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# Oxygen-induced grain boundary effects on magnetotransport properties of $Sr_2FeMoO_{6+\delta}$

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The magnetic, electric, and structural properties of polycrystalline samples of $Sr_2FeMoO_{6+\delta}$ with controlled oxygen content have been investigated for nominal values $\delta=0$ and 0.04. We found that the magnetization and lattice parameters are the same in both samples, while the electric properties are drastically affected. This behavior shows that the difference in the oxygen contents is localized in a region near the surface of the grains, thus changing the transport properties of the grain boundaries (gb's). The sample with $\delta=0.04$ presents a resistivity ($\rho$) that exceeds in more than two orders of magnitude the $\rho$ for $\delta=0$. Also the low-field magnetoresistance is enhanced in $\approx 40\%$ for $\delta=0.04$ and the voltage-current characteristics present appreciable nonlinearities. We discuss these results in terms of a reinforced tunneling barrier due to the formation of an impurity phase at the gb's.

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The recent discovery of room-temperature (RT) magnetoresistance (MR) in the $Sr_2FeMoO_6$ double perovskite has renewed the interest on their transport and magnetic properties.[1] The ideal structure of this $A_2BB'O_6$ double perovskite consists of an ordered array of Fe and Mo atoms alternating on the $B$ and $B'$ site. An antiferromagnetic (AFM) coupling between the $3d^5$ $Fe^{3+}$ ions and the itinerant electrons of the $4d^1$ $Mo^{5+}$ ions predicts a saturated magnetization $M_s=4\mu_B$.[1] However, most of the experiments showed a reduced $M_s$.[1–3] This fact seems to be related to antisite defects, where some of the Fe and Mo ions interchange their crystallographic positions.[4,5] In the perfect ordered material, each Fe ion in the $B$ position is surrounded by six Mo ions at the $B'$ site. However, when disorder is present the AFM superexchange interaction between nearest-neighbor Fe ions reduces the magnetization of the ferromagnetic (FM) Fe sublattice, thus reducing $M_s$. Band structure calculations[1] predict half-metallic behavior, where the electrons at the conduction band are expected to be highly spin-polarized, even at RT. This fact, together with the high magnetic transition temperature ($T_c \approx 410$ K) makes this compound an ideal material to show an appreciable low-field MR (LFMR) in granular samples.

Although the LFMR response of granular samples is a property largely studied in several compounds,[6,7] its origin is still controversial. In the celebrated manganites, several works[8] have shown that this response can be understood as arising from a spin-polarized tunneling of carriers across insulating barriers occurring at the interfaces between ceramic grains. It is well established that the barriers located at the grain boundaries (gb's) strongly affect the resistivity of the samples, but the mechanism by which those barriers give rise to the LFMR is not clear. Experimentally, it has been found that when the resistivity increases the LFMR also does. In the ferromagnetic $CrO_2$ compound, it has been shown[9] that the partial reduction of the grain surface leads to the formation of an insulating $Cr_2O_3$ shell that enhances the resistivity and promotes the appearance of a substantial LFMR.

In the case of polycrystalline $Sr_2FeMoO_6$ the situation is even more complex. It has been shown[2] that annealing treatments under vacuum strongly affect the resistivity of the samples, and this is attributed to the removal of oxygen atoms from the gb's. Usually, the as-made samples present insulating behavior, but after this treatment the resistivity is widely reduced and exhibits an insulator-to-metal transition at $T_c$. This behavior makes evident the effects of the gb's on the transport properties of this compound and the importance of the interplay between these effects and the oxygen control. In spite of these experimental evidences, there have been some claims[10] that the LFMR in double perovskites could be mainly related to the existence of antisite defects. Obviously both interpretations are in knocking contrast and illustrate the limited understanding of the origin of the LFMR in these oxides.

