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Effects of Fe doping of $La_{1.85}Sr_{0.15}CuO_4$

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Abstract

In singly doped samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ and doubly doped samples of $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$, Fe ions substitute for Cu^{2+} at the valence of 3+. The depression of T_c is less sharp in doubly doped samples than in singly doped samples due to the compensation of carriers. We consider that doping with Fe severely disturbs the alignment of $Cu(3d_{x^2-y^2})$ and $O(2p_\sigma)$ orbitals and leads to the formation of CuO_6 clusters. The charge carriers in these CuO_6 clusters lose their itineracy and show localized behaviour. The decrease in T_c caused by Fe doping is due to the localization of carriers but not to the existence of an impurity moment.

1. Introduction

For high-T_c superconductors, study of the depression of T_c caused by impurity substitution at the Cu site of the CuO_2 plane is of considerable importance in research on the mechanism of the superconductivity. The particularly relevant issues in substitution studies are to what degree magnetic and nonmagnetic dopants affect the superconductivity, and how dopants with different electronic structures alter the normal-state transport and magnetic properties. Due to the simple structure of the La214 system, attempts have been made to substitute a great variety of transition metals for copper in $La_{1.85}Sr_{0.15}CuO_4$ [1–5]. $La_{1.85}Sr_{0.15}CuO_4$ is the optimal composition, where the highest T_c-value is attained. The doping of 3d transition metal elements into the Cu sites offers opportunities for study of the interplay between magnetism and superconductivity, and further testing of the Abrikosov and Gork'ov theory which predicts that T_c should decrease in the presence of magnetic impurities in the lattice.

The CuO_2 planes in the parent compounds can be well described in terms of a two-dimensional (2D) $S = \frac{1}{2}$ Heisenberg antiferromagnet [6]. The substitution at the Cu sites ($S = \frac{1}{2}$) of other 3d transition metal elements (Co, Ni, Zn) carries magnetic impurities in the lattice. These impurities essentially cause pair breaking, leading to a reduction of T_c, while leaving the carrier concentration in the CuO_2 plane unaltered [7–9]. However, a high-valence metal doping condition would lead to a change of carrier concentration in the CuO_2 plane. It is known that high-T_c superconductivity is affected by the carrier concentration in the CuO_2

plane. Thus, study of high-valence metal doping is important in efforts to understand the mechanism of the depression of T_c resulting from transition metal doping.

In a previous study we found that double doping is effective in improving the doping at Cu sites with high-valence Mn ions [5]. A double-doping process can be employed to nearly compensate the strong decrease of carrier concentration induced by high-valence ion doping, thus keeping the carrier concentration constant. Fe^{3+} is high valence. Thus a study of double doping with Fe would be helpful. For Fe-doped samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$, x-ray diffraction analysis reveals that only at doping levels $x \leqslant 0.1$ can we obtain pure phase samples. Thus we embarked on a double-doping experiment and successfully synthesized doubly doped samples of $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ ($0 \leqslant x \leqslant 0.5$) which are pure phase. In these samples, Sr^{2+} ions substitute for La^{3+} providing hole carriers, and Fe ions directly substitute at Cu sites in the CuO_2 planes leading to there being extra electrons in the conducting layer [7].

2. Experimental details

Samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ ($x = 0, 0.01, 0.02, 0.03, 0.05, 0.1$) and $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ ($x = 0, 0.01, 0.02, 0.03, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5$) were prepared by means of a conventional solid-state reaction method at sinter temperatures of 1120–1250 °C using high-purity La_2O_3, $SrCO_3$, CuO, and Fe_2O_3. X-ray diffraction (XRD) analysis was carried out using a Rigaku-D/max-γA diffractometer using high-intensity Cu Kα radiation to screen for the presence of an impurity phase and changes in structure. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB MK II spectrometer with a Mg Kα x-ray source and a resolution of 0.9 eV. Resistivity as a function of temperature was measured using a standard four-probe method in a closed-cycle helium cryostat. Magnetic susceptibility was measured by a SQUID susceptometer (Quantum Design MPMS) under field-cooled conditions (field: 10 G).

3. Results and discussion

We obtain pure phase samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ at doping levels $x \leqslant 0.1$. Above this level, impurities emerge. We consider the Cu ion to have the valence of 2+ while the Fe ion has the valence 3+. Doping with Fe would carry extra electrons into the CuO_2 plane and counteract the hole carriers in the CuO_2 plane. At high Fe doping content, this would lead to valence mismatch and further result in instability of the K_2NiF_4-type structure. Thus it is difficult to heavily dope Fe ions into a La214 system without changing the Sr^{2+} doping content. To nearly compensate the strong decrease of hole carrier concentration induced by Fe doping, we carried out a double-doping experiment and successfully synthesized pure phase samples of $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ ($0 \leqslant x \leqslant 0.5$).

