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Tunnel-type giant magnetoresistance in the granular perovskite $La_{0.85}Sr_{0.15}MnO_3$

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The grain-size-dependent transport properties in the granular perovskite $La_{0.85}Sr_{0.15}MnO_3$ have been investigated. A giant magnetoresistance (GMR) effect, similar to that observed in granular transition metals, and a crystal intrinsic colossal magnetoresistance (CMR) have been simultaneously observed. With grain growth, the GMR effect gradually weakens and the intrinsic CMR effect becomes prominent in the present granular system. A resistivity formula originating from interfacial tunneling is obtained and the theoretical calculation is found to be in good agreement with our experimental results. [S0163-1829(97)04437-8]

INTRODUCTION

Since giant magnetoresistance (GMR) was discovered in magnetic multilayers Fe/Cr (Ref. 1) in 1988, the phenomenon has been observed in many other ferromagnets, such as granular transition metals,[2] and heterogeneous magnetic alloys with ferromagnetic grains embedded in nonmagnetic nonmetallic matrix Ni (or Co)-SiO_2.[3] Spin-polarized intergrain tunneling in these ferromagnets has been carefully studied[4] and is known to depend on the grain size and the properties of intergranular material, which constructs the intergrain barrier. Conductive electrons can hop from grain to grain through spin-dependent tunneling.[5] 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 causes a significant increase in the tunnel conductance, thereby reducing resistivity of the granular system.

Recently, the manganese perovskite has been studied extensively since it showed an intrinsic colossal magnetoresistance (CMR) near the Curie temperature T_C.[6] In the ferromagnetic state, the perovskite behaves like a metal in electric properties. In this sense, a granular perovskite is a granular ferromagnets similar to a granular transition metals. However, according to the low-temperature transport properties observed,[7,8] the formation of the intergrain barrier in a granular perovskite may be a little different from that in granular transition metals. Since no nonmagnetic material, which can be the potential barrier between ferromagnetic grains, exists in granular perovskites, the interface between neighboring grains should be take into account as a barrier. The magnetic configuration in the grain surface could be more chaotic than that in the core by considering the facts that (1) the lattice structure in the surface is amorphous, and the magnetic configuration of such material is very structure sensitive.[9] (2) Due to a large number of dangling bonds or noncoordination atoms existing in the surfaces, the coupling among the magnetic ions in the surfaces should be much weaker than that in the cores.[10] Thus the double-exchange interaction,[11] which is often used to explain the conductive behavior of manganese perovskites, could be weaker in the surfaces than in the cores. Then the surfaces between neighboring grains, together with the intergrain distance, can play the part of the potential barrier. The ionic spins in the surface can also be aligned by external field, just like in crystals. Therefore, the barrier height, and also the tunnel resistance could be field reduced. The granular manganese perovskite would be accordingly expected to show a tunnel-type GMR, as suggested by Hwang *et al.*[8] However, unlike the granular transition metals, the magnetic transport behavior of the granular perovskite system can be strongly influenced by intrinsic properties in the cores. Thus, it is possible for us to observe simultaneously both interfacial tunneling and intrinsic transport behaviors, including the two kinds of magnetoresistances, tunnel-type GMR and intrinsic CMR, in the granular perovskite.

In this work, we present a careful study on the interfacial tunneling in the granular perovskite $La_{0.85}Sr_{0.15}MnO_3$. Through considering the difference in the double-exchange interaction between interfaces and cores, we have obtained the expression for the tunnel resistance. The theory is shown to be in good agreement with our experimental results. According to the theory, we conclude that the grain-size-dependent change of transport behavior observed in the granular system just reflects a crossover from the behavior of interfacial tunneling to the intrinsic transport behavior with grain growth.

SAMPLE REPRESENTATION

The samples under investigation were synthesized by the sol-gel method as reported previously.[12] The samples are sintered at different temperatures, from 800 to 1400 °C, to get a series of polycrystalline samples with different grain sizes. The average grain size D was estimated by means of the Scherrer formula[13] through measuring the full width half maximum of x-ray-diffraction (XRD) patterns. The normal-

