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Interfacial tunnel-type GMR in granular perovskite La-Sr-Mn-O system

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The magnetic transport properties in granular perovskite system $La_{1-x}Sr_xMnO_3$ have been investigated. The spin-dependent interfacial tunneling and the corresponding giant magnetoresistance (GMR) effect have been observed in the whole region of temperature below the Curie point T_c for the samples with concentration x from 0.05 to 0.45. Theoretical analysis shows that the interfacial tunneling originates from the difference in magnetism between the grain surfaces and the cores, and the tunnel-type GMR stems from the field-induced change of interfacial magnetic order.

1. Introduction

The observation of giant magnetoresistance (GMR) in fine particle perovskite [1–2] has extended the research of GMR effect in granular ferromagnets. The model of spin-polarized intergranular tunneling suggested by Hwang *et al*. [3] provided a reasonable clue to discuss the magnetic properties in granular perovskites. Our theoretical analysis [4] further showed that the intergranular tunneling resulted from a spin-dependent interfacial effect.

The spin-dependent transport properties in granular ferromagnets have been known to depend on the grain size and intergranular materials [5–7], which construct the intergranular barriers. Conductive electrons can hop from grain to grain through spin-dependent tunneling [8]. The probability of an electron tunneling across the intergranular barrier was calculated by considering an extra magnetic exchange energy arising when the magnetic moments of the neighboring grains are not parallel and the electron spin is conserved in tunneling. Randomly oriented moments of grains can be aligned by an external field. This can significantly reduce the tunnel resistance.

The manganese perovskite is recently studied extensively due to a colossal intrinsic magnetoresistance (CMR) being observed near the Curie temperature T_c [9]. When in ferromagnetic state, the perovskite behaves as a metal in transport properties. In this sense, a granular perovskite is also a conductive granular ferromagnet. However, the transport properties, especially the low-temperature transport properties, observed in granular perovskite with smaller grain size [1–3] are obviously different from that in both single crystals of manganese perovskites and granular transition metals or other ferromagnets. This suggests that the conductive origin of the granular perovskite is somewhat different from that in the both. Now we have known [4] that the transport properties in granular perovskite depend on the magnetic difference between grain surface and the core. This difference makes the surfaces between neighboring grains to be a potential barrier considering that an *extra energy* associated with double exchange interaction (i.e., the difference between the two double exchange energies in cores and surfaces) will arise when the ionic spins in cores are parallel and the ionic spins in surfaces are not parallel, while the spin of itinerant electron is conserved in tunneling. The randomly oriented ionic spins in grain surfaces can also be field-aligned, just like those in films or crystals. Therefore, the resistivity of the system can be reduced by external field, and a tunnel-type GMR can then be observed.

In this paper, we present an observation of the interfacial tunnel-type transport properties in granular perovskite $La_{1-x}Sr_xMnO_3$. We will show that the tunnel-type GMR can exist in all the temperature region below T_c for the samples in a considerably wide range of concentration from ferromagnetic insulator to ferromagnetic metal, even to some samples with mixed magnetic order, but not only for the samples of $La_{0.77}R_{0.33}MnO_3$ (R = Ca, Ba, . . .) [1–2].

2. Sample preparation

The samples under investigation are synthesized by sol-gel method with the nominal concentration x changing from 0.05 to 0.45, and in steps of $\Delta x = 0.05$. Samples

