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Intergranular magnetoresistance in nanomanganites

M A López-Quintela¹, L E Hueso², J Rivas² and F Rivadulla³

¹ Departamento de Química-Física, Facultad de Química, Campus Sur, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain

² Departamento de Física Aplicada, Facultad de Física, Campus Sur, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain

³ Texas Materials Institute, Mechanical Engineering, The University of Texas at Austin, Austin, TX 78712, USA

E-mail: qfarturo@usc.es (M A López-Quintela), fahueso@usc.es, farivas@usc.es and rivadulla@mail.utexas.edu

Received 24 September 2002, in final form 11 December 2002 Published 16 January 2003 Online at stacks.iop.org/Nano/14/212

Abstract

In this paper we present some of the most important magnetic and transport properties of mixed-valence manganite nanoparticles. The samples were prepared by a sol–gel method, which allows us to control particle size and, in this way, to obtain new properties of the archetypal ferromagnetic-metallic compound $La_{2/3}Ca_{1/3}MnO_3$. Magnetic properties allow us to present a model for the nanoparticles based on an ideal inner core and an outer shell in which the magnetism is modified by oxygen non-stoichiometry, vacancies and stress. The experimental results obtained from the electrical transport properties, namely increasing intergranular magnetoresistance (MR) with reducing particle size, tuning of intrinsic colossal MR and low-temperature electrostatic blocking effects, seem to support the proposed model.

1. Introduction

Magnetoresistive effects are nowadays a very interesting topic in both applied and fundamental physics. Their importance was first related to technological applications, principally in magnetic recording or magnetic data storage. However, soon it was noticed that it was worthwhile to study these phenomena in detail from a purely scientific point of view. In 1988, values close to 50% at low temperature were reported in metallic multilayers [1]. Some years after, similar results were obtained in granular metallic systems [2, 3]. Another major boost was promoted by the discovery of fully reproducible magnetoresistance (MR) up to 20%, in small magnetic fields, in permalloy/Al₂O₃/CoFe junctions [4]. All these data show that new tools are now available to obtain artificial MR from metallic compounds just by manipulating the micro/nanostructure of these materials.

In the early 1990s a new kind of MR was rediscovered in mixed-valence manganese oxides (hereafter referred to as *manganites*) [5]. Under a field of several Tesla it was possible to achieve MR values up to 60% at temperatures relatively close to ambient temperature, leading to the name of colossal MR (CMR). This kind of oxide was, in fact, well known in the 1950s [6, 7], when the first studies were carried out on the crystallographic structure, and the basic physical properties and some early theoretical models were developed. Manganites have a general composition $A_{1-x}B_xMnO_3$ (where A is usually a trivalent rare-earth and B a divalent alkaline element). They crystallize in the perovskite structure. This special order, first observed in CaTiO₃, is composed of interpenetrating simple cubic sublattices of A, B and Mn ions with O at the cube faces and edges (see figure 1). In this way, Mn–O–Mn bonds are formed and constitute the basis of the electrical and magnetic properties of these compounds.

The presence of both divalent and trivalent ions in the A site of the structure through chemical doping leads to a charge unbalance that is solved by the appearance of Mn^{3+}/Mn^{4+} pairs. In a cubic lattice environment, the fivefold-degenerate 3d orbitals of Mn^{3+}/Mn^{4+} are split into three lower levels (t_{2g}) and two upper levels (e_g). The large Hund coupling forms a low-energy core with spin 3/2 while the e_g contains one electron with spin parallel to the



Figure 1. Arrangement of ions in a cubic perovskite structure of the typical manganites $La_{1-x}Sr_xMnO_3$.



Figure 2. Schematic density of states of a typical mixed-valence manganite.

inner core (Mn³⁺) or is empty (Mn⁴⁺). The possibility of different doping changes (not only through different cations, but also with different doping levels) leads to a great variety of magnetic and transport ground states, ranging from different antiferromagnetic insulators (e.g. Pr_{2/3} Ca_{1/3}MnO₃ or Nd_{0.5}Sr_{0.5}MnO₃) [8, 9] to ferromagnetic metals (La_{2/3}Ca_{1/3}MnO₃ or La_{2/3}Sr_{1/3}MnO₃) [10, 11]. Among all these different choices, we focus here on the prototypical CMR compound La_{2/3}Ca_{1/3}MnO₃. This compound shows a ferromagnetic metallic state at low temperatures evolving into a paramagnetic insulator one as the temperature rises. The magnetic transition temperature (*T_C*) coincides with the metal–insulator transition temperature (*T_{M-I}*) [10]. Around this temperature (*T_C* \approx *T_{M-I} \approx 260 K), CMR is obtained*.

