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Reassessment of the electronic state, magnetism, and superconductivity in high- T_c cuprates with the Nd_2CuO_4 structure

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Abstract

The electronic phase diagram of the cuprates remains enigmatic and is still a key ingredient to understand the mechanism of high- T_c superconductivity. It has been believed for a long time that parent compounds of cuprates *were* universally antiferromagnetic Mott insulators (charge-transfer insulators) and that high- T_c superconductivity *would* develop upon doping holes or electrons in a Mott-Hubbard insulator (“doped Mott-insulator scenario”). However, our recent discovery of superconductivity in the parent compounds of square-planar cuprates with the Nd_2CuO_4 (T') structure and the revised electronic phase diagram in T' cuprates urged a serious reassessment to the above scenario. In this review, we present the main results derived from our synthesis and experiments on T' cuprates in the undoped or heavily underdoped regime over 20 years, including material issues and basic physics. The key material issue is how to remove excess oxygen ions at O_{ap} without introducing oxygen vacancies in the CuO_2 planes. In order to put this into practice, the basic knowledge of complex solid-state chemistry in T' cuprates is required, which is also included in this review.

1. Introduction

Parent compounds of cuprates have for a long time been believed to be antiferromagnetic Mott insulators (charge-transfer insulators). For example, La_2CuO_4 with the K_2NiF_4 (abbreviated as T) structure is an insulator with no doubt. RE_2CuO_4 (RE: rare-earth element) with the Nd_2CuO_4 (abbreviated as T') structure has also been believed as a Mott insulator since the discovery of “electron-doped” superconductors, $\text{T}'\text{-(RE,Ce)}_2\text{CuO}_4$, in 1989 [1, 2]. In $\text{T-La}_2\text{CuO}_4$, the superconductivity develops by the doping of Sr (or Ca, Ba), i.e., “hole doping”. The superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ appears at $x = 0.05\text{-}0.30$ [3] and T_c is maximized at $x = 0.15$. In $\text{T}'\text{-Nd}_2\text{CuO}_4$, the superconductivity develops by the doping of Ce (or Th), i.e., “electron doping”. The superconductivity in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ appears at $x = 0.14\text{-}0.17$ [2] and T_c is maximized at $x = 0.15$. As shown in Fig. 1, the $T_c\text{-vs-}x$ curves of both of $\text{T-La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{T}'\text{-Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ show a well-known ‘dome’ shape with maximal superconductivity at a doping level of about 0.15 and are roughly symmetrical except for a much larger antiferromagnetic (AF) region and a much smaller superconducting (SC) region in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [4]. Therefore it has been claimed that “electron-hole” symmetry holds for high- T_c superconductivity. Based on this electron-hole symmetry, the doped Mott insulator scenario “high- T_c superconductivity develops upon doping holes or electrons in a Mott-Hubbard insulator” has been a consensus in the field over almost three decades. Along this scenario, many of the strategic searches toward new high- T_c materials were carried out in the past.

Our research on T and T' cuprates (called as “214” cuprates after their chemical formula) started in 1992 by growing epitaxial films of T and T' cuprates by molecular beam epitaxy (MBE). In the growth of $\text{T-La}_{2-x}\text{Sr}_x\text{CuO}_4$, we struggled to obtain superconducting films with T_c comparable to the bulk T_c . The reason for lower T_c in the films is now established to be tensile epitaxial strain due to lattice mismatch between films and substrates (SrTiO_3) [5]. In contrast, $\text{T}'\text{-RE}_{2-x}\text{Ce}_x\text{CuO}_4$ films with good superconducting properties were

easy to grow on any substrates. At that time it was difficult to obtain good superconducting properties in $T'-RE_{2-x}Ce_xCuO_4$ by bulk synthesis, so we had a feeling that thin film growth is more favorable for obtaining high-quality samples of $T'-RE_{2-x}Ce_xCuO_4$ than bulk synthesis. The reason is now understood as follows. In order to achieve superconductivity in $T'-RE_{2-x}Ce_xCuO_4$, post-synthesis reduction in a low- p_{O_2} atmosphere is prerequisite. The reduction is not intended for further electron doping by oxygen deficiencies, but for removal of interstitial oxygen ions at the apical site (O_{ap}), which is empirically known to be very harmful to high- T_c superconductivity. Thin films are advantageous in evacuating interstitial O_{ap} ions due to a large surface-to-volume ratio.

In 1995, we started *in-situ* X-ray photoelectron spectroscopy (XPS) on MBE-grown films and found almost immediately that the parent compound, Nd_2CuO_4 , shows a clear Fermi edge after reduction and that there is no essential difference in the electronic structure between parent Nd_2CuO_4 and electron-doped $Nd_{1.85}Ce_{0.15}CuO_4$ [6]. A significant difference exists rather between as-grown and reduced films of $(Nd,Ce)_2CuO_4$. In fact, reduced films of parent Nd_2CuO_4 and Pr_2CuO_4 are fairly conductive ($\rho(300\text{ K}) \sim 10\text{--}20\text{ m}\Omega\text{cm}$, $d\rho/dT > 0$ down to $\sim 200\text{ K}$) [7]. Our findings disagreed with the consensus at that time that parent Nd_2CuO_4 is a Mott-Hubbard insulator. We speculated that the insulating behavior observed in bulk samples of parent Nd_2CuO_4 and Pr_2CuO_4 may be due to the presence of a large amount of excess oxygen ions at O_{ap} and that parent Nd_2CuO_4 and Pr_2CuO_4 with no excess oxygen ion would be superconducting. Toward this speculation, we attempted at optimizing the growth process as well as the reduction process in the MBE apparatus, but with no quick success. It took more than 10 years to reach superconductivity in $T'-RE_2CuO_4$ [8]. During this period, we had the following important findings.

(1) MBE growth of $T'-La_{2-x}Ce_xCuO_4$

$T'-La_{2-x}Ce_xCuO_4$ is not easy to synthesize by bulk, but is easy by MBE [9]. We found that

the superconducting window of $T'-La_{2-x}Ce_xCuO_4$ extends substantially to a lower Ce doping level than those of $Pr_{2-x}Ce_xCuO_4$ or $Nd_{2-x}Ce_xCuO_4$ and that $T'-La_{2-x}Ce_xCuO_4$ shows $T_c = 31$ K at $x = 0.08$ [9-12]. This result indicates that the T_c -vs- x is not universal in $T'-RE_{2-x}Ce_xCuO_4$ [13].

(2) Insulating $T-La_2CuO_4$ vs metallic $T'-La_2CuO_4$

La_2CuO_4 takes the T structure in standard bulk synthesis. But the selective stabilization of T - and $T'-La_2CuO_4$ can be achieved by MBE via adjusting the growth temperature and choosing the substrate [14]. The electron transport of T - and $T'-La_2CuO_4$ shows a sharp contrast as shown in Fig. 2. $T-La_2CuO_4$ is indeed an insulator whereas $T'-La_2CuO_4$ is conductive with $d\rho/dT > 0$ down to 150 K with $\rho(300\text{ K}) \sim 2\text{ m}\Omega\text{cm}$. The *in-situ* X-ray photoelectron spectroscopy (XPS) also demonstrated a clear Fermi edge for $T'-La_2CuO_4$ but no Fermi edge for $T-La_2CuO_4$. [\[footnote: We could not achieve superconductivity at that time, but achieved in 2014 \[15\].\]](#)

(3) Superconductivity in $T'-(La,RE)_2CuO_4$

As mentioned above in (2), $T'-La_2CuO_4$ can be stabilized by lowering the growth temperature but at the cost of reduced crystallinity. The limited growth temperature leads also to insufficient apical oxygen removal. We suspected that this constraint may be preventing superconductivity in $T'-La_2CuO_4$. With the purpose of relaxing the constraint, we substituted La^{3+} by a little amount of smaller but also trivalent RE^{3+} ions as a T' -phase stabilizer. This led us to the discovery of superconductivity of $T_c \sim 25$ K in $T'-La_{2-x}RE_xCuO_4$ materials ($RE = Sm, Eu, Gd, Tb, Lu, \text{ and } Y$) [7, 16, 17].

The superconductivity in parent $T'-RE_2CuO_4$ was achieved rather accidentally in 2007. In 2006, we started to prepare thin films of $T'-RE_{2-x}Ce_xCuO_4$ by metal organic decomposition (MOD), then soon after we achieved superconductivity in parent $T'-RE_2CuO_4$ ($RE = Pr, Nd, Sm, Eu, \text{ and } Gd$) [8]. The difference between MBE and MOD films exists in

the grain size [18]. MOD films have substantially smaller grain size, which facilitates to evacuate excess oxygen ions at O_{ap} . MBE films have much higher crystallinity that hinders achieving superconductivity.

This review article describes the main results from our MBE and MOD growth of T' cuprates in the undoped or heavily underdoped regime over 20 years, including material issues and basic physics. [foot note: The term “undoped” in this article is defined as chemically undoped, namely neither of addition of aliovalent elements such as Ce or Th nor oxygen nonstoichiometry (excess oxygen or oxygen deficiency). Our “undoped” does not mean that mobile charge carriers are absent. The situation is similar to the case of simple metals such as Al, Cu that have mobile carriers without chemical doping.] The key material issue is how to remove excess oxygen ions at O_{ap} without introducing oxygen vacancies in the CuO_2 planes (see Fig. 3). In order to put this into practice, the basic knowledge of complex solid-state chemistry in T' cuprates is required. This review includes this aspect and is organized as follows. It starts in §2 by the quarter century of the history for the electronic phase diagram for T' cuprates. In §3, the basic solid-state chemistry for 214 cuprates is overviewed. In §4, the details of specific syntheses of undoped superconductors are described. Finally, in §5, the implications of superconductivity in undoped cuprates are addressed toward better understanding high- T_c superconductivity. Section 6 serves as a summary.

2. Past quarter century for superconductivity in T' cuprates - overview

2.1. Early phase diagram in T' cuprates – “electron-doped” superconductors

The first article reporting the discovery of “electron-doped” superconductors demonstrated the following results on T_c as a function of Ce doping (x) in $Nd_{2-x}Ce_xCuO_4$ [1, 2]. Superconductivity of $T_c > 20$ K suddenly appears at $x = 0.14$, and the highest T_c is achieved $x = 0.15$ as shown in Fig. 1. Further Ce doping lowers T_c until superconductivity

disappears at $x = 0.18$. The superconducting window in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ was quite narrow. It was revealed by μSR experiments performed soon after that $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ with $x < 0.14$ exhibits static magnetic order below 300 K, which competes with the superconducting order [19]. Subsequent neutron diffraction studies revealed that the magnetic order is an antiferromagnetic (AF) type [20, 21]. The early reports employed polycrystalline specimens, which were given post-synthesis reduction in $\text{Ar} + \text{O}_2$ mixture of $p_{\text{O}_2} \sim 10^{-4}$ atm at 950-1000°C for 10 hours and subsequent quench to room temperature [2]. At that time, the role of reduction was, although not clear, speculated to be further electron doping by oxygen deficiencies. But later this speculation turned out to be not correct, and it is now established that the reduction is for the removal of interstitial oxygen ions at O_{ap} , which are a strong pair-breaker for high- T_c superconductivity.