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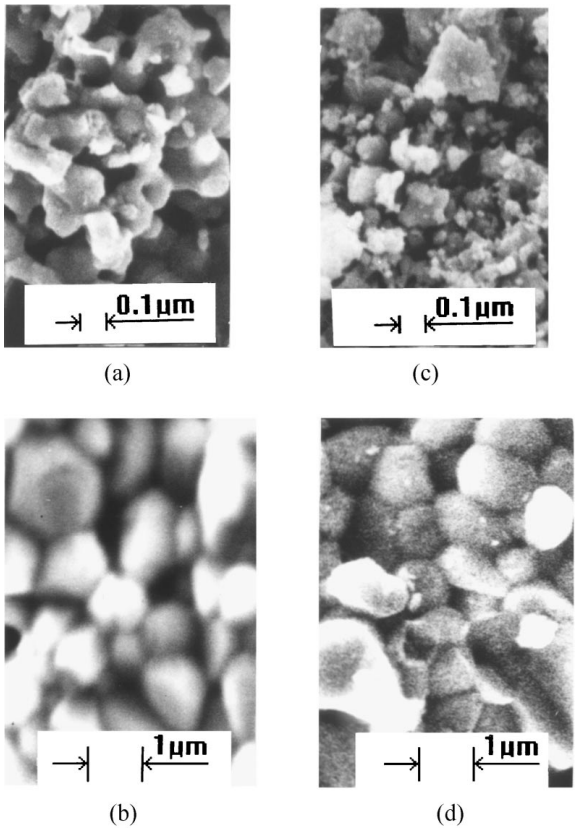


Figure 1 The SEM photographs for (a) 1000 °C sintered $La_{0.85}Sr_{0.15}MnO_z$, (b) 1400 °C sintered $La_{0.85}Sr_{0.15}MnO_z$, (c) 1000 °C sintered $La_{0.65}Sr_{0.35}MnO_z$, and (d) 1400 °C sintered $La_{0.65}Sr_{0.35}MnO_z$.

sintered at two temperatures, 1000 and 1400 °C, are studied. The photographs of scanning electron microscope (SEM) for the samples of $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.65}Sr_{0.35}MnO_3$ are shown in Fig. 1. The average grain size estimated from SEM are 0.08–0.12 μm for 1000 °C sintered samples and 1–1.5 μm for 1400 °C sintered ones. Evidently, the grain size of 1000 °C sintered samples is smaller by two orders in magnitude than that of 1400 °C sintered ones. In addition, the samples are found to be more porous when sintered at lower temperature, as shown in the SEM photographs. This indicates that the conductive channels in low-temperature sintered sample is fewer than that in high-temperature sintered one.

3. Experimental result and discussions

Fig. 2 shows the curves of the resistivity versus temperature at zero field and under an external field $H = 1.5$ T, together with the corresponding magnetoresistances for 1400 °C sintered samples with different concentrations. As can be seen, all the 1400 °C sintered samples show a transport behavior almost the same as that detected from films or crystals [9]. No intergranular tunneling behavior can be observed. Thus we believe that the 1400 °C sintered samples present the intrinsic transport properties.

The electric and magnetic properties of 1000 °C sintered samples are shown in Fig. 3. It can be seen that most of them show a double-peak type curve of resistivity versus temperature (ρ-T), a sharper peak near T_c