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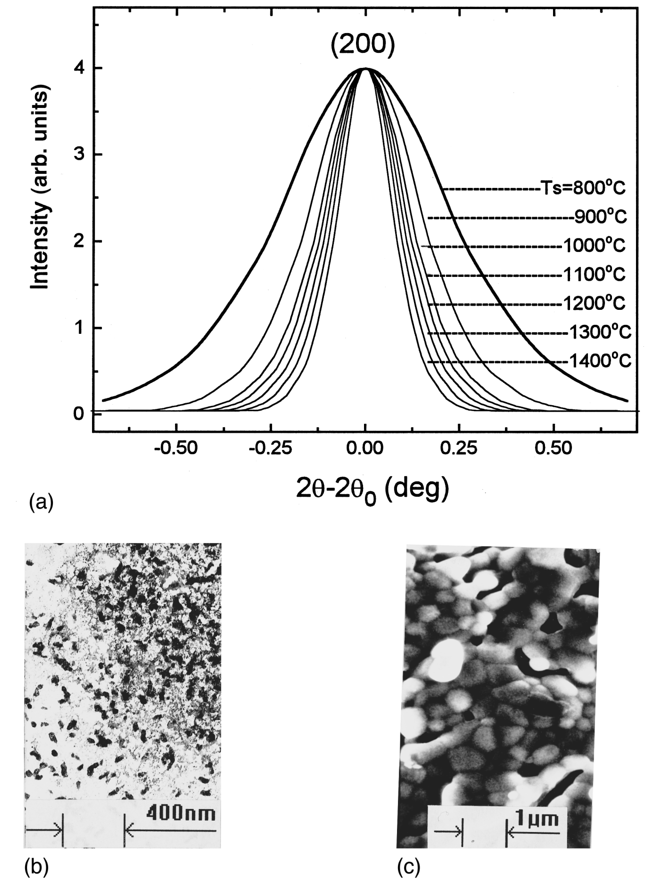

FIG. 1. (a) Normalized XRD profiles of peak [200] for different temperature sintered samples of $La_{0.85}Sr_{0.15}MnO_3$. $2\theta_0 = 46.63°$; (b) TEM photograph for 900 °C sintered sample of $La_{0.85}Sr_{0.15}MnO_3$; (c) SEM photograph for 1300 °C sintered sample of $La_{0.85}Sr_{0.15}MnO_3$.

ized XRD profiles of peak [200] for the different temperature sintered samples are shown in Fig. 1(a). The photograph of transmission electron microscope (TEM) for the 900 °C sintered sample and the photograph of scanning electron microscope (SEM) for the 1300 °C sintered sample are shown in Figs. 1(b) and 1(c), respectively. The relation of D versus sintering temperature T_S is shown in Fig. 2. This result is in good agreement with the TEM photograph but somewhat different from the SEM photograph. In addition, the sample compactness is also found to increase with increasing T_S, also shown in Fig. 2. As can be seen, the sample is porous.

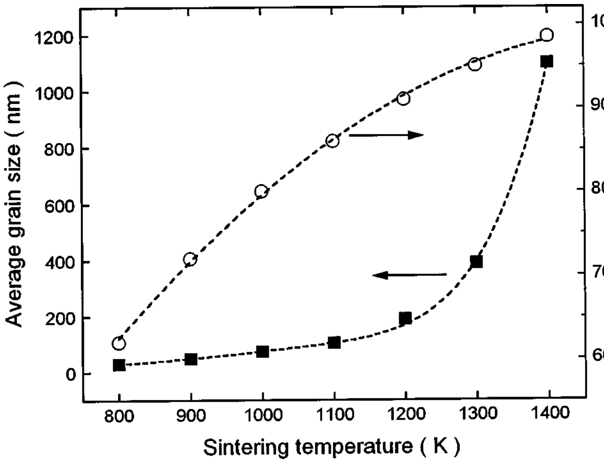

FIG. 2. Sintering temperature dependences of grain size and compactness for sample of $La_{0.85}Sr_{0.15}MnO_3$.

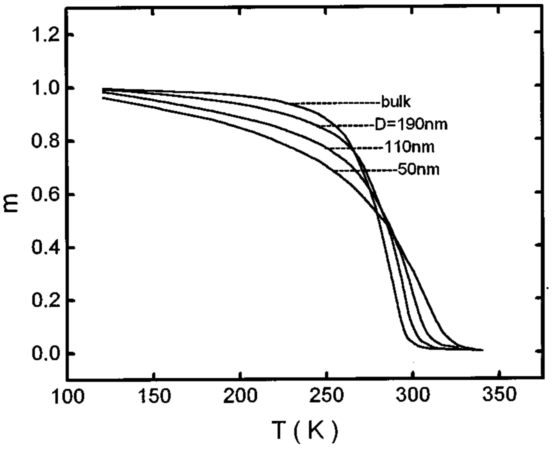

FIG. 3. The temperature dependences of normalized magnetization for the samples of $La_{0.85}Sr_{0.15}MnO_3$ with different grain size.

