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LETTER TO THE EDITOR

Magnetoresistance and paramagnetic anomalies in $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$ ($x = 0.2$)

S L Yuan†, X Y Zeng†, Y Jiang†, J Q Li‡, Y P Yang‡, G Li† and S Z Jin§

† Department of Physics, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

‡ Department of Physics, Wuhan Automotive Polytechnic University, Wuhan 430070, People's Republic of China

§ Structure Analysis Centre, University of Science and Technology of China, Hefei 230026, People's Republic of China

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Abstract. Magnetoresistance (MR) measurements for $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$ ($x = 0.2$) show that the MR effect becomes observable at T_{onset} ($\sim$ 200 K), sharply increases on further cooling and reaches a maximum at T_c ($\sim$ 105 K). Whereas paramagnetic (PM) resonance experiments reveal that PM anomalies occur just below T_{onset}. Above T_{onset}, the g-value keeps constant and the resonance linewidth ΔH_{pp} shows a linear temperature-dependent behaviour, while below T_{onset}, both the g-value and ΔH_{pp} anomalously increase on cooling. It is interesting to find that at the range of $T_c < T < T_{onset}$, both g and ΔH_{pp} show temperature-dependent behaviours similar to that for the MR against T. These findings suggest the same underlying physical origin for the MR effect and the PM anomalies.

In recent years, owing to the discovery of high-temperature superconductivity and the colossal magnetoresistance (CMR) effect, considerable attention has been paid to two types of transition metal (Cu and Mn) oxides. Taking $La_{1+x}Ba_{2-x}Cu_3O_7$ and $La_{1+x}Ba_{2-x}Mn_3O_9$ as examples, it can be seen that both systems have much in common. Most obvious is the fact that both materials are transition metal oxides containing rare-earth metals and incorporating alkaline metals acting as hole dopants. Varying the relative ratio between La^{3+} and Ba^{2+} ions changes mixed-valent behaviour for transition metal ions (Cu^{2+}/Cu^{3+} and Mn^{3+}/Mn^{4+}) that strongly affect physical properties. The similarities between the two systems urge one to investigate the doping effect of Cu on Mn sites of $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$. This has been experimentally studied in our recent work [1]. We show that even for 20%Cu doping, samples of $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$ still show insulator–metal transition and CMR effect.

It has been generally found that for the doped ABO_3-type manganese perovskites, the largest CMR effect appears near the insulator–metal transition, while the transition is accompanied by a simultaneous paramagnetic (PM) to ferromagnetic (FM) transition at almost the same temperature (i.e., the Curie temperature T_c). Therefore, one believes that both the transition and the CMR effect are magnetic in origin. Traditional understanding of these 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 CMR values. It is generally believed that besides the DE [2], other effects should be included, such as small polarons [4], magnetic polarons [5] and spin-polarons [6]. Nevertheless, understanding the cause of the CMR effect is still a matter of controversy. In the present work, we report MR measurements along with PM resonance

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experiments for the 20%Cu doped sample that provide strong evidence for the origin of large MR effects due to the PM anomalies.

Details of preparation, crystalline structure and transport properties (with and without an applied magnetic field) have been reported elsewhere [1] for the $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$ ($0 \leqslant x \leqslant 0.2$) series. Here we only study the 20%Cu doped sample, since its CMR effect is the largest in this series. The phase purity was checked by powder x-ray diffraction analysis that confirmed the present sample to be of single-phase orthorhombic structure ($a = 0.7683/\sqrt{2}$ nm, $b = 0.7862/\sqrt{2}$ nm and $c = 0.7787$ nm). Resistance was measured by the standard four-probe method on cooling. PM resonance 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.