In the present paper we shall provide evidence that the existence of an insulating barrier at the gb's of $Sr_2FeMoO_6$ plays a fundamental role in determining the LFMR. More precisely, in the $Sr_2FeMoO_6$ ceramic samples having the highest LFMR we have identified the presence of a $SrMoO_4$ (insulating) phase at the gb's. We report measurements of magnetization ($M$), resistivity ($\rho$), voltage-current ($V$-$I$) characteristics, and x-ray diffraction (XRD) of polycrystalline samples of $Sr_2FeMoO_{6+\delta}$ with controlled oxygen content, for nominal values $\delta=0$ and 0.04. While the magnetization is similar for both samples, the $\delta=0.04$ one exhibits a much higher resistivity and LFMR. These results are consistent with oxygen-induced gb effects. Indeed, detailed inspection of the XRD data reveals that weak reflections attributed to $SrMoO_4$ appear in the oxygenated ($\delta=0.04$) sample. Likely this insulating shell at the grain surface constitutes the insulating barrier for spin-polarized tunneling.

The $M(T)$ data were obtained in a superconducting quantum interference device (SQUID) magnetometer in the

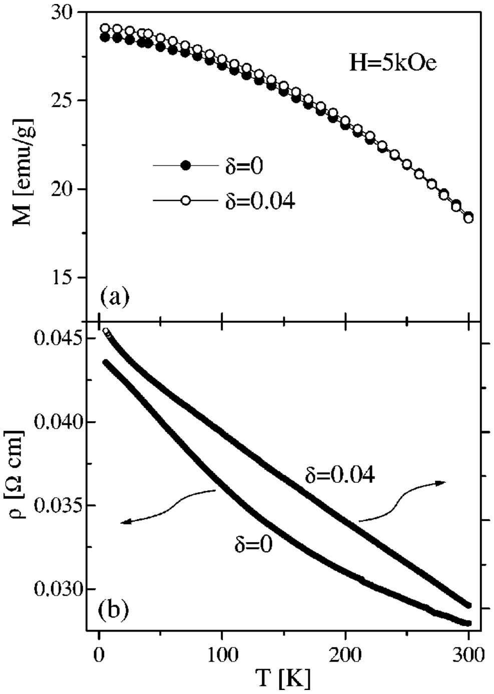

FIG. 1. (a) $M(T)$ data of the as-made ($\delta = 0$) and the oxygenated ($\delta = 0.04$) samples. (b) Resistivity vs $T$ curves. Note that the $\rho$ for $\delta = 0.04$ is about $10^2$ times higher than that for $\delta = 0$.

5–300 K temperature range. The resistivity and the $V(I)$ curves were measured by the usual four-probe method, between 5 and 300 K and with applied magnetic fields ($H$) up to 9 T. The samples for the resistivity measurements were obtained by cutting the sintered pellets in the form of bars, and the XRD experiments were performed on crushed pellets in a Philips PW 1700 diffractometer using Cu $K\alpha$ radiation.

Ceramic samples of $Sr_2FeMoO_6$ were prepared by the solid state reaction technique, as was reported elsewhere.[2] The raw materials were calcinated at 950 °C under an Ar-$H_2$ mixture. The obtained powders were pressed into pellets and a final sinterization treatment was performed under vacuum at 1100 °C. The XRD data indicate a single-phase material with an $I4/m$ tetragonal symmetry. The lattice parameters of the as-made samples obtained by Rietveld refinement[11] were $a = b = 5.5771(2)$ Å and $c = 7.9053(3)$ Å. No secondary phases were also detected by scanning electron microscopy (SEM) observations. This as-made sample corresponds to that labeled $\delta = 0$.

By slow oxidation of the sintered $\delta = 0$ sample we prepared another one with $\delta = 0.04$, making use of a high sensitive thermogravimetric analyzer (TGA).[12] This oxidation was carried out inside the thermobalance at 400 °C under an Ar-$O_2$ mixture, with an oxygen partial pressure $p(O_2) = 6 \times 10^{-5}$ atm. We monitored the mass gain of the sample due to its oxidation. After a certain time the gas flow was interrupted and the sample was quenched to liquid nitrogen temperature. Then, from the gained mass we calculated the new oxygen stoichiometry and obtained the sample labeled as $\delta = 0.04$.