Specimens used in most of early experiments were similar polycrystalline pellets with a small superconducting volume fraction ($\sim 10\%$), a broad superconducting transition, and high resistivity. A subsequent development in single-crystal growth techniques enabled one to produce single-crystalline specimens with a full superconducting volume fraction and low and metallic resistivity (0.5 - 1 $\text{m}\Omega\text{cm}$ at room temperature). However, the initial T_c -vs- x as described above has been believed to be “typical” of T' cuprates over 25 years.

2.2. Toward more complete removal of excess O_{ap} ions

Excess oxygen ions occupying a small percentage of impurity apical sites entirely change the most fundamental properties such as the electronic phase diagram. In 1990's, some efforts were performed toward more complete removal of excess O_{ap} ions, and these efforts indeed demonstrated that the electronic phase diagram shows a dramatic change. In general, it takes longer time to take out excess O_{ap} ions from single crystals due to limited paths of oxygen diffusion than from polycrystalline specimens. Raising the reduction temperature to shorten the reduction time often results in partial decomposition at surface of

single crystals but with a fair amount of excess O_{ap} ions remaining inside. For the purpose of more homogeneous reduction, Brinkmann et al. devised the following method, so-called “protect annealing” [22-24]. They sandwiched $Pr_{2-x}Ce_xCuO_4$ single crystals with polycrystalline pellets of the same composition, and reduced them together in a mixture of $Ar + O_2$ at much higher temperatures (up to $1080^\circ C$) for much longer time (3 days) than in the standard reduction. This method changed the phase diagram dramatically as shown in Fig. 4, which compares the T_c -vs- x by the improved (solid line) and standard (broken line) reduction [22]. With the improved reduction, the superconducting window extends down to $x = 0.04$ and there is a clear tendency of a monotonically increasing T_c with decreasing x .

Another way for more complete removal of excess O_{ap} ions is to employ thin films because oxygen diffusion is prompt in thin films due to a large surface-to-volume ratio and also small grain size. Figure 5 summarizes the T_c -vs- x curves for our MBE-grown $RE_{2-x}Ce_xCuO_4$ thin films with different RE [13]. Table I is a summary of the optimum doping level (x_{opt}) and highest T_c (T_c^{max}) for each RE . T' - $La_{2-x}Ce_xCuO_4$ shows superconductivity in $0.04 < x < 0.22$ with $T_c^{max} = 31.0$ K at $x_{opt} = 0.08$ whereas $Sm_{2-x}Ce_xCuO_4$ shows superconductivity in $0.14 < x < 0.21$ with $T_c^{max} = 19$ K at $x = 0.155$ [9, 11, 25]. In general, the superconducting window for larger RE^{3+} extends to lower doping. Correspondingly, the optimum doping shifts to a lower level and the maximum T_c increases, which leads to non-universal (= RE dependent) T_c -vs- x curve. The trend seems to be in accord with the empirical trend of solid state chemistry in T' cuprates that interstitial O_{ap} ions are easier to remove for larger RE^{3+} (see §3.6).

2.3. Road to “undoped” T' superconductors

The first compounds that were made superconducting without electron doping are T' -(La, RE) $_2CuO_4$, which were grown by MBE [7]. In these compounds, La^{3+} is substituted not by Ce^{4+} but by isovalent RE^{3+} ($RE = Sm, Eu, Gd, Tb, Lu, Y$), which is no effective dopant.

The trend mentioned just above suggests that the best RE^{3+} for superconductivity in T' cuprates is La^{3+} . The obstacle with using La^{3+} is the competing formation of the T-phase of La_2CuO_4 . With the purpose of accessing the heavily underdoped and undoped regime more carefully, we substituted La^{3+} by a little amount of smaller but also trivalent RE^{3+} ions as a T'-phase stabilizer. This led us to the discovery of superconductivity with $T_c > 20$ K in T'- $La_{2-x}RE_xCuO_4$ as shown in Fig. 6. The highest T_c was 26 K in $La_{1.88}Eu_{0.12}CuO_4$. Mysteriously, no superconductivity was observed with $RE = Pr$ and Nd . This mystery may be related to the question why no superconductivity is observed in undoped compounds composed of single RE ions, such as La_2CuO_4 , Pr_2CuO_4 and Nd_2CuO_4 . These observations raised the suspicion that the internal doping may take place in T'- $La_{2-x}RE_xCuO_4$ due to the possible difference in the ionization potential between La and RE in spite of the formally same valence.

The next step came suddenly by changing our synthetic technique from MBE to MOD. This presents one good example for an empirical implication that a new synthesis technique often leads to a breakthrough in the search for new materials. MOD is an inexpensive and easy-to-implement thin film preparation method, which is in contrast to MBE, a leading-edge thin film technology. However, MOD enabled us to explore a wider phase field (temperature and oxygen partial pressure) and provided the answer to the above question: RE_2CuO_4 ($RE = Pr, Nd, Sm, Eu, Gd$) indeed become superconducting with T_c even exceeding 30 K as shown in Fig. 7 and Table II [8, 26, 27]. The key step in synthesis for superconductivity is to fire films in a low- p_{O_2} atmosphere, the aim of which is to minimize the amount of O_{ap} impurities prior to the post-growth reduction process.

2.4. Generic phase diagram in T' cuprates – beyond doping

The above observation of superconductivity in the parent compounds of T'- RE_2CuO_4 further motivated us to reexamine the electronic phase diagram of the doped T' cuprates using

specimens prepared in an almost identical manner; namely, by the low- p_{O_2} MOD synthesis method. We chose the $Nd_{2-x}Ce_xCuO_4$ system, which has been the one most extensively studied among the “electron-doped” cuprates. Figure 8 is a resultant phase diagram [28]. The T_c is the highest (29 K) at $x = 0.00$, and monotonically decreases from 29 K to 24 K with increasing x from 0.00 to 0.15 [footnote: this experiment was performed using $DyScO_3(110)$ substrates in order to increase the Ce solubility limit. The T_c of the films on $DyScO_3(110)$ is slightly (~ 3 K) lower than the T_c on $SrTiO_3(001)$]. The T_c of 24 K at $x = 0.15$ agrees with the established bulk T_c of $Nd_{1.85}Ce_{0.15}CuO_4$. The solubility limit of Ce in our MOD process is $x \sim 0.15$. For $x > 0.15$, the data from our MBE growth are complementary. With the MOD and MBE data together, the T_c of $Nd_{2-x}Ce_xCuO_4$ films monotonically decreases from 29 K at $x = 0.00$ and disappears around $x \sim 0.20$ -0.25.

The new electronic phase diagram is an essential revise of the early one shown in Fig. 1. The origin of the sharp contradiction between the early and new results can be attributed to the different amount of impurity oxygen ions at O_{ap} . The delicate issue of oxygen nonstoichiometry in the T'-cuprates should always be borne in mind: only a minute amount of impurity O_{ap} ions are quite detrimental to superconductivity. However, early works performed more than two decades ago did not pay serious attention to this O_{ap} issue [2]. Our finding provides the following implications on high- T_c superconductivity in cuprates.

(1) Distinct ground states in T- versus T'- La_2CuO_4 with different oxygen coordinations

T'- La_2CuO_4 with square-planar oxygen coordination is superconducting whereas T- La_2CuO_4 with octahedral coordination is insulating. Namely, the ground states of the parent compounds of T' and T cuprates are different.

(2) No electron-hole symmetry

The Ce doping dependence of T_c in T' cuprates is dissimilar to the Sr doping dependence in T cuprates. This is rather natural if one takes account of the difference in the crystal structure.

(3) Beyond doping

The scenario that high- T_c superconductivity develops upon doping holes or electrons in a Mott-Hubbard insulator no longer holds universally. In the case of $T'-RE_{2-x}Ce_xCuO_4$, T_c is the highest at $x = 0.0$ and is reduced by Ce doping. The meaning of doping should be reassessed.

3. Basic solid-state chemistry – “ideal” vs “real” T' cuprates

3.1. 214 cuprates – T , T' , and T^*

The rare earth copper oxides of the general chemical formula RE_2CuO_4 possess a richness of structural and physical properties because of the wide range of the ionic size of RE^{3+} . There are two closely related structures as shown in Fig. 9(a) and (c): the T (K_2NiF_4) and T' (Nd_2CuO_4) structures. The structural difference between T and T' can be viewed as the difference in the $RE-O$ arrangements: rock-salt-like versus fluorite-like or more importantly as the difference in the Cu-O coordination: octahedral CuO_6 versus square-planar CuO_4 . The key parameter determining which of these structures forms is the ionic radius of the RE^{3+} ion. The T structure forms with large La^{3+} whereas the T' structure forms with smaller RE^{3+} ions such as $RE = Pr, Nd, Sm, Eu, \text{ and } Gd$. Employing high-pressure synthesis, the T' structure also forms with Dy to Tm as well as Y (Okada et al., 1990; Bordet et al., 1992) [29, 30]. The T - T' boundary lies in between La^{3+} and Pr^{3+} . There exists a third structure (denoted T^* , Fig. 9(b)), which consists of alternating stacking of T - and T' -slabs. Cuprates with the T^* structure were synthesized first by Sawa et al. in a mixed-lanthanide system such as $(La,RE)_2CuO_4$ ($RE = Sm, Eu, Gd, Tb, \text{ etc.}$) [31]. Therefore it was initially supposed that the stabilization of this structure *would* require two RE ions with significantly different ionic sizes: one large La^{3+} and the other smaller RE^{3+} . Later, however, this turned out not to be a necessary requirement, for pure T^* - La_2CuO_4 has recently been synthesized by MBE using lattice matched substrates [15].

