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Substitution for Cu in the electron-doped infinite-layer superconductor $Sr_{0.9}La_{0.1}CuO_2$: Ni reduces T_c much faster than Zn

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We have substituted magnetic Ni and nonmagnetic Zn impurities at Cu sites, in order to probe the nature of the superconductivity for the electron-doped infinite-layer superconductor $Sr_{0.9}La_{0.1}CuO_2$. We found that T_c was nearly constant until 3% replacement by Zn while the superconductivity was nearly suppressed for a 2% substitution by Ni. This behavior is very similar to that of conventional superconductors, but quite different from typical holed-doped cuprate superconductors.

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I. INTRODUCTION

Magnetic and nonmagnetic impurity substitution at the Cu site in high-T_c cuprates[1,2] has been one of the test probes for the mechanism of superconductivity and the symmetry of the order parameter.[3–33] It has also shed light on the recent striking issue of a normal-state pseudogap.[3–5] The most important observation was that the nonmagnetic Zn ion suppressed T_c at nearly the same rate as a magnetic Ni ion did for hole-doped cuprates such as $(La,Sr)_2CuO_4$,[3,6–8] $YBa_2Cu_3O_{7-\delta}$,[3,6,9–13] $YBa_2Cu_4O_8$,[14,15] $Bi_2Sr_2CaCu_2O_8$,[4,5] etc. This behavior is in strong contrast to that of conventional superconductors, where the reduction of T_c is much stronger for magnetic impurities. This difference led to the theoretical formulation of an unconventional pairing mechanism and a symmetry of the order parameter for hole-doped high-temperature superconductors.[16–27] However, the impurity effect on the superconductivity for the electron-doped high-T_c cuprates has not yet been studied in detail, to our best knowledge.

There are two well-known electron-doped high-T_c cuprates. One is $(Ln,Ce)_2CuO_4$ with $T_c \sim 25$ K; the other is the infinite-layer superconductor $(Sr,Ln)CuO_2$ with $T_c \sim 43$ K where Ln is La, Pr, Nd, etc. The structure of $(Ln,Ce)_2CuO_4$ consists of charge reservoir blocks and CuO_2 planes as in the case of hole-doped cuprate superconductors. In this case, the oxygen content is very important in determining the superconducting transition temperature. The impurity effect on the superconductivity for this compound has been studied, and for the available information on the impurity effect, controlling the impurity and oxygen contents simultaneously is quite essential. Control of the oxygen in $(Ln,Ce)_2CuO_4$ requires rather extreme conditions, such as temperatures as high as $850°-950\,°C$ in Ar, which is not far below the sintering temperature.[7,25,31] Compared with $(Ln,Ce)_2CuO_4$, the infinite-layer superconductor[34,35] has several incomparable merits. This compound contains only the backbone structure, i.e., CuO_2 planes separated only by a metallic spacer layer, and does not contain a charge reservoir block.[36] The absence of the charge reservoir block seems to help make the oxygen content stoichiometric, which was confirmed by neutron-scattering studies.[37] This oxygen stoichiometry allows us to exclude the effect of the oxygen content on the superconductivity. Despite this merit, difficulties in synthesizing high-quality infinite-layer superconductors has hampered the study of the Cu-substitution effect on superconductivity.[38]

Here, we report the effect of the magnetic and the nonmagnetic impurities on the nature of superconductivity for $Sr_{0.9}La_{0.1}Cu_{1-x}R_xO_2$ where R can be magnetic Ni or nonmagnetic Zn. We found that T_c was nearly constant until $x \sim 0.03$ for nonmagnetic Zn substitution while the superconductivity was nearly suppressed for $x \sim 0.02$ with $-dT_c/dx \geqslant 20$ K/% for magnetic Ni. This is quite striking because it is opposite to the general behavior of hole-doped cuprate superconductors, but is similar to that of conventional superconductors.

