Superconductivity in $La_{1.85-4/3x}Sr_{0.15+4/3x}Cu_{1-x}Mn_xO_4$ with x up to 0.2

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The effect of Mn substitution for Cu in mixed-valence Mn-doped $La_{1.85-4/3x}Sr_{0.15+4/3x}Cu_{1-x}Mn_xO_4$ has been investigated by electric resistivity, dc magnetic susceptibility, and electron spin resonance measurements. Robust superconductivity with x up to 0.2 coexisting with ferromagnetism was observed surprisingly. Percolative superconductivity is suggested based on the discussion about the origin of the ferromagnetism.

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I. INTRODUCTION

It is well known that the characteristics of CuO_2 planes are essential to understand the unconventional superconductivity and the anomalous transport behavior of normal state in cuprate superconductors.[1] Continuous efforts have been devoted to the study on effects of substitution for Cu. At the early stage in the cuprate superconductivity research, it was indicated that the impurities on the Cu sites can lead to significant suppression of superconductivity regardless of their spin configurations,[2] which is in contrast to the insensitivity to nonmagnetic impurities in conventional *s*-wave superconductors.[3] Further, it was found that, although both the magnetic and nonmagnetic impurities exhibit similar effects in suppressing superconductivity, the nonmagnetic impurities in *d*-wave cuprates result in stronger impairment of superconductivity. The reason is that the spatial relaxation of spin polarization near the nonmagnetic impurities is slower than that near the magnetic impurities due to the delocalized spatial distribution of the induced moments near the former.[4–6] Besides, it was found recently that the superconductivity can coexist with the "striped" antiferromagnetic order which is induced by an applied magnetic field in a cuprate superconductor.[7]

While a tremendous body of research papers on the effects of impurities substitution on superconductivity provided much insight into the magnetic correlation and the pairing symmetry in the cuprate superconductors, it is a pity that most of the doping research mainly focused on the lightly doped samples and little effort has been made to the effects of heavy doping, except for some cases of doping with Zn and Ni,[2] Li,[8] and Mn (Refs. 9 and 10) (more can be found in Ref. 11 and references therein). This shortage is possibly due to the difficulty that doping with heterovalent cations on Cu sites will lead to valence unbalance thus preventing the formation of pure-phase samples with high dopant concentration. In the existing cases of heavy doping, the localized electrons introduced by the dopants suppress the superconductivity and enhance the resistivity, and relatively little insight into the superconductivity has been found. In our opinion, it is yet natural that the antiferromagnetism induced by an applied field can coexist with the superconductivity because the regions in antiferromagnetic order can be regarded as resistive defects embedded in the superconductor matrix and have little impact on the superconductivity.

Previously we have investigated the heavily Mn doped $La_{1.85}Sr_{0.15}CuO_4$ (LSCO)[12] where the double-doping $La_{1.85-2x}Sr_{0.15+2x}Cu_{1-x}Mn_xO_4$ was used. By virtue of the double doping which means that the Sr^{2+} concentration is increased and the La^{3+} concentration decreased correspondingly when doping more Mn ions on Cu sites, we successfully prepared samples with high doping levels ($0 \leqslant x \leqslant 0.5$) and observed the superconductivity in competition with an antiferromagnetic correlation between Mn ions which is confirmed to be tetravalent. To further explore the relationship between the magnetism and superconductivity, we prepared mixed-valence Mn doped $La_{1.85-4/3x}Sr_{0.15+4/3x}Cu_{1-x}Mn_xO_4$ ($0 \leqslant x \leqslant 0.2$). With this chemical formula we expected that the charge carriers concentration would be kept to 0.15 per Cu site and the atomic number ratio Mn^{3+}/Mn^{4+} would be adjusted to 2/1 which is the most proper ratio leading to ferromagnetism in the colossal magnetoresistance materials. Below we show that mixed-valence Mn doped pure-phase samples with x up to 0.5 were successfully prepared by this double-doping method and surprisingly the superconductivity can even survive a Mn doping level of $x=0.2$ and coexist with ferromagnetism originating from Mn ions in this system.

