Is La$_{1.85}$Y$_{0.15}$CuO$_4$ an oxygen-doped cuprate superconductor?

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(Dated: March 23, 2022)

We report resistivity, Hall effect, Nernst effect, and magnetoresistance measurements on T'-phase La$_{1.85}$Y$_{0.15}$CuO$_4$ (LYCO) films prepared by pulsed laser deposition under different oxygen conditions. Our results show that superconductivity in LYCO originates from an oxygen-doped Mott-like insulator and not from a weakly correlated, half-filled band metal as proposed previously.

PACS numbers: 74.25.Fy, 73.43.Qt, 74.72.-h, 74.78.Bz

The origin of the high-temperature superconductivity in doped copper oxides is one of the major unresolved problems in cuprates. The parent (undoped) compounds, e.g., La$_2$CuO$_4$, are predicted to be half-filled band metals by simple non-interacting electron band models. But experimentally all the copper oxides parent compounds prepared to date are known to be antiferromagnetic (AFM) insulators. Upon doping, superconductivity is achieved with a suppression of antiferromagnetism. This has led to the general belief that electron-electron correlations play a very important role in the normal state and the superconducting properties of this class of copper oxides.

The simplest model used to explain the spin=1/2 antiferromagnetic La$_2$CuO$_4$ (LRCO) is a band metal and not a Mott-like insulator. Small rare earth ions RE$^{3+}$, such as Y$^{3+}$, Tb$^{3+}$, etc., were partially substituted for La$^{3+}$ using a MBE thin film technique. This keeps the total charge the same as in the T'-phase La$_2$CuO$_4$, and implies that no doping occurs. These materials are metastable and cannot be made by conventional bulk growth methods. A very thorough study of the RE doping, preparation conditions, and the properties of these LRCO materials was made. At some RE dopings, superconductivity with Tc’s as high as 23K was found! This was explained as arising from a weakly correlated, half-filled, band metal state. Since this work questions one of the most fundamental assumptions about the possible origin of high-temperature superconductivity in the cuprates, i.e., the Mott-Hubbard parent state, it is quite important to confirm these new experimental results and their interpretations.

In this paper, we show that the doping of a Mott-like insulator is the origin of the physical properties in the LRCO system. Our resistivity, Hall effect, Nernst effect and magnetoresistance data suggest that oxygen reduction of La$_{1.85}$Y$_{0.15}$CuO$_4$ (LYCO) films is responsible for the metallic and superconducting properties. Since oxygen reduction is equivalent to cerium doping in the T'-phase Ln$_{2-x}$Ce$_x$CuO$_4$ (LnCCO), we believe LYCO is an electron-doped superconductor which evolves from a Mott-Hubbard AFM insulating state. Evidence for a spin-density-wave (SDW) or AFM state in the as-grown LYCO films, and a Fermi surface evolution from an electron-like to a two-band system with increasing oxygen reduction were observed. This is the same behavior found in cerium-doped LnCCO materials. Therefore, our data are incompatible with the scenario of a half-filled band metal.

Our c-axis oriented LYCO films were grown by the pulsed laser deposition technique, using a stoichiometric La$_{1.85}$Y$_{0.15}$CuO$_4$ ceramic as a target. The films were deposited first on STO (SrTiO$_3$) or KTO (KTaO$_3$) substrates at 700°C under 230 mTorr N$_2$O pressure, then annealed at 620°C in situ under vacuum of $10^{-6}$ Torr, and finally cooled in the vacuum down to room tempera-
TABLE I: Comparison of the bulk superconducting transition temperature $T_C$ (measured from ac susceptibility), room temperature ab-plane resistivity $\rho^{RT}$, and zero temperature Hall coefficient $R_H^0$, of LYCO films prepared with different substrate, annealing pressure $p$, and annealing time $t$.

| sample | A1 | A2 | A3 | A4 | A5 | A6 | A7 | K1 |
|--------|----|----|----|----|----|----|----|----|
| substrate | STO | STO | STO | STO | STO | STO | STO | KTO |
| $p$ (10$^{-6}$Torr) | 1  | 1  | 1  | 1  | 0.8 | 0.8 | 0.6 | 1  |
| $t$ (minutes) | 0  | 4  | 7  | 9  | 15  | 60 | 11  | 10 |
| $T_C$ (K) | 14.2 | 10.8 | 2.0 | 1.3 | 3.0 | 1.9 | 1.4 |  |
| $\rho^{RT}$ (m$\Omega$cm) | -2.20 | -1.00 | -0.19 | -0.11 | -  | 1  | -  |  |
| $R_H^0$ (ΩA/T) | -220 | -100 | -19  | -11  | -  | 1  | -  |  |