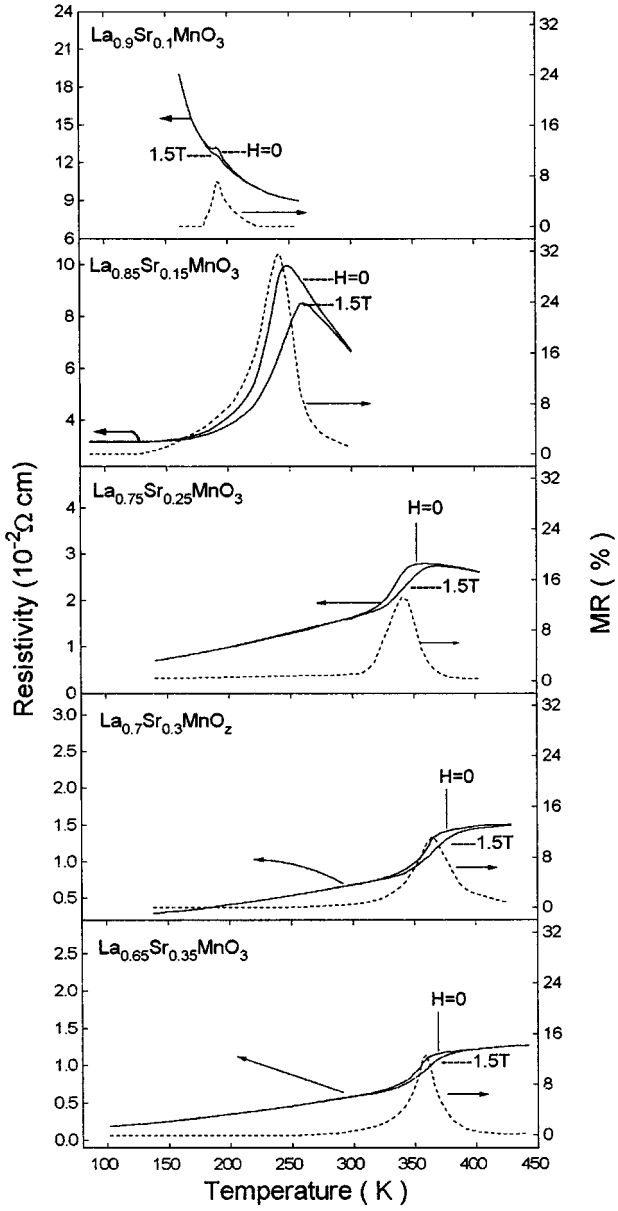


Figure 2 Resistivity versus temperature at zero field and under an external field $H = 1.5$ T and the corresponding MR(T) curves for 1400 °C sintered and different doped $LaMnO_3$, where $MR = [R(0) - R(H)]/R(0)$, $R(0)$ and $R(H)$ are the resistances at zero field and under an external field $H = 1.5$ T, respectively.

with peak temperature T_{pb}, and a broader peak well below T_c with peak temperature T_{pt}. The former obviously reflects the crystal intrinsic transport properties of manganese perovskite, and the latter can be attributed to the interfacial tunneling effect as discussed earlier.

Compared with the curves of $m(T)$ for high-temperature sintered samples, a universally broadening of the Curie temperature T_c has been observed for the low-temperature sintered samples, where m is the normalized magnetization. This point suggests a magnetic surface effect existing in the samples with smaller grain size. According to the early study on surface magnetism, we know that the coupling among the magnetic ions in surface is much weaker than that in the core due to the existence of large number of dangling bonds and non-coordination atoms in surface [10]. Moreover, the lattice structure in surface is often amorphous [11] and the magnetic configuration of such materials being very

structure-sensitive [12]. Thus, the magnetic configuration of the compound can be expected more chaotic in grain surfaces than in cores at a given temperature. In other words, the T_c is expected to be lower in surface than that in core. In practice, in Heisenberg theory of ferromagnetism [13], we have

$$T_c = 2qJ/k, \tag{1}$$

where q is the coordination number, J is the exchange integral between neighboring atoms, and k is the Boltzmann constant. On the one hand, the average coordination number q in surfaces is lower, on the other hand, the overlap between neighboring atoms is also lower due to the lower coordination number, and so the lower exchange integral J, thus the T_c in surfaces is lower than that in cores. Additionally, with increasing sintering temperature, only a little change of oxygen content has been observed in $La_{1-x}Sr_xMnO_3$ system. Taking $La_{0.85}Sr_{0.15}MnO_z$ as an example, as T_s increased from 800 to 1400 °C, the oxygen content z was found to decrease only about 0.01 [14]. According to the data