3.2. Tolerance factor

The crystal chemistry on the structure versus the ionic radius in the rare earth copper oxides has been explained by Bringley et al. (1990) [32] and Manthiram et al. (1990) [33] in terms of the crystallographic tolerance factor (t), which is defined as

$$t = [r_i^{\text{IX}}(\text{RE}^{3+}) + r_i^{\text{VI}}(\text{O}^{2-})]/[\sqrt{2} * [r_i^{\text{VI}}(\text{Cu}^{2+}) + r_i^{\text{VI}}(\text{O}^{2-})]], \quad (1)$$

where $r_i^{\text{IX}}(\text{RE}^{3+})$, $r_i^{\text{VI}}(\text{Cu}^{2+})$, and $r_i^{\text{VI}}(\text{O}^{2-})$ are the ionic radii for RE^{3+} , Cu^{2+} , and O^{2-} ions. The ionic radius depends not only on the valence but also on the coordination, so the coordination number is indicated by a superscript Roman numeral. In the T structure, RE^{3+} is surrounded by nine O^{2-} , therefore $r_i^{\text{IX}}(\text{RE}^{3+})$ should be used in calculation. The tolerance factor (t) was initially proposed to argue the stability of the perovskite structure (ABO_3) by Goldshmidt (1926) [34]. It represents the bond length matching between AO layers and BO_2 layers. Ideal matching corresponds to $t = 1$, and the perovskite structure is stable for $\sim 0.8 < t < 1.0$. This factor can also be used to argue the stability of the K_2NiF_4 structure. The values for t , which are listed in Table III, are calculated using the room-temperature ($\sim 0^\circ\text{C}$) ionic radii by Shannon and Prewitt (1969), and we call them " t_0 ". As we shall see below, the tolerance factor, t , at the synthesis temperature, which slightly differs from t_0 , is more important for the phase stabilization. One can see from Table III that larger RE^{3+} increases t_0 toward 1.0, leading to the stabilization of the T phase. This explains why the T phase forms with large La^{3+} whereas the T' phase forms with smaller RE^{3+} ions.

Next we describe the temperature effect on the tolerance factor. The bond length expands with temperature, so the bond length at the synthesis temperatures ($\sim 1000^\circ\text{C}$) should be used in the discussion of the phase stability. In general, the "ionic" RE-O bond has a larger thermal expansion coefficient than the "covalent" Cu-O bond, which is called as

“thermal expansion mismatch” by Manthiram and Goodenough [35]. The difference in the thermal expansion coefficients between the $RE-O$ and $Cu-O$ bonds leads to the increase of t with temperature ($t = t_0 + \alpha T$, $\alpha \sim 2 \times 10^{-5}$ by rough estimate), where T is measured in $^{\circ}C$. This effect plays an important role in the T-versus-T' phase stability. The threshold for the T to T' transition will be $t_c \approx 0.878$. Therefore, if one *could* synthesize La_2CuO_4 at ambient temperatures ($\sim 0^{\circ}C$), one *would* get T'- La_2CuO_4 since $t_0 = 0.8685$ of La_2CuO_4 is smaller than t_c . In contrast, if the synthesis temperature for La_2CuO_4 is as high as $1000^{\circ}C$, $t_{1000^{\circ}C} = 0.8885$ is larger than t_c and the T phase is stabilized.

Manthiram and Goodenough (1991) succeeded in the selective stabilization of T versus T' in the $La_{2-y}Nd_yCuO_4$ system by changing the synthesis temperature (T_s), which is demonstrated in Fig. 10 [35]. They employed coprecipitated fine powder in solid-state reaction in order to lower the synthesis temperature. $La_{1.5}Nd_{0.5}CuO_4$ ($t_0 = 0.8641$) stabilizes as single-phase T' below $T_s = 625^{\circ}C$ or single-phased T above $T_s = 775^{\circ}C$. A two-phase mixture of T and T' is obtained in between $625^{\circ}C$ and $775^{\circ}C$. At $T_s = 500^{\circ}C$, even La_2CuO_4 becomes not single-phase T but a two-phase mixture of T and T'. By extrapolation of the T/T' phase boundary in the $La_{2-y}Nd_yCuO_4$ system to $y = 0$, it is predicted that La_2CuO_4 can be stabilized as single-phase T' below $T_s = 425^{\circ}C$, which is too low for bulk synthesis, even using coprecipitated powder.

By means of thin-film synthesis, however, the reaction temperature can be lowered significantly since reactants are much smaller in size and also more reactive than in bulk synthesis. Furthermore pseudomorphic stabilization can be utilized by choosing lattice-matched substrates (footnote: The meaning of “pseudomorphic” stabilization is to stabilize quasi-stable phases by clamping those phases of films on lattice-matched substrates via epitaxy). Thereby it was demonstrated that the T' phase of pure La_2CuO_4 can be stabilized by reactive coevaporation technique [14]. Fig. 11 shows an overview of the

selective stabilization of T-, T'-, and T*-phase of La_2CuO_4 in the plane of the growth temperature (T_s) versus the substrate in-plane lattice constant (a_s). The survey was performed at T_s from 425 °C to 725 °C on substrates with $a_s = 3.616\text{--}4.212$ Å. The in-plane lattice constants of T-, T'-, and T* - La_2CuO_4 are indicated by arrows in the figure: $a_0 = 3.803$ Å for T- La_2CuO_4 , 4.026 Å for T'- La_2CuO_4 , and ~ 3.94 Å for T* - La_2CuO_4 . The general trends are as follows.

- (i) Synthesis temperature: high T_s stabilizes T and low T_s stabilizes T', which is in accord with the effect of “thermal expansion mismatch”.
- (ii) Substrate a_s : substrates with $a_s \sim 3.70\text{--}3.85$ Å stabilize T, substrates with $a_s > 3.90$ Å or $a_s < 3.70$ Å stabilize T' or destabilize T, and SrTiO_3 ($a_s = 3.905$ Å) stabilizes T*.
- (iii) Substrate crystal structure: substrates with the K_2NiF_4 -type structure stabilize T.

3.3. Lattice parameters of T' cuprates – RE dependence and Ce doping dependence

T- La_2CuO_4 is located at the borderline of the T stability, and hence it distorts to the orthorhombic structure (LTO: low-temperature orthorhombic phase) at temperatures below 550 K so as to accommodate the large bond length mismatch by tilting of CuO_6 octahedra. On the other hand, T'- RE_2CuO_4 shows no distortion and keeps the original tetragonal ($I4/mmm$) structure except for T'- Gd_2CuO_4 , which is located at the borderline of the T' stability. In this section, we give an overview for the RE dependence and Ce-doping dependence of the lattice parameters obtained by X-ray diffraction. We take a look first at the RE dependence of the lattice parameters of the parent compounds, T'- RE_2CuO_4 . Since the ionic radius of RE^{3+} , $r_i^{\text{VIII}}(\text{RE}^{3+})$, changes from 1.160 Å (La) to 0.977 Å (Lu), the lattice parameters of T'- RE_2CuO_4 changes accordingly. It should be denoted that RE^{3+} is surrounded by nine O^{2-} in the T structure but by eight O^{2-} in the T' structure, therefore $r_i^{\text{VIII}}(\text{RE}^{3+})$ should be used in discussing the structure of T'. One can see a systematic

variation in both of physical and chemical properties with the lattice parameters, which is one benefit to the research of T' cuprates. Table IV summarize the *RE* dependence of the *a*-axis and *c*-axis lattice parameters (a_0 and c_0) [30, 36]. The a_0 shrinks by 4.9 % from 4.026 Å (La) to 3.830 Å (Tm) and the c_0 shrinks by 7.4 % from 12.50 Å (La) to 11.58 Å (Lu).

Next we take a look at the Ce doping dependence of the lattice constants. In general, Ce can be trivalent as well as tetravalent. The early chemical analysis (iodometry titration) by Idemoto et al. gave the Ce valence of +3.84 in T'-Nd_{1.85}Ce_{0.15}CuO₄, which is close to +4 [37]. The ionic radius of tetravalent Ce, $r_i^{\text{VIII}}(\text{Ce}^{4+})$, is 0.97 Å, which is smaller than $r_i^{\text{VIII}}(\text{RE}^{3+})$ of trivalent *RE* ions. Therefore the lattice constants of T' cuprates should decrease with the substitution of Ce for *RE*. As shown in Fig. 12, the c_0 decreases with x in accord with the above expectation whereas the a_0 increase slightly with x , which is opposite to the expectation [2, 36-48]. The increase of a_0 with Ce doping is due to the stretching of the Cu-O bond by filling electrons into the antibonding (σ^*) orbitals. In Fig. 12, both of a_0 and c_0 changes linearly with x in low Ce doping (Vegard's law), but they show no change for x above a certain value, which is the solubility limit (x_c) of Ce: $x_c \sim 0.3$ for La and $x_c \sim 0.1$ for Gd. The extrapolation of the linear part of a_0 and c_0 for each *RE* to $x = 2.0$ appears to converge roughly to one point: $a_0 = 4.0$ Å and $c_0 = 11.0$ Å, corresponding to “hypothetical” Ce₂CuO₄.

3.4. Phase stability

Copper is an element with weak chemical bonding (affinity) to oxygen. Hence copper oxides inevitably decompose at high temperature or in low oxygen partial pressure. This is an obstacle in “reduction” to remove interstitial oxygen ions at O_{ap} . Roughly speaking, the phase stability limit (= decomposition line) of all high- T_c cuprates is close to the phase stability limit of the divalent simple oxide, CuO, since Cu in high- T_c cuprates is essentially divalent. Figure 13 shows a closer comparison between the decomposition lines

of 214 and simple copper oxides (CuO and Cu_2O) [49-52]. It also includes a similar comparison for Ni and Co oxides [53]. The decomposition lines of $\text{T-La}_2\text{CuO}_4$, $\text{T'-Pr}_2\text{CuO}_4$ and $\text{T'-Nd}_2\text{CuO}_4$ are located substantially below that of CuO . One can imagine the reason as follows. The oxygen desorption from the CuO_2 layer triggering the decomposition in 214 cuprates is partially blocked by the RE_2O_3 layers sandwiching above and below. The decomposition lines of La_2NiO_4 and La_2CoO_4 are located at much lower p_{O_2} than those of 214 cuprates. They are also located slightly below the decomposition lines of the simple oxides, NiO and CoO . The large difference in the decomposition line between Ni/Co and Cu oxides reflects much stronger oxygen affinity of Ni/Co than of Cu. These observations indicate that the decomposition in 214 transition-metal (M) oxides is primarily determined by the strength of the M-O bond. The La-O or RE-O bond is much stronger than the M-O bond and is not broken in decomposition.

With regard to the phase stability of $\text{T'-RE}_2\text{CuO}_4$, there exists the following trend, “the larger RE^{3+} , the more stable” (Fig. 14(a)). This trend may be explained partly from the stronger oxygen affinity of larger RE^{3+} . The O^{2-} ion in the CuO_2 is coordinated (surrounded) by two Cu^{2+} and four RE^{3+} ions as shown in the inset of Fig. 14(b). Larger RE^{3+} takes a firmer grip on weakly bound oxygen ions in the CuO_2 layer. The doping of Ce also enhances the phase stability. The decomposition line of $\text{T'-RE}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ locates at higher temperature or equivalently to lower oxygen partial pressure than $\text{T'-RE}_2\text{CuO}_4$ as seen in Fig. 14(a) [50, 54]. The enhanced phase stability by Ce substitution can similarly be explained based on the fact that Ce is nearly tetravalent in T' cuprates and takes a firmer grip on surrounding O^{2-} ions by stronger electrostatic force than trivalent RE as shown in Fig. 14(b).

