Synthesis and characterization of the infinite-layer superconductor Sr$_{0.9}$La$_{0.1}$CuO$_2$

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We report the high-pressure synthesis of the electron-doped infinite-layer superconductor Sr$_{0.9}$La$_{0.1}$CuO$_2$. A Rietveld analysis using X-ray powder diffraction data showed that, within the resolution of the measurement, the sample was purely an infinite-layer structure without any discernible impurities. The superconducting volume fraction and the transition width were greatly improved compared to those in the previous reports. Also the irreversibility field line was much higher than that of (La,Sr)$_2$CuO$_4$. The higher value seems to originate from the strong interlayer coupling due to the reduced average distance between the CuO$_2$ planes.

I. INTRODUCTION

The electron-doped infinite-layer compounds (Sr$_{1-x}$Ln$_x$)$^{+2}$CuO$_2$ (Ln = La, Sm, Nd, Gd, etc.) consist of an infinite stacking of CuO$_2$ planes and metallic (Sr) layers.[1] This is the simplest structure that contains only the key ingredients of all high-$T_c$ cuprates. The charge reservoir block common to other cuprate superconductors does not exist in this compound. Superconductivity in the infinite-layer compounds was first observed by Smith et al. for (Sr$_{1-x}$Nd$_x$)CuO$_2$.[2] Since the structure is so simple, it provides a unique opportunity to explore superconductivity unscreened by the charge reservoir block.

Several interesting properties have been observed for infinite-layer compounds. Since the average distance between CuO$_2$ planes is reduced due to the absence of the charge reservoir block, the interlayer coupling is expected to be very strong, which should strengthen the superconductivity. However, $T_c$ is only about 43 K.[3–10] and neither the size of ionic radius, the magnetic moment, nor the concentration of Ln ions at Sr sites affects $T_c$.[3] Moreover, the oxygen is very stoichiometric; neither vacancies nor interstitial oxygen exists.[3]

So far, the study of superconductivity in these compounds has been hindered by the lack of high quality bulk samples. However, in the case of infinite-layer superconducting films, superconducting transition temperature is much lower than those of bulk samples. For an infinite-layer superconducting film of (Sr$_{1-x}$Nd$_x$)CuO$_2$, the $T_c$ is reduced by about one half.[11,12] High-pressure synthesis is a unique method that now allows infinite-layer compounds to be made in bulk form with various lanthanide ions doped into Sr sites with larger superconducting volume fractions.[3–10]

In this paper, we report the high-pressure synthesis of the infinite-layer superconductor Sr$_{0.9}$La$_{0.1}$CuO$_2$ (Sr(La)-112). To identify the superconductivity, we measured the low-field magnetization. The resulting superconducting volume fraction was found to be greatly improved compared to the results reported so far. The high purity of the samples was confirmed by a Rietveld analysis of the X-ray powder diffraction data. The high-field magnetization curves, along with the resulting irreversibility line showed, that the pinning was unusually high compared to that for hole doped cuprates.

II. EXPERIMENTALS

A cubic multi-anvil-type press was used to synthesize Sr(La)-112.[3] The precursors were prepared by using the solid state reaction method.[3] Starting materials of La$_2$O$_3$, SrCO$_3$, and CuO were mixed to the nominal composition of Sr$_{0.9}$La$_{0.1}$CuO$_2$. The mixture was then calcined at 950 °C for 36 hours with several intermittent grindings. The

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pelletized precursors sandwiched by Ti oxygen getters were put into a Au capsule in a high-pressure cell. A D-type thermocouple was used to monitor the temperature.