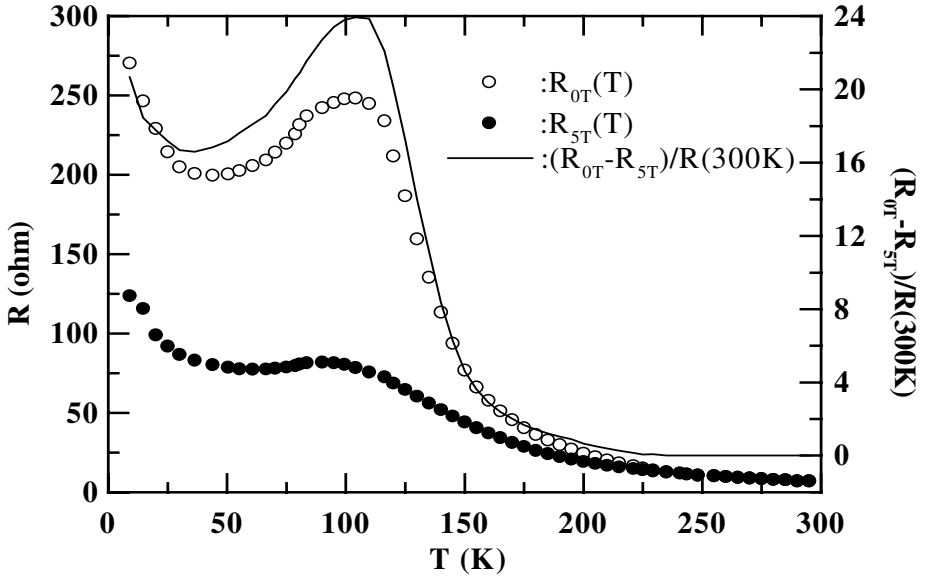

Figure 1. Temperature dependence of resistance for $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$ ($x = 0.2$) in fields of 0 and 5 T. The corresponding magnetoresistance effect is also shown (right-hand axis).

The zero-field R against T dependence for the 20%Cu doped sample is plotted in figure 1. The conductivity shows 'insulating' behaviour at high temperatures, and a transition to 'metallic' behaviour below $\sim$ 105 K. After passing through a minimum, further cooling brings about an increase in resistance, a behaviour different from that in $La_{2/3}Ba_{1/3}MnO_3$. The latter shows insulating behaviour above the Curie temperature T_c but metallic behaviour in the whole range of $T < T_c$. The observed minimum should be caused mainly by the deviation of the Mn^{3+}/Mn^{4+} ratio from the optimal value (2:1). This deviation increases the importance of the antiferromagnetic interaction that prevents the charge carriers transferring. In the present study we are not concerned with the behaviour at low temperatures, but place emphasis upon the conductivity near T_c. Previous measurement [1] of the $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$ ($0 \leqslant x \leqslant 0.2$) series shows that the insulator–metal transition gradually moves towards the low temperature region replacing Mn with Cu. Therefore, it is reasonable to believe that for the present sample the observed resistance maximum at $\sim$ 105 K corresponds to an insulator–

metal transition and the corresponding T_c is approximately determined by the insulator–metal transition temperature, i.e., $T_c \sim 105$ K.

Similar to that in other Mn based oxides, the present sample also shows large MR effects. In figure 1 we plot resistance measured in a magnetic field of 5 T as a function of temperature. Defining the MR effect as $\mathrm{MR} = (R_{0T} - R_{5T})/R(300\ \mathrm{K})$, where R_{0T} and R_{5T} are temperature-dependent resistance values measured in fields of 0 T and 5 T, and $R(300\ \mathrm{K})$ is room-temperature resistance in zero field, the thus obtained MR as a function of temperature is also shown in figure 1. We can see that the MR effect becomes observable below a temperature $T_{onset} \sim 200$ K and negligible above it. At the intermediate temperature range near T_c, the MR effect substantially increases on cooling, reaches a maximum at T_c, and then decreases on further cooling. The largest MR effect is estimated to be $\sim 2.4 \times 10^3\%$. From figure 1, one can also see that the MR effect shows a behaviour similar to that in the zero-field R versus T curve near T_c, suggesting the same underlying physical origin for the MR effect and the insulator–metal transition.

The insulator–metal transition observed in manganese perovskites has traditionally been understood within the framework of the DE mechanism [2]. At $T > T_c$, the system is in a PM state, and the conductivity shows activated insulating behaviour due to disorder scattering from charge carriers with different spin orientations. Below T_c, the DE interaction between Mn^{3+} and Mn^{4+} mediates FM coupling that favours the charge carriers to transfer between adjacent Mn ions, leading to a transition to metallic behaviour. This means that the insulator–metal transition is of magnetic origin. Near T_c, the applied magnetic field tends to align the local spins, and then the charge carrier transfer increases. As a result, applying the field largely enhances the conductance, leading to the so-called CMR effect. Although the DE mechanism is a good physical basis for the discussion of the fascinating properties, theoretical considerations [3] indicate that the DE alone is incompatible with many aspects of the experimental data. It is commonly believed that in addition to DE physics, some other effects should be included.