Early theories tried to explain the low-temperature state and the close connection between T_C and T_{M-I} in terms of the double-exchange models [12, 13]. The basic process implies the transfer of an electron from a Mn³⁺ to a Mn⁴⁺ through the intermediate oxygen: $Mn^{3+}-O^{2-}-Mn^{4+} \rightarrow Mn^{3+}-O^{-} Mn^{3+} \rightarrow Mn^{4+}-O^{2-}-Mn^{3+}$. The spin jump probability depends on the core spin orientations; accordingly, this jump is favoured when spins are parallel and becomes more difficult when orthogonality increases [14]. In conclusion, ferromagnetism and metallicity are clearly linked. However, these theories cannot properly explain either the observed CMR values or other effects like the isotope effect [15] or the giant thermal expansion [16]. For these reasons, more sophisticated theories were developed including, besides the double exchange, other basic properties, like the Jahn-Teller character of the Mn3+ ion by a variable electronphonon coupling [17]. More recently, from theoretical and experimental work, a new picture has evolved suggesting that the physics of manganites, in the CMR regime, is governed by intrinsic electronic inhomogeneities in the form of coexisting competing phases [18].

Almost parallel to the study of the intrinsic CMR, a new kind of MR was discovered in granular manganites samples (both ceramic and also granular thin films) [19-21]. This effect is completely absent in single crystals, and was rapidly related to spin-polarized tunnelling between neighbouring grains [22]. For this reason it is usually denoted (although a general consensus is still lacking) as intergranular MR (IMR). There are great similarities between this MR and the already studied one in ferromagnetic/insulator and ferromagnetic/metal alloys [2, 3, 23], but the MR values reported in these last cases are much higher. The main explanation of this IMR lies again in the intrinsic properties of manganites, derived from their special electronic configuration. Generally, in a ferromagnet, the band structure is spin dependent, and two subbands are found for majority (spin parallel to the magnetization) and minority (spin antiparallel to the magnetization) spins (figure 2). As a result, a net spin polarization (P) takes place. In manganites, there exists a gap in the density of states of minority carriers, and so the total spin polarization is 1. In the spin tunnelling model, IMR depends critically on the spin polarization, and hence the higher P values in manganites lead to higher MR values than those reported for other ferromagnetic alloys.

Following the preliminary results, IMR has been studied in detail in multiple artificial devices. Specifically, the trilayer junction has attracted great attention due to its possibility for replacing conventional ferromagnetic junctions [24, 25]. Other more technologically advanced devices demanding an increase of IMR ratios include, for example, artificial boundaries [26] or laser-patterned junctions [27].

The present approach to the MR problem in manganites is somehow different. Our main aim is to increase the IMR through a micro/nano-structural manipulation via chemical methods, rather than using more sophisticated artificial devices. The surface contact between neighbouring grains can be increased by decreasing the grain size, and the study of the influence of the grain size on the magnetic and electrical properties in manganites is our first objective. Subsequently, many other unexpected effects may appear as a consequence of the particle size reduction. In this paper, we report a detailed study of the sample preparation and characterization. Several of the most characteristic physicochemical properties will be also presented.

2. Sample preparation and characterization

As we have already stated, our first objective is to produce manganite particles with small particle size, more precisely, down to the nanometric range. This size scale is far from the micrometre range usually produced by the conventional ceramic techniques. In this way, the surface/volume ratio is going to be increased proportionally, and we could expect a proportional increase of all the surface-related physical effects. The chosen sample is the prototypical CMR manganite La_{2/3}Ca_{1/3}MnO₃. The reason for this choice is that this is a very carefully studied sample, not only in the bulk form, but



Figure 3. Diagram of the temperature and pH evolution during the gel formation process.



Figure 4. Evolution of the x-ray patterns as the annealing temperature is increased.

also in thin films [7, 10, 20, 26]. At the same time, the T_C value is close to ambient temperature.

