

# Oxygen-doped Mott-Hubbard cuprate superconductor $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_{4-\delta}$ from transport measurements

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We report resistivity, Hall effect, Nernst effect, and magnetoresistance measurements on  $T'$ -phase  $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_{4-\delta}$  (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.

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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.,  $\text{La}_2\text{CuO}_4$ , are predicted to be half-filled band metals by simple noninteracting electron band models. But experimentally all the copper oxide 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 antiferromagnetism on copper sites is the Mott-Hubbard model.<sup>1</sup> Most of the theories attempting to explain the origin of superconductivity in the copper oxides have started from some variation of this basic model for strongly correlated systems.

Recently, a very surprising result was reported, which claimed that the parent, undoped copper oxide system  $T'$ -structure  $(\text{La},R)_2\text{CuO}_4$  (LRCO) (where  $R$  is a rare earth element) is a band metal and not a Mott-like insulator.<sup>2-4</sup> Small rare earth ions  $R^{3+}$ , such as  $\text{Y}^{3+}$ ,  $\text{Tb}^{3+}$ , etc., were partially substituted for  $\text{La}^{3+}$  using a molecular beam epitaxy (MBE) thin film technique. This keeps the total charge the same as in the  $T'$ -phase  $\text{La}_2\text{CuO}_4$ , and implies that no doping occurs. These materials are metastable and cannot be made by conventional bulk growth methods. A very thorough study<sup>2-4</sup> of the  $R$  doping, preparation conditions, and the properties of these LRCO materials was made. At some  $R$  dopings, superconductivity with  $T_C$ 's as high as 23 K 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  $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_4$  (LYCO) films is responsible for the metallic and superconducting properties. Since oxygen reduction is equivalent to cerium doping in the  $T'$ -phase  $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$

(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 electronlike 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 (PLD) technique, using a stoichiometric  $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_4$  ceramic as a target. The films were deposited first on  $\text{SrTiO}_3$  (STO) or  $\text{KTaO}_3$  (KTO) substrates at 700 °C under 230 mTorr  $\text{N}_2\text{O}$  pressure, then annealed at 620 °C *in situ* under vacuum of  $10^{-6}$  Torr, and finally cooled in vacuum down to room temperature. 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 2500 Å 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 structure ( $c \approx 12.4$  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 a STO substrate or a KTO substrate although the annealing time is slightly different. The resistivity of our films is comparable to that of those made by MBE.<sup>4</sup> Our  $ab$ -plane resistivity, Hall effect, and magnetoresistance measurements were performed on Hall-bar patterned films in a Quantum Design physical property measurement system (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 insulatorlike 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

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 substrates, 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
$t$ (min)	0	4	7	9	15	60	11	10
$T_C$ (K)	0	0	4	10	10.5	10.5	11.2	5.5
$\rho^{RT}$ (m $\Omega$ cm)	14.2	10.8	2.0	1.3		3.0	1.9	1.4
$R_H^0$ ( $\Omega$ A/T)	-220	-100	-19	-11			1	-14

emerges and  $T_C$  increases with an increasing annealing time. However, excessive annealing time ( $t \geq 10$  min) under the same pressure does not enhance  $T_C$  (see samples 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.<sup>4</sup> Comparison of  $T_C$  and  $\rho^{RT}$  between our films and the MBE-grown films<sup>2,3</sup> strongly suggests that high-vacuum annealing ( $P \leq 10^{-6}$  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 14 T. The Hall coefficients  $R_H$  from room temperature down to 2 K 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 electronlike 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 that

holelike carriers are introduced. The overall trend of  $R_H$  with annealing is similar to that of the  $n$ -doped cuprates  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ ,  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$  (PCCO), and  $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$  (LCCO) with increasing cerium doping.<sup>5,6</sup> The temperature dependence of  $R_H$  is also similar to that of cerium-doped  $T'$ -structure cuprates.

To further compare with the cerium-doped  $T'$ -phase cuprates, we performed Nernst effect measurements on a  $5 \times 10$  mm<sup>2</sup> LYCO film (sample A5) with  $T_C \approx 10.5$  K. For each temperature, a constant temperature difference between two ends of the sample along the 10 mm 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  $\mu_0 H = 10$  T. Above 20 K, the Nernst signal shows a linear field dependence up to 10 T as shown at a few temperatures in Fig. 4 (inset), characteristic of a normal-state behavior. We note that the sign of the Nernst signal does not represent the sign of the charge carrier.<sup>7</sup> The large amplitude and temperature dependence of  $N$  are comparable to results found in superconducting PCCO films.<sup>8</sup> Below 20 K, a nonlinear  $N$  with magnetic field is found (data not shown), characteristic of the superconducting state.