XRD analysis confirmed that the samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ ($x = 0, 0.01, 0.02, 0.03, 0.05, 0.1$) and $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ ($x = 0, 0.01, 0.02, 0.03, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5$) were all crystallized in a single-phase tetragonal K_2NiF_4-type structure. The unit-cell parameters of the samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ and $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$, obtained by Rietveld analysis of the experimental XRD patterns, are summarized in table 1. Clearly, with increasing Fe doping, the c-parameter contracts and the a-parameter expands slightly for the two series of samples. The changes in unit-cell parameters are similar to the results obtained under other 3d transition metal doping conditions [5, 10, 11].

In order to determine the valence of Fe in different doping conditions, XPS measurements were carried out on Fe, because XPS is a powerful tool for providing information on the

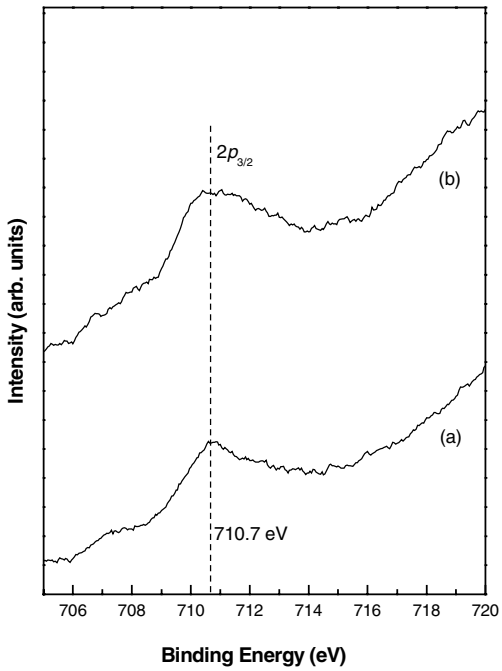

Figure 1. X-ray photoelectron spectra of Fe 2p core level for (a) a $La_{1.85}Sr_{0.15}Cu_{0.9}Fe_{0.1}O_4$ sample and (b) a $La_{1.75}Sr_{0.25}Cu_{0.9}Fe_{0.1}O_4$ sample.

Table 1. The unit-cell parameters of samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ and $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ obtained by Rietveld analysis of the experimental XRD patterns.

	$La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$		$La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$	
x	a (Å)	c (Å)	a (Å)	c (Å)
0.00	3.7790	13.2510	3.7790	13.2510
0.01	3.7800	13.2457	3.7800	13.2460
0.02	3.7806	13.2421	3.7801	13.2448
0.03	3.7820	13.2292	3.7807	13.2405
0.05	3.7849	13.2177	3.7817	13.2382
0.10	3.7877	13.2004	3.7825	13.2263
0.20	—	—	3.7849	13.2115
0.30	—	—	3.7860	13.2040
0.40	—	—	3.7867	13.2006
0.50	—	—	3.7881	13.1911

oxidation state and the electronic structure of the ions. Figure 1 gives the XPS spectrum of the Fe 2p region of a $La_{1.85}Sr_{0.15}Cu_{0.9}Fe_{0.1}O_4$ sample and that of a $La_{1.75}Sr_{0.25}Cu_{0.9}Fe_{0.1}O_4$ sample. The XPS peak at 710.7 eV for the $La_{1.85}Sr_{0.15}Cu_{0.9}Fe_{0.1}O_4$ and $La_{1.75}Sr_{0.25}Cu_{0.9}Fe_{0.1}O_4$ samples corresponds to Fe $2p_{3/2}$. For this spectrum, it was established that Fe 2p line was attributable principally to Fe^{3+}. The XPS results suggest that the Fe ions are at a valence of 3+ for both series of samples.

The temperature dependences of the resistivity for samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ and $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ are shown in figures 2(a) and (b), respectively. From the

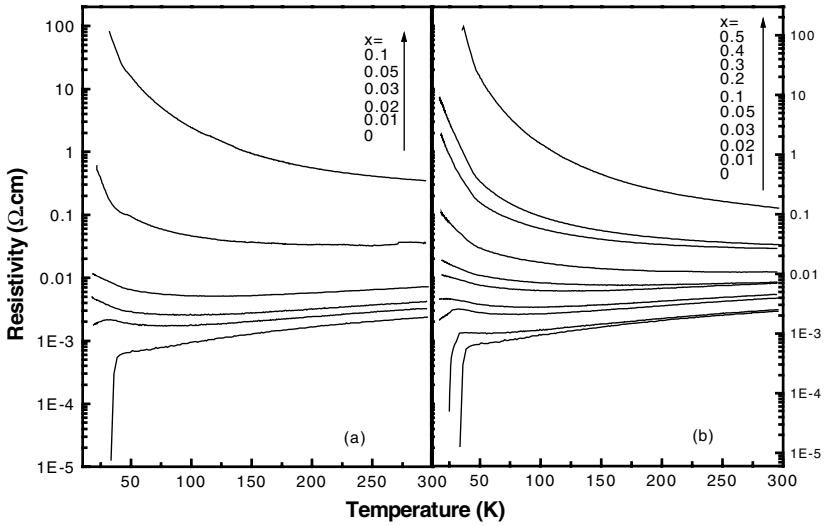

Figure 2. The temperature dependences of the resistivity for (a) samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ and (b) samples of $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$.

