Paramagnetic anomalies above the Curie temperature and colossal magnetoresistance in optimally doped manganites

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Magnetoresistance (MR) and paramagnetic (PM) resonance experiments for $(La_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ ($x=0.15$ and 0.2) show that associated with PM anomalies at $T \leqslant T_{onset}$, the MR becomes observable, especially, both MR and resonance linewidth exhibit similar T-dependent behavior in the temperature range of $T_C \leqslant T \leqslant T_{onset}$, suggesting the evidence of the same underlying origin for both MR and PM anomalies. We argue both PM anomalies and sizable MR to be due to a substantial increase in the volume fraction of the more conductive ferromagnetic domains.

The discovery of colossal magnetoresistance (CMR) in mixed manganese oxides $La_{1-x}B_xMnO_3$ (B=alkaline-earth cation) has aroused renewed interest in these systems.[1] It has been generally found that for the optimally doped oxides ($x \sim 1/3$), the largest CMR effect appears near the insulator-metal (IM) transition, while the transition is accompanied by a simultaneous paramagnetic-ferromagnetic (PM-FM) transition at almost the same temperature (i.e., the Curie temperature T_C). Therefore, one believes that both the IM transition and the CMR are magnetic in origin. Traditional understanding of transport and magnetic properties is generally based on the double exchange (DE) mechanism.[2] However, theoretical considerations[3] indicate that the DE mechanism alone could not quantitatively account for the observed transport properties, and other effects should be included. Electron-phonon coupling,[4] small polarons,[5] magnetic polarons[6], and spin polarons[7] have been commonly invoked in discussing the transport behavior in the manganese perovskites. Nevertheless, understanding the cause of CMR is still a matter of controvery. In the present work, we report magnetoresistance measurements along with electron paramagnetic resonance (EPR) experiments for $(La_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ ($x=0.15$ and 0.2). It is found that in the anomalous PM regime, the MR shows a T-dependent behavior similar to that for the resonance linewidth against temperature, providing an important clue to the understanding of CMR.

Ceramic samples with nominal composition of $(La_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ ($x=0.15$ and 0.2) were prepared by the standard solid-state reaction. The phase purity for each sample was checked by x-ray powder diffraction and no spurious phase was found. Resistance (R) as a function of temperature was measured in applied magnetic fields of $H=0$ and 5 T by the standard four-probe method. EPR experiments were performed at 9.46 GHz using a Bruker (ER-200D-SRC) reflection X-band-type spectrometer at various constant temperatures by sweeping the magnetic field from 0 to 6000 Oe. The temperature for each measurement was controlled to an accuracy of ± 0.1 K using the Bruker N_2 temperature controller.

Figure 1 shows the R-versus-T dependence measured in magnetic fields of $H=0$ and 5 T for both samples. From the zero-field curve, it can be seen that each sample at high temperatures exhibits an activated insulating behavior and undergoes a transition to metallic behavior at low temperatures. The transition temperature T_C is approximately determined to be $\sim$127 K and $\sim$91 K for samples of $x=0.15$ and 0.2, respectively. The application of the magnetic field clearly shifts T_C to a higher temperature and causes a substantial reduction in resistance. This results in the so-called CMR effect. We define the magnetoresistance (MR) as

$$\mathrm{MR}=\frac{R(T,H=0)-R(T,H)}{R(300\ \mathrm{K},H=0)}. \tag{1}$$

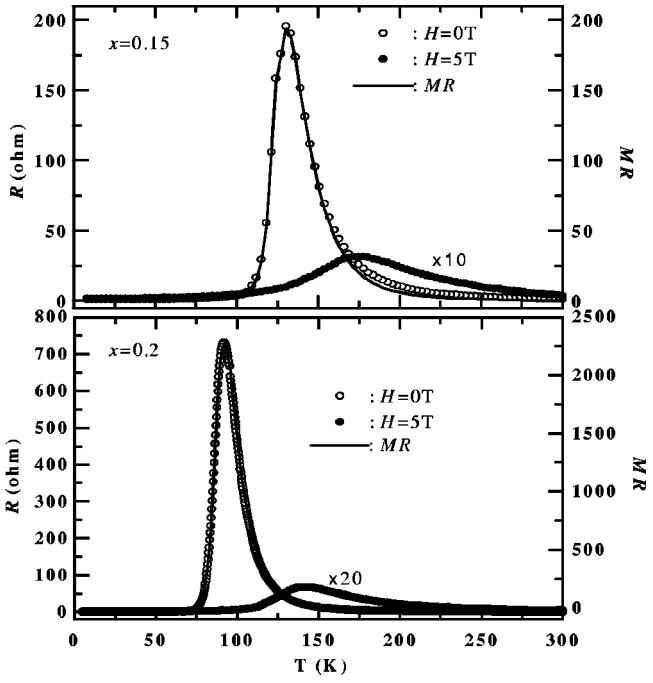

FIG. 1. R versus T curves of $(La_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ ($x=0.15$ and 0.2) measured in magnetic fields of 0 and 5 T. The MR as a function of temperature is also shown (right-hand axis).