In Fig. 1(a) we present $M(T)$ curves for the studied samples, measured with $H = 5$ kOe. Both samples have similar magnetization in the whole temperature range studied, thus the difference in the oxygen content does not significantly affect the magnetic properties. The saturated magnetization is also similar for both samples ($M_s \approx 2.7\mu_B$), therefore the Fe/Mo ordering is not altered by the oxidation process. In contrast, the resistivity behavior is strongly affected. Figure 1(b) shows the $\rho$ data as a function of temperature for both samples, which exhibit insulating behavior as in almost all cases of polycrystalline $Sr_2FeMoO_6$.[1,2] However, the oxygenated sample ($\delta = 0.04$) presents a resistivity more than $10^2$ times higher than the $\rho$ of the $\delta = 0$ sample. Since the magnetic properties of both samples are very similar and the cell parameters were also found to be identical, the difference in the resistivity is a clear signature of the enhanced grain boundary effect in the sample with $\delta = 0.04$. These results indicate that both samples are essentially the same and the difference in the oxygen content must be constrained to the gb region, not affecting the bulk of the compound deep inside the grains. Thus, for the $\delta = 0.04$ sample we expect the actual oxygen content within the grains to be similar to the as-made sample, while gb's are oxygen rich.

In a previous work[2] we have shown that the resistivity of the present compound decreases notably when the oxygen at the gb's is removed. When this occurs, the ceramic samples display the properties of the bulk, thus $\rho$ is metallic as in the case of single crystals.[13] Chmaissem *et al.*[14] studied the electric properties of polycrystalline $Sr_2FeMoO_6$ samples prepared under different conditions. They showed that some of them were insulating and others metallic. In the parent compound $Sr_2FeReO_6$, Kobayashi *et al.*[15] have found similar behavior. The samples made under vacuum show metallic resistivity, and after an annealing process in a stream of Ar gas they become insulating while the magnetization is not altered.[15] These surprising results would be related to different oxygen contents, i.e., the metallic samples would have the lower oxygen content in the grain boundaries region.

It is clear that the properties of the gb's in the $Sr_2FeMoO_6$ double perovskite are strongly coupled to their oxygen content. Based on the present results, we conclude that the oxygen atoms placed at the gb's contribute to reinforce the intergrain tunneling barriers. In this frame, a consequent increase of MR is also expected for the $\delta = 0.04$ sample. This is indeed the observed behavior in Fig. 2, where we show the $\text{MR} = [\rho(H) - \rho_0]/\rho_0$ as a function of $H$ at several temperatures between 5 and 250 K. As observed in other compounds,[9,15] as a result of the increased tunnel barrier the sample with $\delta = 0.04$ effectively presents a higher LFMR. At low $T$, the LFMR for $\delta = 0.04$ is about 40% higher, and the difference slightly decreases with increasing $T$. In the case of the $Sr_2FeReO_6$ compound,[15] the MR is also magnified after the annealing process that produces an increase of the resistivity.

At this point it is absolutely clear that the oxygenated sample ($\delta = 0.04$) has very different transport properties at the gb's, with a higher insulating barrier that leads to an increase of $\rho$ and LFMR. Now we wonder which is the physical origin of this enhanced barrier. The answer to this question is found in the XRD data. In Fig. 3 we show a blow up of the diffractograms at RT of both samples, for $2\Theta$ be-