It is possible for short-range magnetic correlation (or magnetic heterogeneity) to exist well above T_c. Neutron scattering [7,8] and magnetization [9] as well as magnetic susceptibility [10] measurements pointed to short-range magnetic correlation well above T_c. Small-angle neutron scattering measurements [10] showed a large magnetic intensity above T_c, indicating the presence of small FM clusters in the PM background. PM resonance measurements revealed PM anomalies below $\sim 1.04T_c$ for $La_{2/3}Sr_{1/3}MnO_3$ [11], $\sim 1.2T_c$ for $La_{2/3}Ca_{1/3}MnO_3$ [12] and $\sim 2T_c$ for $(La_{0.8}Y_{0.2})_{2/3}Ca_{1/3}MnO_3$ [13]. The question is how does the magnetic heterogeneity correlate to the MR effect? To answer this question, we experimentally study the magnetic behaviour above T_c with the help of the PM resonance technique because of its sensitivity to magnetic heterogeneity.

Shown in figure 2 is resonance spectra measured at various constant temperatures ranging from 435 K to $\sim T_c$. Here the recorded signal is a resonance absorption derivative signal. It can be seen that at high temperatures the spectrum consists of a single line which has a Lorentzian lineshape. The resonance field is independent of temperature. The derivative signal intensity greatly increases on cooling. The symmetric signal with the Lorentzian lineshape is maintained to a temperature (~ 200 K). Below this temperature, some distortions of the lineshape occur: the derivative signal intensity becomes weak, the resonance line largely broadens and the resonance field clearly shifts to a lower field. These observations mean that the complete PM region corresponds to a temperature range of $T > 200$ K, but PM anomalies occur below 200 K. It is interesting to find that the PM anomalous temperature is almost the same as T_{onset} below which the MR effect becomes observable. This finding suggests evidence of some correlation existing between the MR effect and anomalous PM behaviour.

The evidence mentioned above becomes much clearer if we plot both g-value and MR as