The pressure cell was compressed up to 4 GPa and then heat-treated with a graphite-sleeve heater. The temperature of the Au capsule was calibrated to the heating power, and that data allowed us to use the heating power to control the sample-cell temperature. However much of the power from the power-supply was lost to the stray resistance \( R_{\text{stray}} \sim 10^{-2} \Omega \) between the power-supply and the graphite heater \( R_{\text{heater}} \sim 10^{-2} \Omega \). Even though the power was constantly supplied from the power-supply, the actual heating power of the sample fluctuated because \( R_{\text{heater}} \) changed during the synthesis; \( \Delta R_{\text{heater}} / R_{\text{heater}} \sim 0.1 \). The amount of fluctuation was roughly proportional to \( R_{\text{stray}} / R_{\text{heater}} \). To solve this problem, we controlled the heating power across the sample instead of the main power. With this method, a temperature stability of \( \pm 2 ^\circ C \) was obtained for a two-hour heating time under high-pressure conditions.

The heating power was increased linearly and then maintained constant for 2 hours. The synthesizing temperature was about 1000 \(^\circ C\). Then, the sample was quenched to room temperature after an additional postannealing at 500 \(^\circ C\) to 600 \(^\circ C\) for 4 hours. Two conditions were important in obtaining higher quality samples. One was the long-term stability of the synthesizing temperature, and the other was the uniformity of the temperature inside the sample cell, the former being more important. The pressure cell and the heating conditions were optimized after hundreds of trials, very homogeneous samples larger than 200 mg were obtained.

The samples were characterized by powder X-ray diffraction (XRD) measurements using Cu \( K\alpha \) radiation and a SQUID magnetometer (MPMSXL, Quantum Design). Scanning electron microscopy (SEM) and optical microscopy were also used. Zero-field-cooled (zfc) and field-cooled (fc) magnetization \( M(T) \) curves were measured. The structural characterization at room temperature was carried out by using the Rietveld refinement method to analyze the X-ray powder diffraction data. The SEM image showed closely packed grains of uniform size.

### III. DATA AND DISCUSSION

#### A. Structure

It is known that the phase purity obtained from X-ray or neutron powder diffraction does not represent the purity of a superconductor. Previously, it was claimed, based on the XRD data, that infinite-layer compounds were in a pure phase, but with a widely distributed superconducting volume fraction. \[1,2\]

Our powder XRD pattern showed an infinite-layer compound with the tetragonal space group \( P4/mmm \) and lattice parameters \( a = b = 3.956 \text{ Å} \) and \( c = 3.410 \text{ Å} \). The value of 2\( \theta \) was varied from 20\(^\circ\) to 140\(^\circ\) in steps of 0.02\(^\circ\), and the integration time was 15 seconds at each point. The Rietveld refinement program RIETAN-94 by F. Izumi with 50 parameters was used for the analysis. \[3\]

The Rietveld refinement profile is shown in Fig. 1. In that analysis, the thermal factors were assumed to be isotropic, and the coordination of each atom was fixed. We constrained the Sr:La ratio to the nominal stoichiometry of the precursor. \[4,5\] The obtained values of the lattice constants agree well, within 0.001 Å, with those obtained by neutron powder diffraction. \[6,7\] This refinement could not identify, within the resolution, any discernible amount of impurities. The agreement factors, \( R \), between the measured and the calculated diffraction intensities were quite small, and goodness of fit was excellent \( S = 4.0008 \). The refined structural parameters are summarized in Table 1. \[8,9\]

The structural analysis of an infinite-layer compound can also give valuable information about the doping concentration because the lattice constant is sensitive to the doping concentration. \[10\] Note the opposite behavior of the lattice constants with doping; the \( a \)-axis expands while the \( c \)-axis shrinks. The Rietveld refinement showed that the doping concentration in our \( \text{Sr}_{1-x}\text{La}_x\text{CuO}_2 \) was approximately \( x = 0.1 \), which is same as the nominal composition.