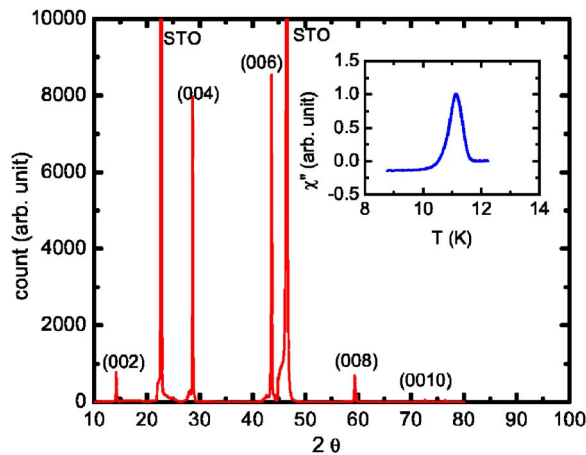


FIG. 1. (Color online) The x-ray diffraction pattern of a  $c$ -axis-oriented  $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_{4-\delta}$  film (sample A7). Inset: The imaginary ac susceptibility  $\chi''$  vs temperature.

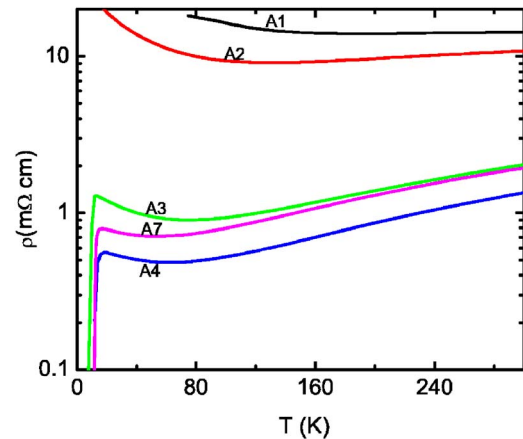


FIG. 2. (Color online) The  $ab$ -plane resistivity of the LYCO films prepared with different annealing conditions. The growth and the annealing conditions for A1, A2, A3, A4, and A7 are shown in Table I.

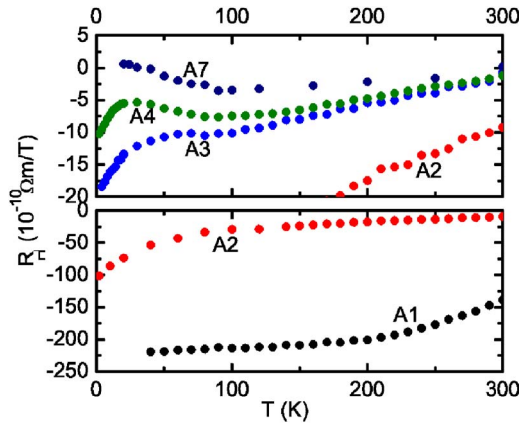


FIG. 3. (Color online) The Hall coefficient of the LYCO films prepared with different annealing conditions. The growth and the annealing conditions for A1, A2, A3, A4, and A7 are shown in Table I.

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 14 T, superconductivity is suppressed at all temperatures. At  $T=2$  K, a negative normal-state magnetoresistance emerges at high fields. The  $H_{C2}$  is about 12 T, 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 those of underdoped PCCO (Ref. 9) and LCCO films.<sup>6</sup> At  $\mu_0 H=14$  T, the LYCO film shows a strong resistivity upturn as the temperature decreases (Fig. 5, inset), suggesting a transition from a superconductor to an “insulatorlike” ground state, similar to underdoped superconducting LnCCO cuprates.<sup>6,9</sup>

These resistivity, Hall coefficient, Nernst effect, and magnetoresistance data strongly suggest that oxygen reduction in  $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_4$  films is equivalent to cerium doping in the  $\text{Nd}_2\text{CuO}_4$ ,  $\text{Pr}_2\text{CuO}_4$ , and  $\text{La}_2\text{CuO}_4$  systems. The low carrier