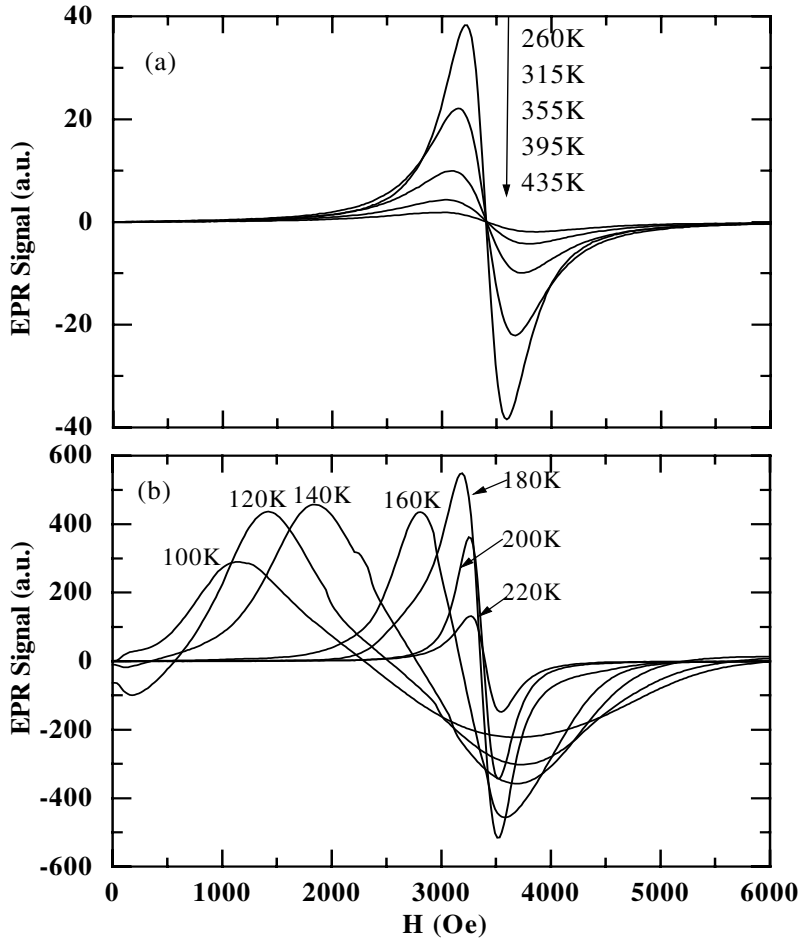

Figure 2. Paramagnetic resonance spectrum as a function of temperature for $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$ ($x = 0.2$).

a function of temperature on the same figure. Such a plot is shown in figure 3(a). One can see that the g-value remains constant until the temperature reaches 200 K, and then largely increases on cooling. On the other hand, no MR effect is observed at $T > 200$ K, and the MR effect becomes measurable just below 200 K. On further cooling, MR sharply increases and reaches a maximum at T_c. From figure 2(a), it is interesting to find that both g-value and MR exhibit similar temperature dependence in the temperature range of $T > T_c$.

Similarly, we plot both linewidth ΔH_{pp} and MR as a function of temperature in the same figure, as shown in figure 3(b). It can be seen that the onset temperature, T_{onset}, for the appearance of the MR effect corresponds to a temperature at which ΔH_{pp} reaches its minimum. Above T_{onset}, no MR effect appears, and ΔH_{pp} linearly decreases on cooling. The linear increase in ΔH_{pp} with temperature has been well predicted by the single-phonon spin-lattice relaxation mechanism [14]. Below T_{onset}, ΔH_{pp} anomalously increases on cooling. On the other hand, as seen in the figure, the MR effect becomes observable just at T slightly lower than T_{onset} and substantially increases on further cooling. Similar to that shown in figure 3(a), one can also see that both MR and ΔH_{pp} show similar temperature dependence in

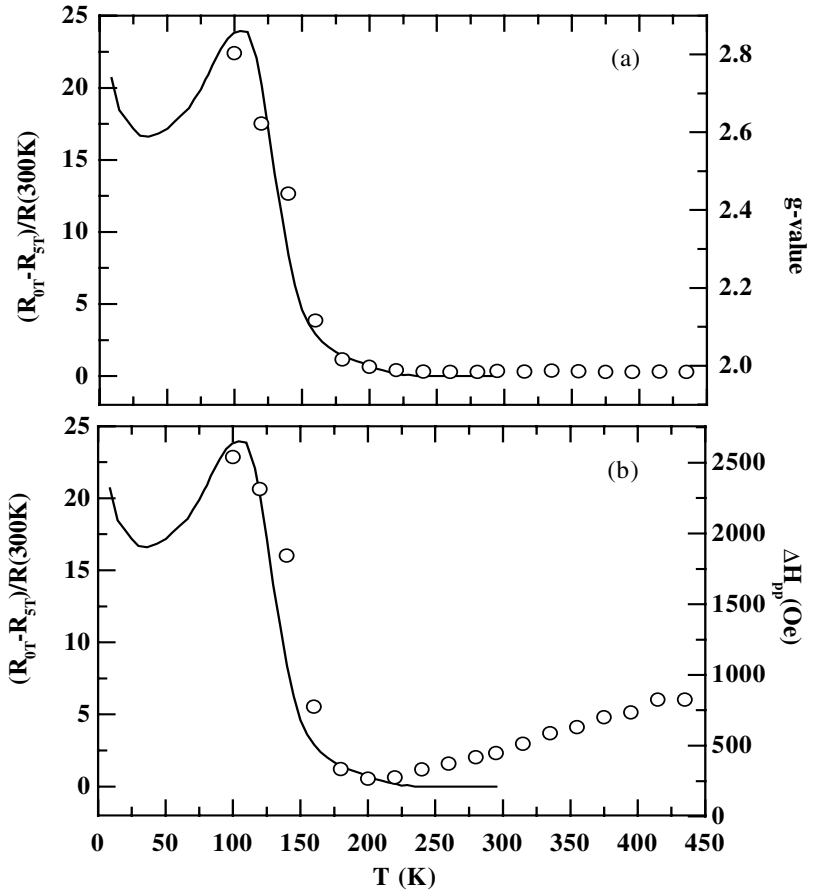

Figure 3. Temperature dependence of MR, g and ΔH_{pp} for $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$ ($x = 0.2$).

the temperature range $T_c < T < T_{onset}$.

