The origin of superconductivity in nominally ‘undoped’ T’-La$_{2-x}$Y$_x$CuO$_4$ films

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Abstract

We have systematically studied the transport properties of La$_{2-x}$Y$_x$CuO$_4$ (LYCO) films with T’-phase (0.05 ≤ x ≤ 0.30). In this nominally ‘undoped’ system, superconductivity was acquired in a certain Y doping range (0.10 ≤ x ≤ 0.20). Measurements of resistivity, Hall coefficient in normal states and resistive critical field ($H_{\rho c2}$) in superconducting states of the T’-LYCO films show similar behavior as the known Ce-doped n-type cuprate superconductors, indicating the intrinsic electron doping nature. The charge carriers are thought to be induced by oxygen deficiency. Non-superconducting Y-doped Pr- or Nd-based T’-phase cuprate films were also investigated for comparison, suggesting a crucial role of the radii of A-site cations in the origin of superconductivity in the nominally ‘undoped’ cuprates. A reasonable scenario is put forward for the microscopic reduction process to explain the experimental observations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

After 20 years of intense research since the discovery of high-temperature superconductivity (HTSC), many interesting physical phenomena unique to the cuprate superconductors are well understood. Although the underlying mechanism for HTSC remains elusive and unresolved, it has been widely accepted [1] that the parent compounds of all the known superconducting cuprates are half-filled Mott antiferromagnetic insulators, in which strong electronic correlation exists. Upon doping holes or electrons into CuO$_2$ sheets, the antiferromagnetism is suppressed, and superconductivity can be induced in a certain concentration range of charge carriers.

Recently, Tsukada et al discovered a new class of cuprate superconducting films, T’-(La, R)$_2$CuO$_4$ (LRCO, R = Sm, Eu, Gd, Tb, Lu, and Y), which are nominally ‘non-doped’ because R$^{3+}$ is a cation that is isovalent with La$^{3+}$ and the substitution cannot provide net charge carriers to the CuO$_2$ planes [2]. In particular, the La-based T’-phase cuprates are metastable, and they have not been obtained by conventional bulk synthesis so far. These T’-phase LRCO films have been synthesized by molecular beam epitaxy (MBE), and $T_c$ as high as 20 K could be achieved at certain R dopings. There are claims that the electron doping via oxygen deficiencies was, at least, not the main source of charge carriers and that T’-LRCO compounds are most plausibly conventional half-filled ‘band superconductors’ with weak electronic correlation [3, 4]. These viewpoints gave rise to strong skepticism because they contradict the acknowledged basic picture of HTSC over the last 20 years.

However, further study of the physical properties of T’-LRCO is still lacking because the sample preparation is quite difficult due to the metastability of the La-based T’-phase structure and the far from satisfactory repeatability by other groups. For example, an unsuccessful attempt was reported recently [5], indicating that the superconductivity of the films is very sensitive to the preparation conditions. By pulsed laser deposition (PLD), Yu et al have also successfully prepared T’-LYCO films with x = 0.15 [6]. At present, it is an urgent
requirement to perform a systematic study on the physical properties of LRCO.

Using dc magnetron sputtering, we have been able to fabricate superconducting La$_{2-x}$Y$_x$CuO$_4$ (LYCO) films of pure c-axis oriented T'-structure with high repeatability [7]. In this study, we systematically investigated the in-plane electronic transport and Hall coefficient of T'-LYCO films with different Y content ($x = 0.05, 0.10, 0.125, 0.15, 0.20$ and 0.30). The superconducting phase diagram and effect of oxygen content on transport properties have been studied. For the films with $x = 0.125$ and 0.20, the magnetic field dependence of superconducting transitions was also measured to obtain the resistive critical field $H_{c2}^r(T)$.

