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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(October 27, 2018)

We report the effect of substitution for Cu on the $T_c$ of the electron-doped infinite-layer superconductors Sr$_{0.9}$La$_{0.1}$Cu$_{1-x}$R$_x$O$_2$ for $R$ = Zn and Ni. We found that $T_c$ was nearly constant until $x \sim 0.03$ for $R$ = Zn while the superconductivity was nearly suppressed for $x \sim 0.02$ with $dT_c/dx \geq 20$ K/% for $R$ = Ni. This behavior is very similar to that of conventional superconductors. These findings are discussed in terms of the superconducting gap symmetry in the cuprate superconductors, including another electron-doped superconductor, (Nd, Ce)$_2$CuO$_{4-y}$.

I. INTRODUCTION

Impurity substitution at the Cu site in high-$T_c$ cuprates [1-3] has been considered to be a test probe for the mechanism of high-temperature superconductivity and the symmetry of the superconducting order parameter [3-33]. It has also shed light on the recent striking issue of a normal-state pseudo-gap. [4-5] The most important observation was that the non-magnetic Zn ion suppressed $T_c$ somewhat more than magnetic ions such as Ni for all kinds of hole-doped cuprates such as (La,Sr)$_2$CuO$_4$, [6-9] YBa$_2$Cu$_3$O$_7$-[4], [10-13] YBa$_2$Cu$_4$O$_8$, [9,10] and Bi$_2$Sr$_2$CaCu$_2$O$_8$. [9,10] The $T_c$ reduction rate for Zn substitution was $dT_c/dx \sim 10$ K/% and was higher for underdoped compounds than optimally or overdoped ones. This behavior of $T_c$ is strongly contrasted with that of conventional superconductors, where the reduction of $T_c$ is stronger for magnetic impurities, but nearly absent for non-magnetic ion impurities. This difference led to the theoretical formulation of an unconventional pairing mechanism and a symmetry of the order parameter for high-temperature superconductor [16-27].

Substitution at the Cu site in ordinary high-$T_c$ cuprates with a charge reservoir block is generally not immune to structural distortion and/or charge carrier transfer between the charge reservoir block and the conducting CuO$_2$ planes, which could affect $T_c$ dramatically. Especially, one must be very cautious about the oxygen content when comparing the amounts of $T_c$ reduction directly. Another complexity is due to the existence of several substitutable sites inside a unit-cell.

Electron-doped infinite-layer superconductors (Sr$_{2+y}$Ln$_{2-y}$)CuO$_2$ (Ln = La, Sm, Nd, Gd, etc.) [34-35] have several incomparable merits for studying the effect of substitution for Cu on $T_c$. Without a charge reservoir block, it has only the back-bone structure common to all high-$T_c$ cuprates, CuO$_2$ planes separated only by a metallic spacer layer. [36] The structure is robust, and oxygen is very stoichiometric and stable: buckling of the CuO$_2$ plane, O interstitials and O vacancies were reported to be nearly absent. [37] The $T_c$ has been found to be very robust against modifications of the structure and changes in the magnetic moment due to doping various lanthanide ions at the Sr sites. [38] Thus, the substitution for Cu in the infinite-layer superconductors has the least possibility of changing $T_c$ via secondary routes, and observations should reveal a more intrinsic change in the $T_c$ of cuprate superconductors. However, difficulties in synthesizing high-quality sample has prohibited intense work on these infinite-layer superconductors. [39] Moreover, no work on the Cu-substitution effect has been reported.

Recently, we succeeded in synthesizing high-quality (Sr$_{0.9}$La$_{0.1}$)CuO$_2$. [40] Here, we report the effect of substitution for Cu on the $T_c$ of the electron-doped infinite-layer superconductors Sr$_{0.9}$La$_{0.1}$Cu$_{1-x}$R$_x$O$_2$ where $R$ = Zn and Ni. We found that $T_c$ was nearly constant until $x \sim 0.03$ for $R$ = Zn while the superconductivity was nearly suppressed for $x \sim 0.02$ with $dT_c/dx \geq 20$ K/% for Ni. This feature is similar to those observed in conventional superconductors.