ρ–T curves we notice that doping with Fe depresses the superconductivity dramatically. When the superconductivity is depressed, these samples show semiconductor-like behaviour. It is obvious that the resistivity is larger in $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ samples than that in $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ samples at the same Fe doping content. We consider the difference in normal-state electrical transport to be the result of the change in hole carrier in the CuO_2 plane for the two series of samples. In singly doped samples, the substitution of Fe^{3+} introduces extra electrons and decreases the hole carrier concentration in the CuO_2 plane. Thus the resistivity is larger in singly doped samples than in doubly doped samples.

Figure 3 gives the temperature dependences of the magnetic susceptibility under field-cooled conditions (field: 10 G) for (a) $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ samples and (b) $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ samples. It shows the diamagnetic signal for $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ samples at $x \leqslant 0.02$; the T_c^{onset}-values are 37, 33, and nearly 0 K for $x = 0$, 0.01, and 0.02 samples, respectively. For $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ samples, it shows the diamagnetic signal at $x \leqslant 0.03$; the T_c^{onset}-values are 37, 35, 31, and 29 K for $x = 0, 0.01, 0.02$, and 0.03 samples, respectively. The Meissner volume decreases sharply with increasing Fe doping content in both series of samples. These results indicate that magnetic Fe ions strongly depress the superconductivity. The T_c^{onset}-values obtained from the χ–T curves are consistent with the results from the ρ–T curves.

The Fe^{3+} ($3d^5$) ion has a high-spin state ($t_{2g}^3e_g^2$) of $S = \frac{5}{2}$ and a low-spin state (t_{2g}^5) of $S = \frac{1}{2}$. Experimental findings and theoretical calculations show that in an octahedron the d^5 ions are exceptionally stable in their high-spin state [12]. According to the suggestion of Xiao *et al* that a magnetic pair-breaking mechanism can account for the depression of T_c, the strong depression of T_c by Fe^{3+} in our experiments also conforms with the occupancy of the high-spin state ($t_{2g}^3e_g^2$, $S = \frac{5}{2}$). The low-spin state of Fe^{3+} ($S = \frac{1}{2}$) possesses the same spin moment as the Cu^{2+} ion.

According to the Abrikosov and Gork'ov theory [13], the T_c-reduction data can be described by the AG equation given as

$$\ln \frac{T_c}{T_{c0}} = \Psi\left(\frac{1}{2}\right) - \Psi\left(\frac{1}{2} + \frac{2J^2S(S+1)N(E_F)x}{2k_BT_c}\right), \tag{1}$$

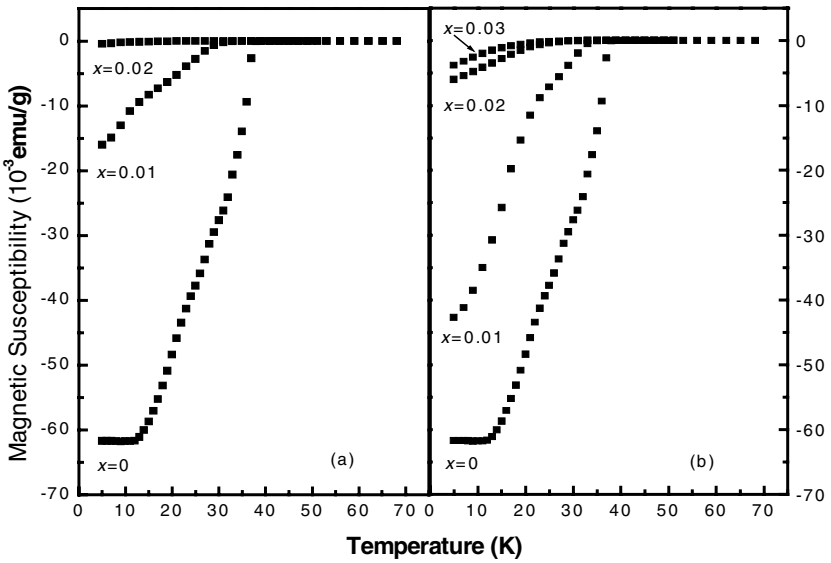

Figure 3. The temperature dependences of the magnetic susceptibility under field-cooled conditions (field: 10 G) for (a) samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ and (b) samples of $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$.