THEORETICAL RESISTIVITY OF GRANULAR MANGANESE PEROVSKITE

To get the resistivity for the porous granular perovskite system, we assume that (1) A grain of the perovskite can be divided into a body phase and a surface phase. The resistivities of the body and surface phases are ρ_b and ρ_t, respectively; (2) The double-exchange interaction is the sole origin of conductive process in the granular perovskite; (3) The Curie temperature in the surface phase is lower than the T_C in the body phase.[10] Our experimental measurement indicates that the ferromagnetic transition temperature continuously broadens as grain size decreases, as shown in Fig. 3. This phenomenon may provide evidence for assumption (3). Thus, the average relative angle of the local spin in surface $\Delta\theta_s$ is larger than that in body phase $\Delta\theta_b$ at a given temperature below T_C, i.e., $\Delta\theta_s \geqslant \Delta\theta_b$ when $T < T_C$.

According to assumption (1), the resistivity for a granular system with compactness c can be written as

$$\rho = \frac{f_b}{c}\rho_b + \frac{f_s}{c}\rho_t, \tag{1}$$

where f_b and f_s are the volume fractions occupied by body and surface, respectively. Denoting the average thickness of the grain surface as w, we have $f_b = (D-2w)^3/D^3$. It gives $f_b \approx 1 - 6w/D$ when $w \ll D$. Noted $f_b + f_s = 1$, we then get

$$\rho = \frac{1}{c}\left[\rho_b\left(1 - \frac{6w}{D}\right) + \rho_t \frac{6w}{D}\right]. \tag{2}$$

If the interface, namely the surfaces between neighboring grains together with the intergranular distance, is considered as the intergrain barrier, as shown in Fig. 4, ρ_t is then the tunnel resistivity. Apparently, the intrinsic and interfacial tunneling transport properties are reflected by ρ_b and ρ_t, respectively, and they should depend, respectively, on the magnetic configurations in core and surface. Letting t denote

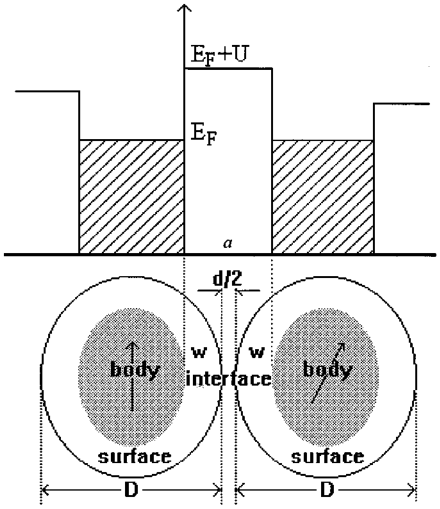

FIG. 4. Schematic illustration of two grains of perovskite separated by intergrain barrier, where $a=2w+d/2$ is the barrier width.

the tunneling probability, we have $\rho_t=\kappa\xi/t$, where κ is a constant and ξ may be called the *double-exchange fraction*. In view of assumption (2), two neighboring grains can be electrically connected only when the intergrain distance is small enough to make the atoms, respectively, located on the edges of two grains (1) overlap each other partly, and (2) form an Mn-O-Mn bond. The former demands the intergrain distance to be about $d/2$, where d is the bond length of Mn-O-Mn, and the latter can be satisfied only when an Mn^{+} ion and an O^{-} ion, respectively, sit at the two sides of a connective point of neighboring grains. For $La_{0.85}Sr_{0.15}MnO_3$, the probability in that case is not greater than 3/25. Moreover, considering surface pollution, such as surface segregation, the probability for double exchange at a given connective point would become further smaller. The surface pollution should be proportional to the number of the most surface atoms, therefore ξ can be simply written as $\xi\propto 1/D$. We accordingly have

$$\rho=\frac{1}{c}\left[\rho_b\left(1-\frac{6w}{D}\right)+\kappa\,\frac{6w}{D^2}\,\frac{1}{t}\right]. \tag{3}$$