All these results show a similar behavior to that of the known electron-doped T'-214 R$_{2-x}$Ce$_x$CuO$_4$ (R = Pr, Nd, Sm) systems, suggesting the same intrinsic electron doping nature in LYCO. The charge carriers in T'-LYCO are considered to be induced by oxygen deficiency during the reduction process. For comparison, we also studied the isovalent substitution in Nd$_2$CuO$_4$ (NCO) and Pr$_2$CuO$_4$ (PCO) systems, and no superconductivity was found. Combining our data with the previous results [2–4], we present a reasonable scenario about the microscopic depletion process of oxygen upon annealing, which is necessary to induce enough carriers to trigger superconductivity in T'-LYCO.

2. Experimental details

The La$^{3+}$ ion is the largest in the lanthanide series. A detailed analysis of the perovskite tolerance factor $t$ [8, 9] revealed that La-based 214 cuprates adopt the T-type phase by high-temperature bulk processes, while the T'-214 phase prefers stabilizing only at low synthesis temperature. By extrapolation of the T/T' phase boundary in the La$_{2-x}$Nd$_x$CuO$_4$ system to $y = 0$, it has been predicted that undoped T'-La$_2$CuO$_4$ can be stable below 425°C [9]. The partial substitution of La$^{3+}$ by smaller Y$^{3+}$ can reduce the average ion radius of the A-site, and slightly shift the T/T' phase boundary to higher temperature. But it is still too low for bulk synthesis of the La-based T'-phase. In comparison with the solid-state reaction process, the preparation of thin films can usually be realized at lower temperature. Furthermore, the appropriate epitaxial strain through the substrates may stabilize some metastable phases [10]. Therefore, we grew c-axis oriented LYCO films of pure T'-phase by dc magnetron sputtering. The stoichiometric ceramic targets are prepared by conventional solid-state reaction. Figure 1 shows the x-ray diffraction (XRD) pattern of a typical LYCO film with $x = 0.15$, which is pure T'-structure of c-axis orientation. Only the (0 0 2l) diffraction peaks appear, and the c-axis lattice constant $c$ is around 12.44 Å. The typical full width at half maximum (FWHM) of the rocking curves at the (006) reflection is only 0.28°, which confirms a good epitaxial growth of the T'-LYCO films.

The XRD pattern of polycrystalline LYCO target for $x = 0.15$ is shown in the inset of figure 1. Except for the trace of unreacted yttrium oxide, all the peaks are well indexed to the La$_2$CuO$_4$-like orthogonal T-214 structure. The calculated lattice constants of the orthorhombic lattice are $a = 5.355$ Å, $b = 5.399$ Å, and $c = 13.136$ Å, which are slightly less than those of undoped La$_2$CuO$_4$, consistent with the partial replacement of larger La$^{3+}$ (the ionic radius is 1.216 Å) by smaller Y$^{3+}$ (1.075 Å). There is a great contrast between the structures for the films and bulk materials, consistent with the above analysis of phase stability.

The optimal growth condition for $x = 0.15$ LYCO films has been discussed in detail elsewhere [7]. Upon increasing Y doping, the average radii of A-site ions decrease, and consequently the T/T' phase boundary shifts to high temperature. Accordingly the optimal deposition temperature $T_0$ is adjusted slightly towards higher temperature with increasing Y doping. After deposition, all the films are annealed at 600°C in high vacuum (near 10$^{-4}$ Pa) and finally followed by a very slow cooling process to room temperature. The Nd$_{2-x}$Y$_x$CuO$_4$ (NYCO) and Pr$_{2-x}$Y$_x$CuO$_4$ (PYCO) films were also prepared by dc sputtering for comparative research, in which the T'-214 structure is intrinsically stable. The reduction process of these films is the same as that of the LYCO films.

The thickness of the typical films for transport measurements is about 3000 Å. The measurements of resistivity and Hall coefficients are carried out in standard six-lead geometry using an ac resistance bridge (LR-700, Linear Research). The Ag electrodes are made by Ag evaporation. Samples are mounted on the top of the variable-temperature loading probe. Low temperature and high magnetic field up to 14 T were supplied by a Teslaron system (Oxford Instruments).

