Transport and magnetic properties in ferromagnetic manganese-oxide thin films

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Abstract

The transport and magnetic properties in ferromagnetic manganese-oxide thin films are studied based on the model of the coupling between the mobile d-electrons and the core spins in Mn ions. The spontaneous magnetization and the resistivity are obtained for various magnetic fields and temperature. The resistivity in absence of magnetic field and the magnetoresistance exhibit maxima near the Curie temperature, the applied magnetic field

moves the position of the resistivity peak to high temperature and suppresses the peak value, which agree with the experimental results. The Hall resistivity is predicted to exhibit maximum near the Curie point. The pressure effect of the magnetoresistance can also be explained qualitatively in this mechanism. The colossal magnetoresistance in ferromagnetic manganese-oxide thin films is attributed to the spin-correlation fluctuation scattering and the low dimensional effect.

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I. INTRODUCTION

In perovskite-type transition-metal oxides, the strong correlated electron systems exhibit many remarkable phenomena. One example of such systems is the high temperature superconductivity in cuprate-oxides $La_{2-x}R_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$. Recently very large negative magnetoresistance (MR), so called colossal magnetoresistance (CMR), has been observed in perovskite-like $La_{1-x}R_xMnO_3$ and $Nd_{1-x}R_xMnO_3$ (R =Ba, Sr, Ca, Pb, etc.) [1 - 4] ferromagnetic metallic thin films. Especially in epitaxial $La_{1-x}Ca_xMnO_3$ and $Nd_{1-x}Sr_xMnO_3$ thin films, the MR ratios under an applied magnetic field, $(R_B - R_0)/R_B$ (B=6 T), are observed more than $10^5\%$ at low temperature, which are much larger than those in ferromagnetic/nonmagnetic metallic multilayers, the resistivity decreases from a typical insulate or semiconductive behavior to metallic behavior. More recently a giant magnetoresistance ratio is also observed to be in excess of $10^4\%$ for polycrystalline La-Y-Ca-Mn-O compounds [5]. Such CMR change provides promising applications such as in magnetic sensor, in magnetic recording media, etc. . It also presents another possible MR mechanism which is very different from that in magnetic multilayer.

Similar to the high temperature superconductive material La_2CuO_4, the undoped $LaMnO_3$ is an antiferromagnetic [6] or a ferromagnetic [7] insulator. X-ray photoemission spectroscopic, and ultraviolet photoemission spectroscopic experiments on pure $LaMnO_3$ [8] show that the on-site Coulomb energy of Mn 3d states is U_{dd}=4.0 eV, the hybridization energy between Mn-O is Δ=3.8 eV, which indicates that La-R-Mn-O compounds are mediated-

strength correlated electron systems. After substitution of some trivalent La ions by Ca, Sr, Pb, Ba or other divalent ions, a fraction of trivalent manganese ions coexist with tetravalent manganese ions in the system, the valence fluctuation of Mn^{+3} and Mn^{+4} is thus assumed to be important and may give rise to the hopping conductivity and other transport properties of these systems [9]. After doped by divalent elements R in these compounds, $La_{2-x}R_xCuO_4$ and $La_{1-x}R_xMnO_3$ become metallic for heavy doping. $La_{2-x}R_xCuO_4$ may lose its resistivity below the superconductive transition temperature, while $La_{1-x}R_xMnO_3$ exhibits giant magnetoresistance around the Curie temperature. The superconductivity in $La_{2-x}R_xCuO_4$ and the CMR effect in $La_{1-x}R_xMnO_3$ are supposed to be related to the magnetic interaction.

The mechanism of CMR has been studied by some researchers. Several mechanisms have been suggested to explain these more than a thousandfold change of resistivity observed in these compounds, such as the double-exchange and magnetic polaron hopping [1-4], the spin spiral states [10], the Jahn-Teller effect [11] and the spin disorder scattering [12]. Some researchers [1-5,13,14] suggested that the magnetic polaron transfer mechanism may play a role for the CMR effect in these systems. As in $La_{1-x}R_xMnO_3$ compounds, the semiconductive behavior in conduction and the negative temperature coefficient of the resistivity above T_c seem to support the thermal hopping of the magnetic polarons [2,13], however, the quantitative calculation shows that there exists considerable discrepancy between experimental and theoretical results for the resistivity in magnetic field [11]. Besides,it seems that magnetic polaron is hardly to form for heavy doped $La_{1-x}R_xMnO_3$ and $Nd_{1-x}R_xMnO_3$ systems ($x > 0.3$). Another suggestion is that the CMR is related to the spin disorder scattering