The intergrain tunneling probability t can be estimated from the early discussion on tunneling theory of spin-polarized electrons[5]

$$1/t=1+[(E_F+U)^2/4E_FU)]\sinh^2(\beta a), \tag{4}$$

where E_F is Fermi energy of itinerant electrons, U is the barrier height above the Fermi surface, $a(=2w+d/2)$ is the barrier width (see Fig. 3), $\beta=[2mU/\hbar^2]^{1/2}$, m is the electronic mass, and $\hbar$ is Planck's constant divided by 2π. When βa is much greater than 1, Eq. (4) can be simplified as

$$\begin{aligned}\frac{1}{t}&=1+\frac{(E_F+U)^2}{16E_FU}\exp(2\beta a)\\&\approx\exp(2\beta a).\end{aligned} \tag{5}$$

We can then replace Eq. (3) by

$$\rho=\frac{1}{c}\left[\rho_b\left(1-\frac{6w}{D}\right)+\frac{6w\kappa}{D^2}\exp(2\beta a)\right]. \tag{6}$$

The next step is to express the barrier height U in terms of measurable quantities. According to the theory of double exchange, the hopping amplitude for an itinerant electron, which comes from the $3d$ shell e_g orbit of Mn^{3+} ion, between neighboring Mn ions is given by $\widetilde{t}_{i,j}=t_{iJ}\cos(\Delta\theta/2)$, where $t_{i,j}$ is the transfer integral between neighboring Mn sites. For the body and surface phases, we have

$$\widetilde{t}_{b(i,j)}=t_{b(i,j)}\cos(\Delta\theta_{b(i,j)}/2),$$

$$\widetilde{t}_{s(i,j)}=t_{s(i,j)}\cos(\Delta\theta_{s(i,j)}/2).$$

The double-exchange energy in the body and surface phases can be, respectively, written as[11]

$$E_{dB}=-Nx\sum_i t_{b(i,j)}\langle\cos(\Delta\theta_{b(i,j)}/2)\rangle, \tag{7}$$

$$E_{dS}=-Nx\sum_i t_{s(i,j)}\langle\cos(\Delta\theta_{s(i,j)}/2)\rangle, \tag{8}$$

where x is the concentration, N is the number of magnetic ions per unit volume, the sum Σ_i extends to the nearest neighbors of the Mn sites, and the $\langle\,\rangle$ symbol represents a thermal average on the possible states of the ionic spins. Thus, the barrier height U should be considered as the difference of the two energies of double exchange, namely $U=E_{ds}-E_{db}$. Combining this with Eqs. (7) and (8) gives

$$\begin{aligned}U=&-Nx\left[\sum_i t_{s(i,j)}\langle\cos(\Delta\theta_{s(i,j)}/2)\rangle\right.\\&\left.-\sum_i t_{b(i,j)}\langle\cos(\Delta\theta_{b(i,j)}/2)\rangle\right]\\=&Nx[\Phi_B\cos(\Delta\theta_b/2)-\Phi_S\cos(\Delta\theta_s/2)],\end{aligned} \tag{9}$$

where $\Phi_B=\Sigma_i t_{b(i,j)}$ and $\Phi_S=\Sigma_i t_{s(i,j)}$. Inserting Eq. (9) into Eq. (6), yields

$$\begin{aligned}\rho=\frac{1}{c}&\left\{\rho_b\left(1-\frac{6w}{D}\right)+\frac{6w\kappa}{D^2}\exp\left[b\left(\Phi_B\cos\frac{\Delta\theta_b}{2}\right.\right.\right.\\&\left.\left.\left.-\Phi_S\cos\frac{\Delta\theta_s}{2}\right)^{1/2}\right]\right\},\end{aligned} \tag{10}$$

where $b=(2w+d/2)\sqrt{2mNx/\hbar^2}$. Furthermore, we make use of the following relation:[11]

$$\langle\cos(\Delta\theta_{i,j}/2)\rangle=(3+2m^2)/5, \tag{11}$$

respectively, to the body and surface phases, where m is the magnetization normalized to the saturation value. We then get