3.5. Refined crystal structure and oxygen defects in T' cuprates

Oxygen nonstoichiometry is a phenomenon prevalent in cuprates, which is due to the

weak nature of a Cu-O bond and to the multivalent character of Cu (Cu^0 , Cu^{1+} , Cu^{2+} , Cu^{3+} , *etc.*). Oxygen loss in the CuO_2 layer starts to occur in low p_{O_2} prior to phase decomposition, deteriorating superconductivity. In high p_{O_2} , excess oxygen ions occupy the interstitial site in the RE_2O_2 layer in 214 cuprates: the tetrahedral site in T (the position close to O2 in T') and the apical site (O_{ap}) in T'. It is well known that interstitial excess oxygen ions in $\text{T-La}_2\text{CuO}_4$ provide the CuO_2 layer with holes, achieving high- T_c superconductivity without Sr substitution. In contrast, interstitial oxygen ions at O_{ap} in T' cuprates are harmful to high- T_c superconductivity. Therefore the precise knowledge of the oxygen chemistry is essential to achieving the best superconductivity in T' cuprates. There are two regular and one interstitial sites in the T' structure: the O1 site in the CuO_2 layer, the O2 site in the fluorite layer, and the interstitial apical site (O_{ap}) (Fig. 15). A systematic study by neutron diffraction on the variation of the occupancies at O1, O2 and O_{ap} as a function of p_{O_2} and T are highly required. There are dozens of such investigations on T' cuprates, but the data are not converging [55-61]. The problem exists not in diffraction experiments but in sample preparation.

Table V shows one result from the powder neutron diffraction experiments by Petrov et al. [62], which, we believe, are the most reliable. It includes the data for both of oxygenated and reduced $\text{Nd}_{1.9}\text{Ce}_{0.1}\text{CuO}_4$ samples. As seen from Table V, in the oxygenated sample (annealed in air at 950°C , and then quenched to room temperature), a significant amount of oxygen (~ 0.08 ions/formula unit) is present at O_{ap} . On the other hand, in the reduced sample (annealed in $p_{\text{O}_2} = 4.57 \times 10^{-2}$ atm at 1200°C , and then quenched to room temperature), the occupancy of O_{ap} is reduced to ~ 0.04 ions/formula unit. With regard to the regular oxygen sites, the occupancy of O2 is essentially full (2.00) and unchanged by reduction whereas the occupancy of O1 is slightly less than 2.00 even in the oxygenated sample. The experimental results by Petrov et al. in Table V appear to show no substantial change in the O1 occupancy by reduction, but many other results indicate that oxygen

vacancies at O1 increases by reduction, especially in samples with no or low Ce doping [55].

The results can be summarized as follows: oxygen vacancies at O1 and interstitial oxygen ions at O_{ap} coexist with their occupancies in thermal equilibrium. This makes quite complex the oxygen chemistry of T' cuprates, resulting in the defect structure dependent on the temperature, oxygen partial pressure, cerium content, and even *RE*. Interstitial oxygen ions at O_{ap} are very harmful to superconductivity and that “reduction” to remove oxygen ions at O_{ap} is a key step for achieving superconductivity in T' cuprates. But excessive reduction generates oxygen vacancies at O1, which deteriorates and eventually kills high- T_c superconductivity. Therefore it is essential toward the best superconductivity in T' cuprates to minimize the disorder in the oxygen sublattice, which should be carried out based on the precise knowledge of the oxygen chemistry in T' cuprates.

There are also the complementary experimental data by means of chemical analysis such as iodometry titration, thermogravimetry, *etc.*, but the results are again not converging [37, 43, 54, 62-75]. Even the presence of excess oxygen ions is not supported by some articles. Early iodometry titration experiments, which is employed for evaluation of the absolute value (y) of oxygen in T'-(*RE*,Ce) $_2$ CuO $_y$, often concluded $y < 4.0$. The behavior of conductivity of T' cuprates, increasing monotonically with lowering p_{O_2} , was also erroneously interpreted on early days as a typical behavior of *n*-type oxides with oxygen deficiencies. However, the presence of excess oxygen ions at the apical site (O_{ap}) is in no doubt from our systematic photoemission spectroscopy [6].

Here, selecting several careful studies, we give our understanding for the oxygen nonstoichiometry in T' cuprates, specifically best studied T'-Nd $_{2-x}$ Ce $_x$ CuO $_y$, as follows.

- Oxygen loss and excess oxygen coexist in T' cuprates. Even with $y = 4.00$, the oxygen sublattice is not perfect. It is very difficult (almost impossible) to remove O_{ap} impurities without introducing oxygen deficiencies in the CuO $_2$ layer.
- The maximum occupancy at O_{ap} is ~ 0.10 at $x = 0.00$ and decreases to ~ 0.05 at $x = 0.15$.

Interstitial oxygen ions of 0.02-0.04 remain at O_{ap} even after reduction.

- The maximum amount of oxygen deficiencies in the CuO_2 layer is ~ 0.05 at $x = 0.00$ and is reduced to $\sim 0.02-0.03$ at $x = 0.15$. Oxygen deficiencies may not be filled up completely even after annealing in 1 atm of oxygen.

Finally we point out two empirical trends about the RE dependence of the oxygen chemistry in T' cuprates:

- The binding energy of O1 in the CuO_2 layer is larger for larger RE^{3+} , which was explained in §3.4.
- The binding energy of O_{ap} in the RE_2O_2 layer is smaller for larger RE^{3+} , which is not easily explained, so should be regarded as an empirical law [71, 72].

Both of the trends suggest that more perfect oxygen sublattice can be realized with larger RE^{3+} such as Pr^{3+} , Nd^{3+} , which agrees with the empirical trend to have better superconductivity in T' cuprates. The substitution of Ce also influences the oxygen chemistry. As was explained in §3.5, Ce substitution increases the binding energy of O1, thereby allows stronger reduction than for Ce-free compounds. Oxygen diffusion is also an important factor in low-temperature reduction. The reduction time required for homogeneous oxygen is a function of the sample size/thickness, grain size, *etc.* Thin films with small grain size may be the best to achieve homogeneous oxygen distribution in short time.

3.6. “Real” T' cuprates with O_{ap} ions remaining (1) – resistivity upturn

So far we have described how to approach ideal T' cuprates with perfect oxygen sublattice, but it is almost impossible to synthesize ideal T' cuprates in practice. Real

specimens, which we can synthesize, contain more or less excess oxygen ions at O_{ap} . The presence of excess oxygen O_{ap} ions is manifested by a slight elongation of the c -axis lattice constant (up to ~ 0.05 Å). Although the structural change is not drastic, surprisingly a minute amount ($\delta \sim 0.02$) of excess O_{ap} ions causes serious influences on the physical properties, which we describe in the following two sections. We start by the resistivity upturn at low temperatures.

Figure 16 shows the resistivity-vs-temperature (ρ - T) curves of two T' - $La_{1.9}Ce_{0.1}CuO_4$ films grown by MBE with identical growth parameters but reduced differently. One film was reduced in vacuum for 10 min at $T_r = 580^\circ\text{C}$ whereas the other film at $T_r = 500^\circ\text{C}$. The former film is superconducting with $T_c = 30$ K, but the latter is not superconducting and also has extra scattering. The extra scattering is almost constant (~ 300 $\mu\Omega\text{cm}$) down to 100 K, but it grows up below 100 K, resulting in a resistivity upturn with the resistivity minimum at ~ 65 K. Such a resistivity upturn is often observed in T' cuprates, especially with low Ce doping. This upturn strongly correlates with the suppression of T_c . This correlation was first pointed out by Brinkmann et al. in the form “the larger residual ρ_R , the lower T_c ” [23]. Empirically, specimens containing a larger amount of residual O_{ap} impurities show a more prominent upturn in low-temperature resistivity. Hence the above correlation expresses that O_{ap} impurities are a strong scatterer to increase ρ_R as well as a strong pair-breaker to lower T_c . It appears that O_{ap} impurities in T' cuprates behave like magnetic impurities in conventional superconductors.

It is important to elucidate the origin of a resistivity upturn. For this purpose, Sekitani et al. performed transport measurements in high magnetic fields up to 40 T [76, 77]. Figure 17 shows the data for two films: nonsuperconducting $Pr_{2-x}Ce_xCuO_4$ film with $x \sim 0.10$ and superconducting $Nd_{2-x}Ce_xCuO_4$ with $x \sim 0.13$, both grown by MBE. In the latter film, the normal-state behavior is revealed by suppressing superconductivity by magnetic fields. In both of the films, the upturn has a $\log$ - T dependence below the resistivity minimum

temperature but saturates to a finite value toward lowest temperatures. In addition, the upturn is suppressed in magnetic fields (negative magnetoresistance) with a $\log-B$ dependence. The two main features, the $\log-T$ -dependent upturn and the $\log-B$ -dependent negative magnetoresistance, can be explained either by two-dimensional (2D) weak localization or by Kondo scattering, which caused some controversy. The former possibility has been pointed out by several authors [78-81]. The 2D weak localization predicts, for simplest cases, a $\log-T$ -dependent divergence (with no saturation) of resistivity toward $T = 0$ K with the universal (= material independent) coefficient ($\sigma_{2D} = \alpha \times e^2/\pi h \times \ln T$, α is a constant of order unity). But the observed upturn does not diverge and the coefficient is strongly material-dependent ($\alpha = 0.9 \sim 15$), indicating that this possibility may be ruled out. Then we need to resort to the other possibility, i.e. the Kondo effect. The coefficient of the $\log-T$ -dependent upturn strongly depends on the reduction, namely on the amount of excess O_{ap} ions, which gives a hint on the origin of the Kondo impurities. One can speculate the following scenario. Regardless of the Ce doping level, Cu^{2+} is nonmagnetic in the “ideal” T’ cuprates with no excess O_{ap} ion left (although such samples have not yet been synthesized). But the presence of an interstitial O_{ap} ion drives Cu^{2+} just beneath to be magnetic (see the inset of Fig. 16). Hence the Kondo impurity is identified as magnetic Cu^{2+} induced by an interstitial O_{ap} ion. The Kondo effect causes strong carrier scattering as well as pair breaking as in the case of magnetic impurities in conventional superconductors.

3.7. “Real” T’ cuprates with O_{ap} ions remaining (2) - magnetism

Next we discuss the magnetism. In the previous section, we speculated that regular Cu^{2+} is nonmagnetic and only irregular Cu^{2+} beneath an interstitial O_{ap} ion is magnetic. The amount (δ) of interstitial O_{ap} ions is estimated to be 0.02-0.10, depending on the reduction, which appears to indicate that there are not many magnetic Cu^{2+} ions. But, in reality, AF order, either static long-range or dynamic short-range, is often observed in T’ cuprates. In

this section, we first summarize the magnetism observed for “real” T’ cuprates with O_{ap} ions remaining and next discuss the origin of AF order from our point of view.

