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The dependence of the magnetoresistance on the magnetic history for $La_{2/3}Ca_{1/3}Mn_{0.85}Cu_{0.15}O_3$

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Abstract. A study of the dependence of the magnetoresistance on the magnetic history for a polycrystalline sample of $La_{2/3}Ca_{1/3}Mn_{0.85}Cu_{0.15}O_3$ at temperatures of 4.2 K and 77 K has been carried out experimentally. It was found that the magnetoresistance dependence at 4.2 K is quite different from that at 77 K. The former shows a remarkably large loop during the variation of the magnetic field while the latter does not. The relaxation behaviours of the magnetoresistance in some constant magnetic fields both at 4.2 K and at 77 K also show a great difference. Magnetization measurement shows that Cu doping at Mn sites may give rise to an antiferromagnetic phase in addition to the original ferromagnetic one. These two coexisting magnetic structures at 4.2 K are likely to be responsible for the above differences.

1. Introduction

The distorted ABO_3-type perovskite oxides with the form $RE_{1-x}AE_xMnO_3$ (RE = trivalent rare-earth ions, AE = divalent ions like Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+}) have recently been the subject of extensive investigation because of their unusual and potentially useful magnetic properties [1]. These properties include the colossal-magnetoresistance (MR) effect and complex physical phase transitions. The physics of manganites has primarily been described by the double-exchange (DE) model proposed by Zener [2] and de Gennes [3]. There are two magnetic couplings involved in the model: one is the on-site ferromagnetic coupling (Hund's rule coupling) between e_g electrons and local t_{2g} spins, which follows Hund's rule; the other is the inter-magnetic coupling between the neighbouring manganese ions mediated by oxygen anions. The latter coupling can be either a ferromagnetic or an antiferromagnetic one, or, in some cases, the two kinds of coupling can coexist according to the ability of the e_g electrons to move. In fact, in some temperature regions where antiferromagnetic and ferromagnetic interactions become comparable, one would observe a canted (ferromagnetic) or helical (antiferromagnetic) spin arrangement or spin glass due to local magnetic structure inhomogeneities [4]. When such a magnetic structure appears and under certain conditions, the magnetoresistance curves show a remarkable hysteresis and the resistance becomes dependent on the magnetic history, and a relaxation behaviour of the resistance also appears [5]. The authors of [5] found that the relaxation of the resistance has a logarithmic time dependence for $La_{2/3}Ca_{1/3}MnO_{3+\delta}$ magnetic thin films, which is a well-known feature of the relaxation of the magnetic moment of hard magnets, blocked superparamagnets and also spin glasses. Here we report the dependence of the magnetoresistance on the magnetic history for

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$La_{2/3}Ca_{1/3}Mn_{0.15}Cu_{0.15}O_3$ at 77 K and 4.2 K. It was found that the dependence at 4.2 K is quite different from that observed at 77 K, but very similar to the behaviour of the structure relaxation detected in metallic glass systems. On the basis of the magnetization measurement carried out at 4.2 K, we proposed that Cu doping at Mn sites may introduce an antiferromagnetic phase in addition to the original ferromagnetic one, and suggested that these two coexisting magnetic structures at low temperature (4.2 K) are likely to be the origin of the differences.

2. Experimental procedure

The sample, with nominal composition $La_{2/3}Ca_{1/3}Mn_{0.15}Cu_{0.15}O_3$, was prepared by conventional solid-state reaction with the starting materials La_2O_3, $MnCO_3$, $CaCO_3$ and CuO of high purity (>99.9%). The details of the preparation conditions have been described elsewhere [6]. The XRD pattern of the sample obtained with Cu Kα radiation has revealed its single-phase perovskite structure. Resistance measurements (dc) were performed by a standard four-probe technique at temperatures of 4.2 K and 77 K on the sample with dimensions $10 \times 4 \times 1.5$ mm. An 8 T superconducting magnet produced magnetic fields. Firstly, the sample was zero-field (ZF) cooled to 77 K. After that, the sample was ZF warmed up to 300 K and again ZF cooled to 4.2 K. The dependence on the magnetic history of the resistance was measured with constant temperatures of 77 K and 4.2 K. The field-scanning speed was fixed at 0.42 T min^{-1} throughout the whole experiment.