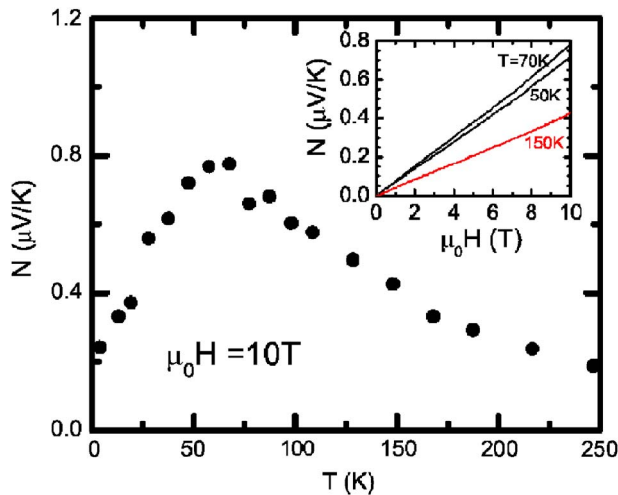


FIG. 4. (Color online) A Nernst signal of a LYCO film (sample A5) with  $T_C \approx 10.5$  K. The growth and the annealing conditions for A5 are shown in Table I.

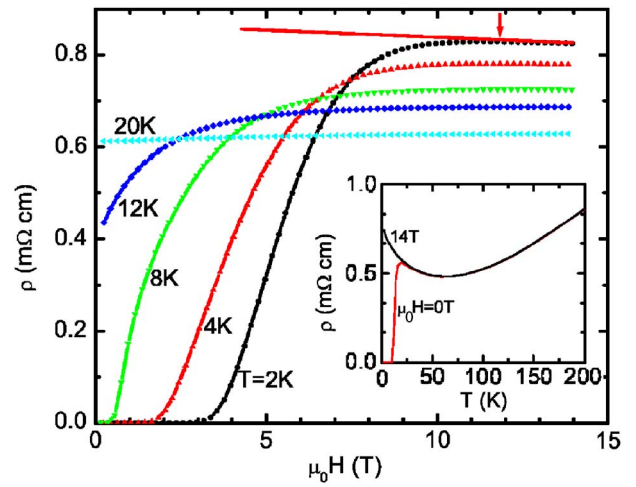


FIG. 5. (Color online) The low-temperature transverse magnetoresistance of a LYCO film (sample A4) with  $H \parallel c$ . Inset: The temperature dependence of the zero-field and the normal-state ( $\mu_0 H=14$  T) *ab*-plane resistivity.

density of as-grown LYCO films, about 0.03 electrons/Cu determined by the Hall coefficient (from  $R_H = 1/ne$  at 2 K), supports the view that LYCO originates from a doped insulator, rather than a half-filled band metal.<sup>2,4</sup> On oxygen reduction, both the resistivity and Hall coefficient first decrease significantly, which suggests that more electronlike carriers are introduced.<sup>10</sup> On further reduction, the sign change of the Hall coefficient (sample A7) and the large Nernst signal (sample A5) suggest a Fermi surface with both electronlike and holelike carriers, as has been found in cerium-doped LnCCO cuprates by transport<sup>11</sup> and angle-resolved photoemission spectroscopy<sup>12,13</sup> measurements. This Fermi surface evolution from an electronlike 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.<sup>14,15</sup> The similar value of  $H_{C2}$  of LYCO to that of the cerium-doped cuprates, as shown by the magnetoresistance measurements, again suggests a similar band structure 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.<sup>16</sup> The previous work<sup>2-4</sup> on LRCO 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 Refs. 2-4 is that carrier doping is not necessary for superconductivity because LRCO is intrinsically a band metal. But the authors of Refs. 2-4 present no quantitative evidence to support their hypothesis of carrier localization. In contrast, our transport data suggest a significant increase of the carrier density with increasing oxygen reduction in order to achieve superconductivity on  $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_4$  films.

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  $La_{1.85}Y_{0.15}CuO_{4-\delta}$  film (sample A7) has a resistivity and Hall coefficient similar to those of  $La_{2-x}Ce_xCuO_4$  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  $Nd_2CuO_4$  after vacuum annealing.<sup>17</sup> Another point to note is that superconductivity has not been achieved in  $T'$ -structure  $La_2CuO_4$  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  $R^{3+}$  substitution for  $La^{3+}$ .<sup>2</sup> This may be similar to the enhanced oxygen intake found in  $La_{2-x}Sr_xCuO_{4+\delta}$  films caused by a strain effect from the substrate.<sup>18</sup> In that case, a significant increase in  $T_C$  was observed.<sup>18,19</sup> So it appears that the role of oxygen stoichiometry and disorder is complicated and poorly understood in both hole-doped and electron-doped cuprates. These

are issues for future study and are beyond the scope of the results we present here.

In summary, we have prepared superconducting  $T'$ -structure  $La_{1.85}Y_{0.15}CuO_4$  films by pulsed laser deposition. 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  $(La,R)_2CuO_4$  is an undoped, half-filled band metal.<sup>2-4</sup>

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