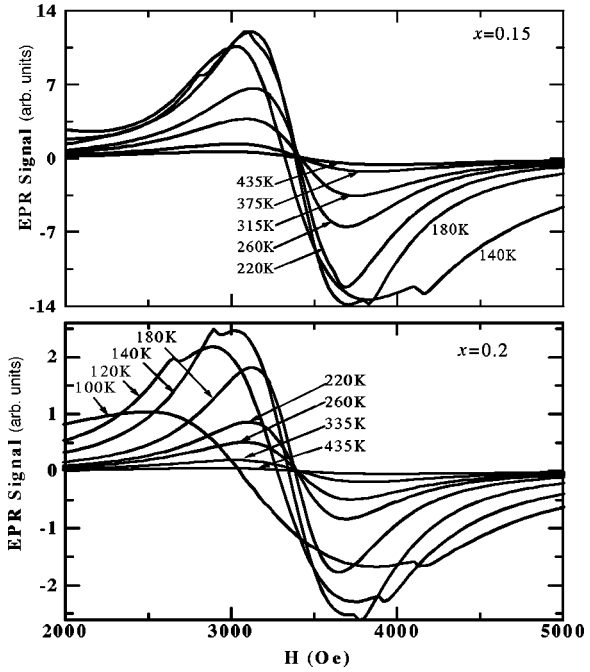

FIG. 2. EPR spectrum as a function of temperature for $(La_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ ($x=0.15$ and 0.2).

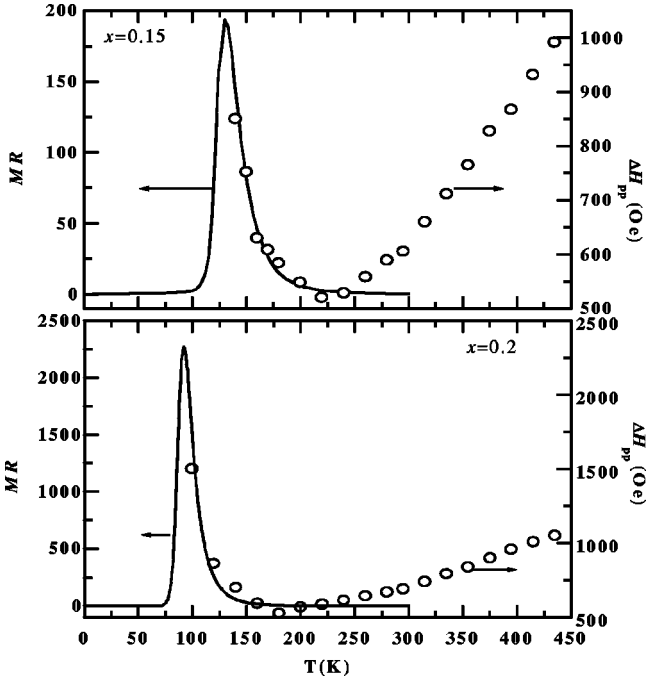

FIG. 3. MR as a function of temperature together with $\Delta H_{pp}(T)$ obtained from EPR experiments for $(La_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ ($x=0.15$ and 0.2).

The thus obtained MR as a function of T is also plotted in Fig. 1 for the field of $H=5$ T. We can notice that the MR becomes observable only at the intermediate temperature regime near T_C and negligible outside this range. At the intermediate temperature regime near T_C, the MR substantially increases upon cooling, reaches the maximum at $\sim T_C$, and then sharply decreases upon further cooling. The largest MR values are estimated to be $\sim 2\times 10^4\%$ and $\sim 2.3\times 10^5\%$ for $x=0.15$ and 0.2, respectively. One can also notice that the MR shows T-dependent behavior similar to that for the zero-field R against T, suggesting the same underlying physical origin for both the CMR and the IM transition.

Since the IM transition is shown to occur near the Curie temperature,[8] there is every reason to believe that the transition is of magnetic origin. Previous investigations on magnetic properties have generally placed emphasis upon measurements of magnetization below and susceptibility above T_C. From these measurements, one concludes that the optimally doped system shows PM behavior above T_C. However, the question of the ground state at $T>T_C$ is subtle. It has been commonly proposed that the Mn-based oxides with perovskite-related structures can accomplish a dynamic phase segregation that may creat domains of short-range FM ordering within the PM matrix.[9] As a result, the magnetic heterogeneity would be introduced into the system. The measurement of scanning tunneling spectroscopy (STS) directly domenstrates the coexistence of PM and FM regions near T_C.[10] Experiments, such as neutron scattering[11,12] and small-angle neutron scattering[13] measurements, give an evidence for the presence of magnetic heterogeneity above T_C. If this is present, it can be checked with the help of the EPR technique because of its sensitivity to magnetic heterogeneity.