mechanism due to the field-induced change in the canting angle of manganese spins [12]. A strong external magnetic field will induce the spin canting of Mn ion. However, as indicated by the experiments [3,4], the magnetic field about 1 *Tesla* can saturate the magnetization, further increasing magnetic field does not change the spin configuration significantly, so the spin-disorder scattering shouldn't change the resistivity by several orders in magnitude. Therefore the spin disorder scattering may be not the main mechanism of the CMR in these systems.

As seen from the above discussion, these mechanisms did not give a satisfactory explain regarding the CMR behavior under strong magnetic field over all the temperature ranges. In this paper, we present another possible mechanism of the CMR in these ferromagnetic $La_{1-x}R_xMnO_3$ and $Nd_{1-x}R_xMnO_3$ thin films. This paper is organized as follows, the proposed model and formalism is described in Sec.II., Sec.III gives the results and discussions , and the conclusion is given in Sec.IV.

II. MODEL AND FORMALISM

Because of the crystalline field effect, the 3d energy level of the Mn ion in $La_{1-x}R_xMnO_3$ and $Nd_{1-x}R_xMnO_3$ compounds is split into a low-energy triplet(t_{2g}) and a high-energy doublet(e_g), therefore three d-electrons of Mn ions will fill the low d- t_{2g} band with same spin, and the extra d-electrons in Mn^{+3} will fill in to the higher d-e_g band. These two bands are separated about 1.5 eV [15]. The three electrons in the filled d-t_{2g} band form a

localized core spin of S=$\frac{3}{2}$ by Hund's rules [9,11,12], these core spins tend to align parallelly through the double exchange interaction between Mn^{+3} ions and Mn^{+4} ions [9] and can be considered as a localized ferromagnetic background. The electrons in d-e_g band are mobile by hopping between Mn^{+3} and Mn^{+4} ions as an itinerant electron which is responsible for electric conduction in these systems. The Coulomb interaction of the localized d-electrons and the conduction d-electrons can be attributed to a s-d like exchange coupling. In this model, the Hamiltonian of this system is described as:

$$H = H_0 + V \tag{1}$$

$$H_0 = \sum_{k\sigma}(\epsilon_k - \sigma\mu_B B)c^\dagger_{k\sigma}c_{k\sigma} - \sum_{<ij>} A\mathbf{S}_i \cdot \mathbf{S}_j - \sum_i g\mu_B B S^z_i \tag{2}$$

$$V = -\frac{J}{N}\sum_{ikq}\sum_{\mu\nu} e^{i\mathbf{q}\mathbf{R}_i}\mathbf{S}_i \cdot c^\dagger_{k+q\mu}\sigma_{\mu\nu}c_{k\nu} \tag{3}$$

where H_0 describes the bare energies of the mobile d-electrons and the ferromagnetic background, V is the interaction between the mobile electrons and the localized core spins S_i on ith site. In Eq.(2), ϵ_k is the energy spectrum of mobile electrons with respect to the Fermi energy E_F, A is the effective ferromagnetic exchange constant between manganese ions, and only the nearest-neighbor interaction is considered. -gμ_BB is the Zeemann energy in the magnetic field $\mathbf{B}$. In Eq.(3) the mobile electron is scattered from state kν to state k+qμ by the localized spin $\mathbf{S_i}$; J is the coupling constant between the mobile electrons and the core spins. We notice that in the external magnetic field and in the internal molecular field of ferromagnetically ordered state, the mobile (or conduction) band of the system will be split. This splitting will move the position of the conduction band with respect to the Fermi surface, therefore the mean-field spectrum of the conduction electron with state $\mathbf{k}\sigma$ is

$\epsilon_{k\sigma} = \epsilon_k - \sigma(\mu_B B + J < S^z >)$.