As mentioned in §2.1, the first magnetic measurement on T’-RE_{2-x}Ce_xCuO₄ was μ SR by Luke et al. performed just after the discovery of “electron-doped” superconductors [19]. The experiments by Luke et al. were performed on Nd_{2-x}Ce_xCuO₄ samples that were not well-characterized, especially in oxygen homogeneity, but the results were basically supported by later μ SR experiments [82, 83] and also by neutron diffraction. The early neutron diffraction experiments by Matsuda et al. on single crystals of Nd_{2-x}Ce_xCuO₄ and Pr₂CuO₄ are one of the most extensive works on the magnetism of T’ cuprates [20, 21]. In the parent compounds, Nd₂CuO₄ and Pr₂CuO₄, the Cu²⁺ spin has a magnetic moment of $\sim 0.4\mu_B$, and the AF order develops below $T_N = 255$ K. In the parent compounds, no significant change was observed in the magnetic behavior by heat treatment in Ar or in O₂. On the other hand, a large change was observed by heat treatment in Ce-doped compounds. In as-grown samples with Ce doping of $x = 0.15$, the AF order remains with T_N varying from 125 K to 160 K (T_N of as-grown samples is indicated by the broken line in Fig. 1). After reduction (950°C/20 hr in Ar followed by 500°C/20 hr in O₂), the superconducting phase was predominant but with the AF phase remaining in 10% or more volume of a specimen. The essence of these early results can be summarized as follows.

- (i) The parent compounds show static AF order. The Neel temperature (T_N) for 3D long-range order is about 250 K, which is comparable to $T_N = 250$ -300 K in T-La₂CuO₄.
- (ii) The initial decrease of T_N with x is more gradual than in T-LSCO. There is an abrupt drop of T_N from ~ 80 K at $x = 0.14$ to < 5 K at $x = 0.15$. Superconductivity appears after long-range AF order disappears.
- (iii) In specimens not reduced, the AF order remains and no superconductivity appears even at $x = 0.15$.

One might imagine that the Neel temperature (T_N) of the AF order in the

$T'-(RE,Ce)_2CuO_{4+\delta}$ *would* depend primarily on the Ce concentration. But it has to be emphasized from the above observation by Matsuda et al. that the T_N depends more strongly on the amount of residual O_{ap} ions [21] and varies from 0 K in well-reduced $Nd_{1.85}Ce_{0.15}CuO_4$ to 125-160 K in as-grown ones. The presence of O_{ap} ions causes a significant effect not only on the superconductivity (T_c -vs- x) but also the magnetism (T_N -vs- x) in the CuO_2 layer [84]. Phenomenologically, it appears that the tiny amount of impurity apical oxygen in the T' cuprates plays a role as a switch that turns the magnetic order on or off. Since the first μ SR measurements on $T'-RE_{2-x}Ce_xCuO_4$ [19], magnetic studies on T' cuprates have been continuing for more than 20 years, but experimental results are sometimes contradictory and none of them are definitive, which is somewhat similar to the situation for oxygen nonstoichiometry. The reason for this controversy is, at least in part, again inhomogeneity of oxygen distribution in specimens. Especially neutron diffraction experiments require large single crystals, in which homogeneous oxygen distribution is hard to achieve. One has to pay attention to how carefully O_{ap} impurities are removed in each article.

Finally we present our view on the magnetism in T' cuprates. If one assumes that the superconductivity is an intrinsic phenomenon of oxygen-stoichiometric $Nd_{1.85}Ce_{0.15}CuO_4$, the AF correlation that kills superconductivity in oxygen-nonstoichiometric $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ has to be regarded as an extrinsic phenomenon induced by impurity O_{ap} ions. We believe that this statement holds not only for $x \sim 0.15$ but also over the whole range of x , including $x = 0.00$. According to the experiments by Matsuda et al., the Neel temperature (255 K) of the parent compounds, Nd_2CuO_4 and Pr_2CuO_4 , did not change by post-synthesis heat treatment. As mentioned in §3.5, however, the Ce-free parent compounds are easier to decompose than Ce-containing compounds, therefore the reduction to remove excess O_{ap} ions is more delicate. The early experiments by μ SR and neutron diffraction concluded without much care of impurity O_{ap} ions that the magnetism in $T'-RE_{2-x}Ce_xCuO_{4+\delta}$ *were* similar to that in $T-La_{2-x}Sr_xCuO_4$. But the magnetism in

$T'-RE_{2-x}Ce_xCuO_{4+\delta}$ should be distinguished from that in $T-La_{2-x}Sr_xCuO_4$ that shows an intrinsic AF order.

4. Synthesis of undoped T' superconductors

In this section, we introduce the synthesis of undoped T' superconductors by various methods. So far superconducting films of $T'-RE_2CuO_4$ have been synthesized by MOD and MBE with subsequent post annealing or *in-situ* by MBE with no post annealing. Bulk samples of $T'-RE_2CuO_4$ are yet to be superconducting. But bulk samples of superconducting $T'-(La,RE)_2CuO_4$ can be synthesized either by low-temperature liquid-phase reaction using molten alkaline hydroxides or topotactic reduction using CaH_2 with subsequent reoxidation. Each synthesis is briefly described.

4.1. MOD synthesis of $T'-RE_2CuO_4$ thin films

Our synthesis of superconducting $T'-RE_2CuO_4$ films by MOD was carried out in a standard procedure except that films are fired in low p_{O_2} , and the synthetic conditions are summarized in Table VI. Briefly, stoichiometric amounts of RE - and Cu-naphthenate solutions were spin-coated on substrates, either (001)SrTiO₃ or (110)DyScO₃. As RE , Pr~Tb were employed. The films were calcined at 400°C in air to obtain precursors and then fired at 850-900°C in a tubular furnace under a mixture of O₂ and N₂ ($p_{O_2} = 2 \times 10^{-4} - 2 \times 10^{-3}$ atm). Finally the films were reduced in vacuum ($p_{O_2} < 10^{-6}$ Torr) at 420-460°C for 10 min.

The low p_{O_2} firing is a key step for achieving superconductivity [8]. Figure 18 shows the effect of p_{O_2} during firing, which compares the resistivity of two Sm₂CuO₄ films (A and B) on (001) SrTiO₃ substrates: film A fired at 900°C for 1 hour in $p_{O_2} = 1$ atm, followed by reduction at 750°C in 10 min, and film B fired at 850°C for 1 hour in $p_{O_2} = 2.8 \times 10^{-3}$ atm, followed by reduction at 440°C in 10 min. The resistivity of Film A is ~ 100 mΩcm at 300 K and metallic down to 180 K with, but shows an upturn at lower temperatures. By contrast,

the resistivity of film B is $900 \mu\Omega\text{cm}$ at 300 K, metallic all the way, and shows superconductivity at $T_c^{\text{onset}} = 28 \text{ K}$ ($T_c^{\text{end}} = 25\text{K}$). In both the films, the reduction recipe was optimized. Films fired in low- p_{O_2} do not stand against reduction at temperatures higher than 500°C whereas films fired in $p_{\text{O}_2} = 1 \text{ atm}$ do against reduction temperatures as high as 750°C . The dramatic effect of low- p_{O_2} synthesis is actually corroborated from the structural aspect. The c_0 value of film A ($11.97 \text{ \AA}$) is in good agreement with the c -axis length of bulk samples ($11.972 \text{ \AA}$) [41], whereas the c_0 of film B is substantially shorter ($11.94 \text{ \AA}$). A c -axis length shorter than the bulk values as well as enhanced conductivity in film B indicates that the amount of residual O_{ap} ions present may be small.

Next we demonstrate the results of a systematic study of the reduction dependence on the ρ - T , T_c , and c_0 of the films [85]. The reduction condition can be varied by either the temperature ($T_{\text{red}} = 230\sim 600^\circ\text{C}$) or by the duration ($t_{\text{red}} = 5\sim 60 \text{ min}$). Figure 19 shows one example, i.e., the c_0 value of $\text{T}'\text{-Sm}_2\text{CuO}_4$ films as a function of T_{red} in (a) and the ρ - T curves for different T_{red} in (b). All the films were fired in a low- p_{O_2} atmosphere ($p_{\text{O}_2} = 2.8 \times 10^{-3} \text{ atm}$), and then reduced in vacuum at different T_{red} for 10 min. The c_0 value monotonically decreases with increasing T_{red} , indicating that the evacuation of impurity O_{ap} ions proceeds. The resistivity value of the as-grown film is in the range of Ωcm and shows semiconducting behavior. After vacuum reduction, the resistivity value drops in the range of $\text{m}\Omega\text{cm}$. The film reduced at $T_{\text{red}} = 420^\circ\text{C}$ is metallic with a broad superconducting transition but the resistivity upturn observed at low temperatures is indicative that a small amount of O_{ap} ions are left (§3.6). The films reduced at $440\text{-}460^\circ\text{C}$ show superconductivity with no resistivity upturn. Upon further increase of T_{red} , superconducting properties deteriorate and no superconductivity is observed for $T_{\text{red}} = 520^\circ\text{C}$. Our present reduction is not a thermal equilibrium process. We speculate that the binding energies of impurity O_{ap} and regular O1 ions are comparable in magnitude in $\text{T}'\text{-Sm}_2\text{CuO}_4$, but the loss of O1 ions is a kinetically slower process than the removal of O_{ap} ions. At high T_{red} , loss of regular O1 ions is

predominant, therefore degrades superconductivity. The synthesis in a low- p_{O_2} and subsequent reduction at low temperatures allows us to evacuate most of impurity O_{ap} sites while preserving regular O1 sites occupied.