II. EXPERIMENTAL DETAILS

A series of polycrystalline samples of the general formula $La_{1.85-4/3x}Sr_{0.15+4/3x}Cu_{1-x}Mn_xO_4$ ($0 \leqslant x \leqslant 0.2$) was prepared by the conventional solid-state reaction method. Powder x-ray-diffraction (XRD) analysis was carried out by a Rigaku-D/max-γA diffractometer using high-intensity Cu $K\alpha$ radiation. The infrared (IR) transmission spectra were obtained (MAGNA-IR 750) using powder samples with KBr serving as a carrier. Raman scattering spectra were recorded (JY LABRAM-HR) using a 514.5 nm laser, with the power 15 mW and exposure time 5 min. The electric resistivity as a function of temperature over the range 15–280 K was measured with a four-probe method in a circular helium refrigerator. The temperature dependence of dc magnetic susceptibility was measured on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) under a field of 10 Oe (5–150 K) and 40 kOe (5–300 K) in (ZFC) mode. The electron spin resonance (ESR) spectra over a temperature range of 110–400 K were obtain at 9.07 GHz (X band) with a JEOL JES-FA 200 spectrometer.

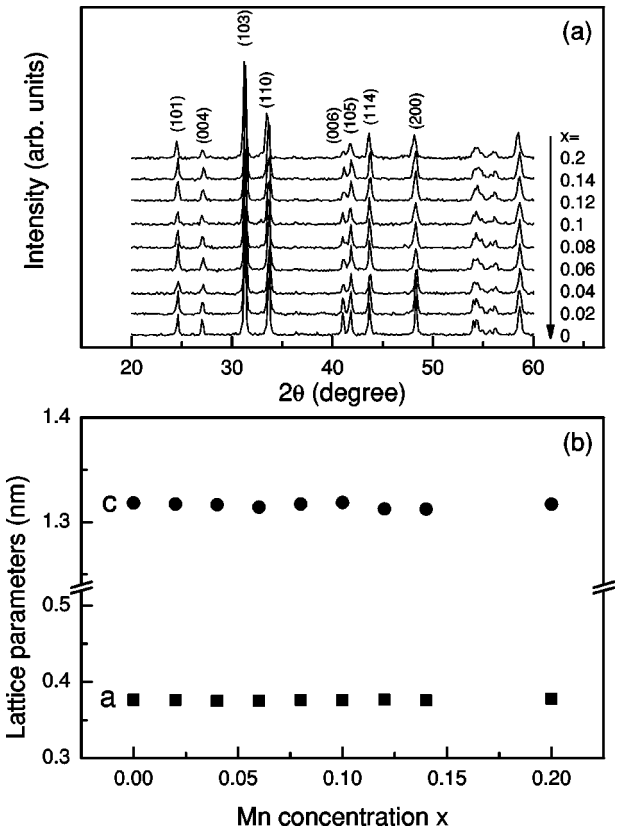

FIG. 1. Powder XRD patterns (a) and Mn concentration x dependence of lattice parameters a and c (b) for all the samples at room temperature.

III. RESULTS AND DISCUSSION

A. Dopant Mn matching matrix closely

As shown in Fig. 1(a), the diffraction peaks in the XRD patterns for $(0 \leqslant x \leqslant 0.2)$ can be indexed according to the single tetragonal phase with K_2NiF_4 structure. Standard least-squares refinement of the patterns revealed that the lattice parameters a and c, as shown in Fig. 1(b), are nearly unchanged upon Mn doping for all the samples. This is consistent with the facts that the radii of Mn^{3+} and Mn^{4+} ions are similar to that of Cu^{2+} ions and that manganese oxides $La_{1-x}Sr_{1+x}MnO_4$ with the same K_2NiF_4 structure as LSCO can form with $0 \leqslant x \leqslant 0.75$.[13–16] Based on the early results, the two IR modes at about 510 and 680 cm^{-1} in Fig. 2(a) are assigned to the A_{2u} stretching mode of apical oxygen atoms and the stretching mode of in-plane oxygen atoms, respectively;[17] The two Raman scattering peaks at about 430 and 680 cm^{-1} in Fig. 2(b) are ascribed to the A_{1g} vibration of apical oxygen atoms along the tetragonal axis and the symmetry-forbidden in-plane oxygen vibration induced to be Raman active by local disorder, respectively.[18] Because all these IR and Raman vibration modes are closely related to the Cu-based K_2NiF_4 structure; i.e., $(La/Sr)_2CuO_4$, the absence of each mode splitting into two modes of different frequencies upon increasing doping reveals that the Mn doping does not lead to the change in structure and vibration spectra, and the dopant Mn can match the matrix closely.