3. Results and discussion

Figure 1 shows for the sample $La_{2/3}Ca_{1/3}Mn_{0.15}Cu_{0.15}O_3$ the temperature dependence of the resistance in zero field and in an applied magnetic field of 6 T. In zero field, the resistance reaches a remarkable maximum at about 80 K, which is defined as T_p. On applying a magnetic field of 6 T, the maximum is greatly suppressed, thus leading to the enormous magnetoresistance of four orders of magnitude in this region (right-hand-side axis). Here the magnetoresistance MR is defined as a function of temperature in the temperature range of 4.2 K to 300 K at a

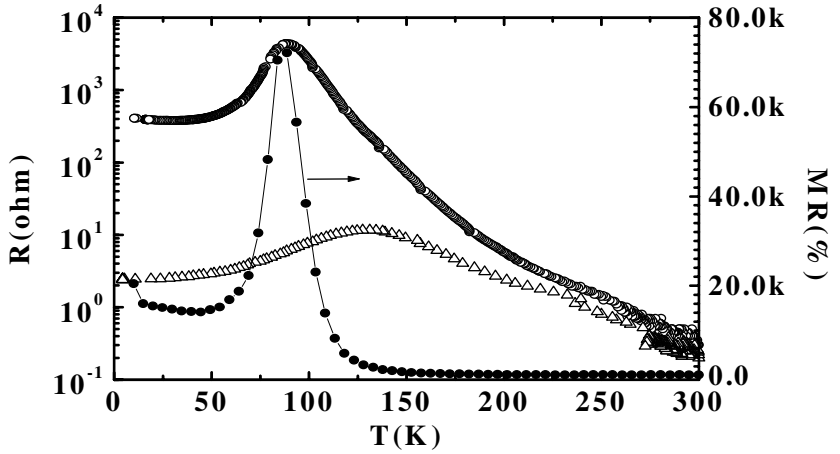

Figure 1. The temperature dependence of the resistance for $La_{2/3}Ca_{1/3}Mn_{1-x}Cu_xO_3$ ($x = 0.15$) in zero (◯) and 6 T (△) magnetic fields and the magnetoresistance MR versus T. Here, MR (%) = $\{[R(0) - R(H)]/R(H)\} \times 100$.

fixed magnetic field of 6 T: MR (%) $= \{[R(0) - R(H)]/R(H)\} \times 100$. From figure 1, one can see that although the temperature reaches 4.2 K, the resistance of the sample without an applied field around this point is still large. On applying a magnetic field of 6 T, the resistance at this point is suppressed by nearly three orders of magnitude. The temperature dependence of MR (right-hand-side axis) shows an enormous hysteresis below 80 K. This prompted us to carry out a study on the dependence on the magnetic history of the magnetoresistance for $La_{2/3}Ca_{1/3}Mn_{0.15}Cu_{0.15}O_3$ both at 4.2 K and at 77 K.

Figure 2(a) shows the magnetic field dependence of the resistance of the sample at 77 K obtained by sweeping the field from 0 to 7 T, and then again back to 0 at a fixed field-scanning speed of 0.42 T min^{-1} after the sample was ZF cooled from 300 K. During the process, the magnetic field was kept constant for 10 min both at 0.4 T and 1.2 T to allow the relaxation of the resistance. A similar procedure has been carried out at 4.2 K, as shown in figure 2(b). From figure 2(b), one can see that the resistance firstly decreases rapidly as the field increases to 1 T, then decreases sharply when the applied field is switched on when 3.5 T is reached