The scattering rate of the conduction electrons scattered by the localized spins is:

$$\omega = \frac{2\pi}{h} \sum_m | < f|V|m > |^2 \delta(E_f - E_m) \tag{4}$$

where $|f>$ refers the final equilibrium state and $|m>$ denotes the possible intermediate state of the system during the scattering process. Since the conduction electrons are scattered into various intermediate states, summing over all the intermediate states of the system at temperature T, one can obtain:

$$\omega = \frac{\pi}{h} \frac{J^2 D(0)}{4} \sum_{kq\sigma} f_{k\sigma}(1 - f_{k\sigma}) f_{k+q\bar{\sigma}}(1 - f_{k+q\bar{\sigma}})[< S_q^- S_{-q}^+ > + \tag{5}$$

$$< S_q^+ S_{-q}^- > + 8 < S_q^z S_{-q}^z >].$$

Where D(0) is the density of states of the conduction electrons near the Fermi surface, Dirac-Fermi distribution function f_k is $f_k = 1/[e^{\beta(\epsilon_k - \epsilon_F)} + 1]$. As pointed out above, the magnetic interaction dominates the properties in thses systems, the resistivity from other scattering might be neglected. The lifetime of the conduction electrons between two scattering is $\tau = \omega^{-1}$, therefore the resistivity is given by the Drude formula,

$$\rho = \frac{m^*}{ne^2\tau} = \frac{m^*\omega}{ne^2}. \tag{6}$$

where n is the carrier density, m^* is the effective mass of carriers. Accordingly, for certain doped concentration, the effective mass and the concentration of carriers are almost fixed, hence the resistivity can be determined by the scattering rate of the conduction electrons. One can obtain the temperature-dependent and field-dependent resistivity ρ(T,B) as

$$\rho(T, B) = \sum_q F(q, T, B)[< S_q^- S_{-q}^+ > + < S_q^+ S_{-q}^- > + 8 < S_q^z S_{-q}^z >] \tag{7}$$

where the temperature factor F(q,T,B) is defined as:

$$F(q,T,B) = \frac{\pi D(0) m^* J^2}{4hne^2} \sum_{k\sigma} f_{k\sigma}(1 - f_{k\sigma}) f_{k+q\bar{\sigma}}(1 - f_{k+q\bar{\sigma}}). \tag{8}$$

The resistivity mainly depends on the temperature factor F(q,T,B) and the spin-spin correlation functions (longitudinal and transverse), $< S_q^z S_{-q}^z >$ and $< S_q^+ S_{-q}^- >$. When T << T_c, or $< S_z > \approx$ S, the long-range magnetic order exists, both the transverse and the longitudinal correlations have the same order of magnitude contributions to the resistivity. The transverse spin-spin correlation functions are chosen from Ref. [16]:

$$< S_q^+ S_{-q}^- > = \frac{2 < S^z >}{exp(\beta\omega_q) - 1} \tag{9}$$

where $\omega_q = g\mu_B + zA(1 - \gamma_q)$ is the ferromagnetic spin wave spectrum, and the longitudinal spin-spin correlation function $< S_q^z S_{-q}^z >$ is obtained by the Green's function technique and it may be rather complicated when T < T_c. When T >> T_c, or $< S_z > \approx 0$, the long-range magnetic order doesn't exist, and only the longitudinal correlation $< S^z S^z >$ plays a role [17],

$$< S_q^z S_{-q}^z > = \frac{CT}{T - T_c - T_c(\gamma_q - 1)} \tag{10}$$

where C is the Curie constant and γ_q the structure factor. when T $\approx$ T_c, the spin-spin correlation function near the transition temperature is also chosen from Ref.[16].

For the case of steady-state, we can easily derive the Hall conductivity as:

$$\sigma_H = \frac{\sigma^2}{ne} B_{eff}, \tag{11}$$

or the Hall resistivity as

$$\rho_H = \frac{ne}{B_{eff}} \rho^2, \tag{11'}$$

where B_{eff} is an effective field,

$$B_{eff} = |\mathbf{B} + zA \ < \mathbf{S} \ > /\mu_B|.$$

From Eqs.(7) and (8) we can qualitatively understand the temperature-dependence of the resistivity. Since

$$F(q,T,B) \propto \sum_{k\sigma} f_{k\sigma}(1-f_{k\sigma})f_{k+q\bar{\sigma}}(1-f_{k+q\bar{\sigma}})$$