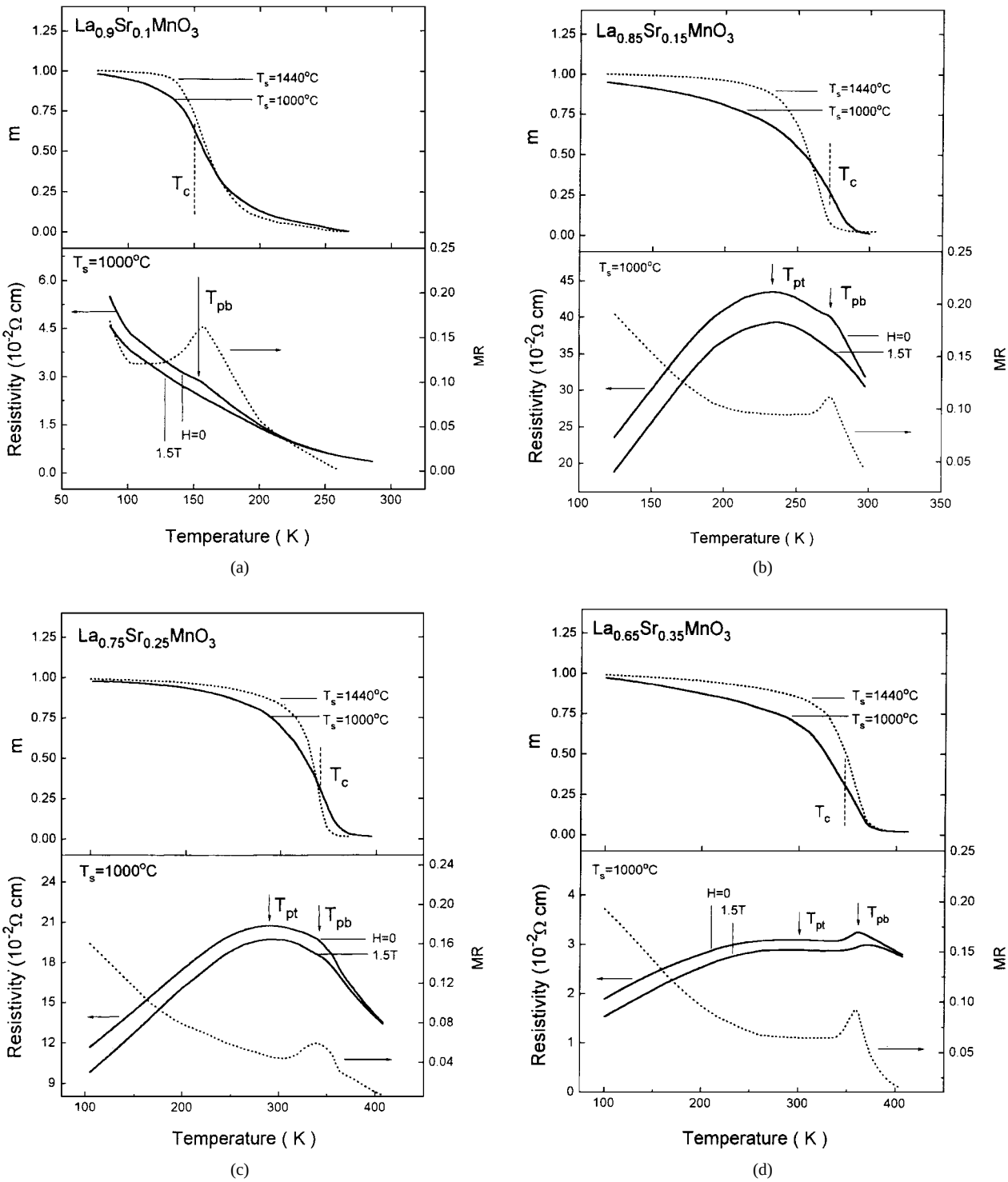
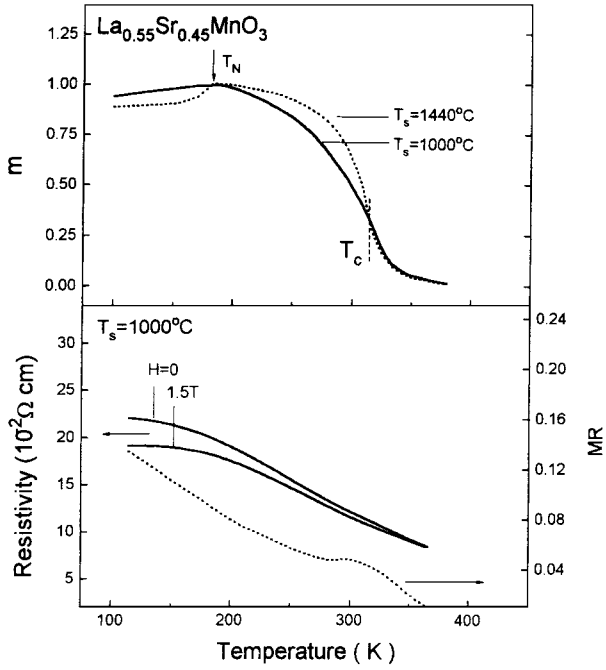