3. Experimental results

3.1. Superconductivity and resistivity of T'-LYCO

We first focus on the temperature-dependent resistivity $\rho(T)$ of T'-LYCO in zero magnetic field. Figure 2 shows the evolution
of $\rho(T)$ with different Y dopings ($0.05 \leq x \leq 0.30$). The film with $x = 0.05$ (plotted in the inset of figure 2) shows an insulating behavior in the whole temperature range like heavily underdoped or oxygenated cuprates such as NCCO (Nd$_{2-x}$Ce$_x$CuO$_4$) [11, 12]. All the other films show metallic behavior ($d\rho/dT > 0$) in the high-temperature range. In contrast to the familiar linear temperature dependence in the hole-doped cuprates (such as YBCO and LSCO), a nearly quadratic behavior of $\rho(T)$ in the normal state is observed (a detailed analysis is presented elsewhere [7]). This kind of behavior is a common feature in the known electron-doped superconducting cuprates near optimal and over doping, such as Ln$_{2-x}$Ce$_x$CuO$_4$ (Ln = La, Pr, Nd, and Sm) [13–16]. It is usually considered as a quasi-2D Landau–Fermi liquid behavior due to electron–electron scattering [17]. The metallic behavior is maintained down to the resistivity minimum ($T_{\text{min}}$). Below $T_{\text{min}}$, the resistivity shows an upturn as in either hole or electron cuprates at low Y dopings. The insulating upturns at low temperature are commonly interpreted in terms of 2D weak localization [18] or Kondo scattering by the uncompensated Cu$^{2+}$ spins [19].

Although the Y$^{3+}$ ion doping cannot bring net charge by substitution of La$^{3+}$, the resistivity of films reduces with increasing Y content until the minimum near $x = 0.20$, suggesting more electron doping by Y doping. As shown in figure 2, superconductivity occurs when $0.10 \leq x \leq 0.20$. But further doping leads to the increase of $\rho$ and the disappearance of superconductivity. This is consistent with the evolution of Hall coefficients (as discussed below). The superconducting phase diagram for Y doping is plotted in figure 3. Superconductivity exists in a narrow Y doping range, i.e., $0.10 \leq x \leq 0.20$, which is in agreement with the previous results [3]. The best $T_{\text{cZero}}$ is 13.5 K near the optimal doping $x = 0.15$. $T_{\text{cZero}}$ does not vary much with doping, differing from the usual superconducting ‘dome’ of other cuprates in the diagram. One should note that the Y content is not proportional to the concentration of charge carriers. In contrast, heavy Y doping leads to larger resistivity and the insulating behavior, instead of more metallic behavior induced by overdoping in other cuprates.

3.2. Resistive critical field $H_{\text{c2}}$

The magnetic field dependence of superconducting transitions for the two T'-LYCO films (x = 0.125, 0.20) is shown in figures 4 and 5. The magnetic field was applied parallel to the c-axis (shown in the main figures) or parallel to the ab plane (shown in the upper-right insets of figures 4 and 5). For $H \parallel c$, the superconducting onset temperature ($T_{\text{cOnset}}$) for both of the films decreases and the width of the transition slightly broadens at $\mu_0H = 1$ T. Upon increasing the magnetic field, the transition shifts to lower temperature and the $R(T)$ curves are roughly parallel to each other, and no further broadening is found. The field of 7 T along c-axis is enough to kill the superconducting transition of T'-LYCO film with $x = 0.125$. 

![Figure 2](image2.png)  
**Figure 2.** Resistivity versus temperature for T’-LYCO films with various Y contents: $x = 0.10, 0.125, 0.15, 0.20$, and $0.30$. The inset shows $\rho(T)$ of the film with $x = 0.05$. The reduction process for all these films after deposition is the same.

![Figure 3](image3.png)  
**Figure 3.** Phase diagram of T’-LYCO films as a function of Y content $x$, determined from the resistivity data in figure 2. Solid circles and squares represent $T_{\text{cZero}}$ and $T_{\text{cOnset}}$ respectively.

