Superconductivity in the $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{Ag}_x\text{O}_{4-\delta}$ system

J.W. Chen and Fu-An Yang

Department of Physics, National Taiwan University, Taipei, Taiwan

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We report AC electrical resistance $R(T)$ and DC magnetization measurements on N_2 -annealed $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{Ag}_x\text{O}_{4-\delta}$ samples with $0 \leq x \leq 0.6$. $R(T)$ measurements reveal that the undoped $\text{La}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ is an insulator. However, as Ag is substituted for Cu, a superconducting transition starts to occur at ~ 24 K for $x \geq 0.2$. The normal state resistance $R(T)/R(280 \text{ K})$ varies systematically with x , and the resistance ratio $R(24 \text{ K})/R(280 \text{ K})$ reaches a minimum for $x=0.4$. Although DC magnetization measurements reveal superconducting signals for samples with $x \geq 0.1$, the superconducting volume fractions obtained are quite small ($< 2\%$) for all samples. In addition, the low-temperature inverse magnetic susceptibility $\chi^{-1}(T)$ curve reveals that the valence of the Ce ions in this system is close to $3+$. The $H_{c2}(T)$ data for the $x=0.4$ sample are also obtained.

The discovery of superconductivity in the La–Ba–Cu–O system at 34 K by Bednorz and Müller [1] has attracted a lot of research interest in the cuprate compounds. Until now, superconducting systems with a transition temperature as high as 125 K have been discovered [2–8]. All the systems mentioned in refs. [1–8] contain CuO_2 planes and the Cu valence in these materials plays a very important role for the appearance of superconductivity. The Cu valence can be changed by either changing the oxygen content or by certain cationic substitutions. Until now, chemical substitutions can either lead to a Cu formal valence greater than 2 (such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [2–4]), or reducing the Cu formal valence (such as $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$) [9].

Following the discovery of superconductivity in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ at 23 K, so called electron doped superconductors have been found in the $\text{R}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($\text{R} = \text{Pr}, \text{Nd}, \text{Sm}$ and Eu) [10] and $\text{R}_{2-x}\text{Th}_x\text{CuO}_{4-y}$ ($\text{R} = \text{Pr}, \text{Nd}$ and Sm) [10–12] compounds. In this paper, we report our results on the $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{Ag}_x\text{O}_{4-\delta}$ system. We found that by substituting Ag for Cu, superconductivity can be induced as the silver concentration $x \geq 0.1$.

The samples used in this study were prepared using the solid-state reaction method. Stoichiometric mixtures of high purity La_2O_3 , CeO_2 , CuO and Ag_2O powders were ground thoroughly and heated in air

at 1000°C for 1 day and furnace cooled to room temperature, reground and heated in air at 1000°C for 1 day and furnace cooled to room temperature. The resulting powders were then reground and pressed into pellets and sintered in flowing N_2 gas at 1100°C with a rising rate of $15^\circ\text{C}/\text{min}$ for 1 day and cooled to room temperature in flowing N_2 with a cooling rate of $1^\circ\text{C}/\text{min}$. AC electrical resistance $R(T)$ measurements on bar-shaped samples were performed with the four-wire technique using a Linear Research Model LR 400 AC resistance bridge operating at a frequency of 16 Hz with Si-diode and germanium thermometers as temperature sensors. DC magnetization measurements were performed using a Quantum Design MPMS SQUID magnetometer in various fields.

The normalized AC electrical resistance $R(T)/R(280 \text{ K})$ as a function of temperature T curves for various values of x of the $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{Ag}_x\text{O}_{4-\delta}$ samples are shown in fig. 1. For $x=0$, the sample is insulating and the $R(T)$ curve is not shown here. For $x=0.1$, $R(T)$ increases monotonically as the sample cooled from room temperature. However, a sudden drop in the $R(T)$ curve occurs at ~ 24 K, indicating the occurrence of superconductivity below this temperature, but zero resistance is not reached at 4 K. As the Ag concentration x increases, the increasing rate of the normal state resistance $R(T)/R(280 \text{ K})$

Fig. 1. Normalized electrical resistance $R(T)/R(280 \text{ K})$ as a function of temperature T curves for $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{Ag}_x\text{O}_{4-\delta}$ with various values of x . (a) $x=0.10, 0.20, 0.30$ and 0.35 . (b) $x=0.40, 0.45, 0.50$ and 0.60 .

with decreasing temperature T decreases monotonically and the superconducting transition becomes sharper for $x \leq 0.4$. For $x \geq 0.4$, the increasing rate of $R(T)/R(280 \text{ K})$ starts to increase with increasing x and the transition width becomes broader as x increases. For $x=0.4$, $R(24 \text{ K})/R(280 \text{ K})$ reaches a minimum value of 1.1 for all values of x studied. The midpoint transition temperature $T_c(50\%)$ is 19 K and the transition width ΔT_c ($T_c(90\%) - T_c(10\%)$) is about 7 K for this sample.