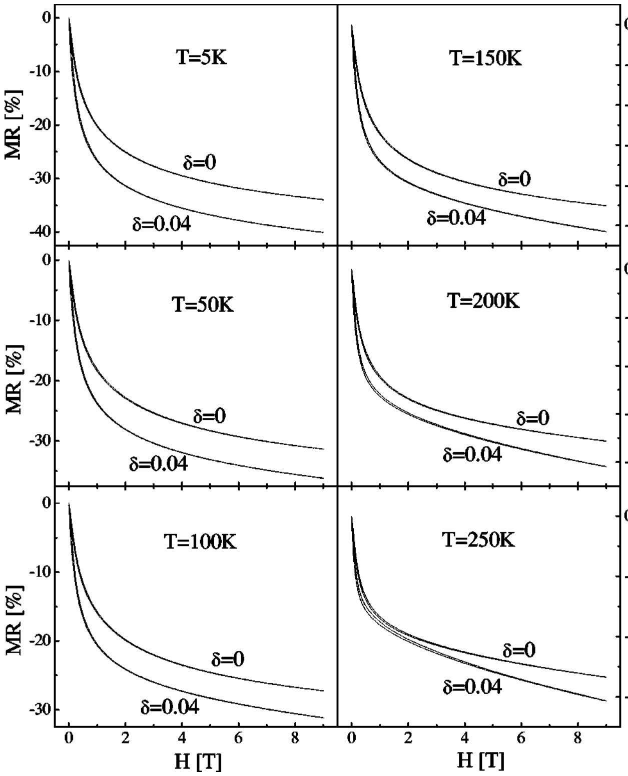

FIG. 2. Magnetoresistance (MR) vs applied field at several temperatures. At any temperature the MR of the $\delta = 0.04$ sample is higher than that of the $\delta = 0$ one.

tween 18° and 36°. All the lines corresponding to the $Sr_2FeMoO_6$ compound are exhibited at the very same position by the spectra of both samples, and a Rietveld profile refinement of the complete spectra indicates that they have the same lattice parameters. On the contrary, only the $\delta = 0.04$ sample clearly displays a weak peak at $2\Theta \approx 27.7°$. This peak corresponds to the (112) reflection of a small amount of the $SrMoO_4$ compound. Therefore, since both samples present the same magnetization and lattice parameters and such a different resistivity response, we conclude that in the oxidation process the nonmagnetic $SrMoO_4$ impurity phase is induced to appear at the gb's. It is well known that the oxygen diffusion coefficient is much higher at the gb's than in the bulk, so the oxidation process must necessarily be much more important at the gb's. Also, the low temperature used during the oxidation for obtaining the $\delta = 0.04$ sample (400 °C) is not enough to substantially modify the bulk of the compound. Thus, the $SrMoO_4$ phase is expected to be located at the gb's, with the consequent enhancement of the intergrain insulating barrier. The spin-polarized transport across this barrier promotes a substantial rising of the LFMR. We have to note that, since the parent compound is $Sr_2FeMoO_6$, selective precipitation of $SrMoO_4$ at the gb's must also precipitate a Sr/Fe-rich phase in the neighborhood. Although the XRD pattern does not show any trace of Fe precipitates, recent detailed magnetic measurements in the paramagnetic phase of these oxides have indeed revealed the existence of minor traces ($\approx 0.05\%$) of ferromagnetic Fe impurities.[16] A more deep insight must be done in order to understand the precise microstructure of the gb region.

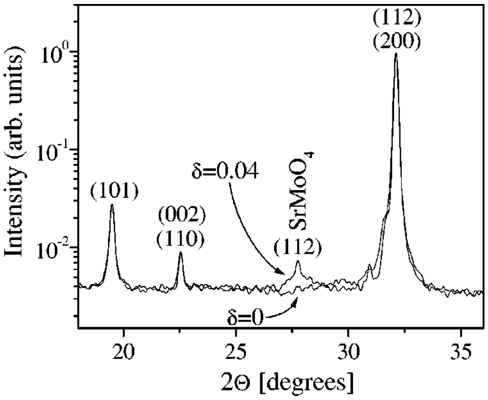

FIG. 3. Blow up of the x-ray diffractograms of the $Sr_2FeMoO_{6+\delta}$ samples. The peak at 27.7° for $\delta = 0.04$ corresponds to the nonmagnetic and insulating $SrMoO_4$ impurity phase.

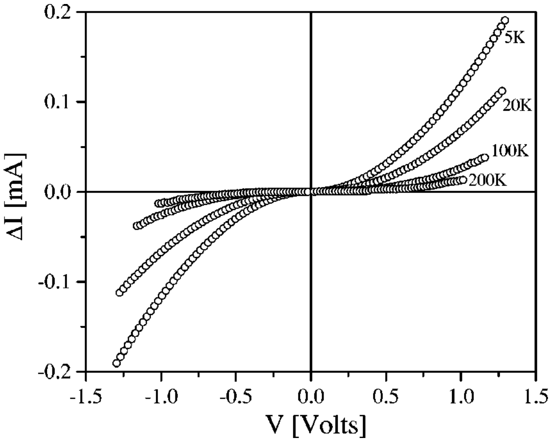

FIG. 4. $V$ vs $I$ characteristics for the $\delta = 0.04$ sample. The $\Delta I$ is the excess current with respect to the linear response, thus the $\Delta I \neq 0$ indicates a nonlinear behavior.