where T_{c0} is the value of T_c at $x = 0$. J is the constant for exchange between the hole spin and the spin of the 3d metal ions. The quantity $N(E_F)$ is the density of states at the Fermi level. When x is small, equation (1) can be interpreted as

$$T_{c0} - T_c = \frac{\pi^2 J^2 S(S+1) N(E_F) x}{2k_B}. \tag{2}$$

If $N(E_F)$ remains constant with increasing doping content, formula (2) can be interpreted as

$$T_{c0} - T_c = Ax. \tag{3}$$

In the two series of samples, Fe^{3+} ions occupy high-spin states and possess the spin moment $S = \frac{5}{2}$. From the magnetic susceptibility results, we notice that the superconductivity is depressed at different Fe doping levels ($x = 0.02$ for $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ and $x = 0.03$ for $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$). The T_c^{onset}-values for $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ samples are 37, 33, and nearly 0 K for $x = 0$, 0.01, and 0.02 samples, respectively. For doubly doped $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ samples, there is a diamagnetic signal at $x \leqslant 0.03$. The T_c^{onset}-values are 37, 35, 31, and 29 K for $x = 0$, 0.01, 0.02, and 0.03 samples, respectively. In figure 4 we present the dependence on the Fe content x of T_c^{onset}. It is obvious that the depression of T_c does not obey formula (3) for samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$. For samples of $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$, it seems to obey formula (3) for $x \leqslant 0.03$. According to formula (3), the T_c^{onset}-value would drop to zero at doping content $x = 0.138$, while the experimental results suggest no superconducting transition for $x = 0.05$ samples. These results suggest that the suppression of superconductivity does not result from magnetic pair-breaking effects. We consider that doping with Fe severely disturbs the alignment of $Cu(3d_{x^2-y^2})$ and $O(2p_\sigma)$ orbitals because it is hard to form FeO_6 octahedra in K_2NiF_4-type structures. The doping of Fe blocks the arrangement of CuO_6 octahedra and leads to the formation of CuO_6 clusters. Due to the blocking of Cu–O–Cu long-range hybridization by Fe, the carriers in these CuO_6 clusters lose their itineracy and show localized behaviour. Thus the superconductivity

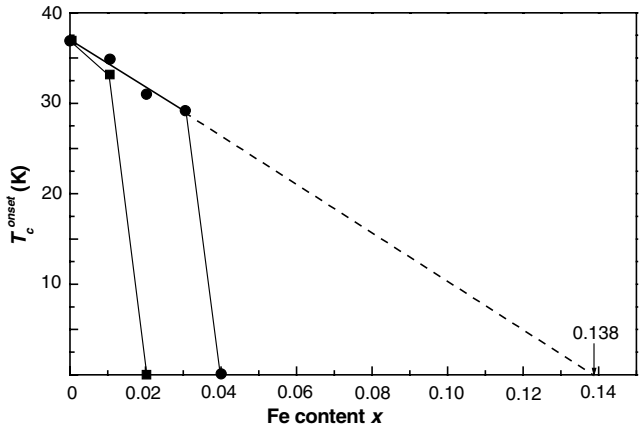

Figure 4. Variation of T_c^{onset} with the Fe doping content x (solid squares: $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ samples; solid circles: $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ samples).

is suppressed. For singly doped $La_{1.85}Sr_{0.15}Cu_{1-x}Fe_xO_4$ samples, the doping of high-valence Fe ions into Cu sites leads to a reduction in carrier concentration, while for doubly doped $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_4$ samples, the reduction in carrier concentration is compensated by regulation of the Sr doping content. Thus the suppression of superconductivity is less severe in doubly doped samples than in singly doped samples. On the other hand, the double-doping process is effective in compensating the reduction of the carrier concentration by high-valence Fe-ion doping. As a result, the double-doping process is not only effective in stabilization of the K_2NiF_4-type structure, but also leads to a smaller resistivity in normal-state samples and a higher T_c as compared to those of singly doped samples. These results reveal that the decrease in T_c caused by Fe doping is due to the localization of carriers but not to the existence of an impurity moment.

4. Conclusions

In summary, the effects of Fe doping of $La_{1.85}Sr_{0.15}CuO_4$ have been studied by means of measurements of the electrical transport and magnetic susceptibility. The double-doping process is effective in improving the doping at the Cu site with high-valence transition elements due to the compensation of charge carriers in the CuO_2 plane. The suppression of superconductivity is less severe in doubly doped samples than in singly doped samples. Doping with Fe leads to the formation of CuO_6 clusters and thus localizes the movement of hole carriers. The decrease in T_c caused by Fe doping is due to the localization of carriers but not to the existence of an impurity moment.

Acknowledgments

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