It may be valuable to overview the correlation between the superconductivity and the oxygen nonstoichiometry in $T'-RE_2CuO_4$. Although a quantitative evaluation of the amount of residual O_{ap} ions is difficult in thin films, the above result in Fig. 19(a) suggests that the c_0 value is a good measure for it. Fig. 20 is a summary of our comprehensive investigation. We plotted the $\rho(300\text{ K})$ and T_c as a function of c_0 for all RE_2CuO_4 ($RE = \text{Pr, Nd, Sm, Eu, Gd, and Tb}$) films, which we synthesized [85]. On decreasing c_0 from the as-grown value, the $\rho(300\text{ K})$ decreases and superconductivity appears. A further reduction in c_0 degrades superconductivity. Zero-resistivity is observed in the samples with the c_0 values in the shaded ranges. This range becomes narrower from $RE = \text{Pr and Nd}$ to Gd . For each RE_2CuO_4 , there is an optimal c_0 value, at which the highest T_c is achieved. Figure 21 shows the transport properties of the RE_2CuO_4 films, for which the synthesis and reduction conditions are optimized [85]. The resistivity value increases monotonically in descending order of the ionic radius of RE^{3+} from Pr to Tb . RE_2CuO_4 with $RE = \text{Pr, Nd, and Sm}$ show a residual resistivity ratio (RRR) larger than 10 whereas Eu_2CuO_4 films show a RRR of 3 as well as broader superconducting transition. Gd_2CuO_4 films are metallic down to 30 K but a resistivity upturn is observed below 30 K. Tb_2CuO_4 films show a resistivity upturn at 50 K and no superconducting transition. The induction of superconductivity into $T'-RE_2CuO_4$ strongly depends on the RE^{3+} ionic size. This trend may be explained by RE -dependent oxygen chemistry in T' cuprates. For smaller RE^{3+} , the thermodynamic boundary condition becomes tighter. In Gd_2CuO_4 and Tb_2CuO_4 , the binding energy of impurity O_{ap} atoms might be larger than that of regular O1 atoms.

The structural characterizations for superconducting Nd_2CuO_4 films prepared by MOD were carried out using the X-ray diffraction and AFM [18]. The XRD results indicate

that Nd_2CuO_4 films prepared by MOD are *c*-axis oriented and in-plane aligned, namely single-crystalline and shows a high degree of structural perfection, which is achieved via solid-state epitaxy. The AFM pictures confirm that the morphology of the film consists of 3D grains and the grain size appears to be as small as or less than 1000 Å. This grain size is smaller than that reported for MBE-grown films (2000-3000 Å). The small grain size facilitates to evacuate impurity O_{ap} ions.

4.2. MBE (1) 2-step annealing process

The synthesis of superconducting RE_2CuO_4 films by MOD was reproduced soon after by MBE [86, 87]. In 1990's, as mentioned in §.1, superconducting RE_2CuO_4 had never been obtained by MBE with our standard growth and reduction conditions. Now, however, it is demonstrated that MBE is capable to synthesize superconducting thin films of RE_2CuO_4 in two different ways. The first method is similar to the MOD synthesis and employs two-step annealing whereas the second method is direct growth without post annealing. We describe the first method in this subsection and the second method in the next subsection.

The two-step annealing method has so far been applied to MBE-grown films of Pr_2CuO_4 , Nd_2CuO_4 , and Sm_2CuO_4 . The difference between the standard and two-step annealing processes is illustrated in Fig. 22(a). Our standard reduction process is to anneal films *in-situ* at 550-650°C for 10 min in vacuum immediately after growth. The two-step process is to anneal films *ex-situ* in a quartz tube furnace equipped with a turbo molecular pump and high precision p_{O_2} control system. The two-step annealing process consists of the first high-temperature annealing (750–850°C and $p_{\text{O}_2} \sim 8 \times 10^{-2}$ Torr) and subsequent low-temperature annealing (450–700°C) in vacuum. The details of the process in the case for Nd_2CuO_4 are shown in Fig. 22(b). We have often grown initial thin films of RE_2CuO_4 intentionally at temperatures lower than optimal to reduce crystallite dimensions, which are advantageous for a homogeneous annealing experience.

It is intriguing to understand the microscopic processes involved at each step in the two-step annealing process. In order to reveal the oxygen diffusion processes involved at each step, we incrementally determined electronic conduction as well as crystallographic dimensions before and after each annealing step. The results are visualized in Fig. 23. The as-grown crystal contains more than the stoichiometric amount of oxygen, which are randomly distributed at apical sites (Fig. 23(a)). After the first annealing step, the films are less conductive than the as-grown films (Fig. 23(c)). As the X-ray diffraction pattern did not vary, neither by intensity nor by peak positions (Fig. 23(f)), we concluded that the reduced conductivity is a consequence of the creation of O1 vacancies. After the second annealing step, the c -axis length as well as the electronic conduction vary significantly (Fig. 23(d)(g)). The reduction in the c -axis length can be as large as 0.06 Å and the low-temperature conductivity rises by at least 5 orders of magnitude. We conclude the following scenario. In the second annealing step, oxygen vacancies at O1 created during the first annealing step are being occupied by apical oxygen ions. Hence, the second annealing step might be considered as a repairing procedure to defects brought by the first annealing step.

4.3. MBE (2) direct growth

As discussed in §4.2, large efforts need to be taken in order to bring as-grown, off-stoichiometric $\text{Pr}_2\text{CuO}_{4+\delta}$ close to stoichiometry, i.e. $\delta \approx 0.00$. Annealing is a diffusion process that requires detailed knowledge of the spatial dimensions of the crystallites and of the oxygen diffusion parameters in order to meet the boundary conditions, i.e., evacuation of apical sites while preserving the CuO_2 plane's integrity. Moreover, such *ex-situ* annealing procedures are incompatible with certain measurement techniques, e.g., angle-resolved photoemission spectroscopy, due to their sensitivity to surface conditions. Therefore one would actually strive to synthesize superconducting $\text{Pr}_2\text{CuO}_{4+\delta}$ *in-situ* without further actions.

Toward this direction, we carefully analyzed the thermodynamic stability conditions

of T' - Pr_2CuO_4 so as to minimize the amount of O_{ap} impurities taken during growth [88]. Typically, Pr_2CuO_4 thin films are grown at 650–750°C and 5×10^{-6} Torr of ozone gas ($\text{O}_2 + \text{O}_3$, ~10% O_3 concentration). This synthesis phase field is located well above the phase stability limit and hence results in the intake of a fair amount of O_{ap} impurities. Bringing the synthesis conditions closer to those for the thermodynamic stability of Pr_2CuO_4 may reduce the intake to a significantly lesser amount. To synthesize Pr_2CuO_4 in the phase field closer to the thermodynamic stability, namely at a higher growth temperature and/or in a reduced flow of ozone gas, we utilized pseudomorphic stabilization due to epitaxy.

Figure 24(a) shows the plots of temperatures at which Pr_2CuO_4 thin films were grown on various substrates. The partial pressure of ozone gas during synthesis was kept constant at 5×10^{-8} Torr. In general, lattice mismatch $\beta = (a_s - a_0)/a_s$, where a_s and a_0 are the in-plane lattice constants of the substrate and thin film, respectively, is crucial for pseudomorphic stabilization. Thin films grow coherently on substrate materials with an in-plane lattice constant close ($|\beta| < 10^{-2}$) to the bulk value of Pr_2CuO_4 ($a_0 \approx 3.9588 \text{ \AA}$). For cuprate superconductors, coherent growth was demonstrated earlier for the synthesis of $\text{T}(\text{La}, \text{Sr})_2\text{CuO}_4$ films on LaSrAlO_4 , infinite-layer $(\text{Sr}, \text{La})\text{CuO}_2$ on DyScO_3 , and infinite-layer CaCuO_2 on NdGaO_3 . As clearly seen in Fig. 24(a), good lattice matching between Pr_2CuO_4 and GdScO_3 results in enhanced thermodynamic stability of the T' phase. Substrate temperatures as high as 850°C and ozone flow rates as low as 0.1 sccm are not detrimental to the phase formation on (110) GdScO_3 substrates. However, such synthesis conditions are unsuitable for other substrate materials, e.g., SrTiO_3 , and Pr_2CuO_4 does not form on them. Figure 24(b) is a plot of the resistivity of as-grown Pr_2CuO_4 as a function of temperature. The resistivity values at 300 and 30K are 640 and $105 \mu\Omega \cdot \text{cm}$, respectively, resulting in a RRR ($= \rho(300\text{K})/\rho(30\text{K})$) of 6.1. The superconducting transition monotonously shifts in magnetic fields from 26.0 K at 0 T to 12.2 K at 3.5 T (inset of Fig. 24(b)).

The next example for pseudomorphic stabilization is La_2CuO_4 . As mentioned in

§3.2, we demonstrated in 2002 that both of the T and T' phase of La_2CuO_4 can be stabilized in MBE growth [14]. T'- La_2CuO_4 grown at that time was metallic but not superconducting. But the same strategy employed in Pr_2CuO_4 , namely bringing the synthesis conditions closer to the thermodynamic stability, enabled us to synthesize superconducting films of T'- La_2CuO_4 . The growth of superconducting T'- La_2CuO_4 films employed PrScO_3 ($a_s = 4.022 \text{ \AA}$) substrates. Furthermore single-phase T*- La_2CuO_4 was also stabilized on lattice matched DyScO_3 ($a_s = 3.944 \text{ \AA}$). The growth of T- La_2CuO_4 employed well-known LaSrAlO_4 ($a_s = 3.755 \text{ \AA}$). These combinations realize coherent growth. Figure 25 compares the electrical resistivity of three different La_2CuO_4 with octahedrally (T-phase), pyramidally (T*-phase), and square-planar (T'-phase) coordinated Cu^{2+} [15]. While T- and T*- La_2CuO_4 have an insulating ground state, T'- La_2CuO_4 is a metal with a superconducting ground state. Three “isomers” of La_2CuO_4 have different ground states. This observation provides a good example demonstrating an intimate relation between the electronic conduction and the oxygen coordination.

4.4. Low-temperature bulk synthesis via a molten-alkaline hydroxide route

In the previous three subsections, the synthesis of thin films of undoped T' superconductors were described. Now we move to the synthesis of bulk powders of these compounds. Bulk samples have a disadvantage against thin films in removing excess O_{ap} ions, but bulk samples with a full superconducting volume fraction are required in some experiments such as neutron diffraction to determine the site-specific occupancies at the oxygen sites. Until now, superconducting T'- RE_2CuO_4 bulk samples have not yet been synthesized. Here we describe the synthesis of superconducting T'- $\text{La}_{2-x}\text{Sm}_x\text{CuO}_4$ powder samples via a molten alkaline hydroxide route [89-91]. So far the superconductivity is observed in the samples with $x = 0.05$ to 1.0 and the superconducting volume fraction is nearly 100% at $x = 0.3$ – 0.7 .

Low-temperature synthesis is required to obtain single-phase T' - $\text{La}_{2-x}\text{Sm}_x\text{CuO}_4$. We attempted to prepare T' - $\text{La}_{2-x}\text{Sm}_x\text{CuO}_4$ with $x = 0.7$ by conventional solid-state reaction at rather low temperatures (800°C), and the resultant samples are a two-phase mixture of T' and T , indicating that the La-rich region of T' - $\text{La}_{2-x}\text{Sm}_x\text{CuO}_4$ is difficult to access in this method. Therefore it is necessary to employ synthetic techniques by soft-chemistry relying on chemical energy instead of thermal energy. One such technique is a molten alkaline hydroxide route. This method enables the synthesis of cuprate powder samples at temperatures as low as $300\text{--}400^\circ\text{C}$ [92-96].