As a possible signature of the presence of the gb insulating barrier, we present $V$ vs $I$ characteristics where a nonlinear response is observed only for the oxygen-rich sample. In Fig. 4 we show the excess current $\Delta I$ as a function of applied voltage for the $\delta = 0.04$ sample. The $\Delta I$ is defined as

$$I = \frac{V}{R_0} + \Delta I(V), \tag{1}$$

where $R_0$ is the resistance in the limit $V \rightarrow 0$. Then, $\Delta I$ is the voltage-induced excess current with respect to the linear response. In Fig. 4 a nonlinear behavior ($\Delta I \neq 0$) is clearly observed at low temperatures, and the effect diminishes with increasing $T$. The $\Delta I$ at $T = 5$ K corresponds to a decrease of the resistance of approximately 4% between $V = 0$ and 1.3 V. Nonlinear $V(I)$ characteristics in granular samples may arise from a number of reasons. Coulomb blockade[7,17] has been identified in samples formed by nanometric grains and is usually accompanied by a $\rho(T) \propto \exp\sqrt{(\Delta/T)}$ dependence. However, our samples are micrometric and the observed temperature dependence of $\rho$ [Fig. 1(b)] does not follow the predicted behavior. Therefore, grain charging is not at the origin of the observed nonlinearity. In contrast, nonlinear $V(I)$ characteristics naturally appear in the tunneling process.[18]

In a recent paper, García-Hernández *et al.*[10] suggested that the LFMR in the FeMo double perovskites is mainly determined by the concentration of antisite defects. In our case, this concentration is expected to be the same for both samples. The oxidation treatment for obtaining the $\delta=0.04$ sample was performed at 400 °C, a very low temperature at which the Fe/Mo ordering cannot be changed.[5] The similar magnetizations in both samples and the remarkable coincidence of the intensities of the (101) superstructure peak[5] confirm that expectation. Then, our increase of the LFMR is univocally related to the enhancement of the intergrain barrier, and not to a disorder-induced effect.

Recently, in order to explain the effect of the intergrain tunneling barrier on the LFMR, Dai and Tang[19] have suggested the existence of a spin-independent conduction channel. This conductance would be given by higher-order inelastic hopping through localized states due to imperfections in the barrier. As the barrier thickness increases this term would become less important as compared with the elastic tunneling of the spin-dependent channel,[19] thus enhancing the LFMR. On the other hand, it is well established that the angle $\theta$ between the magnetizations of neighboring grains at zero field determines the LFMR.[8] Recent results[20] suggest that when the intergrain barrier diminishes, the itinerant electrons in the surface of each grain become delocalized between the two neighboring grains. This delocalization would take place by reducing the misalignment between the localized $t_{2g}$ spins located at the surface of the two grains, thus reducing the effective $\theta$. This reduction implies a decrease of the LFMR as the intergrain barrier is diminished.

In summary, we studied the magnetic and electric properties of the $Sr_2FeMoO_{6+\delta}$ compound, for $\delta=0$ (the as-made sample) and 0.04. We found that the oxidation process to obtain the $\delta=0.04$ sample just induces the formation of a nonmagnetic $SrMoO_4$ impurity phase in the grain boundaries region. This impurity leads to the enhancement of the intergrain tunneling barrier, with the consequent increase of the resistivity and the low-field magnetoresistance. On the other hand, since the impurity phase is located in the grain boundaries region, the magnetization and structure of the sample are not altered. This behavior opens the possibility of a meticulous control of the magnetotransport properties of the high-temperature half-metallic ferromagnets through the oxygen-induced grain boundary effects.

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