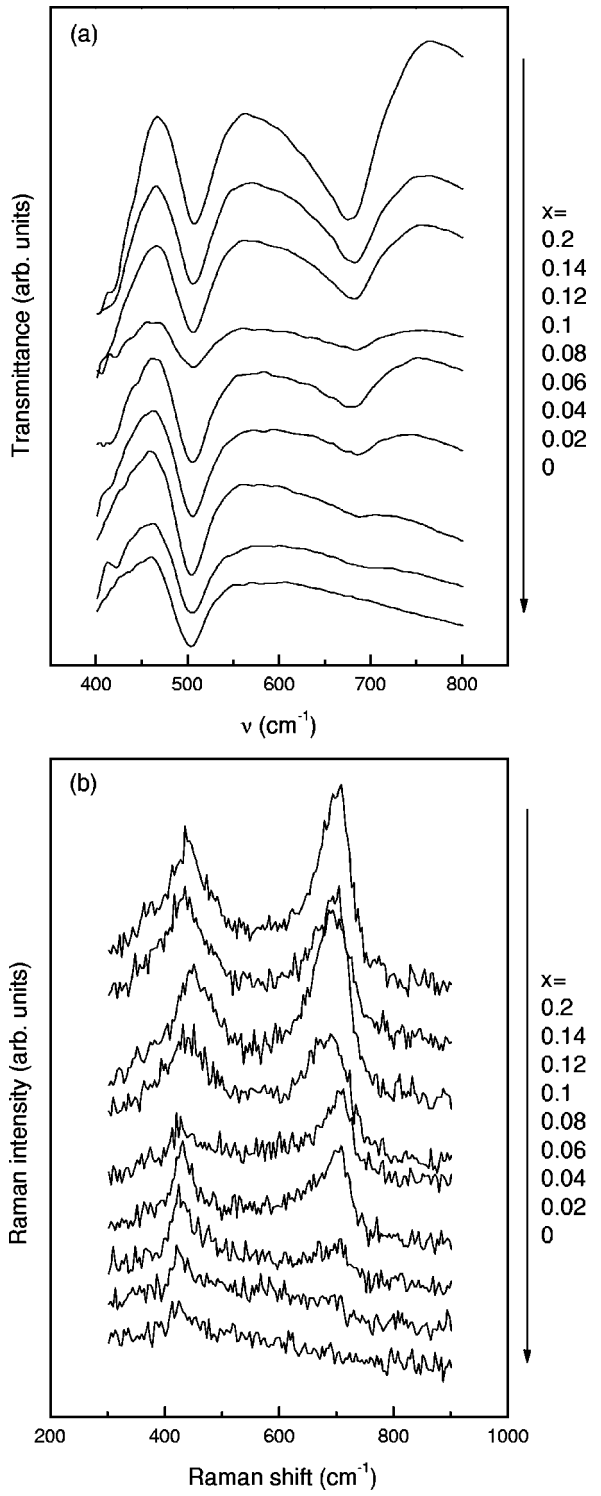

FIG. 2. IR spectra (a) and Raman spectra (b) for all the samples at room temperature.

B. Coexistence of superconductivity and ferromagnetism

1. Superconductivity surviving Mn doping level of $x = 0.2$

Figure 3 shows the temperature dependence of resistivity for $0 \leqslant x \leqslant 0.2$. For $0 \leqslant x \leqslant 0.06$ [curves (a)–(d) in Fig. 3], the resistivity decreases abruptly at about 37 K, manifesting the occurrence of superconductivity, and the superconducting