The synthesis of polycrystalline samples of $\text{La}_{2-x}\text{Sm}_x\text{CuO}_4$ is described in Ref. [89, 90]. Here we repeat only the essence. In the synthesis of samples with $x = 0.6\text{--}2.0$, all the starting powders (CsOH , Cu_2O , La_2O_3 , and Sm_2O_3) were placed in a 25 ml Ag crucible and heated at $420\text{--}480^\circ\text{C}$ for 48–72 h in flowing N_2 gas. The synthesis for $x = 0.0\text{--}0.5$ is slightly different. First the starting powders of Cu_2O and CsOH alone without La_2O_3 and Sm_2O_3 were placed in a 25 ml Ag crucible and melted at 400°C for several hours in flowing N_2 gas. Subsequently powders of La_2O_3 and Sm_2O_3 were added quickly into the melt of CsOH and Cu_2O , and the crucible was held at 400°C for another 48–72 h in flowing N_2 gas. This procedure is necessary to obtain single phase T' - $\text{La}_{2-x}\text{Sm}_x\text{CuO}_4$ with $x = 0.0\text{--}0.5$ since Cs contamination takes place at reaction temperatures below 400°C , which results in the formation of the T phase of $(\text{La,Cs})_2\text{CuO}_4$. The purpose of adding La_2O_3 and Sm_2O_3 powders later is to prevent them from reacting with CsOH below 400°C . The synthesis in flowing pure O_2 instead of pure N_2 tends to yield T -phase contamination. In order to improve the superconducting volume fraction of samples, however, synthesis in air appears to provide better results.

After the reaction, the melt was decanted and the product was quenched to ambient temperatures. A black polycrystalline powder was isolated by dissolving the flux in water. Reduction for removal of excess O_{ap} ions was performed in vacuum of $p < 10^{-4}$ Torr at

600–750°C for 48–96 h. The synthesis and reduction conditions for each x are summarized in Table VII. The reduction temperature (T_{red}) is slightly below the decomposition temperature for each x . The decomposition of samples can be noticed by Cu metal deposited on a quartz tube of a reduction furnace (not the same as the synthesis furnace). The T_{red} increases almost monotonically with x .

The XRD patterns confirmed that the powder samples of $\text{La}_{2-x}\text{Sm}_x\text{CuO}_4$ are nearly single-phase T' with no inclusion of the T phase. $\text{La}(\text{OH})_3$ and Ag were sometimes detected as impurity phases. $\text{La}(\text{OH})_3$ is unreacted reactant dissolved in the flux, and Ag is due to flakes from an Ag crucible, which often precipitated during prolonged heating time. Since Ag and $\text{La}(\text{OH})_3$ are nonmagnetic, they do not affect magnetization measurements. Both of the lattice parameters (a_0 and c_0) decrease almost linearly in the whole range of x from 0.0 to 2.0 (Vegard's law), indicating that T'- La_2CuO_4 and T'- Sm_2CuO_4 form a continuous series of solid solution in the entire range of x . The reduction decreases the c_0 noticeably (by 0.01–0.06 Å) and increases the a_0 slightly (0.005 Å at most). In thin films of superconducting T'-(La,RE) $_2\text{CuO}_4$ and T'- RE_2CuO_4 , the a_0 does not change by reduction [16]. We have not yet understood the reason for the different behavior in a_0 between thin films and bulk powders.

Figure 26 shows the zero-field-cooled (ZFC) magnetization curves of reduced $\text{La}_{2-x}\text{Sm}_x\text{CuO}_4$ samples with various x . In this figure, $\chi = -1$ represents full shielding. We observed a diamagnetic signal for $x = 0.05$ –1.0. The diamagnetic signal is substantial (≥ 20 –30%) for $x = 0.2$ –0.9. The signal is the largest for $x = 0.7$ whereas the T_c is higher for $x = 0.2$ –0.4. Figure 27 shows the superconducting T_c and volume fraction at 5 K of the samples as a function of x . The T_c is ~ 25 K for $x = 0.05$ and gradually decreases with x , which is in good agreement with the value and also the x dependence observed in thin films of T'-(La,Sm) $_2\text{CuO}_4$ [7]. The superconducting volume fraction is 2–3% for $x = 0.05$, but it increases rapidly as x increases and becomes nearly or more than 100% at $x = 0.3$ –0.7 except

for $x = 0.5$, where the synthesis was not optimized. The result clearly indicates that $\text{La}_{2-x}\text{Sm}_x\text{CuO}_4$ with $x = 0.3\text{--}0.7$ is a bulk superconductor. Reduction for 48 h and 96 h showed no significance difference in the superconducting volume fraction. In general, 48 h reduction is sufficient and 96 h reduction is sometimes excessive as seen at $x = 0.4$.

Another synthetic technique to prepare bulk samples of $\text{T}'\text{-La}_2\text{CuO}_4$ or $\text{T}'\text{-(La,RE)}_2\text{CuO}_4$ is to transform T-phase materials into the T' phase via a two-step topotactic reaction using CaH_2 [36, 97]. For example, $\text{T-La}_2\text{CuO}_4$ is at first reduced by CaH_2 at 200°C to $\text{La}_2\text{CuO}_{3.5}$, which can be subsequently reoxidized to $\text{T}'\text{-La}_2\text{CuO}_4$ at 300°C in air. This technique was first proposed by Chou et al. in 1990 [36]. At that time, $\text{La}_2\text{CuO}_{3.5}$ was supposed to adopt the Sr_2CuO_3 type "S-phase" structure, which has been taken for granted for almost 20 years. Recently, however, it has been demonstrated that $\text{La}_2\text{CuO}_{3.5}$ constitutes an oxygen deficient T' -framework, with copper in 4-fold planar and 2-fold linear dumbbell coordination [98]. Employing this technique, Takamatsu et al. successfully synthesized bulk powder samples of superconducting $\text{T}'\text{-La}_{1.8}\text{Eu}_{0.2}\text{CuO}_4$ with $T_c \sim 20$ K [99]. Furthermore they attempted Sr doping (hole doping) into $\text{T}'\text{-La}_{1.8}\text{Eu}_{0.2}\text{CuO}_4$ and claimed that Sr was successfully doped [100]. If it is true, this is the first demonstration of hole doping into T' cuprates. However, the T_c was reduced to ~ 13 K against expectation.

5. Implication of undoped superconductors

5.1. Electronic structure of T' vs T (1): Ionic model

$\text{T}'\text{-La}_2\text{CuO}_4$ is a superconductor whereas $\text{T-La}_2\text{CuO}_4$ is an insulator. The compounds of the same chemical formula but with different oxygen coordinations (square-planar versus octahedral) have distinct ground states. This fact is at odds with the past conjecture that Cu^{2+} oxides *would* universally have an insulating ground state. However, it can be explained rather naturally from a simple electrostatic consideration (ionic model), which we introduce in this subsection.

The ionic model is grounded on the fact that T-La₂CuO₄ with odd-number electrons is not a metal but an insulator. The electronic configuration in (La³⁺)₂Cu²⁺(O²⁻)₄ is basically Cu3d⁹ since La³⁺ and O²⁻ have a closed shell. The band theory predicts T-La₂CuO₄ to be a metal, but T-La₂CuO₄ is in fact an insulator. The contradiction can be eliminated if the *d* orbitals of Cu²⁺ in La₂CuO₄ are localized as in an isolated Cu²⁺ ion. In this case, electron transfer to the neighboring *d* orbitals requires Coulomb energy, leading to the insulating conduction (see Fig. 28). The same scenario may apply to T'-La₂CuO₄, but T'-La₂CuO₄ is metallic (superconducting). What is the difference between T-La₂CuO₄, and T'-La₂CuO₄? In order to answer this question, a schematic view for the electronic state of oxides developed by Zaanen-Sawatzky-Allen (ZSA) is helpful [101].

Before going into the ZSA scheme, we evaluate the electron transfer energy in the simplest case for an isolated ion [102]. Based on Fig. 28, the Coulomb energy for transition-metal ions (M^{v+}) to transfer an electron to the neighboring site can be approximated by the energy difference between the ionization potential I_{v+1} of M^{v+} and the electron affinity $A (=I_v)$ of M^{v+} in the following equation,

$$U_0' = I_{v+1}(M) - I_v(M) - \frac{e^2}{d_{M-M}}. \quad (2)$$

The last term e^2/d_{M-M} is the attraction energy between the excited electron and hole left behind (excitonic effect). For Cu²⁺, U_0' is ~12.8 eV, assuming $d_{M-M} = 3.80 \text{ \AA}$. In solids, however, this bare U_0' in an isolated Cu ion is substantially reduced by the effect of the overlap between ions (covalency/hybridization, screening, electronic polarizability, *etc.*).

In copper oxides, the O2p orbitals play an important role since the Cu 3d orbitals are deep in energy due to large nuclear charge and approach the O2p orbitals. The charge transfer energy (Δ_0) of an electron from O²⁻ to M^{v+} can also be approximated in a similar way,

$$\Delta_0 = e\Delta V_M + A(O^-) - I_v(M) - \frac{e^2}{d_{M-O}}, \quad (3)$$

where $A(O^-)$ ($= -7.70$ eV) is the electron affinity of O^- , equivalent to the ionization energy of O^{2-} . The negative sign means that 7.70 eV is released by removing an electron from O^{2-} . The Δ_0 includes the difference ($\Delta V_M = V_M(O) - V_M(Cu)$) of the electrostatic potentials (called the Madelung potential) between the oxygen site and the copper site, which can be calculated numerically. In solids, the bare Δ_0 is again substantially reduced by overlap. We write U' and Δ to represent the Coulomb and charge transfer energy in solids. In solids, both of the $Cu3d$ and $O2p$ levels are broadened to have a certain band width (W).

