Impact of Ru doping in bilayered manganese oxide La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$

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The Ru doping effect on the bilayered manganese oxide La$_{1.2}$Sr$_{1.8}$(Mn$_{1−y}$Ru$_y$)$_2$O$_7$ has been investigated in the range of $0≤y≤0.2$. The ferromagnetic transition temperature ($T_C$) increases, while the saturated magnetization decreases, with Ru doping. These indicate that in addition to the doping-induced suppression of charge-orbital correlation, the antiferromagnetic coupling between the Ru and the Mn moments is relevant to the enhancement of $T_C$. The axis of easy magnetization changes from within the in plane to along the $c$ axis with Ru doping, owing to the strong magnetic anisotropy of Ru spins. © 2005 American Institute of Physics. [DOI: 10.1063/1.1947900]

Impurity doping into a colossal magnetoresistive manganite is known to cause a nontrivial modification in the electronic and magnetic properties. For example, a several-percent substitution of Cr for Mn in half-doped manganites such as Pr$_0.5$Ca$_0.5$MnO$_3$ induces the phase transition from a charge-orbital ordered state to a ferromagnetic metal state. This is because the quenched disorder arising from the doped impurities suppresses the long-range charge-orbital ordered state and alternatively induces the other competing phase, namely, the ferromagnetic metal state. Many kinds of dopant (Fe, Co, Ni, Ru, etc.) can induce such a metal-insulator transition. Among them, Ru doping can most effectively stabilize the ferromagnetic state. Raveau et al. proposed that in addition to the randomness effect, the double-exchange interaction between Mn and Ru is relevant to the effective stabilization of the ferromagnetic metal state.

La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$, which is composed of bilayer slices of a MnO$_2$ plane, shows the colossal magnetoresistance (CMR) around $T_C = 125$ K. The competition between the charge-orbital ordered state and ferromagnetic metal state may be responsible for its CMR as well as in other CMR manganites, since the short-range charge-orbital correlation has been observed above $T_C$. Therefore, the Curie temperature can be increased largely by suppressing the charge-orbital correlation by means of impurity doping. In this Letter, we have investigated the Ru-doping effect on La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$. The Curie temperature increases up to 167 K (by 30%) with 20% Ru doping. On the other hand, the magnetization $M$ decreases with Ru doping $y$, almost following the relation that $M$ decreases with $y$. This suggests that the Ru moments couple antiferromagnetically with the Mn moments, which is inconsistent with the double-exchange scenario mentioned above.

Single crystals of La$_{1.2}$Sr$_{1.8}$(Mn$_{1−y}$Ru$_y$)$_2$O$_7$ ($y=0$, 0.03, 0.05, 0.07, 0.10, and 0.20) were grown by the floating zone method at a rate of 15 mm/h in a 10-atm Ar/O$_2$ (O$_2$ ~ 10%) mixture gas. While clear Laue patterns were obtained, the powder x-ray diffraction reveals a trace of an impurity phase of insulating (La,Sr)$_2$ (Mn,Ru)O$_4$ in Ru-doped samples, which does not affect at least the resistivity. We measured the in-plane resistivity as a function of temperature and magnetic field with a standard four-probe method in a physical-property measurement system (PPMS, Quantum Design Inc.). The magnetization was measured in a magnetic property measurement system (MPMS, Quantum Design Inc.).

Figure 1 shows temperature and magnetic-field dependences of resistivity for La$_{1.2}$Sr$_{1.8}$(Mn$_{1−y}$Ru$_y$)$_2$O$_7$ ($0≤y≤0.2$). As reported previously, the resistivity in zero field for $y=0$ increases rapidly with decreasing temperature and shows an abrupt decrease around 125 K. The peak temperature in the resistivity curve ($≈125$ K) corresponds to the ferromagnetic transition temperature. At low temperatures ($≤50$ K), the resistivity gradually increases, following the relation of $\sigma = 1/\rho = \sigma_0 + AT^{1/2}$, which is expected in the case of weak localization in a three-dimensional system. A similar behavior was previously observed for La$_{1.3}$Sr$_{1.7}$Mn$_2$O$_7$. As the magnetic field is increased, the resistivity decreases in a