![Figure 4](image4.png)  
**Figure 4.** Superconducting transition in the resistivity of T’-LYCO with $x = 0.125$ at different magnetic fields. The derived temperature dependence of $H_{\text{c2}}$ is shown in the bottom-right inset.
but insufficient for \( x = 0.20 \). The higher upper critical field may be due to the stronger vortex pinning by in-plane oxygen deficiencies or the local distortion of the lattice induced by Y substitution in fluorite layers in the T'-structure.

In figures 4 and 5, the most remarkable character is the strong anisotropy in the effect of suppressing superconductivity by a magnetic field. When \( H \parallel \text{CuO}_2 \) planes, a field up to 13.5 T only slightly reduces \( T_c \) by a few kelvins. This strong anisotropy is a common feature in high-\( T_c \) cuprates due to their low dimensionality and a strong fluctuation effect. From these \( R(T) \) data in different magnetic fields, one can derive a characteristic field, which is often referred to as the resistive upper critical field \( H_{c2}^R \). The choice of the criterion to determine \( H_{c2}^R \) remains more or less uncertain and arbitrary because of the broadened flux-flow resistivity curves. But as pointed out in \cite{20} and \cite{21}, the general trend of \( H_{c2}^R \) is very insensitive to the criterion used in electron-doped NCCO and PCCO (Pr\textsubscript{2}−\textsubscript{x}Ce\textsubscript{x}CuO\textsubscript{4}). Here we adopt the zero resistivity temperature \( T_{c2}^{\text{Zero}} \). Other criteria (10% and 50% of the transition) were tested, and also gave a similar trend of \( H_{c2}^R \) in the case of T'-LYCO. \( H_{c2}^R \) for \( H \parallel c \) and \( H \perp c \) are shown in the bottom-right insets of figures 4 and 5. For \( H \perp c \), the derived values are quite close to \( T_c \) because of our experimental limits. It is difficult to deduce the accurate trends towards low temperature. For \( H \parallel c \), anomalously positive curvature of \( H_{c2}^R(T) \) was observed in both of the films, which seems to deviate from the conventional WHH theory \cite{22}.

The behavior of \( H_{c2}^R(T) \) in PCCO \cite{20} and NCCO \cite{21} has been found to have a similar temperature dependence. It has been pointed out by Ong and collaborators \cite{23, 25} that the resistivity is a bad diagnostic to determine intrinsic \( H_{c2}(T) \). \( H_{c2}^R(T) \) in cuprates determined by resistivity measurements can actually be correlated with the irreversibility line defined at the onset of flux flow and near the crossover from the vortex solid to liquid in the \( H-T \) phase diagram in the superconducting state. Only a very rough criterion corresponding to a full recovery of the normal-state resistivity for \( x = 0.15 \) brings the characteristic field temperature dependence close to the expected behavior described by WHH theory. Because of the absence of a pseudogap above \( T_c \) in electron-doped cuprates, the Nernst measurements are expected to serve as a much more accurate probe for \( H_{c2}(T) \) in T'-LYCO, as done in NCCO \cite{24, 25}.