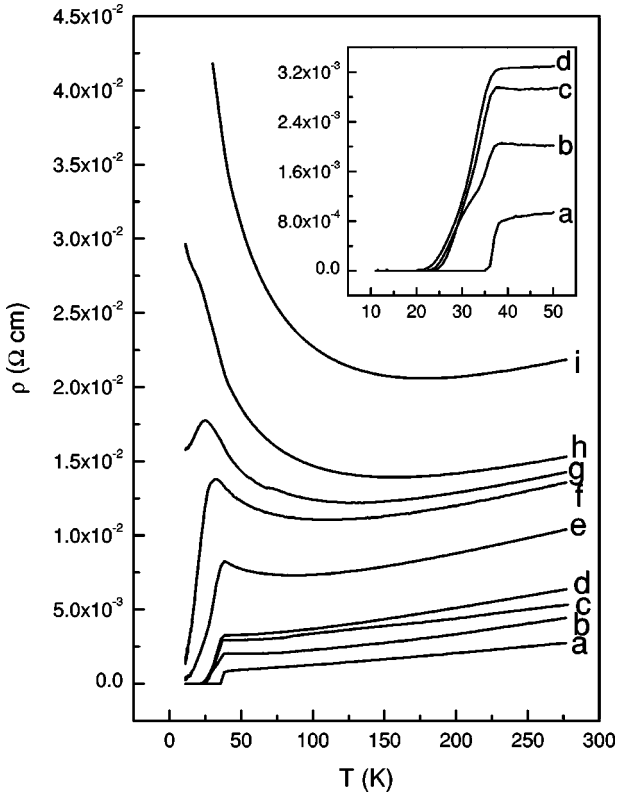

FIG. 3. Temperature dependence of electrical resistivity for (a) $x=0$, (b) $x=0.02$, (c) $x=0.04$, (d) $x=0.06$, (e) $x=0.08$, (f) $x=0.1$, (g) $x=0.12$, (h) $x=0.14$, and (i) $x=0.2$. Inset is the enlarged view around the superconducting transition for (a)–(d).

transition get broadened upon increasing of x. For $x \geqslant 0.08$, all the curves exhibit a minimum; for $x=0.08$, 0.1, and 0.12 [curves (e)–(g) in Fig. 3], there is an abrupt decrease in resistivity at 36, 31, and 25 K, respectively, exhibiting the characteristics of superconductivity; For $x=0.14$ [curve (h) in Fig. 3] there is a kind at 18 K; For $x=0.2$ [curve (i) in Fig. 3] the resistivity versus temperature relationship exhibits semiconductorlike behavior. Upon doping more Mn ions, the resistivity increases rapidly: For example, the resistivity at room temperature (275 K) for $x=0$ is about $2.2\times10^{-3}\ \Omega$ cm, while for $x=0.12$ it is about $1.4\times10^{-2}\ \Omega$ cm. Taking the kink on the curve for $x=0.12$ as the evidence of the superconductivity, obviously it can be understood that the superconducting drop of resistivity is blurred by the background of the high resistivity.

The dc magnetic susceptibility measured under low field of 10 Oe (ZFC) as shown in Fig. 4 is consistent with the results in Fig. 3. For $0 \leqslant x \leqslant 0.08$, increasing Mn doping leads to decreasing Meissner signals. For $x=0.1$, 0.12, and 0.14, the susceptibility decreases at the same temperatures as given by the resistivity results and shows diamagnetic signals at lower temperature eventually. Even for a sample with $x=0.2$, which shows no trace of superconductivity in Fig. 3, the diamagnetic signal is revealed by the rapidly decreasing susceptibility at low temperature. The magnetic results thus confirm that the superconductivity can survive upon replacing 20% of planar Cu ions with Mn ions. To our knowledge, critical doping levels higher than this one have not been reported so far.