At zero-temperature limit (T $\rightarrow$ 0 K), F(q,T,B) approaches zero because of the Pauli exclusion principle, so $\rho(T \rightarrow 0) \approx 0$. However, at high temperature limit (T $>>$ T_c, E_F), F(q,T,B) $\approx$ *const*, the resistivity is entirely determined by the spin-spin correlation functions, and the correlation functions are independent of the magnetic field. In this case the resistivities under different applied magnetic fields should approach to the same value. In the mediated temperature range (0<k_BT << E_F), F(q,T, B) doesn't vanish and the spin-spin correlation functions are also finite, then the resistivity from the spin-correlation-dependent scattering is not zero. Especially, at the temperature near the Curie point (k_BT $\approx$ T_c << E_F), the temperature factor F(q,T,B) is smooth, the spin-spin correlation functions have maxima, therefore the resistivity exhibits a maximum at the transition temperature when the magnetic field is absent.

III. RESULTS and DISCUSSIONS

We have evaluated the resistivity ρ(T ,B) according to Eqs.(7) and (8) to compare with the experimental data. We should point out that in order to carry out a quantitative calcu-

lation, we need the exact forms of the transverse and the longitudinal spin-spin correlation functions over all the temperature region and under any magnetic field. However, such exact correlation functions are not available for two and three dimensional Heisenberg ferromagnets since the exact solution of the Heisenberg ferromagnet hasn't yet been obtained [16]. In this work the approximate forms of the longitudinal and the transverse correlation functions in Eq.(9) (T< T_c) and the longitudinal correlation function in Eq.(10) (T> T_c) are adopted for our calculations. In quasi-two-dimensional systems, the lattice constant is a=3.89 $\mathring{A}$, and the coordinate number is z=4. Although the theoretical parameters is chosen from La-Ca-Mn-O system only, the results may be applied in other similar systems.

The temperature-dependence of the spontaneous magnetization in different magnetic fields is calculated self-consistently and shown in Fig.1. The ferromagnet-paramagnet transition occurs within a wide temperature range in Fig.1. Because of the critical fluctuation and the low-dimensional character in z-direction, the spontaneous magnetization has a long tail, the ferromagnet-paramagnet transition is broaded. Although the exchange integral is the same as that in the bulk, the Curie temperatures of these quasi-two dimensional systems decrease significantly.

The temperature-dependence of the diagonal resistivity in La-Ca-Mn-O systems is shown in Fig.2. The resistivity in different magnetic fields exhibits maximum within the magnetic transition region, where the spin-correlation scattering rate ω is very large. With the increase of the magnetic field, the resistivity peak is driven to higher temperature and the maximum value is reduced. This can be explained as the following. A strong field aligns all spins in the

systems and suppresses the correlation fluctuation of spins at different sites, thus reduces the spin correlation scattering between the conduction electrons and the local spins. Because the applied field stabilizes the magnetic order and to destroy the magnetic order needs much high temperature (about Zeemann energy -gμ_BB), the maximum of the correlation function are be moved to higher temperature region in a strong applied magnetic field. These unusual transport behaviors due to the spin-spin correlation fluctuation scattering agree with the recent experiment [7]. The resistivity maximum in absence of magnetic field appears exactly at the Curie point.

As pointed out in Sec.II, because of the thermal effect, the high-temperature resistivity should tend to the same value with respect to different magnetic field, however this cannot been seen clearly in Fig.2. It is believed that this is due to the approximation we have used in the calculations. In high temperature region, the thermal fluctuation is strong enough to destroy the spin alignment due to the applied magnetic field and the exchange interaction, so the effect of the magnetic field is smaller over the high temperature region.

The dependence of the Hall resistivity on temperature is shown in Fig.3. The electrons moving in the transverse direction are also scattered by the spin-spin correlation fluctuation near the critical point, therefore the Hall resistivity also exhibits a maximum. In the meantime, the magnetic field **B** affects the cyclotron movement of the conduction electrons, the Hall resistivity decreases with increasing of **B**, so the maximum of the Hall resistivity will not appear at the same position as that of the diagonal resistivity, the position of the maximum moves to lower temperature. Since the transverse movement of the conduction

electrons is affected both by the magnetic field and by the spin-correlation scattering, the change of the Hall resistivity may be much larger than that of the diagonal resistivity with the variation of the magnetic field.