Shown in Fig. 2 are EPR spectra measured at various constant temperatures for both samples. It seems that there exists a distinguishable temperature T_{onset}. This temperature is estimated to be ~ 220 K ($\approx 1.7T_C$) for $x=0.15$ and ~ 180 K ($\approx 2T_C$) for $x=0.2$, respectively. For each sample, the resonance spectrum at high temperatures consists of a single line with a Lorentzian line shape. With decreasing temperature, the resonance field remains constant, the derivative signal intensity greatly increases, and the peak-to-peak linewidth ΔH_{pp} becomes narrow. The symmetric signal with the Lorentzian line shape is maintained at the temperature T_{onset}. Below this temperature, some distortions in resonance behavior occur: the signal does not keep symmetry any longer, the resonance line broadens substantially, and the resonance field clearly shifts to a lower value. These observations suggest that the real PM region corresponds to a temperature range of $T>T_{onset}$, but in the temperature range of $T_C<T<T_{onset}$, the anomalous PM phenomena occur. Similar anomalous PM behaviors were previously also observed[14,15] below $\sim 1.04T_C$ and $\sim 1.2T_C$ for both samples of $La_{2/3}Sr_{1/3}MnO_3$ and $La_{2/3}Ca_{1/3}MnO_3$, respectively.

One can notice that the only difference in systems mentioned above is the average A-site ionic size $\langle r_A\rangle$ which in turn controls the bandwidth (W) of the conduction band. Our results along with the previous observations on both samples of $La_{2/3}Sr_{1/3}MnO_3$ and $La_{2/3}Ca_{1/3}MnO_3$ seem to show that the relative onset temperature (T_{onset}/T_C) for the occurrence of PM anomaly increases substantially with narrowing W. On the other hand, the MR is commonly shown to increase substantially with narrowing W. Also, it is interesting to notice that the T_{onset} determined from the anomalous PM is almost the same as the temperature below which the MR becomes observable. These facts indicate some correlation between the MR and the PM anomaly. Such a correlation becomes clearer if one plots both MR and ΔH_{pp} as functions of temperature in the same figure, which are shown in Fig. 3 for both samples studied here. It can be found that ΔH_{pp} decreases almost linearly with decreasing T and reaches a

minimum at T_{onset}. Its physical origin has been discussed in Ref. 16: it is explained as being caused by both spin-lattice and exchange-narrowing spin-spin interactions. When temperature is decreased from T_{onset}, one finds that ΔH_{pp} increases anomalously with decreasing temperature. On the other hand, a substantial increase in MR occurs in the temperature range of $T_C < T < T_{onset}$. It is interesting to find that in the anomalous PM regime, the MR shows a T-dependent behavior similar to that for ΔH_{pp} against T, indicating the evidence for the same underlying origin of both CMR and PM anomaly.

Manganese perovskites contain both Mn^{3+} and Mn^{4+} ions. Because of the DE, Mn^{3+} ions are ferromagnetically coupled to adjacent Mn^{4+} ions to form Zener pairs (i.e., ''Mn^{3+}-Mn^{4+}'' pairs). At high temperatures, these pairs are isolated and hence the system is still PM as a whole. Goodenough and Zhou[9] called it superparamagnetic (''PM'' for short) to distinguish it from conventional PM systems. As is well known, manganese perovskites can accomplish a dynamic phase segregation that makes Zener pairs condense into FM domains within the ''PM'' matrix. As long as no magnetic correlation exists between the domains, the system is still ''PM.'' On cooling, the FM domains grow in size, or equivalently, the separation distance between adjacent domains becomes shorter. On cooling below T_{onset}, the FM domains themselves are no longer isolated, and one needs to consider the FM coupling between them. Because of the coupling, the system does not show ''PM'' behavior any longer, leading to the occurrence of some distortions in the resonance behavior. On further cooling below T_C, the domains tend to touch, so that the system enters a long-range FM regime. It is reasonable to suppose the conductivity to be metallic within the FM domains and insulating in the ''PM'' regions. When temperature is decreased, the volume fraction of the more conductive FM domains increases, so that they touch to each other below T_C. As a result, a transition to metallic behavior occurs below T_C. Near T_C, applying the field accelerates the growth of the domains in size, resulting in CMR. The feature mentioned here is in agreement with STS experiments. STS measurements directly demonstrate that both metallic and insulating regions coexist in the system near T_C, and a considerable fraction of insulating regions can be converted into metallic regions on the application of magnetic fields.[10]

In summary, both MR and anomalous PM behaviors have been experimentally studied for $(La_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ ($x = 0.15$ and 0.2). We explain both the MR and the PM anomalies observed below T_{onset} to be a result of substantial increase in the volume fraction of metallic FM domains. Based on STS experiments, Fath *et al.*[10] explained the MR to be due to a percolation of metallic FM domains. To our opinion, however, it is also likely to explain the experimental observations on the basis of a network of magnetic coupled junctions, each consisting of a PM region sandwiched between two FM domains. In such a scenario, the observed PM anomalies are due to the FM coupling between the domains, and the MR is due to the increase in the FM coupling between the domains that is favorable for the charge carriers to tunnel from one domain to next.

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