We have selected the sol–gel method as an alternative method to solid-state reaction, usually used for manganite bulk samples [10, 19]. This method allows us a more accurate control of the sintering temperatures and of the final particle sizes [28–30]. We have employed an aqueous solution of La(NO₃)₃·6H₂O, Ca(NO₃)₂·4H₂O and Mn(NO₃)₃·6H₂O in the stoichiometric proportions and urea (NH₂CONH₂) as gelificant agent. Final correct stoichiometry is related to the ratio between the metallic ions in the solution and the gelificant agent. There is an optimum urea concentration that favours the stoichiometrical reaction between the ions in the solution, which was found to be [urea]/([La³⁺]+[Ca²⁺]+[Mn²⁺]) = 10. Gel formation is achieved by slow evaporation of the solvent up to 137 °C (melting point of urea). In figure 3 we can observe the temperature and pH evolution during this process.

The cold gel is further decomposed by heating at 250 °C for 3 h, yielding the precursor to prepare the final samples. This precursor is then annealed at different temperatures up to 1100 °C (6 h). Complete crystallization is already observed at 600 °C (see figure 4). Cell parameters of the different samples were obtained by fitting the x-ray powder diffraction patterns by the Rietveld method. The results are consistent with the data of ceramic samples and only slight variations were found between the different samples.

Particle size was checked by scanning electron microscopy (SEM) (see figures 5 and 6 as examples). In figure 7,



Figure 5. SEM photography of a sol–gel sample annealed at 800 °C.



Figure 6. SEM photography of a sol–gel sample annealed at 1100 °C.



Figure 7. Comparison between particle (\blacktriangle) and crystallite ($\textcircled{\bullet}$) sizes for different annealing temperatures.

we can compare the crystallite sizes obtained from the width of the x-ray diffraction peaks and particle sizes obtained from SEM. Particle size increases as the sintering temperature increases, showing a dispersion of the data around the mean size close to 15% in every case. It can also be seen that each grain is composed of several crystallites, probably due to internal stresses or defects in the structure.

A particularly interesting point in manganites (as in other related oxides), is the control of the oxygen stoichiometry. This parameter, which directly affects the Mn³⁺/Mn⁴⁺ ratio, is very important in governing the physical properties of these compounds [31, 32]. In the sol–gel technique, as the sintering temperatures are not very high, the oxygen content control is specially difficult. As we can observe in figure 8, the Mn⁴⁺ percentage is different from the stoichiometric one, specially



Figure 8. Evolution of % Mn⁴⁺ for different annealing temperatures.

for the lower-temperature sintered samples. However, for the reasons given below, we believe that the oxygen faults are not randomly distributed in each particle, but mainly on the grain surface. This assumption is further confirmed by the magnetism and electrical transport data, which support a model of the particles composed of two different parts: an inner core with physical properties similar to the bulk, and an outer shell with oxygen faults, vacancies, etc. We will explore this model in detail in the next paragraphs.

3. Experimental results and data analysis

3.1. Magnetic properties

In figure 9, we can observe the temperature variation of magnetization for the different samples. Despite the particle size difference, the magnetic transition temperature $(T_C,$ defined as the temperature of the minimum in dM/dT) is the same. However, the saturation magnetization is reduced linearly with the surface/volume ratio (D^{-1}) (see figure 10). These data confirm the particle model presented in the previous section. The almost identical T_C indicates that the innercore contribution to the magnetization is nearly the same; that is, the stoichiometry is similar. On the other hand, the saturation magnetization is reduced because the influence of the outer layer increases as the particle size decreases. Surface contribution is larger for smaller particles and therefore the magnetization is diminished in a proportional way. We can then propose a model of the particles (figure 11) in which the inner part would have the same properties as the bulk compound (oxygen stoichiometry, magnetic and transport properties), but the outer layer (width t) would contain most of the oxygen defects and faults in the crystallographic structure that will lead to a magnetically disordered state. For simplicity, we will assign a zero magnetization to this shell.

With this simple model we can estimate that the width of the magnetically disordered outer layer (t) is approximately 3 nm. Certainly, this contribution is more important as the particle size becomes smaller, i.e. the relative surface contribution increases, but its absolute value remains almost unchanged for all the samples as it has to be more important for the smallest particle size samples.

A consequence of this model can be explored by means of the magnetocaloric effect (MCE); that is, the magnetic entropy



Figure 9. Temperature dependence of the magnetization for samples with different particle sizes.



Figure 10. Saturation magnetization versus the surface/volume ratio for samples with different particle sizes.



Figure 11. Proposed model for manganite nanoparticles. M_C and M_S are the magnetizations of the core and outer shell of the particles, respectively. *t* is the shell thickness.