The field-dependence of the diagonal and the Hall resistivities at different temperature are shown in Fig.4 and Fig.5 respectively. We can see that the diagonal and the Hall resistivities decrease monotonously when the magnetic field increases. The results of the diagonal resistivity agree with the experiments [1-4]. We can see from Fig.4 that the diagonal resistivity ratio $\Delta R_B/R_B$ at field B=6 T can be as high as 1000%. The descent resistivity with the increase of magnetic field is caused by the suppress of the spin-spin correlation fluctuation scattering .

The resistivity due to the $s-d$ exchange interaction expressed in Eq.(3) was studied by a number of researchers, such as Fisher [18], Kubo and Ohata [19], Searle and Wang [20], and Furukawa [12]. Fisher's work does not consider the finite size character and the spin-splitting of the conduction electrons from the internal molecular field and the external magnetic field, which may be important for the MR effect in ferromagnetically ordered state. The others' studies disregard the spin-spin correlation functions and contain only the resistivity from spin-flip scattering. The present work has shown that the spin-spin correlation scattering is essential and should be responsible for the CMR. The effect due to the spin-spin correlation and the spin fluctuation is considerable large near the Curie point. These theoretical results agrees with the experimental data very well [1-4,13,14].

Another interesting effect is the pressure-dependence of the CMR in these systems, which

is reported recently [21, 22]. The pressure has the similar influence on the resistivity as the magnetic field does, this can be explained qualitatively within the present model. When the pressure is increased, the exchange integral between Mn ions also increases, correspondingly, the Curie temperature T_c raises and the spin correlation fluctuation is suppressed, the resistivity maximum will move to high temperature region due to the presence of pressure. Therefore the pressure has similar effect on the resistivity as the magnetic filed does.

IV. CONCLUSION

From the above discussions, we can see that, (a) If the measured temperature is far below or above the critical point T_c, the MR ΔR_B is smaller. (b) If the critical transition range is very wide, a CMR can be observed within a wide temperature region. These observations are very important in applications. It suggests that if we want to find or explore a new material which can be used at the room temperature for magnetic recording and sensitive detection, the critical point of this material should be near the room temperature, and it should be low dimensional system, such as thin film. Especially, for the magnetic/nonmagnetic multilayers, if the MR is measured near its transition temperature, it would be expected a much higher MR ratio than that observed currently. (c) the temperature dependence of the Hall resistivity will exhibit a maximum below the peak position of the diagonal resistivity. Further experiments is desired to verify these predictions.

In conclusion, we have calculated the transport properties, such as the diagonal and the Hall resistivity, and magnetic properties of the ferromagnetic manganese-oxide compounds,

which are in agreement with the experimental data. The the CMR in La-R-Mn-O and Nd-R-Mn-O compounds near the phase transition point can be attributed to the spin-spin correlation scattering between the conduction electrons and the localized spins. The CMR effect in thin films is enhanced by the low dimensional effect.

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Figures Captions

Fig.1 . Temperature-dependence of the spontaneous magnetization in different magnetic fields for La-Ca-Mn-O systems. Parameters: A=245 K, J=500 K. (1) B=1.0 T, (2) B=15 T.

Fig. 2. Temperature-dependence of the diagonal resistivity in different magnetic fields for La-Ca-Mn-O systems. Theoretical parameters: A=245 K, J=500 K. (1) B=1.0 T, (2) B=15 T

Fig. 3. Dependence of the Hall resistivity on the temperature in different magnetic fields. Theoretical parameters: A=245 K, J=500 K. (1) B=1 T, (2) B=15 T

Fig. 4. Field-dependence of the diagonal resistivity for La-Ca-Mn-O systems. MR ratio is 1000% for B=6 T. Theoretical parameters: A=245 K, J=500 K, (1) T=50 K, (2) T=100 K.

Fig. 5. Dependence of the Hall resistivity on the magnetic field for La-Ca-Mn-O systems. Theoretical parameters: A=245 K, J=500 K, (1) T=50 K, (2) T=100 K.