II. EXPERIMENT

Starting materials of La_2O_3, $SrCO_3$, CuO, and ZnO (NiO) with nominal compositions were calcined at $920°-945\,°C$ for 36 h with several intermittent grindings. A pelletized precursor sandwiched between two Ti oxygen-getter slabs was put in a Au or Pt capsule. The capsule, together with an insulating wall and a graphite-sleeve heater, was closely packed inside a high-pressure cell made of pyrophillite. Details of the sintering under high pressure[38,39] and determination of the charge-carrier type[40] were reported elsewhere. The masses of the homogenous samples obtained in one batch were larger than 200 mg.

The low-field magnetization was measured in the zero-field-cooled state by using a superconducting quantum interference device magnetometer (MPMS*XL*, Quantum Design) at 10–20 Oe. The powder x-ray diffraction (XRD) was measured using a Rigaku x-ray diffractometer. Energy dispersive spectroscopy using an electron probe microanalyzer (EPMA) and a field-emission scanning electron microscope (SEM) (JSM-6330F, Jeol) was also used.

III. DATA ANALYSIS AND DISCUSSION

Figure 1(a) shows the x-ray powder-diffraction patterns of $Sr_{0.9}La_{0.1}Cu_{1-x}Zn_xO_2$ for $x=0$, 0.01, and 0.03 and of $Sr_{0.9}La_{0.1}Cu_{1-x}Ni_xO_2$ for $x=0.01$ and 0.02. The intensity of

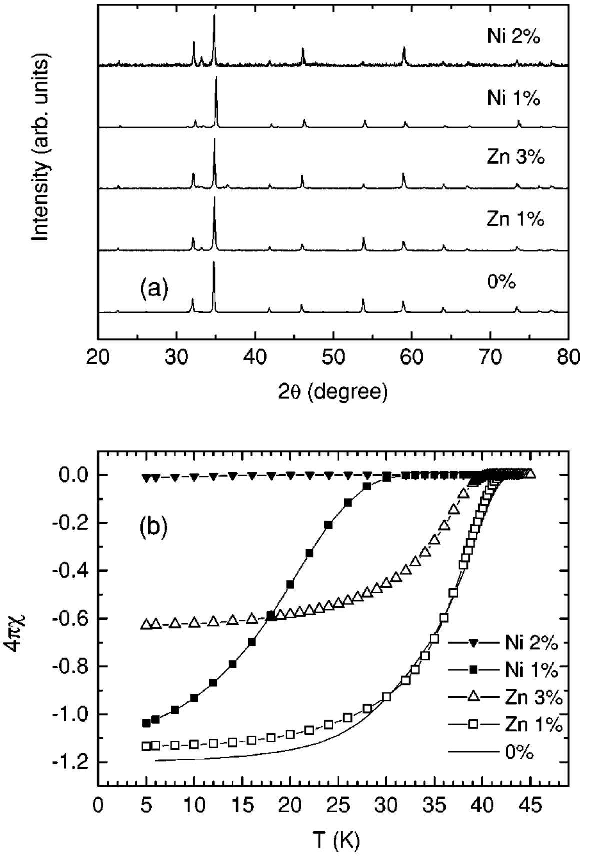

FIG. 1. (a) X-ray powder-diffraction patterns for $Sr_{0.9}La_{0.1}Cu_{1-x}Zn_xO_2$ ($x=0$, 0.01, and 0.03) and $Sr_{0.9}La_{0.1}Cu_{1-x}Ni_xO_2$ ($x=0.01$ and 0.02). The intensity of each pattern was normalized to the intensity of the (101) peak and offset vertically for clear comparison. (b) Magnetic susceptibility, $4\pi\chi(T)$, curves for the samples.

each pattern was normalized to the intensity of the highest peak (101) and offset vertically for clear comparison. These XRD patterns show that a nearly single phase with an infinite-layer structure was formed. Peaks corresponding to Zn oxide, Ni oxide, and La oxide could not be identified within the resolution. The smaller peaks at $2\theta\sim 33.5°$ and 37.5° were also found to exist for the unsubstituted $Sr_{0.9}La_{0.1}CuO_2$ sample with nearly the same diamagnetic signal and same T_c; so they neither correspond to Zn oxide or Ni oxide, nor have an effect on T_c.[41] These smaller peaks were assigned to Cu_2O and $LaCuO_3$ previously.