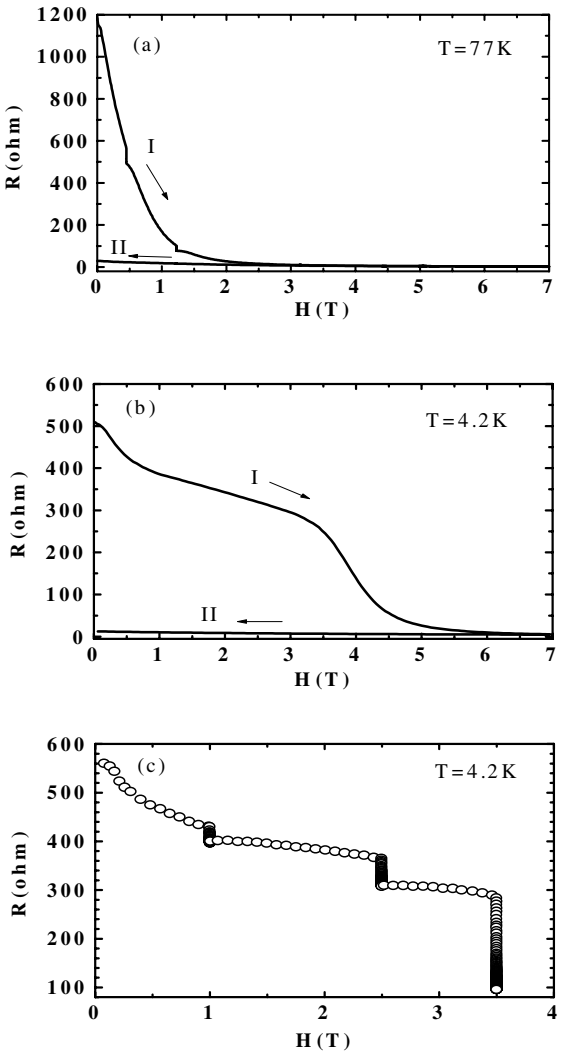

Figure 2. Resistance versus H at 77 K (a), 4.2 K (b) and 4.2 K (c). I: field increasing; II: field decreasing. In (a) and (c) the magnetic fields are kept constant at 0.5 T and 1.2 T at 77 K, and at 1 T, 2.5 T and 3.5 T at 4.2 K for a few minutes to allow observation of the magnetoresistance hysteresis.

during the process of sweeping the field upwards. As shown in figure 2(c), the magnetic field was kept constant for about 10 min at 1 T, 2.5 T and 3.5 T at 4.2 K to allow the relaxation of the resistance during field scanning.

From figures 2(a) and 2(b), one finds a hysteresis loop for both increasing (I) and decreasing (II) magnetic field. However, the magnetoresistance dependence at 4.2 K is quite different from that at 77 K. The former shows a remarkably large loop as compared to the latter. The time dependence of the resistance is shown in figures 3(a) and 3(b), corresponding to 77 K and 4.2 K at different constant fields, respectively. It was found that the relaxation of the resistance has a logarithmic time dependence for 77 K, which is a well-known feature of the relaxation of the