The results given above strongly demonstrate the same underlying physical origin for both the MR effect and the PM anomaly. Therefore, in order to understand the true nature of the MR effect, it is necessary to first clarify the possible origin of the PM anomaly in manganese perovskites. As is well known, manganese perovskites are typical systems of narrow band containing Jahn–Teller ions. For such systems, a strong electron–phonon interaction arising from the Jahn–Teller effect should play a crucial role. Of particular importance are the vibrations of lighter oxygen atoms. This may lead to the occurrence of cooperative atomic displacements. Associated with cooperative atomic displacements, the Mn based oxides with perovskite-related structures can accomplish a dynamic phase segregation that creates some domains of short-range FM ordering, separated by the PM regions [15]. At high temperatures, these FM domains are isolated within the PM matrix. Therefore, the system in magnetism still shows PM behaviour as a whole, as long as no magnetic correlation exists between FM domains. Goodenough *et al* [15] called it superparamagnetic to distinguish it from conventional paramagnetic. On cooling, the FM domains grow, 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 magnetic correlation between them. Because of the magnetic correlation, the system below T_{onset} does not show superparamagnetic behaviour any longer. This leads to the occurrence of some distortions in resonance spectrum including the distorted lineshape, the large increase in g and the anomalous rise in $\Delta H_{pp}(T)$. On further cooling below T_c, the FM domains tend to overlap, so that the system enters a long-range FM regime.

It is reasonable to suppose that the conductivity is metallic within a FM domain, but insulating in the PM region due to disorder scattering from charge carriers with different spin orientations. Therefore, the system shows metallic conductive behaviour below T_c due to the overlapping of FM domains. Whereas above T_c, the system exhibits insulating behaviour, since the PM regions are sandwiched between FM domains. Application of a magnetic field increases the volume fraction of the more conductive FM domains, so the resistance decreases, leading to the observable MR effect below T_{onset}.

In summary, both the MR effect and anomalous PM behaviour have been experimentally studied for $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$ ($x = 0.2$). We show that in the anomalous PM region, both g and ΔH_{pp} have temperature dependence similar to that for the MR against T, providing strong evidence of the same underlying physical origin for both the MR effect and anomalous PM behaviour. Further experimental and physical considerations are needed to understand the origin of anomalous PM behaviour above T_c. Also, further theoretical developments on the MR effect in manganese perovskites should consider the present experimental fact.

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References

[1] Yuan S L *et al* 2000 *Phys. Rev.* B **61** 3211
[2] Zener C 1951 *Phys. Rev.* **82** 403
De Gennes P-G 1960 *Phys Rev.* **118** 141
[3] Millis A J *et al* 1995 *Phys. Rev. Lett.* **74** 5144
Roder H *et al* 1996 *Phys. Rev. Lett.* **76** 1356
[4] Mott N F 1993 *Conduction in Non-Crystalline Materials* (Oxford: University Press)
[5] Kusters R M, Singleton J, Keen D A, McGreevy R and Hayes W 1989 *Physica* B **155** 362
[6] Zhang S 1996 *J. Appl. Phys.* **79** 4542
[7] Lynn J W *et al* 1996 *Phys. Rev. Lett.* **76** 4046
[8] J M De Teresa *et al* 1996 *Phys. Rev.* B **54** 1187
[9] Sun J Z *et al* 1996 *Appl. Phys. Lett.* **69** 1002
[10] J M De Teresa *et al* 1997 *Nature* **386** 256
[11] Causa M T *et al* 1998 *Phys. Rev.* B **58** 3233
[12] Oseroff S B *et al* 1996 *Phys. Rev.* B **53** 6521
Rettori C *et al* 1997 *Phys. Rev.* B **55** 3083
[13] Yuan S L *et al* 2000 *J. Phys.: Condens. Matter.* **12** L109
[14] Huber D L and Seehra M S 1975 *J. Phys. Chem. Solids* **36** 723
[15] Goodenough J B and Zhou J S 1997 *Nature* **386** 229