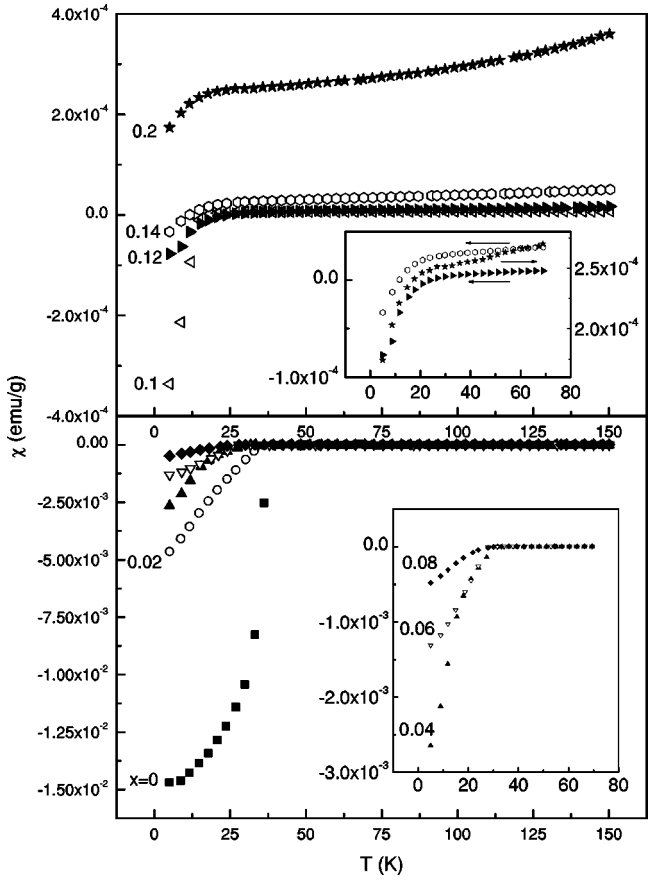

FIG. 4. Temperature dependence of dc magnetic susceptibility for all the samples. ZFC and $H=10$ Oe. Insets are the enlarged views around superconducting transition for $x=0.04$, 0.06, 0.08, 0.12, 0.14, and 0.2.

2. Ferromagnetism in superconductor

It can be seen from Fig. 4 that the susceptibility in normal state is zero for $x \leqslant 0.08$ and shows a small positive value for higher doping level $x \geqslant 0.1$. This observation motivated us to further measure the susceptibility of the samples under a high field of 40 kOe (ZFC), as shown in Fig. 5. Clearly, an upturn in susceptibility can be observed at low temperature for samples with higher doping levels where the superconductivity is weak and is suppressed by the external high field. This behavior cannot be simply related to the paramagnetism. To understand why the superconductivity can survive 20% Mn substitution for Cu and the magnetization results, we carried out ESR experiment.

Figure 6 shows the ESR spectra for several typical samples at different temperatures. For each doping concentration, the paramagnetic (PM) signal corresponding to Lande factor $g \sim 2.0$ as marked by the vertical line can be observed clearly. Also found is another feature besides the PM signal, i.e., another clear ferromagnetic (FM) signal corresponding to $g > 2.0$ as marked by the filled triangle can be observed under low field at low temperatures. There is only the PM signal at temperatures higher than 370 K below which the FM signal can also be observed. This temperature is in accordance with the ferromagnetic critical temperature

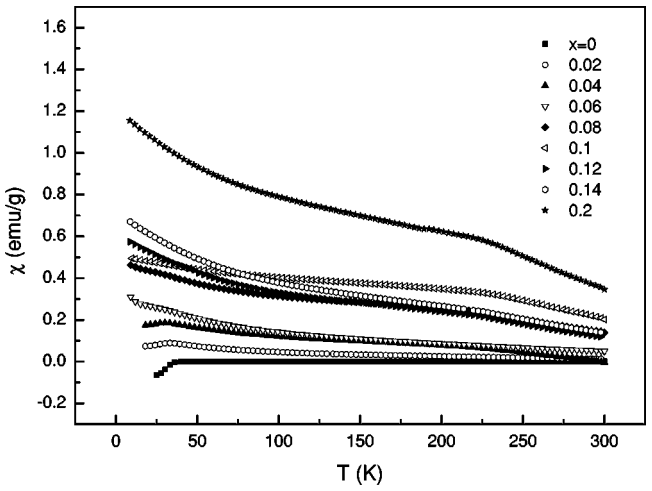

FIG. 5. Temperature dependence of dc magnetic susceptibility for all the samples. ZFC and $H=40$ kOe.