The lattice constants are $a=b=3.928$ (3.950) Å and $c=3.433$ (3.410) Å for insulating $SrCuO_2$ (superconducting $Sr_{0.9}La_{0.1}CuO_2$).[37,41,38] The expansion of the a-axis lattice constant is known to be due to the transfer of electron carriers to the CuO_2 planes, and the shrinking of the c-axis lattice constant is simply due to the ionic size effect.[34] The lattice constants from the XRD patterns in Fig. 1(a) for $Sr_{0.9}La_{0.1}Cu_{0.98}Ni_{0.02}O_2$ and $Sr_{0.9}La_{0.1}Cu_{0.97}Zn_{0.03}O_2$ are $a=b=3.943$ Å and $c=3.417$ Å and $a=b=3.950$ Å and $c=3.408$Å, with an error bar of about 0.001 Å, respectively. Note that the lattice constants of $Sr_{0.9}La_{0.1}Cu_{0.98}Ni_{0.02}O_2$ remain much closer to those for superconducting $Sr_{0.9}La_{0.1}CuO_2$ than to those for insulating $SrCuO_2$. We also examined whether Zn was uniformly distributed within the samples of $Sr_{0.9}La_{0.1}Cu_{1-x}Zn_xO_2$ with $x=0.03$ and found that the average Zn concentration was close to the nominal value. Since the entire heating process was done inside a sealed Au capsule under high pressure, a net loss of metallic ions was not likely to occur.

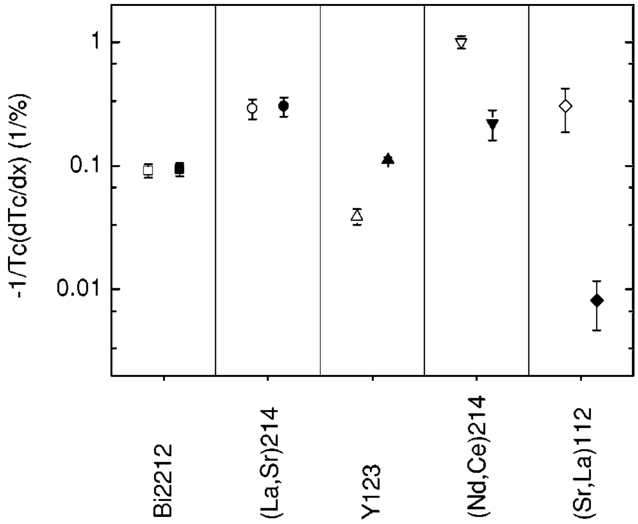

FIG. 2. Normalized reduction rates of T_c, $-1/T_c\times dT_c/dx$, for Cu-site substitution in high-T_c cuprates are displayed in units of 1/%. Open symbols are for Ni substitution, and closed symbols are for Zn substitution. The squares are for $Bi_2Sr_2CaCu_2O_8$, the circles for $(La,Sr)_2CuO_4$, the up triangles for $YBa_2Cu_3O_{7-\delta}$, the down triangles for $(Nd,Ce)_2CuO_4$, and the diamonds for $Sr_{0.9}La_{0.1}CuO_2$. All data, except that for $Sr_{0.9}La_{0.1}CuO_2$, are from the references shown in the text. Note that nonmagnetic Zn hardly suppresses the T_c of an infinite-layer superconductor.