Figure 3 Upper panels: Normalized magnetization vs. temperature for 1000 °C and 1440 °C sintered samples. Lower panels: Resistivity vs. temperature at zero field and under an external field $H = 1.5$ T and the corresponding MR(T) curves for 1000 °C sintered samples, where $MR = [R(0) - R(H)]/R(0)$, T_s is the sintering temperature, T_N is the Néel temperature. (*Continued*).



(e)

Figure 3 (*Continued*).

provided by Ju *et al.* [15], so little change of oxygen cannot give rise to much influence on magnetic properties. We, therefore, conclude that T_c broadening for the samples with smaller grain size may provide an evidence for T_c-decreasing in surfaces. Thus the relative angle of local spin is larger, and the energy of double exchange [16] should be higher in surfaces than in cores.

Dividing a grain into body phase and surface phase, and denoting the resistivities of body and surface as ρ_b and ρ_t, respectively, the resistivity of a granular system should be

$$\rho = \frac{1}{c}\left[\left(1 - \frac{3w}{D}\right)\rho_b + \frac{3w}{D}\rho_t\right], \tag{2}$$

where c is the compactness of the system, D is the average diameter of grains, w reflects the average thickness of surfaces, $3w/D$ represents the volume fraction occupied by surface phase. If the interface, i.e., the surfaces between neighboring grains together with the intergranular distance (if there exists), is considered as the tunneling barrier, ρ_t will be the tunnel resistivity. From the early discussion on tunneling theory of spin-polarized electrons [8], we have

$$\rho_t \propto \exp(2\beta a), \tag{3}$$

where a is the barrier width, $\beta = [2\mu U/\bar{h}^2]^{1/2}$, μ is the electronic mass, and $\bar{h}$ is Planck's constant divided by 2π, U is the barrier height, which can be considered as the difference of the energies of double exchange in body and surface. In the theory of double exchange, the double exchange energy can be expressed as [16]

$$E_d = -Nx\sum_i t_{(i,j)}\left\langle \cos\left(\Delta\theta_{(i,j)}/2\right)\right\rangle, \tag{4}$$

where x is the concentration, N is the number of magnetic ions per unit volume, the sum $\sum_i$ extends to the nearest neighbors of Mn sites, the $\langle\,\rangle$ symbol represents a thermal average on the possible states of the ionic spins. Denoting the surface and the core with foot notes s and b, respectively, then the double exchange energy in surfaces and cores can be respectively written as

$$E_{db} = -Nx\sum_i t_{b(i,j)}\left\langle \cos\left(\Delta\theta_{b(i,j)}/2\right)\right\rangle, \tag{5}$$

$$E_{ds} = -Nx\sum_i t_{s(i,j)}\left\langle \cos\left(\Delta\theta_{s(i,j)}/2\right)\right\rangle. \tag{6}$$

The barrier height then should be

$$U = E_{ds} - E_{db} = Nx[\Phi_b\cos(\Delta\theta_b/2) - \Phi_s\cos(\Delta\theta_s/2)], \tag{7}$$

where $\Phi_b = \sum_i t_{b(i,j)}$ and $\Phi_s = \sum_i t_{s(i,j)}$. Making use of the following relation [16]

$$\langle\cos(\Delta\theta_{i,j}/2)\rangle = \cos(\Delta\theta/2) = (3 + 2m^2)/5,$$