$$\cos(\Delta\theta_b/2)=(3+2m_b^2)/5, \tag{12}$$

$$\cos(\Delta\theta_s/2)=(3+2m_s^2)/5, \tag{13}$$

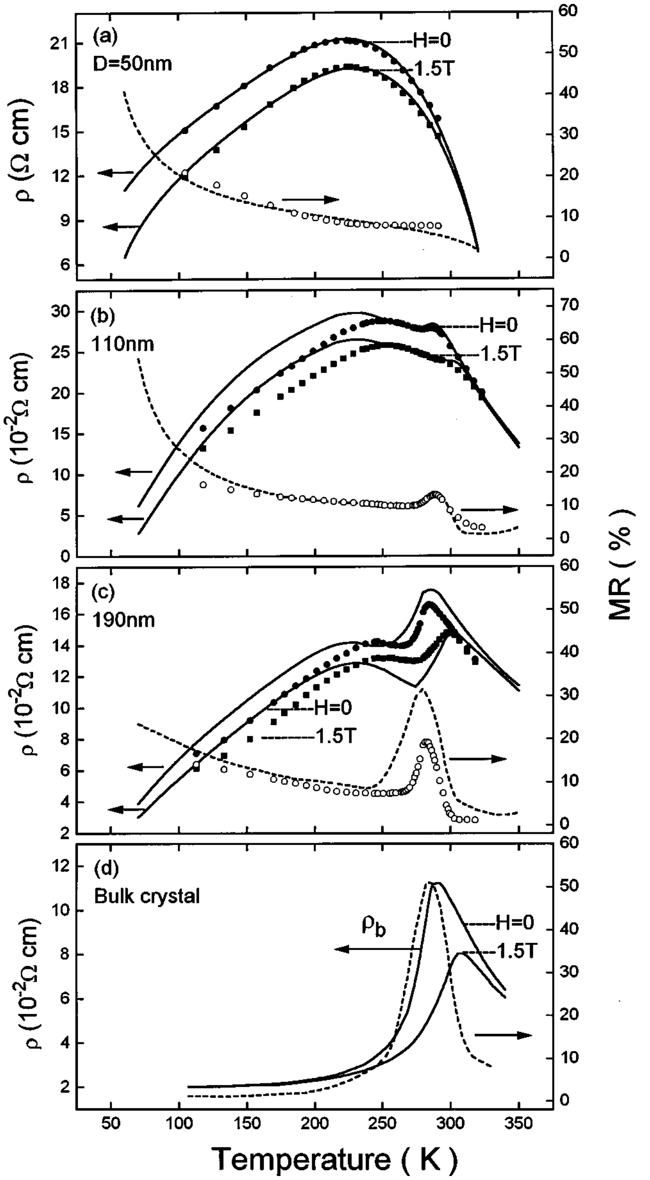

FIG. 5. (a), (b), and (c) Temperature dependences of resistivity at zero field (solid circles) and under an applied field of $H=1.5$ T (solid squares), and the corresponding temperature dependences of MR for the samples of $La_{0.85}Sr_{0.15}MnO_3$ with different grain size from experiments (open circles) and calculations (dashed lines) by Eq. (16); (d) the experimental data of ρ vs T and MR vs T for a bulk crystal sample of $La_{0.85}Sr_{0.15}MnO_3$.

where m_b and m_s are the normalized magnetizations in body and surface, respectively. They should meet the following relation:

$$m=(1-6w/D)m_b+(6w/D)m_s. \tag{14}$$

Additionally, we use the molecular field approximation to surface

$$m_s=C(H/M_0+\lambda m)/T, \tag{15}$$

where C is the Curie constant, M_0 is the saturated magnetization, H is the applied field, λ is the proportional constant of the molecular field. The product $C\lambda$ can be considered here as the surface Curie temperature T_{Cs}. Collecting the results from Eq. (10) to Eq. (14), we consequently obtain

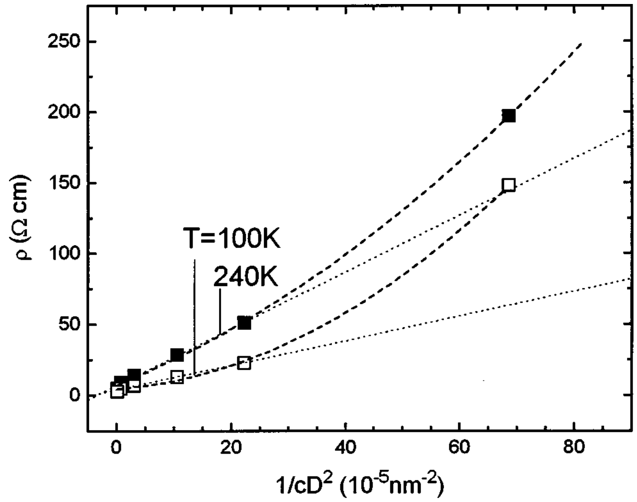

FIG. 6. The resistivity as a function of $1/cD^2$ for the granular $La_{0.85}Sr_{0.15}MnO_3$ system. The square points and the dashed curve are from experiment.