We measured the low-field magnetization and calculated the magnetic susceptibility, $4\pi\chi(T)$, as shown in Fig. 1(b). For Ni substitution, both T_c and the superconducting volume fraction drastically decrease for $x=0.02$, and the superconductivity nearly vanishes. (Here, the T_c was determined to be the onset temperature.) The average T_c reduction rate was $-dT_c/dx\geqslant 20$ K/%. However, for Zn substitution, the change in T_c was less than about 2 K until $x\sim 0.03$ where the superconducting volume fraction became less than about half that of the unsubstituted sample. For $x\gtrsim 0.03$, a single phase was hard to obtain.

Figure 2 shows the normalized reduction rate of T_c, $-1/T_c\times dT_c/dx$, for Cu-site substitution in other high-T_c cuprates in the literature and in $(Sr_{0.9},La_{0.1})CuO_2$ in our study: $Bi_2Sr_2CaCu_2O_8$,[4,5] $(La,Sr)_2CuO_4$,[3,6–8] $YBa_2Cu_3O_{7-\delta}$,[3,6,9–13] $(Nd,Ce)_2CuO_4$,[7,25,31] and $(Sr_{0.9},La_{0.1})CuO_2$. The open and filled symbols represent the cases of Ni and Zn substitution, respectively. As noted previously, in hole-doped cuprate superconductors, the $-1/T_c\times dT_c/dx$ for nonmagnetic Zn is nearly the same as that for magnetic Ni substitution, which is in contrast to the behavior in conventional superconductors. However, not all cuprates are the same. For example, in the electron-doped superconductor $(Ln,Ce)_2CuO_4$, a magnetic impurity reduces T_c about three times faster than does a nonmagnetic impurity. In this study, a similar behavior was also observed in

$(\mathrm{Sr}_{0.9},\mathrm{La}_{0.1})\mathrm{CuO}_2$. In other words, impurity effect on T_c is similar for two well-known *n*-type cuprates; that is, Ni ''kills'' the superconductivity faster than Zn. However, in $(\mathrm{Sr}_{0.9},\mathrm{La}_{0.1})\mathrm{CuO}_2$, the nonmagnetic impurity kills the superconductivity more than ten times more slowly than do the magnetic impurities, which is closer to behavior observed in conventional superconductors.

The effects of impurities in cuprates with different superconducting gap symmetries have been discussed quite intensively.[16–27] Also, phase-sensitive Josephson tunneling or the existence of a half flux quantum in a tricrystal ring[28] could be another test of the gap symmetry. Such approaches require high-quality thin films, and are not feasible for infinite-layer superconductors.[42] In addition, the pairing symmetry of $(Ln,\mathrm{Ce})_2\mathrm{CuO}_4$ still remains controversial.[29,30]

In addition to the impurity effect, quite a few other experiments have indicated that $(\mathrm{Sr}_{0.9},\mathrm{La}_{0.1})\mathrm{CuO}_2$ is very similar to conventional superconductors. For example, equilibrium magnetization measurements showed that, even in the zero-temperature limit, the superconductivity has a three-dimensional nature.[43,44] Another example is the recent observation of scanning tunneling spectra[45] in $(\mathrm{Sr}_{0.9},\mathrm{La}_{0.1})\mathrm{CuO}_2$, which showed the absence of a zero-bias conductance peak (superconducting gap $\Delta\sim13$ meV) and a pseudogap. The absence of the pseudogap was also observed in nuclear-magnetic-resonance experiments.[46]

IV. SUMMARY

We found that in the electron-doped infinite-layer superconductor $\mathrm{Sr}_{0.9}\mathrm{La}_{0.1}\mathrm{Cu}_{1-x}\mathrm{R}_x\mathrm{O}_2$ substitution of the nonmagnetic Zn ion in the CuO_2 plane hardly suppressed T_c ($-dT_c/dx\leqslant0.5$ K/% for $x\leqslant0.03$) while substitution of the magnetic Ni ion kills the superconductivity at only $x\sim0.02$ ($-dT_c/dx\geqslant20$ K/%). This behavior is similar to that observed for conventional superconductors and is also consistent with recent observations, such as the absence of the pseudogap and a stronger three-dimensional superconductivity.

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