in the (La/Sr)MnO system. The FM signal shifts to lower field upon further cooling, revealing a stronger ferromagnetic correlation at lower temperature. Although the lowest temperature which was reached in the ESR experiment is 110 K, there is good reason to believe that the ferromagnetism would coexist with paramagnetism at low temperature as in the case of 110 K. This is because from Fig. 4 we can see that the magnetization under the field of 10 Oe at low temperature is nearly unchanged with respect to that at 110 K. It is known that superexchange interaction between neighboring Mn ions can result in the ferromagnetism. In cuprate superconductors, the superexchange interaction through $pd\sigma$ hybridization causes the antiferromagnetic correlation between the Cu^{2+} spins. Because the hybridization strength between Mn3*d* and O2*p* states is quite different from that between Cu3*d* and O2*p* states,[19,20] it is less possible that the correlation between Mn and Cu can be established. So, when mixed-valence Mn ions are introduced into the CuO_2 planes, it can be expected that the superexchange interaction between Mn^{3+} and Mn^{4+} will form and lead to the ferromagnetism. However, given the homogeneous distribution of Mn ions in samples with a low doping level $x=0.02$, 0.04, etc., it is hard to hope for the superexchange ferromagnetism of Mn ions. In fact, as revealed by the ESR spectra, the distribution of Mn ions is inhomogeneous microscopically, and there are two kinds of steric states of Mn ions in the CuO_2 planes. One corresponds to the randomly distributed and isolated Mn ions which are in paramagnetic state, and the other corresponds to the Mn ions which have other Mn ions in their neighborhood and form clusters. These clusters exhibit ferromagnetism which coexists with the superconductivity. The two states of Mn ions in the CuO_2 planes is reasonable because as we know, both the $(La/Sr)_2CuO_4$ and the $(La/Sr)_2MnO_4$ have the same K_2NiF_4 structure and can exist independently. When prepared by the conventional solid-state reaction method, it is very possible for the $(La/Sr)_2MnO_4$ to exist independently in the $(La/Sr)_2CuO_4$, so the Mn—O—Mn and Cu—O—Cu can exist in the same planes.

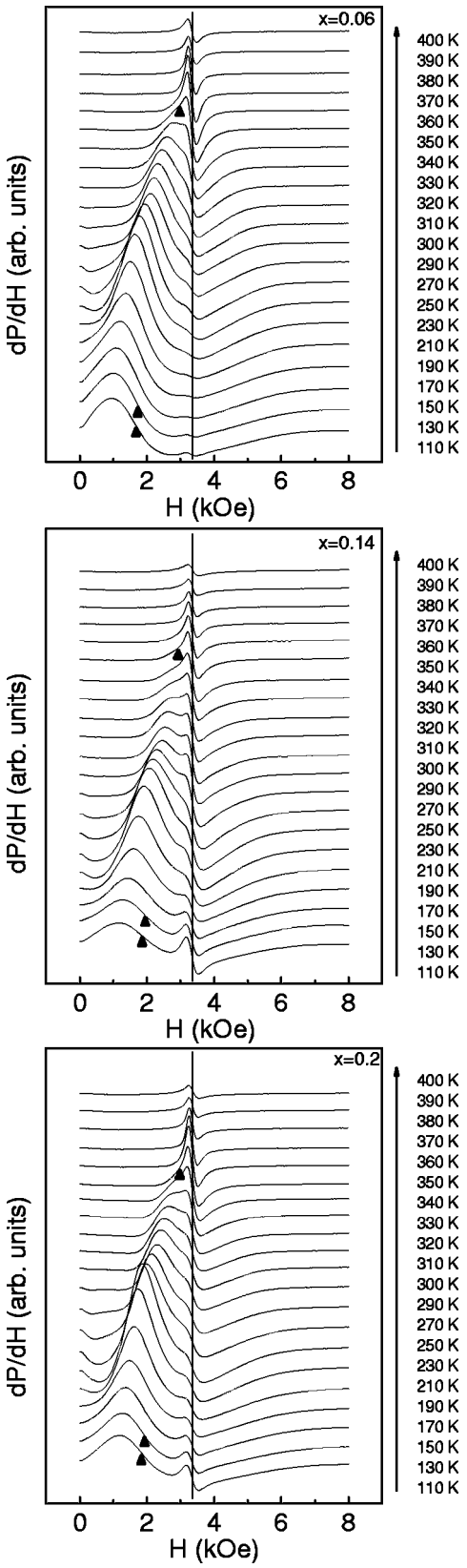

FIG. 6. ESR spectra for samples with $x=0.06$, 0.14, and 0.2 at different temperatures. The straight lines and filled triangles denote the positions of the paramagnetic and ferromagnetic signals, respectively.