II. EXPERIMENTAL

Starting materials of La$_2$O$_3$, SrCO$_3$, CuO, and ZnO (NiO) with a nominal composition were calcined at 920 – 945 °C for 36 hours 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 is found elsewhere. [41] 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 SQUID magnetometer (MPMS.XL, Quantum Design) at 10 \textdegree\sim 20 \textOE. The powder X-ray diffraction (XRD) was measured using a RIGAKU X-ray diffractometer. Energy dispersive spectroscopy (EDS) using an electron probe microanalyzer and a field emission scanning electron microscope (JSM-6330F, JEOL) were 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$_x$O$_2$, $x = 0, 0.01, 0.03,$ and Sr$_{0.9}$La$_{0.1}$Cu$_{1-x}$Ni$_x$O$_2$, $x = 0.01$ and 0.02. The intensity of each pattern was normalized to the intensity of the (101) peak and offset vertically for clear comparison. 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$^\circ$ and 37.5$^\circ$ were also found to exist for unsubstituted pristine Sr$_{0.9}$La$_{0.1}$Cu$_2$O$_2$ sample with nearly the same diamagnetic signal; thus they do not correspond to Zn oxide or Ni oxide.

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$_{0.1}$Cu$_2$O$_2$). 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. 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, respectively. The error bars are about 0.003 Å.

We also examined whether Zn was uniformly distributed within the samples of Sr$_{0.9}$La$_{0.1}$Cu$_{1-x}$Zn$_x$O$_2$ with $x = 0.03$. The microscopic composition of the sample was measured over tens of grains, each with a smaller detecting area of $3 \times 3$ $\mu$m$^2$. The average diameter of a grain was about 10 $\mu$m, and the Zn concentration in the grains was 3±1%. The average Zn concentration was also closer to the nominal value. Since the entire heating process was done inside a Au capsule, a net loss of metallic ions is not likely to occur for the high-pressure synthesis technique. For other samples, the resolution of the EDS was rather insufficient to determine the stoichiometry.

We measured the low-field magnetization and calculated the magnetic susceptibility, $4\pi\chi(T)$, to determine the effect of substitution at the Cu site on $T_c$. Figure 1(b) shows magnetic susceptibility, $4\pi\chi(T)$, curves for the above samples. The data for $x = 0$ were from a previous result. For Ni substitution, both $T_c$ and the superconducting volume fraction drastically decrease, and superconductivity nearly vanishes for a 2% substitution with an average $T_c$ reduction rate of $dT_c/dx \geq 20$ K/%. This behavior was confirmed for several samples with $x = 0.02$. 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 pristine sample. For samples with $x \geq 0.03$, growth of singl-phase samples was very difficult. Though we did not confirm the uniformness of Ni inside the sample due to the resolution limit of EDS, the result for $dT_c/dx$ should be a lower bound on the real value. The nearly total suppression of superconductivity in Sr$_{0.9}$La$_{0.1}$Cu$_{0.98}$Ni$_{0.02}$O$_2$ seems not to result from the lattice effect because the lattice constants remain much closer to those for superconducting Sr$_{0.9}$La$_{0.1}$Cu$_2$O$_2$ than those for insulating SrCuO$_2$. This means that the reduction of the electron carrier density in the CuO$_2$ plane does not play a dominant role in killing the superconductivity.

Figure 2 shows the reduction rate, $dT_c/dx$, for Cu-site substitution in high-$T_c$ cuprates: Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, [4,5] (La,Sr)$_2$CuO$_4$, [37–39] YBa$_2$Cu$_3$O$_7$–$\delta$, [4,5] (Nd,Ce)$_2$CuO$_4$, [4,5] and (Sr$_{0.9}$La$_{0.1}$)Cu$_2$O$_2$. We also examined whether Zn was uniformly distributed within the samples of Sr$_{0.9}$La$_{0.1}$Cu$_{1-x}$Zn$_x$O$_2$ with $x = 0.03$. The microscopic composition of the sample was measured over tens of grains, each with a smaller detecting area of $3 \times 3$ $\mu$m$^2$. The average diameter of a grain was about 10 $\mu$m, and the Zn concentration in the grains was 3±1%. The average Zn concentration was also closer to the nominal value. Since the entire heating process was done inside a Au capsule, a net loss of metallic ions is not likely to occur for the high-pressure synthesis technique. For other samples, the resolution of the EDS was rather insufficient to determine the stoichiometry.

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As noted previously, the $T_c$ reduction rate is higher for Zn substitution in 2-dimensional hole-doped cuprate superconductors, which occupies the majority of high-$T_c$ cuprates. However, this trend was first reversed for an electron-doped superconductor such as (Nd,Ce)$_2$CuO$_4$–$\delta$, which is just one step toward a conventional superconductor in terms of charge carrier type. Our finding for (Sr$_{0.9}$La$_{0.1}$)Cu$_2$O$_2$ seems to be the next step. Two kinds of representative n-type cuprates show similar behaviors for the substitution effect on $T_c$. Ni killing the superconductivity faster than Zn. However the difference is that the substitution effect in (Sr$_{0.9}$La$_{0.1}$)Cu$_2$O$_2$ is much closer to those in conventional superconductors with respect to the exact value of the $T_c$ reduction rate $dT_c/dx$.