#### B. Superconducting properties

Typical low-field susceptibility \( 4\pi \chi(T) \) data for three different samples are shown in Fig. 2. In this figure, the curves labeled as \( \chi_{\text{zfc}} \) and \( \chi_{\text{fc}} \) were measured in the zero-field-cooled and the field-cooled states, respectively. The nominal superconducting volume fraction, \( f_{\text{nom}} \), in Fig. 3 was obtained by using the relation \( f_{\text{nom}} = -4\pi \chi_{\text{fc}}(T < T_c) \) and is not corrected for the demagnetization factors. \[11\] The superconducting volume fractions were much higher, especially in the high magnetic field region, compared to previous results, as shown in Fig. 3. \[12,13\]

The superconducting transition onset in Fig. 2 appears at 43 K, which is the value typically reported for the \( \text{Sr(La)}-112 \) compound. \[14,15\] However, we can see some notable differences from the previous reports. One is a very sharp transition near \( T = 43 \text{ K} \), and another is a well-developed saturation of the susceptibility at low temperatures, which reflects the formation of a high quality superconducting \( \text{Sr(La)}-112 \) phase. To quantify the sharpness of the
magnetization near $T_c$, we introduced $T_{\text{mid}}$ such that $\chi(T_{\text{mid}}) = 0.5 \times \chi(T \sim 0.1 \times T_c)$. The $T_{\text{mid}}$ for sample A is 40.5 K, and $T_c - T_{\text{mid}}$ was only half the smallest value reported until now, a clear indication of the sharpness of the superconducting transition. The saturated values of $4\pi\chi_{\text{zfc}}$ at low temperatures are about $-1.0$, $-1.17$, and $-1.22$ for samples A, B, and C, respectively.

For a superconducting sphere with a radius $R$, $4\pi\chi(T)$ is given by the Shoenberg formula

$$-\frac{3}{2}(1 - (3/x) \coth x + 3/x^2),$$

where $x = R/\lambda_{\text{avg}}(T)$ and $\lambda_{\text{avg}}(T)$ is the average magnetic penetration depth, i.e.,

$$\lambda_{\text{avg}} = (\lambda_{ab}\lambda_c)^{1/3}.$$  

In the limit of $x \gg 1$, the absolute value of $-4\pi\chi$ is $\sim 1.5$, which, due to the demagnetization effect, is 50% larger than the ideal value. If we take the typical value of $\lambda \sim 2000$ Å for high-$T_c$ cuprates and the grain size $R \sim 5 \mu$m obtained from the SEM image, the value of $4\pi\chi$ is estimated to be about $-1.3$, which is close to the above measured value. Thus, the real superconducting volume fraction of our sample should be close 100%.

Diamagnetic shielding fraction from $\chi_{\text{zfc}}$ is basically same for 100 Oe as it is for 10 Oe, as can be seen in Fig. 2. This is quite typical for all of our samples. By measuring the point at which magnetic hysteresis curve $M(H)$ deviates from linearity, we could identify the lower critical field $H_{c1}$, and our value was above $10^2$ Oe, as are the values for other high-$T_c$ cuprates. Previously, it was claimed that $H_{c1}$ was significantly less than 100 Oe.

While the low-field magnetization demonstrated a highly enhanced superconducting volume fraction, the irreversible field $H_{\text{irr}}(T)$ from the high-field magnetization up to 5 Tesla showed that pinning was very strong in this compound. In Fig. 3 the magnetization curves for fields higher than 1 Tesla and the resulting $H_{\text{irr}}(T)$ are presented. The criterion for the reversible point was set as $|M_{\text{zfc}} - M_{\text{fc}}| = 0.1$ emu/cm$^3$. The irreversible field was fitted with $H_{\text{irr}}(T) = H_0(1-T/T_c)^n$. The best parameters were $H_0 = 55.7$ Tesla, $T_c = 42.6$ K, and $n = 1.99$. The quite interesting point is that the $H_{\text{irr}}(T/T_c)$ of Sr(La)-112 is about 2 times higher than that of (La,Sr)$_2$CuO$_4$ even though the superconducting transition temperature of both compounds are similar. If the criterion is chosen more strictly as $|M_{\text{zfc}} - M_{\text{fc}}| = 0.01$ emu/cm$^3$, the irreversible field is increased by a factor of two.