$$\rho=\frac{1}{c}\left(\rho_b\left(1-\frac{6w}{D}\right)+\frac{6w\kappa}{D^2}\exp\left\{b\left[f+\frac{2\Phi_B}{5}\frac{(Dm-6wm_s)^2}{(D-6w)^2}-\frac{2\Phi_S}{5}m_s^2\right]^{1/2}\right\}\right), \tag{16}$$

where $f=(3/5)(\Phi_B-\Phi_S)$, m_s should be obtained through Eq. (15). Roughly take $\Phi_B=\Phi_s$ and $6w\ll D$, it yields

$$\rho\approx\frac{1}{c}\left(\rho_b\left(1-\frac{6w}{D}\right)+\frac{6w\kappa}{D^2}\exp\left\{\sigma\left[\frac{D^2m^2}{(D-6w)^2}-m_s^2\right]^{1/2}\right\}\right), \tag{17}$$

where $\sigma=(2w+d/2)\sqrt{4mNx\Phi_B/5\hbar^2}$. Equations (16) or (17) express just the resistivity for the granular magnetic perovskite. It is worthwhile to point out that only double-exchange-type interfacial tunneling has been included in deriving ρ_t, while the intrinsic transport properties should be reflected by ρ_b, which can be obtained from experimental data for crystals.

EXPERIMENTAL RESULT AND DISCUSSION

It is generally believed that a surface includes about four or five atom layers. Taking the thickness per atom layer as a bond length of Mn-O-Mn d, the thickness of surface w could be about 2 nm in magnitude.

Figure 5 shows the ρ-T curves at zero field and under an applied field $H=1.5$ T obtained from experiments (solid squares and circles) and calculated from Eq. (16) (solid lines), together with the corresponding MR-T curves from experiment (open circles) and calculation (dash lines), for the samples with different grain sizes, where MR$(=[R(0)-R(H)]/R(0))$ is the value of magnetoresistance. The ρ_b-T curve in Fig. 5 was obtained through measuring a bulk crystal sample of $La_{0.85}Sr_{0.15}MnO_3$ which was prepared through a standard ceramic method. The magnetization m for calculating ρ was also obtained from experimental data, as shown in Fig. 3. It can be seen that the calculated curves are basically compatible with the measured results, especially for the samples with smaller grain size.

From Eq. (16), we can conclude that (1) The resistivity peak at temperature well below T_C, which can be seen in Fig. 5 and in Ref. 7, does not mean a metal-insulator-like transition for the granular system but reflects the interfacial tunneling due to the difference in magnetic order between surface and core. The peak temperature can be obtained from the relation $\partial\rho/\partial T=0$. From earlier discussions, we can expect that the resistivity should decrease with increasing temperature when the surface becomes a paramagnetic state $(m_s\approx 0)$, while the body phase is still in the ferromagnetic state. As a result, the low-T resistivity peak appears at T_{Cs}, the surface Curie temperature, approximately; (2) At a given temperature lower than T_C, the resistivity is roughly proportional to $1/cD^2$ when the grain size is not very small, considered $w\ll D$, then $D/(D-6w)$ basically invariant in that case [see Eq. (17)]. In other words, we can neglect the change of the barrier height versus grain size in that case. However, the rule may be deviated somewhat when the grain size is so small that the change of intergrain barrier cannot be neglected. This point can be seen in Fig. 6. Evidently, the resistivity growth with decreasing grain size mainly originates from surface expansion and conductive channels reduction; (3) Spin-dependent tunneling and intrinsic transport properties can simultaneously exist in the present system. And the two effects can be simultaneously observed in a sample with a suitable grain size. This is just the case displayed by the double-peak-type ρ-T curves in Figs. 5(b) and 5(c). Otherwise, the extreme cases, i.e., the tunnel-type or the intrinsic effect, are observed, as shown in Figs. 5(a) and 5(d), respectively; (4) The magnetoresistance effect well below T_C can be attributed to the ionic spins in the surface being aligned by external field, this causes the magnetic difference between body and surface, then the barrier height of the intergrain decreases.

ACKNOWLEDGMENT

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