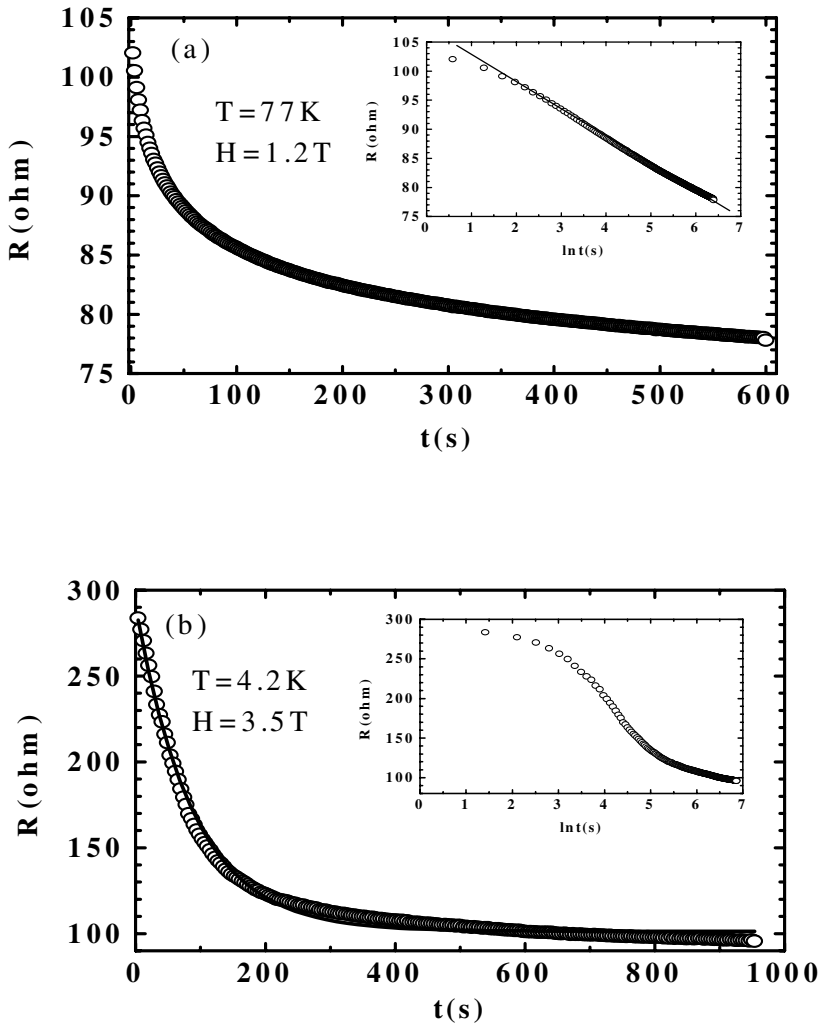

Figure 3. The magnetoresistance relaxation in a 1.2 T field at 77 K (a) and in a 3.5 T field at 4.2 K (b). The resistance (R) data versus logarithmic time ($\ln t$) are re-plotted in the insets of (a) and (b). There is clearly a linear relationship between R and $\ln t$ at 77 K, as the solid line shows in the inset of (a). The inset of (b) does not show such a relationship. Contrarily, as shown in (b), the experimental data are well fitted by equation (1). Here the parameters are $R_0 = 101.3\ \Omega$, $R_1 = 190\ \Omega$, $\tau_1 = 88.6$ s.

magnetic moment of hard magnets, blocked superparamagnets and also spin glasses; this is shown in the inset of figure 3(a). This feature is similar to what has been found in [5]. But it is not the case for 4.2 K with applied fields of 1 T, 2.5 T and 3.5 T, as in the example for $H = 3.5$ T shown in the inset of figure 3(b), in which it does not have a logarithmic time dependence. The behaviour could be well fitted, however, to the following equation, represented by the solid line in figure 3(b):

$$R = R_0 + R_1 e^{-t/\tau_1}. \tag{1}$$

Here R_0, R_1 and τ_1 are fitting parameters. These parameters have their self-evident physical meanings, which will be explained later. It should be noted that the cases for 4.2 K with applied fields of 1 T and 2.5 T have similar results, but different fitting parameters. Such behaviour is very similar to that of the structure relaxation observed in metallic glass systems [7]. In those systems, it was found that many physical parameters, such as the magnetization and resistance, have the following time dependence relationship:

$$A(t) = A(\infty) + Ae^{-t/\tau}. \tag{2}$$

Here $A(t)$ represents a physical parameter, $A(\infty)$ is the value of $A(t)$ when $t \to \infty$, i.e. the value for a stable state, τ the characteristic relaxation time, and A a constant value. It should be noted that this is not the case for $T = 77$ K.

Obviously, the large MR ratio found for the sample is due to grain boundary transport to some degree. One may at first think of the grain boundary transport as being the origin of the above-mentioned observations. Some experiments [8] have proved that the grain boundary dominates the resistance of polycrystalline samples. However, although the high-field slopes in figures 2(a) and 2(b) are consistent with the 2% T^{-1} seen by Hwang *et al* [8], the low-field effects in the figures are very large by comparison. This cannot be simply explained by grain boundary transport, especially for the case in figure 2(b): the slope is too large when H is around 3.5 T. The $M(H)$ data at 4.2 K in figure 4 confirm the discovery of a bulk effect, since M is not very sensitive to the grain boundary material which dominates the grain boundary transport. This forces us to make the supposition described below.