 (ΔS_M) change produced by changes in the magnetic field applied to the system. MCE can be calculated from initial magnetization curves through simple equations derived from basic thermodynamics relations [33]. In figure 12, we can see a typical MCE curve. It shows a clear peak around the magnetic phase transition temperature, increasing with the applied magnetic field. The MCE is larger for the bigger particles (figure 13), and it reduces in a linear proportion with the surface/volume ratio. This result, far from surprising, is again related to the model for the nanoparticles presented above. The outer-layer contribution to the overall MCE effect is almost negligible (due to the assumed disordered magnetic state) and, in that way, total effect reduces as particle size diminishes and the superficial contribution is bigger.



Figure 12. Temperature dependence of the MCE, at different magnetic fields, for a sample with D = 60 nm.



Figure 13. Linear relationship between the MCE and the surface/volume ratio of the particles.

Linked with the MCE results, we should indicate the change in the nature of the ferromagnetic–paramagnetic phase transition for the smallest particles. The magnetic phase transition in $La_{2/3}Ca_{1/3}MnO_3$ is a first-order one [34]. This result has been confirmed for the bigger nanoparticles by means of pure magnetic measurements [35]. Instead of that, a second-order magnetic phase transition is identified in the smallest particles. The reason for that behaviour lies again in the different magnetic transition at T_C , the disordered magnetic state of the outer layer is more likely to undergo a second-order transition [36]. By a pure bulk measurement (magnetization), the global result is a second-order transition hiding the intrinsic behaviour.

3.2. Electric transport properties

The electrical transport constitutes probably the most attractive physical property of the manganites. We should not forget that CMR was one of the main reasons for the new investigations into these compounds. As we have already cited in the introduction, the resistivity of high-temperature sintered ceramic samples is characterized by a metal–insulator transition at a temperature $T_{M-I} \approx 260$ K [10]. Around this temperature (almost coincident with T_C), an applied magnetic field leads to the huge decrease in resistivity usually denoted as CMR. This behaviour is observed for the biggest nanoparticles



Figure 14. Temperature dependence of the resistivity for samples with different particle sizes.



Figure 15. Logarithmic linear relationship between the resistivity and the surface/volume ratio of the particles.

produced by the sol-gel method (see figure 14). However, the smaller particles show a larger resistivity and T_{M-I} is reduced in a nearly 80 K from the bulk value, for the 60 nm particles. The increasing resistivity with reducing particle size (figure 15) can be attributed to the potential barrier between particles. This logarithmic linear relation shown in figure 15 can be understood because the surface/volume ratio depends as D^{-1} , and the behaviour is similar to that found in granular metallic samples in insulator matrices [37].

A successful model of the nanoparticle resistivity has been done in terms of a simple model proposed by Zhang et al [38]. The basic assumptions of this model agree perfectly with the model proposed for the particles and the magnetic measurements; namely, the existence of both nucleus and an outer surface layer, as well as a lower magnetic transition temperature for that layer. The low transition temperature for the layer can be assumed because of the magnetically disordered state in the surface. This model contains a few fitting parameters, but many of them can be fixed by independent measurements (such as the particle size, the compactness or the outer disordered magnetic layer width). The achievement of this model is mainly to probe that the changes in resistivity are caused by the change in the potential barrier between the particles due to the grain size change.

Another probe of this model can be achieved with samples with the same particle size, but electrochemically treated to induce oxygen vacancies only in the surface of the particles [32]. In these samples (see figure 16), the metal– insulator transition temperature is reduced by reducing the bulk



Figure 16. Temperature dependence of the normalized resistivity for samples (D = 95 nm) with different oxygen content.

oxygen content, while T_C remains constant. This is the same result as that already presented for particles with reducing grain size via the sol–gel method.

The MR in polycrystalline manganites shows two clearly different behaviours. Intrinsic CMR response is shown around the metal-insulator transition temperature but superimposed to this, IMR appears, as a consequence of the granular morphology of the samples. In figure 17 we can observe the results of both contributions in the nanoparticles. CMR around T_{M-I} can be tuned by means of particle size variations. Actually, we believe that the intrinsic response of the material does not disappear for the smallest particles, but is being hidden by the increasing intergranular response. The temperature dependence of MR for the smallest particles, close to T_{M-I} , does not show any peak, but it shows the usual linear behaviour of IMR. At temperatures much lower than the metal-insulator transition, only the intergranular response is present. The typical dependence of the MR with the applied magnetic field is shown in figure 18. Two different regions can be distinguished in the IMR magnetic field response. The low-field region, which corresponds to magnetic fields typically lower than 5 kOe, is dominated by the quickly magnetic domain rotation and produces huge values of MR at relatively low fields. The high-field region, observed at fields typically larger than 5 kOe, shows an almost linear dependence with the applied field, without any sign of saturation. The highly disordered superficial shell of the particles dominates this region. These spins are difficult to align in the magnetic field direction, as they are suitable to be pinned by defects and vacancies. In that way, a small percentage of spins affect significantly the intergranular magnetotransport properties.