**TABLE I.** Structural parameters for Sr$_{0.9}$La$_{0.1}$CuO$_2$ from Rietveld refinement using X-ray powder diffraction pattern for sample A. The values in parentheses are reported ones based on neutron powder diffraction. Ref 4.

| Parameter | Value |
|-----------|-------|
| $a = b$ (Å) | 3.950 42(3.950 68) |
| $c$ (Å) | 3.410 20(3.409 02) |
| $V$ (Å$^3$) | 53.219(53.212) |
| $\alpha = \beta = \gamma$ | 90.000 0 |
| Sr,La$^a$ | $x = y = z$ | 0.5 |
| | $n$ | 1 |
| Cu | $x = y = z$ | 0 |
| | $n$ | 1 |
| O | $x$ | 0.5 |
| | $y = z$ | 0 |
| | $n$ | 2 |
| Agreement factor | Value(%) |
| $R_{wp}$ (%) | 7.48(16.0) |
| $R_p$ (%) | 4.68 |
| $R_e$ (%) | 2.21 |
| Goodness of fit, $S$ | 3.3853 |

$^a$Constraint: n(Sr):n(La)=0.9:0.1.
IV. SUMMARY

We synthesized the infinite-layer compound Sr$_{0.9}$La$_{0.1}$CuO$_2$. Its improved superconducting properties were confirmed by a structural analysis and low-field magnetization measurements. The high superconducting quality was confirmed by the high superconducting volume fractions and the sharp transition near $T = 43$ K. The irreversibility field $H_{irr}(T)$ was much higher than that of (La,Sr)$_2$CuO$_4$, which indicated an enhanced interlayer coupling between the CuO$_2$ planes due to a shortening of the c-axis lattice constant. A sufficient quantity of high quality infinite-layer superconducting samples will ignite research on the superconductivity in electron-doped infinite-layer superconductors.

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FIG. 1. Rietveld refinement of the X-ray powder diffraction pattern of sample A. The dots are the raw data including background, and the solid line is the calculated profile. The vertical tick marks below the profile represent the positions of allowed diffractions in the tetragonal $P4/mmm$ space group. A difference curve (observed pattern minus calculated pattern) is also plotted at the bottom.

FIG. 2. Magnetic susceptibility, $4\pi\chi(T)$, of Sr$_{0.9}$La$_{0.1}$CuO$_2$ for zero-field-cooling and field-cooling from the low-field magnetization $M(T)$ at 10 and 100 Oe. For calculating the nominal superconducting volume fraction $f_{\text{nom}}$, we used a low-temperature density of 5.94 g/cm$^3$ from Ref. 10. (a) Sample A, $f = 100\%$, (b) Sample B, $f = 117\%$, and (c) Sample C, $f = 122\%$. 
FIG. 3. Comparison of the nominal superconducting volume fraction $f_{\text{nom}} = -4\pi \chi (T \ll T_c)$. The squares labeled with sample A, sample B, and sample C are data for our samples. The up-triangle is from Ref. 7, the down-triangle is from Ref. 4, the circles are from Ref. 6, the diamond is from Ref. 10, the open circle is from Ref. 14, and the open square is from Ref. 15.

FIG. 4. $4\pi M(T)$ curves of sample A at fields higher than 1 Tesla and irreversibility field $H_{\text{irr}}(T)$: (a) $4\pi M(T)$ curves at 1, 2, 3, 4, and 5 Tesla, and (b) irreversible field fitted with $H_{\text{irr}}(T) = H_o (1 - T/T_c)^n$. The criterion was chosen as $|M_{\text{zfc}} - M_{\text{fc}}| = 0.1$ emu/cm$^3$. The error bar in terms of temperature is less than 0.2 K. The fit was excellent with the parameters $H_o = 55.7$ Tesla, $T_c = 42.6$ K, and $n = 1.99$. The top axis denotes the normalized temperature $T/T_c$. The filled triangles were obtained with the criterion $|M_{\text{zfc}} - M_{\text{fc}}| = 0.01$ emu/cm$^3$. 