Vacuum annealing of the $T'$-structure cuprates is known to remove oxygen from the sample (i.e., oxygen reduction). Under these conditions, a c-axis oriented $T'$-phase LYCO is well established. Typical film thickness is about 2500Å and $T_C$ depends on the annealing time and pressure (see Table I). The X-ray diffraction pattern and ac susceptibility of a superconducting film (sample A7) are shown in Fig. 1, indicating the $T'$-phase ($c \approx 12.4$Å) and bulk superconductivity. To our knowledge, this is the first time the standard PLD method has been used without a buffer layer to achieve La-based $T'$-phase superconducting films. The transport properties are similar for films made with an STO substrate or a KTO substrate although the annealing time is slightly different. The resistivity of our films is comparable to those made by MBE [4]. Our ab-plane resistivity, Hall-effect, and magnetoresistance measurements were performed on Hall-bar patterned films in a Quantum Design PPMS. Nernst effect measurements were conducted in the PPMS with a home-built Nernst setup.

For films grown under different oxygen conditions, the ab-plane resistivity and bulk $T_C$ are shown in Table I and in Fig. 2. The as-grown film A1, which is cooled under vacuum after deposition, shows a metallic behavior close to room temperature, followed by an insulator-like resistivity upturn at low temperatures. Longer annealing time under the same annealing pressure results in a decrease of the resistivity, by one order of magnitude, and a shift of the resistivity upturn to lower temperatures (sample A1 to A4). Superconductivity emerges and $T_C$ increases with an increasing annealing time. However, excessive annealing time ($t \geq 10$ minutes) under the same pressure does not enhance $T_C$ (see sample A5 and A6 in Table I), and severe chemical decomposition is clearly observable under an optical microscope. Indeed, better vacuum with shorter annealing time seems to further enhance $T_C$ as shown by sample A7 (Table I). Our PLD chamber can only reach $\sim 10^{-6}$ Torr, which probably limits the $T_C$ of our films, as compared with MBE-grown films [4]. Comparison of $T_C$ and $\rho^{RT}$ between our films and the MBE-grown films [2, 3] strongly suggests that high-vacuum annealing ($P \ll 10^{-6}$ Torr) is necessary to achieve higher $T_C$'s in the LYCO system.

The normal state Hall resistivity of these films was measured with fields up to 14T. The Hall coefficients $R_H$ from room temperature down to 2K are shown in Fig. 3. It is evident that the Hall coefficient changes dramatically with increasing annealing time. For films A1 to A3, the amplitude of $R_H$ decreases by about one order of magnitude while remaining negative, which is consistent with the decrease of resistivity shown in Fig. 2.
if more electron-like carriers are being created. With further annealing under higher vacuum, the Hall coefficient changes sign from negative to positive at low temperature as shown by sample A7, which suggests hole-like carriers are introduced. The overall trend of $R_H$ with annealing is similar to that of the n-doped cuprates Nd$_2$Ce$_2$CuO$_4$ (NCCO), Pr$_2$Ce$_2$CuO$_4$ (PCCO) and La$_2$Ce$_2$CuO$_4$ (LCCO) with increasing cerium doping. The temperature dependence of $R_H$ is also similar to these cerium-doped T’-structure cuprates.

To further compare with the cerium-doped T’-phase cuprates, we performed Nernst effect measurements on a 5mm×10mm LYCO film (sample A5) with $T_C \approx 10.5K$. For each temperature, a constant temperature difference between two ends of the sample along the 10mm direction was stabilized by a heater. By applying a magnetic field along the c-axis, a transverse electric field $E_y$ was induced due to the Nernst effect. The Nernst signal N, defined as $E_y/\nabla_x T$ where $\nabla_x T$ is the longitudinal temperature gradient, is shown as a function of temperature at a constant field $\mu_0 H = 10T$. Above 20K, the Nernst signal shows a linear field dependence up to 10T as shown at a few temperatures in Fig. 4 (inset), characteristic of a normal-state behavior. The amplitude and temperature dependence of N are comparable to results found in superconducting PCCO films [3, 4]. Below 20K, a non-linear N with magnetic field is found (data not shown), characteristic of the superconducting state.

Now we report the transport properties of the superconducting state. The transverse magnetoresistance of a superconducting LYCO film (sample A4) was measured at low temperatures, as shown in Fig. 5. By increasing the magnetic field to 14T, superconductivity is suppressed at all temperatures. At $T = 2K$, a negative normal-state magnetoresistance emerges at high fields. The $H_{C2}$ is about 12T, which is estimated by the field where the normal-state resistivity is recovered. The negative magnetoresistance behavior at high fields and the value of $H_{C2}$ are similar to that of underdoped PCCO [5] and LCCO films [6, 7]. At $\mu_0 H = 14T$, the LYCO film shows a strong resistivity upturn as the temperature decreases (Fig. 5 inset), suggesting a transition from a superconductor to an “insulator-like” ground state, similar to underdoped superconducting LnCCO cuprates [8, 9].