### 3.3. Hall coefficient and origin of the charge carrier in T'-LYCO

At present, T'-LYCO films behave very similarly to the Ce-doped n-type cuprates. No distinct difference is observed in the above experiments. To clarify the sign and concentration of charge carriers in T'-LYCO, we examined the Hall coefficient of T'-LYCO with different Y doping, as shown in figure 6. All the films show negative \( R_H \) near room temperature. This confirms the intrinsic electron-doped nature in T'-214 LYCO films. For the non-superconducting film with \( x = 0.30 \), \( R_H \) decreases with lowering temperature and becomes divergent when approaching \( T = 0 \). This is a typical behavior observed in lightly doped n-type cuprates, such as NCCO \cite{12}, PCCO \cite{15} and LCCO \cite{13}. Our results also agree with the recent work in Greene’s group \cite{6}. \( R_H \) of \( x = 0.125 \) resembles the behavior for \( x = 0.30 \) except for the upturn at low temperature and its smaller absolute value, indicating more concentration of electron carriers. For \( x = 0.15 \), \( R_H \) decreases gradually with decreasing temperature from room temperature down to about 100 K. A slight upturn toward zero occurs upon decreasing the temperature further, which is analogous to slightly underdoped NCCO or LCCO near the optimal doping in the phase diagram, while for \( x = 0.20 \), the upturn at low temperature is observed, and \( R_H \) changes from negative at high temperature to positive at low temperature. Such a behavior is similar to that in electron-doped cuprates near optimal doping, which can be considered as a direct evidence for two types of charge carrier \cite{11}.

From the above analysis of \( R_H \), the variation of electron doping \( n_e \) with different Y content is clear: \( n_{e|\text{LYCO}|=0.20} > n_{e|\text{LYCO}|=0.15} > n_{e|\text{LYCO}|=0.125} > n_{e|\text{LYCO}|=0.30} \), which is consistent with the resistivity data shown in figure 2. Because Y\textsuperscript{3+} and La\textsuperscript{3+}...
are isovalent, no net charge can be provided by Y doping. The most natural assumption is that the charge carriers arise from oxygen deficiencies since the superconductivity can only be acquired by annealing films in high vacuum. But there is still no way to determine the oxygen content in thin films accurately and straightforwardly at present. To confirm this assumption, we deposited LYCO \( (x = 0.15) \) films at the optimal temperature \( (T_D = 690 \, ^\circ C) \), but annealed them in lower vacuum \( (P_{O_2} \sim 0.6 \times 10^{-2} \, Pa) \). These films are of pure T'-214 phase with less oxygen deficiency. Their resistivity become much larger and an insulating behavior lowering temperature. The absolute value of \( R_H \) in the whole temperature range and decreases sharply with decreasing temperature, as shown in the inset of figure 7. The corresponding Hall coefficient \( R_H \) is shown in figure 7, together with \( R_H \) of optimal T'-LYCO \( (x = 0.15) \) for comparison. \( R_H \) of oxygenated films is negative in the whole temperature range and decreases sharply with lowering temperature. The absolute value of \( R_H \) is much larger than that for optimal films, indicating much less effective carrier density. This behavior coincides with the observation by Yu et al., where a systematical variation of oxygen concentration has been performed on LYCO \( (x = 0.15) \). Similar phenomena were observed during the oxygenation of optimal NCCO [11] and PCCO [15]. It suggests that oxygen deficiency is the source of electron doping in T'-LYCO films.

3.4. Comparative research on Y-doped Pr- and Nd-based T'-phases
From the above results, we can conclude that ‘undoped’ T'-LYCO is actually intrinsically electron-doped and its charge carriers and subsequent superconductivity in T'-LYCO film are induced by oxygen deficiency. T'-LYCO seems to be an electron-doped counterpart of the hole-doped superconductor La\(_2\)CuO\(_{4+y}\), whose superconductivity is induced by excess oxygenation. Besides reducing the \( t \) factor to improve the stability of T'-structure slightly, the role of Y in superconducting T'-LYCO is still elusive. It is found that the superconductivity occurs only in a certain Y doping range \( 0.10 \leq x \leq 0.20 \). Does superconductivity exist in other ‘undoped’ T'-structure systems? To find an answer to this question, comparative research on other T'-214 lanthanide cuprates is necessary.