Impurity substitution effects in hole-doped cuprates and electron-doped cuprates have been discussed in terms of the superconducting gap symmetry, $d$-wave and $s$-wave, respectively [16–27]. Phase-sensitive Josephson tunneling or the presence of a half flux quantum at the center of the tricrystal ring [28] could be a direct test of $d$-wave superconductivity, but would require high-quality thin films, which have not been feasible for infinite-layer superconductors due to difficulties in film growth. In addition, the pairing symmetry of the (Nd,Ce)$_2$CuO$_4$ compound remains to be controversial. [24,30]

Many experimental observations indicate that (Sr$_{0.9}$La$_{0.1}$)Cu$_2$O$_2$ has properties which are the most similar to those of conventional superconductors. This compound was reported to have more 3-dimensional superconductivity with the $c$-axis coherence length, even near zero temperature, being larger than the $c$-axis lat-
The undoped antiferromagnetic insulator Ca$_{0.85}$Sr$_{0.15}$CuO$_2$ has been reported to have more 3-dimensional magnetic coupling and that material has been reported to have a stronger 3-dimensional character than other parent insulators of cuprate superconductors, such as YBa$_2$Cu$_3$O$_6$, La$_2$CuO$_4$, and Sr$_2$CuO$_2$Cl$_2$. For example, an estimate of the ratio of the out-of-plane to the in-plane coupling constants for Ca$_{0.85}$Sr$_{0.15}$CuO$_2$ was two to three orders of magnitude larger than the corresponding values for YBa$_2$Cu$_3$O$_6$ and La$_2$CuO$_4$. A very recent observation of scanning tunneling spectra in (Sr$_{0.9}$La$_{0.1}$)CuO$_2$ support the existence of an s-wave gap with a superconducting gap $\Delta \sim 13$ meV, as well as the absence of pseudogap.

IV. SUMMARY

We found that in electron-doped infinite-layer superconductors Sr$_{9-x}$La$_{x}$Cu$_{1-y}$R$_{y}$O$_2$, substitution of the nonmagnetic Zn ion in the CuO$_2$ plane hardly suppresses $T_c$ ($dT_c/dx \leq 0.5$ K/% for $x \leq 0.03$) while substitution of the magnetic Ni ion kills the superconductivity at only $x \sim 0.02$ ($dT_c/dx \geq 20$ K/%). This behavior is similar to that observed for conventional superconductors. This behavior is also consistent with many recent observations, such as the existence of s-wave gap, the stronger 3-dimensionality in superconducting and antiferromagnetic properties.

ACKNOWLEDGMENTS

We greatly appreciate valuable discussions with D. Pavuna, K. Maki, Yunkyu Bang, N.-C. Yeh, A. V. Balatsky, and M. Sigrist. For the EPMA and SEM measurements, we are thankful to Mr. Dong Sik Kim at the Department of Materials Science & Engineering at Pohang University of Science and Technology. This work is supported by the Ministry of Science and Technology of Korea through the Creative Research Initiative Program.

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FIG. 1. (a) X-ray powder diffraction patterns for Sr$_{0.9}$La$_{0.1}$Cu$_{1-x}$Zn$_x$O$_2$ ( $x = 0, 0.01, 0.03$) and Sr$_{0.9}$La$_{0.1}$Cu$_{1-x}$Ni$_x$O$_2$ ( $x = 0.01$ 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.

FIG. 2. $T_c$ reduction rate, $dT_c/dx$, for Cu-site substitution in high-$T_c$ cuprates; open symbols are for Ni substitution and closed symbols are for Zn substitution. The squares are for Bi$_2$Sr$_2$CaCu$_2$O$_8$, the circles for (La,Sr)$_2$CuO$_4$, the up-triangles for YBa$_2$Cu$_3$O$_7$-$\delta$, the down-triangles for (Nd,Ce)$_2$CuO$_4$, and the diamonds for Sr$_{0.9}$La$_{0.1}$CuO$_2$. Note that non-magnetic Zn hardly suppresses the $T_c$ of an infinite-layer superconductor.
Figure 1, C. U. Jung et al.
Figure 2, C. U. Jung et al.