C. Percolative superconductivity

Earlier research showed that, despite the different spin configurations of the dopants on the Cu sites, the impurities suppress superconductivity dramatically through the interaction with the magnetic correlation in the CuO_2 planes, resulting in the critical doping levels of only several percent.[2,4–6] By contrast, in the mixed-valence Mn doped $La_{1.85-4/3x}Sr_{0.15+4/3x}Cu_{1-x}Mn_xO_4$ here, the Mn ions in the clusters establish a ferromagnetic relation with one another and may have no influence on the magnetic correlation in the CuO_2 which is responsible for the superconductivity. Thus the suppression of the superconductivity is alleviated, and a much higher critical doping level can be expected. Because the dopant Mn ions reside on the Cu sites, naturally the superconductivity in this system will take place in the form of percolative superconductivity. This is illustrated by the presence of the diamagnetic signal (Fig. 4) and the absence of an obvious decrease of resistivity (Fig. 3) for $x=0.2$, because the superconducting grains are separated from one another and fail to form uninterrupted channels and the general conductivity for the higher doping level $x=0.2$ is poor thus making small change less discernable.

D. Retrospection and appeal

As the ground state of the undoped cuprates is an antiferromagnetic Mott insulator with nearest-neighbor $Cu^{2+}—Cu^{2+}$ antiferromagnetic exchange interaction in the CuO_2 planes, the relationship between the antiferromagnetism and the superconductivity in the CuO_2 has been the focus of the cuprate superconductivity research, while the relationship between ferromagnetism and superconductivity in the CuO_2 planes is seldom reported. However, things are different in other systems, such as the cobalt oxyhydrate $Na_xCoO_2 \cdot yH_2O$.[21] This hydrated compound superconductor possesses layered structure as the cuprate superconductors, consisting of triangular CoO_2 sheets separated by insulating blocks of Na^+ ions and H_2O molecules, which donate electrons to create Co^{3+} ions with zero spin in a background of Co^{4+} ions with spin $S=1/2$ and increase the sheets separation, respectively. There has been no consensus to date for the mechanism of the superconductivity in these electron-doped possibly Mott-insulating CoO_2 sheets, and especially it is controversial whether the dominant in-plane magnetic correlation is ferromagnetic or antiferromagnetic. On the one hand, some researchers tried[22–26] to understand the superconductivity using the resonating valence bond idea[27] which describes a singlet quantum spin liquid ground state stabilized by frustration, and high temperature susceptibility measurement suggested the antiferromagnetic coupling between nearest-neighbor spins.[28,29] On the other hand, several studies examined the possibility of spin-triplet superconductivity,[22,30–32] and evidences in favor have been gained from resonance[29] and neutron inelastic scattering[33] experiments. Moreover, a brief historical retrospect will tell that the relationship between ferromagnetism and superconductivity has been a topic of research interest. Early research found that in some rare earth metal compounds, notably $ErRh_4B_4$,[34] $HoMo_6S_8$,[35] and $ErNi_2B_2C$,[36] the ferromagnetic nuclear-spin order and the superconductivity compete with each other, the nuclear and electronic system being only weakly coupled. Recently, in close examination inspired by the identification of the spin-triplet superfluid phase in ^3He which naturally led to theoretical prediction that spin-triplet superconductivity would be favored in a metallic state close to the border of ferromagnetism, the coexistence of superconductivity and ferromagnetism has been observed in UGe_2,[37] $ZrZn_2$,[38] and URhGe,[39] where spin-triplet superconductivity induced by magnetic fluctuation was suggested. All these interesting observations provide useful information for expanding our general understanding of the superconductivity and also calls for further efforts.

IV. CONCLUSION

To summarize, the percolative superconductivity which is coexisting with the ferromagnetism or superparamagnetism originating from the $Mn^{3+}—O—Mn^{4+}$ superexchange interaction can survive a Mn doping level of $x=0.2$ in mixed-valence Mn doped $La_{1.85-4/3x}Sr_{0.15+4/3x}Cu_{1-x}Mn_xO_4$.

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