It is well known that in n-type superconducting cuprates the CuO\(_2\) network is under tensile strain because of the bond length mismatch between the CuO\(_2\) sheets and Ln\(_2\)O\(_2\) fluorite layers [26, 27]. The tensile CuO\(_2\) sheets are apt to receive electron doping. Doping electrons into CuO\(_2\) planes increases the Cu–O bond length and releases the tension. Larger cations can introduce more tensile strain. Naturally more stretch increases the capability to receive electron doping by CuO\(_2\) sheets. In contrast, if the Cu–O bond length in the T' structures is too small, as in the Gd214 system \( (a \sim 3.89 \, \text{Å}) \), the planes do not readily accept electron doping, and no superconductivity is found with Ce substitution [28]. In [2], the series of \( R_2\)CuO\(_4\) films with increasing radii of the \( R^{3+} \) ions \( (R = \text{Tb}, \text{Gd}, \text{Eu}, \text{Sm}, \text{Nd}, \text{Pr}, \text{La}) \) was fabricated by MBE. Their resistivity decreases gradually with increasing ionic radius (shown in figure 3 in [2]); the trend is consistent with the above analysis. The Cu ions are reduced by in-plane deficiency and the stretch can be partly released since the binding energy of the Cu–O bond is less than R–O [29]. It suggests that it is more likely that the main oxygen deficiency is mostly introduced at O(1) sites (in the CuO\(_2\) planes), while O(2) sites (out of the CuO\(_2\) planes) remain intact in the reduction. The in-plane oxygen defects created by reduction have been evidenced in infrared transmission, Raman and ultrasonic studies in NCCO [30, 31] and PCCO [32] systems.

In our work, we have prepared Nd\(_{2−x}\)Y\(_x\)CuO\(_4\) (NYCO) and Pr\(_{2−x}\)Y\(_x\)CuO\(_4\) (PYCO) films with Y content \( x = 0.15 \). The temperature dependence of resistivity is shown in figure 8 for NYCO and PYCO films. Here the T'-214 structure is intrinsically stable even for \( x = 0 \) and the role of Y to stabilize the T'-structure is not required. It is convenient to study the size effect at the A-site in the T'-phase. Furthermore, to study the effect of cation disorder, undoped Pr\(_2\)CuO\(_4\) (PCO) films
were also prepared for comparison. All the films are of pure c-axis oriented T'-phase, and they were annealed in high vacuum. The NYCO and PYCO films show an insulating behavior and no superconductivity is found. The resistivity of PYCO films is smaller than that of NYCO, which is consistent with above analysis because of the larger average ion radius at the A-site in PYCO. In the T'-phase, the larger cations at the A-site lead to the stronger driving force for the acceptance of electrons into CuO2 planes. During the reduction process, oxygen vacancies lead to further electron doping, as observed in many early experiments on the preparation of T'-214 cuprate ceramics [27, 34, 35].

To find the reason why PYCO and NYCO are not superconducting in contrast to LYCO, we measured their Hall coefficients from 280 K down to 20 K, as shown in figure 9. The temperature dependence of $R_H$ of superconducting LYCO films ($x = 0.15$) is also plotted for comparison. The Hall coefficients $R_H$ of PYCO and NYCO films are both negative in the whole temperature range and they decrease gradually upon lowering temperature with a slight upturn below 50 K. The absolute value of $R_H$ is much larger than that for LYCO films, indicating much lower effective carrier density, consistent with the resistivity data. As pointed out in [26], the critical amount of electron doping necessary to induce a transition from antiferromagnetic insulator to superconductor is nearly fixed in cuprates. The low carrier density should be the main reason for the absence of superconductivity in NYCO and PYCO.

For comparison, the resistivity of PYCO and undoped PCO is shown in the inset of figure 8. The partial substitution of Y for Pr greatly reduces the resistivity, suggesting that more oxygen vacancies are induced by Y doping. Although at present there is no the quantitative theoretic calculation and direct experimental evidence of the oxygen deficiency, we suppose that it is a reasonable microscopic scenario that the local distorted fluorite structure weakens the local binding of Ln–O and causes the further loss of oxygen in the fluorite layer. Therefore, Y doping leads to the additional oxygen deficiency and consequently the increase of the effective charge carriers.