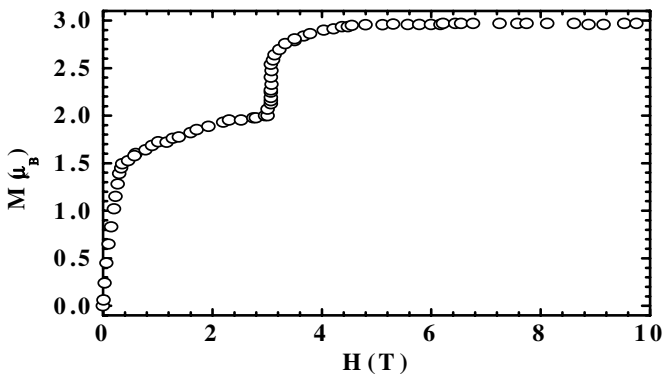

Figure 4. The variation of the magnetization (M) of $La_{2/3}Ca_{1/3}Mn_{1-x}Cu_xO_3$ ($x = 0.15$) at 4.2 K with the magnetic field up to 10 T. M is normalized to a Bohr magneton per Mn site. A jump of M is clearly observed when $H \sim 3.5$ T.

By supposing that in the system studied by us, ferromagnetic and antiferromagnetic structures coexist at 4.2 K, the above-mentioned relaxation behaviour can be well explained. In low magnetic fields, the antiferromagnetic structure cannot have been destroyed at 4.2 K. Both

the ferromagnetic and antiferromagnetic structures are near to their ideal structures. In this case, the magnetoresistance relaxation may originate from the ferromagnetic diffusion after-effect, which is widely observed in ferromagnetic materials. However, in high magnetic fields, such coexisting structures will be destroyed, i.e. the antiferromagnetic one will be destroyed and turned into a new ferromagnetic structure.

This supposition could also be proved from the M–H magnetization curve measured at 4.2 K, as shown in figure 4. It is clear that when the applied magnetic field is lower than 3.5 T, the magnetization seems to reach a saturation of 2.0 μ_B per Mn site at $H > 0.3$ T. However, when H exceeds 3.5 T, the magnetization jumps to a new value of about 3.0 μ_B per Mn site. From a sample calculation, one can find that this value corresponds to the ideal saturation value when all the magnetic moments of manganese ions align in the same direction. This means that a phase transition occurs at $H \sim 3.5$ T. We think that at low magnetic field, the antiferromagnetic phase still remains in the background of the original ferromagnetic one. The antiferromagnetic phase turns into a new ferromagnetic one when the applied magnetic field is high enough. Besides the magnetic phase transition in higher magnetic fields investigated by magnetization measurements, a similar transition is also found in electron transport experiments when the magnetic field is beyond 3.5 T, as shown in figure 2(b). One may note that the resistance at 4.2 K is decreased significantly when the magnetic field exceeds 3.5 T. We think that it corresponds to a magnetic phase transition—an antiferromagnetic structure turns into a ferromagnetic one. The ferromagnetic state favours e_g electron motion and hence sharply decreases the resistance.

The coexistence of ferromagnetic and ferromagnetic phases implies that it is not easy to arrange all the magnetic domains to form a well-ordered ferromagnetic state [9]. In other words, the ferromagnetic Mn^{3+}–O–Mn^{4+} interaction is weakened due to Cu doping, and Cu doping gives rise to antiferromagnetism in addition to the original DE ferromagnetism. The reason for this can be regarded as the amount of manganese ions in the system decreasing as Cu is substituted for Mn and the doping of Cu tending to break down the long-range ferromagnetic order. The disordered distribution of Cu in the system may easily bring about antiferromagnetism.

In summary, we have reported the dependence on the magnetic history of the magneto-resistance for $La_{2/3}Ca_{1/3}Mn_{1-x}Cu_xO_3$ ($x = 0.15$) both at liquid nitrogen and at liquid helium temperature. We found that the behaviour at liquid helium temperature is quite different from that observed in the liquid nitrogen regime, which seems like that of superparamagnets and ferromagnets, but very similar to the behaviour of the structure relaxation detected in metallic glass systems. On the basis of the hypothesis that Cu doping at Mn sites may give rise to an antiferromagnetic phase in addition to the original ferromagnetic one, we propose that these two coexisting magnetic structures at low temperature bring about the above differences.

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