From low-temperature MR measurements we can extract the low-field MR (LFMR), defined as the zero-field extrapolation of the high-field slope. This value gives us an idea of the pure intergranular processes. As we can see in figure 19, we can also obtain a linear relationship between LFMR and the surface/volume ratio of the particles; moreover, it seems that higher values of MR could be achieved by reducing further the particle size.

A suitable prediction of the LFMR curves can be done by means of the spin-polarized tunnelling model as MR \propto $T^{-1}[m^2(H, T) - m^2(0, T)]$ [22] (figure 20). In this model, MR is related with magnetization (*m*) and, in this manner, MR can be calculated from magnetization hysteresis loops. Although



Figure 17. MR around the metal-insulator transition for samples with different particle sizes.



Figure 18. Typical low-temperature IMR for a sample with D = 95 nm.



Figure 19. LFMR versus the surface/volume ratio of the samples.

the fit is not perfect, it reproduces the main features of the MR magnetic field dependence. However, the model is not adequate to reproduce the MR temperature dependence. The MR and the square of magnetization temperature dependences are different, and a variable term has to be added to fit both quantities in all the temperature range (figure 21). In any case, the spin-polarized tunnelling model seems to be, at this moment, the most accurate one to explain the IMR in polycrystalline manganites.

In the observed temperature dependence of resistivity curves, an unexpected increase at low temperatures was found, being more prominent in the smallest particle size samples (see again figure 14). This effect, related to the IMR, is absent



Figure 20. Typical LFMR (open circles) and magnetization-based prediction (curve).



Figure 21. Comparison between normalized MR and magnetization.

in high-quality single crystals, and can be tentatively related to an electrostatic blockade of carriers between grains. This model predicts a temperature dependence for the resistivity in the form $\rho(T) \propto \exp(A/T)^{1/2}$. This functional form can be observed in the fits of figure 22. The slope of those lines (A) is somehow proportional to the electrostatic blocking energy, E_C [39, 40]. As we can see in figure 23, the proportional constant increases with the surface/volume ratio of the particles. This indicates the increasing influence of the barrier between particles with reducing grain size. From voltage-intensity curves it is possible to calculate the tunnelling resistance. This can be fitted by the Simmons equation for square barriers [41], and from the fits, one can obtain the potential energy barrier between nanoparticles. The electrostatic charging energy for the smallest particles (D = 60 nm) is estimated to be $E_C = 0.3 \text{ eV}$.

4. Conclusions

In this paper, we have studied the magnetic and electric transport properties of manganites $La_{2/3}Ca_{1/3}MnO_3$ nanoparticles. We have shown that by the sol–gel method one can produce nanoparticles of this compound down to a range of 60 nm. Crystallographic and morphological studies of the particles allowed us to characterize them, but an ideal model of the particles is based basically on the magnetic properties. The linear reduction of both, saturation magnetization and MCE, with the surface/volume ratio of the particles, leads



Figure 22. Reduced resistivity versus $T^{-1/2}$ for particles with different grain size. Lines are fits to the data.



Figure 23. Variation of the fitting factor (*A*), for low *T* resistivity, with surface/volume ratio of the particles.

to an image of the particles composed of an inner core with unchanged intrinsic properties and an outer shell in a different magnetic state, caused by oxygen vacancies and superficial stress. Some electrical transport properties are found to vary with the surface/volume ratio of the particles. IMR is increased for the smaller particles but intrinsic CMR is reduced in the same way. Spin-polarized tunnelling seems to be a first approximate valid description of these effects. Simultaneously, low-temperature electrostatic blocking effects appear in the smallest particles as a consequence of the potential barriers between them. The energy barrier height is obtained in the tunnelling scenario.

Acknowledgments

Fruitful discussions and experimental support from R D Sánchez and A Fondado are deeply acknowledged. The authors want to thank financial support from FEDER project MAT2001-3749, DGI, MCyT, Spain.

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