These resistivity, Hall coefficient, Nernst effect, and magnetoresistance data strongly suggest that oxygen reduction in La$_{1.85}$Y$_{0.15}$CuO$_4$ films is equivalent to cerium doping in the Nd$_2$CuO$_4$, Pr$_2$CuO$_4$, or La$_2$CuO$_4$ systems. The low carrier density of as-grown LYCO films, about 0.03 electrons/Cu determined by the Hall coefficient (from $R_H = 1/ne$ at 2K), supports the view that LYCO originates from a doped insulator, rather than a half-filled band metal [2, 4]. By oxygen reduction, both resistivity and Hall coefficient first decrease significantly, which suggests that more electron-like carriers are introduced [2, 4]. By further reduction, the sign change of the Hall coefficient (sample A7) and the large Nernst signal (sample A5), suggests a Fermi surface with both electron-like and hole-like carriers, as has been found in cerium-doped LnCCO cuprates by transport [10] and ARPES [11, 12] measurements. This Fermi surface evolution from an electron-like to a two-band structure with increasing carrier density has been proposed to result from the destruction of an AFM, or SDW gap, by doping [12, 14]. The similar value of $H_{C2}$ of LYCO with that of the cerium-doped cuprates, as shown by the magnetoresistance measurements, again suggests a similar band struc-
ture and a similar mechanism for superconductivity. All of our transport data suggest that LYCO originates from an antiferromagnetic Mott-like insulator and is electron-doped by oxygen reduction. This is the main conclusion of this paper.

In the cerium-doped cuprate superconductors, oxygen reduction has been shown to trigger the superconductivity primarily by the suppression of a disorder induced pair breaking effect [17]. The previous work on LRCO [2-4] argued for a similar disorder induced pair breaking effect and a carrier localization to explain the semiconducting resistivity of the as-grown films. The hypothesis of ref. [2-4] is that carrier doping is not necessary for superconductivity because LRCO is intrinsically a band metal. But the authors of ref. [2-4] present no quantitative evidence to support their hypothesis of carrier localization. In contrast, our transport data on LYCO suggests a significant increase of the carrier density with increasing oxygen reduction. This means that carrier doping is necessary to drive LYCO to the metallic and superconducting state.

We now discuss oxygen reduction (by vacuum annealing) in LYCO films. It is likely that all the carriers are introduced by oxygen deficiency, because the valence of $Y^{3+}$ is not expected to change with oxygen reduction. Our best-annealed $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_4-\delta$ film (sample A7) has a resistivity and Hall coefficient similar to $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ with $x = 0.08 - 0.10$, which would correspond to an oxygen deficiency of $\delta = 0.04 - 0.05$ in LYCO. This amount of oxygen deficiency is not unreasonable, since an oxygen deficiency of 0.06 was found in Nd$_2$CuO$_4$ after vacuum annealing [16]. Another point to note is that superconductivity has not been achieved in T'-structure La$_2$CuO$_4$ by oxygen reduction. Therefore, it seems that oxygen reduction is strongly affected by the rare-earth ionic environment, possibly because of the lattice distortion created by RE$^{3+}$ substitution for La$^{3+}$ [2]. This may be similar to the enhanced oxygen intake found in La$_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ films caused by a strain effect from the substrate [17]. In this case, a significant increase in Tc was observed [17, 18]. So it appears that the role of oxygen stoichiometry and disorder is complicated and poorly understood in both hole-doped and electron-doped cuprates. There are issues for future study and are beyond the scope of the results we present here.

In summary, we have prepared superconducting T'-structure $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_4$ (LYCO) films by the pulsed laser deposition for the first time. Our systematic transport studies, including resistivity, Hall effect, Nernst effect, and magnetoresistance measurements, suggest that LYCO evolves from an antiferromagnetic insulator to a two-band metal with increasing oxygen reduction. This implies that oxygen reduction in LYCO causes electron doping, and superconductivity in LYCO originates from a doped Mott-like insulator. Our results contrast with the prior proposal that (La, RE)$_2\text{CuO}_4$ (LRCO) is an undoped, half-filled band metal [2-4].

This work is supported by NSF under contract DMR-0352735. It is also supported by the W. M. Keck Foundation and by the NSF-UMD-MRSEC SEF. The authors would like to thank Professor A. J. Millis and Dr. J. S. Higgins for beneficial discussions.

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