of a sample with 15% in volume of alumina. After the final sintering process, we can observe grains with a mean grain size around 500 nm. Brightest regions are alumina grains detected by energy dispersive microanalysis (EDAX).

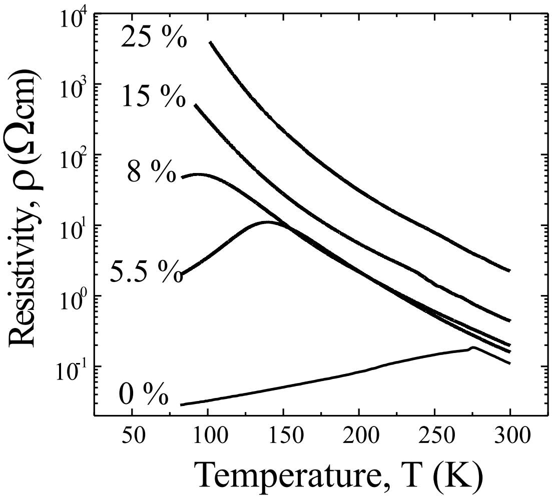

Fig. 2. Temperature dependence of the electrical resistivity for several alumina percentage in the final composite.

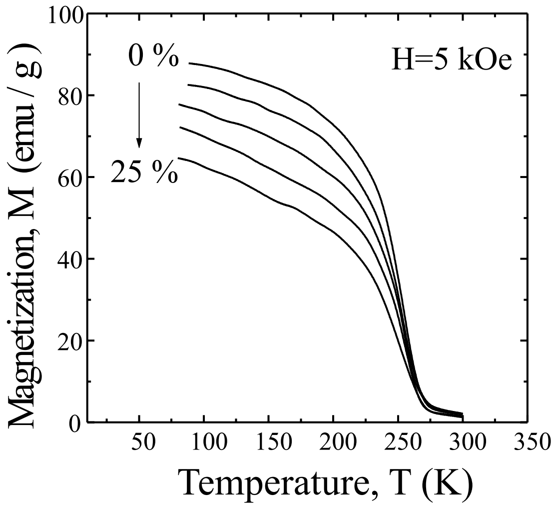

Fig. 3. Magnetization versus temperature dependence for the whole manganite/alumina series studied. It is clear that the reduction of low temperature magnetization is due to inert alumina presence.

temperature range can be adjusted by a two conducting channel model (insulator and metallic) with a different influence according to alumina proportion (see Fig. 4). This model is merely composed by two resistances in parallel with a different weighting factor which represents their different contributions to the resistivity. The first one corresponds to the conduction inside manganite grains (obtained form high temperature sintered ceramic samples) and the second one to the extra electronic scattering created by alumina particles [21].

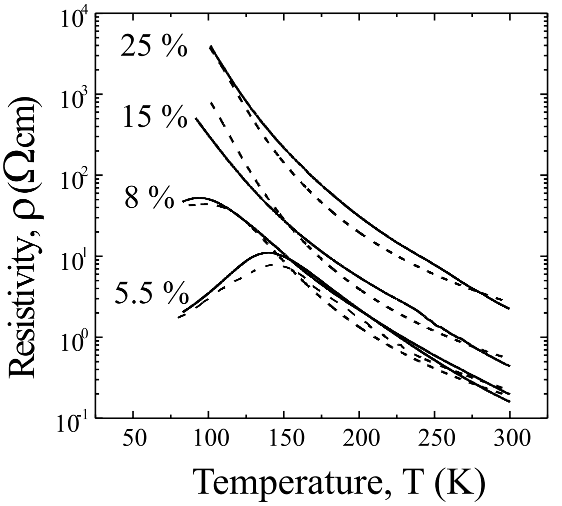

Fig. 4. Experimental resistivity (solid lines) and fits to the model proposed in the text and in [21] (dashed lines).

The abrupt increase in resistivity for an Al_2O_3 composition around 10% (see Fig. 5) may due to a percolation of alumina grains, but the threshold value obtained seems to be very small with the purpose of justify the breakdown of conductivity in our network. However, by comparing sample and crystalline densities, we have estimated that more than 20% in volume of our samples is composed of air pores and defects. In that case, around 20% of non-conducting elements could easily justify a percolation transition [22]. The resistivity increase seems to be directly related to the enhancement of low temperature MR, which is the most stimulating result in these kind of samples (see Figs. 5 and 6). We can amplify MR response and also MR sensibility at low fields just by determining the percolation threshold of our samples. The critical state of the formation of an infinite cluster just in the percolation, as cited before, could explain for the special response of the material.

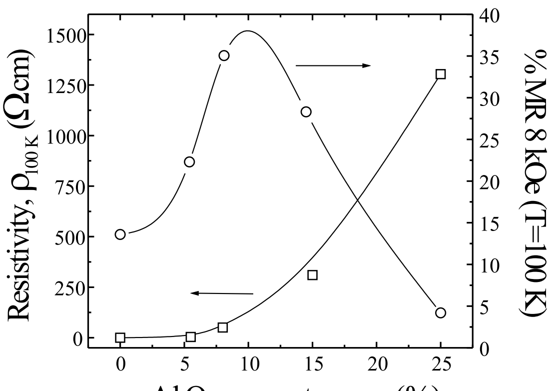

Fig. 5. Resistivity at 100 K (left axis) and MR at $T = 100$ K (right axis) versus alumina percentage. The optimum value for MR enhancement is coincident with the increase in resistivity around 10% of Al_2O_3. Lines are drawn as guides to the eye. The errors in the data are of the order of the site of the data symbols.

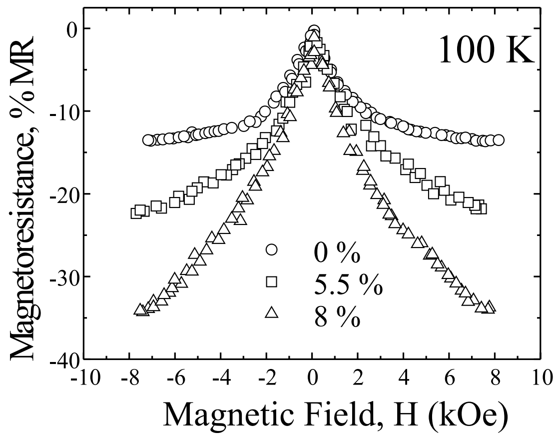

Fig. 6. MR isotherms at $T = 100$ K.

4. Conclusions

In this work we have explored the magneto-transport properties of manganite–alumina nanocrystals composites. The main experimental results presented here are the progressive destruction of conductivity and the increase in the MR response at low temperatures when increasing alumina percentage. The first one is a result of the disorder introduced by the insulating alumina grains and the second one is closely related to the percolation threshold around 10% alumina in volume. Both effects can be qualitatively explained in terms of a theory developed for granular ferromagnetic metals in an insulator matrix.

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