respectively to surfaces and cores, it gives

$$\cos(\Delta\theta_b/2) = \left(3 + 2m_b^2\right)/5, \tag{8}$$

$$\cos(\Delta\theta_s/2) = \left(3 + 2m_s^2\right)/5, \tag{9}$$

where m is the total magnetization normalized to the saturation value, m_b and m_s are the normalized magnetizations in core and surface, respectively. In addition, for the present granular system we have

$$m = (1 - 3w/D)m_b + (3w/D)m_s, \tag{10}$$

Collecting all the results from Equations 7 to 10, and roughly take $\Phi_b = \Phi_s$, we consequently obtain

$$U \approx \frac{2}{5}Nx\Phi_b\left[\frac{(Dm - 3wm_s)^2}{(D - 3w)^2} - m_s^2\right]. \tag{11}$$

It is generally believed that a surface includes about four or five atom layers. Taking as the thickness of per atom layer a bond length of Mn–O–Mn (~4 Å), w is about 2 nm. Thus, noted that $3wm_s \ll Dm$ when $D > 100$ nm, it furthermore gives from Equation 3,

$$\rho_t = \frac{k}{D}\exp\left\{b\left[\frac{m^2}{(1 - 3w/D)^2} - m_s^2\right]^{1/2}\right\}, \tag{12}$$

where k is a constant relative to the chemistry inhomogeneity of the grain surface, which can be estimated from the resistivity of the system at zero temperature, $b = 2a\sqrt{mNx\Phi_b/5\bar{h}^2}$. Inserting Equation 12 into Equation 2, we have

$$\rho = \frac{1}{c}\left\{\left(1 - \frac{3w}{D}\right)\rho_b + \frac{3w\kappa}{D^2}\exp\left\{b\left[\frac{m^2}{(1 - 3w/D)^2} - m_s^2\right]^{1/2}\right\}\right\}. \tag{13}$$

Equation 13 is just the resistivity formula for granular manganese perovskite. The first and second terms in the bracket represent the transport properties of body phase and surface phase respectively.

From Equation 13, we conclude that: (1) The tunnel resistance is strongly influenced by the magnetism in body phase and will disappear with m tending to zero. Since the Curie point in surface is lower than that in the cores, the m_s should disappear before m tending to zero; (2) Using the method of molecular field approximation to surface ($m_s = C(H/M_0 + \lambda m)/T$, where C is the Curie constant, M_0 the saturated magnetization, H the applied field, λ the proportional constant of molecular field), and considering m as a function of temperature, the tunnel resistance undergoes a maximum with increasing temperature due to the relative change of m_s to m. A resistivity peak well below T_c, with peak temperature T_{pt}, is therefore observed. The origin of the peak is qualitatively different from that of the intrinsic resistivity peak near T_c, with peak temperature T_{pb}. The former stems from the change of interfacial tunneling and the later is considered to be reflecting a process of intrinsic metal-insulator-like transition [9]; (3) The resistivity depends not only on the magnetic difference between the surface and the core but also on the grain size. Thus the resistivity is not the same though above T_c, where the surface layer is gone, for the 1000 and 1400 °C sintered samples; (4) The magnetization in surface can be increased by external field, thus an interfacial tunneling GMR can be observed; (5) The tunneling GMR only demands a magnetic difference between core and surface but not limits the magnetic order of body in ferromagnetism. The tunneling GMR can therefore be expected to take place not only in the samples with their concentration in the regime of ferromagnetic metal but also in part regime of ferromagnetic insulator, even in some samples with different magnetic orders in different region of temperature respectively, such as for $La_{0.55}Sr_{0.45}MnO_z$, which shows a antiferromagnetic order below 180 K, as shown in the top panel of Fig. 3e. In addition, when the magnetic difference between core and surface disappears, i.e., $m \approx m_s$, we can not observe any tunneling GMR. This will be hold for the grains of $D > 100$ nm due to $D \gg w$ in that case. All the conclusions above can be seen in the lower panels of Fig. 3 respectively.

In summary, the transport properties of the granular manganese perovskite depend on magnetic difference between body and surface but not on magnetic moments of the neighboring grains. This discriminates a granular perovskite from other granular ferromagnets in transport mechanisms.

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