4. Discussion

We have shown that T'-LYCO is in nature electron-doped, like other Ce-doped cuprate superconductors such as NCCO and PCCO. The electron doping is considered to originate from oxygen deficiency. Although the strain effect caused by the substrates may help to stabilize the T' structure to some degree, this kind of effect can be negligible because the films we used in measurements are much thicker than 1000 Å. In addition, two kinds of substrate, SrTiO3 (STO) and [(LaAlO3)0.3(Sr2AlTaO6)0.7] (LSAT), were used and no apparent difference was found in the transport properties in our experiments. The apical or interstitial oxygen is thought deleterious to superconductivity and is also excluded, because these films are sufficiently annealed in a vacuum where the oxygen partial pressure is far below the level in reducing single crystals or ceramics in flowing inert gas. The removal of apical oxygen is complete and the actual stoichiometric ratio for oxygen should be less than 4.0, according to a previous determination of the oxygen content in the bulk after sufficient reduction [27].

Based on our present results and the data from Tsukada et al [2, 3], we present a most likely and reasonable mechanism of the superconductive in T'-214 cuprates. The electron doping originates from two different microscopic processes of oxygen deficiency, and each of them is indispensable to trigger superconductivity.

First, the large average radius of cations at the A-site should make the CuO2 sheets sufficiently tensile. The tensile strain becomes the internal driving force for the acceptance of electrons into CuO2 planes to release the stretch strain. Driven by the internal stress, an oxygen deficiency is produced in the reduction process, mainly at the O(1) position in the CuO2 planes because of the lower binding energy at the O(1) site than that at the O(2) site in La2O2 fluorite layers. The larger cations at the A-site introduce more oxygen vacancies, which are responsible for more charge carriers. It has been found in the previous experiments that there are more oxygen vacancies produced as the average ion radius of the A-site increases in T'-214 systems during a constant reduction process [26, 34]. This is consistent with the results that the resistivity decreases gradually with increasing lanthanide ionic radius in annealed undoped Ln2CuO4 (Ln = Tb, Gd, Sm, Eu, La, Pr, Nd) as shown in figure 3 of [2].

Furthermore, the various A-site ions in the T’-structure also lead to different additional dopings by various oxygen deficiency, which modifies the superconducting phase diagram as a function of Ce content $x$ in known Ce-doped n-type cuprate films (as shown in figure 1 in [2]). The shift of the highest $T_c$ towards lower Ce concentrations is also observed with the increasing substitution of La in PCCO [33] or NCCO [34, 35] bulk systems.

Nevertheless, in undoped T'-214 cuprates the charge carriers induced only by in-plane vacancies are not enough to drive the CuO2 into a superconducting state. One has not
been able to achieve superconductivity in undoped or low-doped T'-214 cuprates in different families by reduction. An opposite example is that excess oxygen can turn undoped T'-La$_2$CuO$_4$ into a hole-doped superconductor. Additional oxygen deficiency in the fluorite layers is needed. However, in undoped Ln$_2$CuO$_4$, the binding energy in the Ln–O bond is always larger than that in the in-plane Cu–O bond, so that O(2) can be too hard to remove before the excess in-plane oxygen vacancies destabilize the T’-structure and lead to chemical decomposition of samples during the further reduction.

Second, the partial substitution of smaller Y$^{3+}$ ions for La$^{3+}$ leads to local strong distortion in the fluorite Ln$_2$O$_2$ layers. It can be apt to further produce oxygen vacancies during the reduction. The strong distortion in fluorite layers by Y substitution is thought to decrease the local binding energy to be overcome, and then creates additional oxygen vacancies in fluorite layers in reduction. This has been demonstrated in the comparison of doped and undoped PCO films.