Figure 2 shows the midpoint transition temperature $T_c(50\%)$, the transition width ΔT_c ($T_c(90\%) - T_c(10\%)$), and the resistance ratio $R(24 \text{ K})/R(280 \text{ K})$ as a function of the Ag concentration x . A strong correlation between T_c , ΔT_c and $R(24 \text{ K})/R(280 \text{ K})$ is observed. The superconducting transition temperature T_c increases monotonically as x gets close to 0.4, while the transition width ΔT_c gets smaller and $R(24 \text{ K})/R(280 \text{ K})$ becomes smaller as x approaches 0.4. This kind of behavior is similar to

Fig. 2. (a) $R(T_c(\text{onset}))/R(280 \text{ K})$ as a function of the Ag concentration x for the $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{Ag}_x\text{O}_{4-\delta}$ system. (b) The superconducting transition $T_c(50\%)$ (solid circles) and the transition width ΔT_c (vertical bars) as a function of the Ag concentration x for the $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{Ag}_x\text{O}_{4-\delta}$ system. Solid lines are guides to the eye.

that observed for the electron doped superconductors, such as $\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_{4-\delta}$ [9–12]. This indicates that the mechanism of superconductivity in the system studied here and the electron doped superconductors may be of the same origin.

DC magnetization measurements reveal both the shielding effect (zero field cooling) and Meissner effect (20 G field cooling) for samples that exhibit the superconducting transition in the $R(T)$ measurements. However, the superconducting volume fractions in all samples as calculated from $M(T)$ measurements are quite small ($< 2\%$) for all values of x measured. Shown in fig. 3(a) are the DC magnetization curves taken at zero field and 20 G for $x=0.4$, the sample that shows best behavior in the $R(T)$ curve. Both Meissner and shielding curves indicate

Fig. 3. (a) Magnetization vs. temperature for the $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{0.6}\text{Ag}_{0.4}\text{O}_{4-\delta}$ sample. The upper curve is the field cooling curve in a field of 20 G and the lower curve is the shielding curve. (b) The inverse magnetic susceptibility as a function of temperature T for the $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{0.6}\text{Ag}_{0.4}\text{O}_{4-\delta}$ sample with an applied field of 5 kG.

the onset of the superconducting transition at 20 K. But the superconducting volume fraction obtained is only about 1%. Similar curves have been obtained for other values of x . In fig. 3(b), the inverse magnetic susceptibility χ^{-1} as a function of temperature T is displayed. Although no single straight line can be fit to the curve above 100 K, at low temperatures (below ~ 80 K) this curve follows a Curie-Weiss behavior with a moment of $0.35\mu_B$. Similar behaviors have been obtained for other Ag concentrations. If we assume that this moment comes from the Ce ions, then the effective moment obtained for the Ce ions is around $2.4\mu_B$, which is close to the moment of an Ce^{3+} . This indicates that the valence of the Ce ions in this system is close to 3+.

The superconductivity in the system studied here

is quite stable. Figure 4(a) shows the $R(T)$ curves in various magnetic fields for $x=0.4$ one month after the sample has been made. Both T_c and ΔT_c remain essentially unchanged. Increasing the magnetic field shifts the transition curve to lower temperature and broadens the transition width. Shown in fig. 4(b) are the upper critical magnetic field $H_{c2}(T)$ data obtained from fig. 4(a) where a solid circle represents $T_c(50\%)$ and a horizontal bar represents a transition width ΔT_c . Similar to what has been reported for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{3.98}$ and $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$, the H_{c2} curve exhibits a positive curvature throughout the whole temperature range [13,14]. The initial slope ($-dH_{c2}/dT$) estimated from the data below 1 T is 0.24 T/K. Above 1 T, H_{c2} increases rapidly with slight upward curvature with a slope ($-dH_{c2}/$

Fig. 4. (a) Normalized electrical resistance $R(T)/R(40\text{ K})$ as a function of temperature T for $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{0.6}\text{Ag}_{0.4}\text{O}_{4-\delta}$ in applied magnetic fields up to 5 T. (b) Upper critical magnetic fields $H_{c2}(T)$ determined from the data in fig. 4(a). The solid line is a guide to the eye.

$dT)=0.6$ T/K. If we apply the weak-coupling formula [15]

$$H_{c2}(0) = -0.69 T_c (dH_{c2}/dT)_{T=T_c}$$

then the $H_{c2}(0)$ obtained is only about 3.2 T, which is too small to describe the data here. This indicates that paramagnetic effects may be important for this system. More studies are in progress in order to understand the behavior of $H_{c2}(T)$ in this system.

In conclusion, we have shown that superconductivity can be included in the $\text{La}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{Ag}_x\text{O}_{4-\delta}$ system as $x \geq 0.1$. The superconducting volume fraction obtained in this system is small. The low-temperature inverse susceptibility $\chi^{-1}(T)$ curve indicates that the valence of the Ce ions in this system is close to 3+. $H_{c2}(T)$ data obtained for $x=0.4$ cannot be described by the weak-coupling formula and this indicates that the paramagnetic effects of the Ce^{3+} ions may be important for this system.

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