![FIG. 1. (a)–(f) Temperature dependence of oh-plane (in-plane) resistivity in various magnetic fields for the single crystals of La$_{1.2}$Sr$_{1.8}$(Mn$_{1−y}$Ru$_y$)$_2$O$_7$ with various $y$. The peaks, corresponding to the Curie temperatures, are shown by closed triangles.](image-url)
Corresponds to the Curie temperature, increases with Ru doping, indicated by closed triangles, which approximately the Ru-doped crystal. Importantly, the peak or the kink temperature becomes steeper with further Ru doping. The three-dimensional variable-range-hopping feature ($ln\rho \sim aT^{1/4}$) is observed for $y=0.1$ and 0.2. This is because the disorder introduced by the Ru doping strongly scatters almost fully spin-polarized charge carriers. While the metallic ground state ($\sigma>0$ at $T=0$) is not observed in the heavily doped region of $y \geq 0.05$, the ferromagnetism is even more stabilized. The resistivity curves in $H=0$ for $0.03 \leq y \leq 0.10$ show pronounced peaks around 130–150 K. The kink around 160 K in the resistivity of the $y=0.20$ crystal for $H=0$ is the remnant of such a resistivity peak. These are indications of the ferromagnetic transition. The CMR can be observed around these temperatures also in the Ru-doped crystal. Importantly, the peak or the kink temperature indicated by closed triangles, which approximately corresponds to the Curie temperature, increases with Ru doping.

We show the temperature variation of the magnetization in $H=0.01$ T along the c axis in Fig. 2(e). The magnetization for $y=0$ begins to increase at around 125 K and saturates around 80 K. The onset temperature corresponding to the Curie temperature increases with Ru doping, being consistent with the resistivity data. In the temperature-dependent magnetization of the Ru-doped crystals, the nonmonotonic behavior is observed below the Curie temperature. This is due to the temperature variation of the coercive force and/or the magnetic anisotropy. The magnetization curves at 5 K for the $y=0$, 0.03, 0.07, and 0.20 crystals are shown in the Figs. 2(a)–(d). The magnetization of the $y=0$ crystal for $H \parallel c$ saturates at a low field ($\sim 0.1$ T), while the saturation field for $H \parallel c$ is around 3 T. The easy axis gradually changes from within the in plane to along the c axis with Ru doping. The saturation field for $H \parallel c$ decreases with Ru doping, while the magnetization for $H \perp c$ in the low-field region decreases. In the magnetization curve of the $y=0.20$ crystal for $H \parallel c$, a clear hysteresis loop is observed. The strong spin-orbit coupling and resultant single-ion anisotropy of Ru 4d spins modify the anisotropy of the net magnetization through the coupling with the surrounding Mn spins. The temperature and doping variations of the magnetic anisotropy and domain structure are discussed in more detail using Lorentz transmission electron microscopy in a separate paper. The magnetization in the both configurations is observed to almost saturate in the high field region ($\sim 5$ T) for all the crystal. The saturated magnetization decreases with Ru doping, indicating that the Ru spins couple antiferromagnetically with the Mn spins.

In Fig. 3(a), we show the Curie temperatures determined by the resistivity and magnetization data. The both quantities similarly increase with Ru doping. The fluctuation of charge-orbital order is responsible for the steep increase of resistivity toward low temperature down to $T_C$. The Ru-doping-induced enhancement of the Curie temperature is partly due to the disorder-induced suppression of such charge-orbital correlation. In addition, the magnetic coupling between Ru and Mn moments may also be relevant to the increase of the Curie temperature as discussed below. In Fig. 3(b), the magnetization at 5 T is plotted against the doping concentration $y$. The magnetization $M$ decreases with Ru doping almost in parallel with the relation that $M=3.6–5y$, although the...
observed magnetization is slightly smaller than the relation. This relation is expected for the case where the Ru and Mn spins couple antiferromagnetically as shown in the inset of Fig. 3. It is worth noting that the both cases of possible Ru valence values, Ru$^{4+}$ and Ru$^{5+}$, satisfy the relation. Previously, the double-exchange interaction between the Ru and the Mn spins was proposed as an origin of the strong stabilization of the ferromagnetic metal state by Ru doping in perovskite manganese oxides. This cannot explain the present results because Ru spins are revealed to couple antiferromagnetically with Mn spins. The antiferromagnetic superexchange coupling between Mn and Ru spins is relevant to the stabilization of the ferrimagnetic state at least in the present case. The obtained conclusion is in good agreement with the recent X-ray magneto-optical study on the polycrystalline La$_{1.2}$Sr$_{1.8}$($\text{Mn}_{1-x}\text{Ru}_x$)$_2$O$_7$.6

In conclusion, we have investigated the Ru-doping effect in single crystals of the bilayered manganese oxide La$_{1.2}$Sr$_{1.8}$($\text{Mn}_{1-x}\text{Ru}_x$)$_2$O$_7$. Owing to the disorder caused by Mn-site substitution, the resistivity in the low temperature region steeply increases with Ru doping. Strong magnetic anisotropy of the Ru spin increases the coercive force and changes the easy axis of magnetization. The Curie temperature increases but the saturated magnetization decreases with Ru doping. The origin of the enhancement of the Curie temperature is ascribed to the disorder-induced suppression of the charge-orbital ordering instability as well as to the antiferromagnetic superexchange interaction between the Ru and the Mn moments.

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