Therefore, the total oxygen deficiency created in two ways is adequate to induce superconductivity in T'-LYCO. As proposed by Zhu and Manthiram [26], the transition from antiferromagnetic insulator to superconductor occurs at the critical amount of electron concentration, $n_c$, which is nearly fixed in n-type cuprates. Although the Madelung energy or charge transfer gap $\Delta$ decreases upon increasing ion radius at the A-site, its effect on $n_c$ is negligible. Increasing Y doping leads to an introduction of more charge carriers. However, excess Y doping induces the decrease of the average size of Ln at the A-site, which will hinder the oxygen depletion at the O(1)-site. Furthermore, the disorder induced by Y doping localizes the charge carriers. Therefore, excess Y will kill the superconductivity in an extreme case. This accounts for the increasing resistivity and the absence of superconductivity in the T'-LYCO films with high doping ($x = 0.30$).

Our analysis above can naturally explain the results of Tsukada and co-workers [2]. Superconductivity has been found in many ‘non-doped’ T’-(La, RE)$_2$CuO$_4$ cuprates such as RE = Sm, Eu, Gd, Tb, Lu, and Y, but neither Pr nor Nd. Pr and Nd are closer to La in the lanthanide series. The difference of ion radius between Pr (or Nd) and La is not as distinct as for other lanthanides. This suggests that the local distortion caused by Pr or Nd substitution is not as remarkable as that by Y. The fluorite structure remains almost intact during the usual annealing process. Oxygen vacancies mainly exist in the CuO$_2$ network, and they cannot afford the necessary doping to trigger superconductivity unless there is extra charge induce by alloyation Ce substitution in charge reservoir layers such as in the (La, Nd, Ce)$_2$CuO$_4$ system [34].

Our present results provide a more comprehensive understanding of this new class of cuprates as well as the microscopic process of oxygen reduction which is necessary to obtain superconductivity in electron-doped cuprates. Because of the metastability of the La-based T'-214 structure, one can obtain superconducting T’-LYCO only in the form of thin films so far. Therefore, it is difficult and even impossible to determine directly the oxygen occupancy at O(1) and O(2) sites in films within present technologies such as conventional x-ray or neutron diffraction. Bulk T’-La$_2$CuO$_4$ [36] and even superconducting La$_{2-x}$Ce$_x$CuO$_4$ [37] have been synthesized in special precursor route. This indicates that the bulk synthesis of superconducting T’-LYCO seems to be possible. Such attempts are still underway. For the second processes of oxygen reduction we propose above, more powerful experimental methods such as Raman, extended x-ray absorption fine structure (EXAFS), and x-ray absorption near edge structure (XANES) measurements are expected to detect the distortion of the local atomic structure and thereafter its quantitative effect on oxygen depletion.

5. Conclusion

In summary, we systematically investigated the transport properties of the newly discovered nominal ‘non-doped’ La$_{2-x}$Y$_x$CuO$_4$ (0.05 $\leq x \leq 0.30$). Detailed studies of the resistivity, Hall coefficient, and strong anisotropic $H_C(T)$ with positive curvature show clearly the similarity to the known Ce-doped electron-type cuprates such as NCCO or PCCO. This kind of so-called ‘non-doped’ superconductor is intrinsically electron-doped. The effect of oxygen content on the superconductivity and transport properties indicates that the charge carriers mainly arise from oxygen deficiency obtained during the reduction process.

Comparative experiments on non-superconducting Y-doped Pr- and Nd-based T’-214 films exhibit the crucial role of cation radius played in the oxygen depletion during the reduction. The cooperation of large-sized La$^{3+}$ ions with smaller Y$^{3+}$ enables sufficient oxygen deficiency in the T’-structure to induce superconductivity in T’-LYCO. We propose a reasonable scenario for the microscopic reduction process. The large La$^{3+}$ ions at A-sites keep the CuO$_2$ in adequate tensile strain which enhances in-plane oxygen deficiency during reduction. The appropriate substitution of smaller Y$^{3+}$ for La$^{3+}$ leads to strong local distortion and the lowering of the binding energy to be overcome in the oxygen depletion from fluorite layers. They are two indispensable keys to induce enough electron doping to trigger superconductivity in the nominally ‘undoped’ cuprates.

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