The ZSA scheme distinguishes two different types of insulators as shown in Fig. 29. One is Mott-Hubbard insulators for $U' < \Delta$, in which the energy gap is given by U' . The other is charge transfer insulators for $U' > \Delta$, in which the energy gap is given by Δ . In both cases, if the band width W is sufficiently large, the energy gap collapses, then resulting in conducting oxides. Based on the ZSA scheme, Torrance et al. reached an empirical criterion to predict whether an oxide is insulating or conducting, using bare U_0' and Δ_0 [102]. They pointed out that oxides, either simple or perovskite-type oxides, satisfying $U_0' \leq 11$ eV or $\Delta_0 \leq 10$ eV are conducting. This criterion applied to copper oxides correctly predicts that perovskite $LaCuO_3$ ($\Delta_0 = 8.59$ eV, $U_0' = 14.64$ eV) and $T-LaSrCuO_4$ ($\Delta_0 = 8.17$ eV, $U_0' = 14.55$ eV) with Cu^{3+} are predicted to be conducting whereas $T-La_2CuO_4$ ($\Delta_0 = 13.67$ eV, $U_0' = 12.76$ eV) with Cu^{2+} is insulating. However, Cu^{2+} oxides are not always predicted to be insulating since Δ_0 , which includes ΔV_M , is material dependent. Figure 30 is a summary of Δ_0 as well as $-eV_M(O)$ and $-eV_M(Cu)$ for $T'-RE_2CuO_4$ and $T-La_2CuO_4$. The Δ_0 of $T'-La_2CuO_4$ is 10.26 eV, smaller by 3.56 eV than Δ_0 of $T-La_2CuO_4$, predicting $T'-La_2CuO_4$ to be possibly conducting [footnote: It should be noted that $T'-Gd_2CuO_4$ with $\Delta_0 = 11.71$ eV is

superconducting against the Torrance's criterion ($\Delta_0 \leq 10$ eV). It appears to imply that square-planar cuprates have a stronger tendency to be conductive than expected from the Torrance's criterion]. The difference in Δ_0 between T- and T'-La₂CuO₄ comes mostly from the difference in $-eV_M(O)$. The Madelung potential energy, $-eV_M(Cu)$ (>0), which an electron ($-e$) at Cu feels, is substantially smaller in T'-La₂CuO₄ than in T-La₂CuO₄ primarily due to the absence of apical oxygen. Then both of the upper and lower Hubbard bands of Cu3d_{x²-y²} in T'-La₂CuO₄ are lowered relatively to those in T-La₂CuO₄ as shown in Fig. 30(b) (the position of the O2p band is almost unchanged in the two compounds). This may substantially decrease or even collapse the charge-transfer gap (Δ) in T'-La₂CuO₄. For such a situation, it is not appropriate to start from the ionic picture but it may be better to start from the band picture, which will be discussed in the next section.

5.2. Electronic structure of T' vs T (2): Band model

In most of oxides, the chemical bonds are essentially ionic due to the large electronegativity of oxygen. For example, the typical perovskite oxide, SrTiO₃, is built up by attractive electrostatic forces between cations (Sr²⁺ and Ti⁴⁺) and an anion (O²⁻): Sr²⁺Ti⁴⁺O₃²⁻ = (Sr²⁺O²⁻)(Ti⁴⁺O₂²⁻). Band calculations also predict that the O2p bands derived from oxygen 2p orbitals are located more than 5 eV below Ti 3d bands and filled by electrons fully, leading to divalent O²⁻ [103]. On going to the right in the periodic table, the 3d electrons see an increasing effective nuclear charge, and thereby the 3d orbitals become deeper in energy. Figure 31 illustrates a semi-empirical energy diagram for the 3dⁿ manifolds at divalent first-row transition-metal ions at octahedral sites (also pyramidal or square-planar sites for Cu²⁺) in an oxide, relative to the edges of the empty cation-4s and filled O-2p bands, which was drawn initially by Goodenough et al. [104]. As seen in this figure, the energies of O2p and Cu3d_{x²-y²} of Cu²⁺ are close, hence one has to take account of hybridization between them. Furthermore, according to the discussion in §5.1, the energy of Cu3d_{x²-y²} at square-planar sites

is still deeper than at octahedral sites, which leads to stronger hybridization and makes the bonds in square-planar cuprates covalent rather than ionic.

The band calculations for T' cuprates were performed immediately after the discovery of superconductivity in the compounds in 1989. Figure 32 shows one early example (APW calculation) for T'-Nd₂CuO₄ calculated by Massidda et al. [105]. The energy bands are highly two-dimensional. Two strongly *k*-dispersive bands are the bonding and antibonding bands (thick lines), which are truncated by many non-bonding or π -bonding bands derived from Cu3*d* and O2*p* orbitals. Near the Fermi level, the band structure is very simple. The Fermi level crosses the antibonding band at the middle, namely half-filled position. The resultant Fermi surface is hole-like and has a rounded square shape centered at around the X point. The Fermi level is raised by ~ 0.2 eV for a doping of Ce by $x = 0.15$. The above band calculation predicts metallic nature for T' parent compounds. Therefore the insulating behavior of initial samples of T' parent compounds again led to a skepticism to the reliability of band calculations for cuprates. As mentioned in §3.6, however, the apparent insulating behavior of T' parent compounds may be an artifact derived from early experiments on non-qualified specimens, and the generic behavior may be quite different (metallic and superconducting).

Recently the difference between T-La₂CuO₄ and T'-La₂CuO₄ was revealed by LDA (local-density approximation) + DMFT (dynamical mean field theory) calculations suitable for treating many-body (correlation) effects [106-109]. Weber et al. carried out calculations based on the three-band (Cu3*d*_{*x*²-*y*²} and O2*p* σ orbitals) model Hamiltonian [106, 107]. According to their calculations, T-La₂CuO₄ is a charge-transfer insulator where Mott-physics plays an essential role, but the parent compounds with the T'-structure are essentially metallic. The metallic ground state competes with the Slater insulating state caused by magnetic Bragg reflections due to the AF long range order. Unfortunately, even with the modern calculation approach, it is difficult to predict by *ab initio* calculations whether a metallic state or a

magnetically ordered state, e.g., spin density wave (SDW), is more stable. Other calculations have reached nearly the same conclusions. Das and Saha-Dasgupta have also performed similar DMFT calculations on the 2D single-band (= antibonding $pd\sigma$ band) Hubbard Hamiltonian, which is derived from the LDA calculations [109]. And they pointed out that introducing correlation effects to a one-electron band structure provides an insulating solution to T'-La₂CuO₄ but a metallic one to T'-La₂CuO₄ under an assumption that $U' = 4.5$ eV. Ogura and Kuroki employed the three-band model and took account of the electron correlation effect by the two-particle self-consistent (TPSC) method developed by Vilk and Tremblay. Their calculations reproduce the monotonously increasing T_c in T'-RE_{2-x}Ce_xCuO₄ with decreasing x .

5.3. Experiments on undoped superconductors (1) μ SR

A few measurements on the physical properties in undoped superconductors have started using thin films. As we have mentioned repeatedly, “ideal” T' cuprates have not been synthesized, so the experimental results require careful interpretation. Some observations arise from the presence of excess O_{ap} ions and may not be intrinsic to oxygen-defect free T' cuprates.

The first experiment presented is the depth-resolved μ SR measurements conducted by Kojima et al. on T'-La_{1.9}Y_{0.1}CuO_{4+ δ} (LYCO) films with $T_c \simeq 21$ K [110]. The work confirmed the bulk nature of superconductivity and also elucidated that Cu²⁺ is nonmagnetic except at the surface region. The LYCO films were grown by MBE on YAlO₃ substrates with a thickness ($2D = 275$ nm) comparable to the penetration depth. The film surface was covered by a thin layer ($d_0 = 20$ nm) of silver to protect the surface. The μ SR measurements using low-energy muons have been performed at the Paul Scherrer Institute, Switzerland [111, 112]. A muon beam ($//z$) with an implantation energy (E_μ) ranging from 4 to 23 keV was transported to sample position with an initial muon polarization $\mathbf{P}_\mu(0)$ ($//x$). An incident

muon stops at some depth in the films, and the implantation energy determines its stopping profile $n(z, E_\mu)$, which shows a maximum at d_p called as peak implantation depth.

Two types of experiments were carried out: transverse-field (TF-) μ SR and zero-field (ZF-) μ SR. In the TF- μ SR (see a schematic configuration in Fig. 33(a)), a weak magnetic field ($B_0 = 7$ mT) ($//y$) is applied parallel to the film surface after zero-field cooling down to ~ 5 K. The magnetic field is attenuated inside the film by the Meissner effect. Implanted muons probed the local transverse field, $B_y(z)$, since $\mathbf{P}_\mu(t)$ precesses around the local field. The time evolution of an implanted muon polarization described by $G_x(t) = \cos(\gamma_\mu B_y(z)t + \phi)$, where $\gamma_\mu (= 2\pi \times 135.53$ MHz/T) is the muon gyromagnetic ratio and ϕ is the initial phase. In principle, $B_y(z)$ is estimated from the experimental $G_x(t)$ by deconvolution under several reasonable assumptions.

There is one complexity that does not allow simple deconvolution procedure. That is, mesoscopic, highly disordered magnetic domains develop with decreasing temperature below ~ 80 K, which is manifested by a signal component with an enhanced depolarization. Fortunately the depolarization rates due to the weak and disordered magnetism are substantially higher ($\sim 2 \mu\text{s}^{-1}$) than those in the nonmagnetic domains, so it is rather easy to distinguish the magnetic and nonmagnetic components. Furthermore the preliminary analysis indicates that the mean field B_m originating from the magnetic domain is considerably smaller than $B_y(z)$. Then, if one assumes that superconductivity occurs in the nonmagnetic domains (with a volume fraction f_p) and that the depolarization in the magnetic domain (with a volume fraction $1-f_p$) can be described by an appropriate formula, then the mean local field $\langle B_y(z) \rangle$ is deduced as shown in Fig. 33(c). One can observe a clear decrease of $\langle B_y(z) \rangle$ at 5 K with increasing depth over a distance of ~ 100 nm underneath the Ag layer. This magnetic field gradient is completely absent at 25 K ($> T_c$). From this data, λ_{ab} is estimated to be 465 nm. These values are in line with earlier λ_{ab} by mutual inductance measurements on “electron-doped” $\text{T}'\text{-La}_{2-x}\text{Ce}_x\text{CuO}_4$ and “undoped” $\text{T}'\text{-La}_{2-x}\text{Y}_x\text{CuO}_4$ films:

320 nm for $\text{La}_{1.91}\text{Ce}_{0.09}\text{CuO}_4$ [113] , 354 nm for $\text{La}_{1.91}\text{Y}_{0.09}\text{CuO}_4$ [113, 114] and 408 nm for $\text{La}_{1.88}\text{Y}_{0.12}\text{CuO}_4$ [113, 114]. It should be denoted that the presence of a magnetic domain near the surface layer might weaken the shielding current, so that the “local λ ” might be depth-dependent. However, the observed depth profile of $\langle B_y(z) \rangle$ is well reproduced by a simple $B_0 \cosh(z/\lambda)/\cosh(D/\lambda)$ ($2D$: film thickness), suggesting that the model provides a reasonable description of the Meissner effect with λ as a mean value averaged over $20 \leq d_p \leq 120$ nm.

The above analyses also yield the depth profile of the nonmagnetic (= superconducting) volume fraction f_p , which is shown in Fig. 33(d). The f_p exhibits a gradual increase with an increasing d_p . The microscopic detail of the magnetic domain is inferred also from depth-resolved ZF- μ SR measurements, where the presence of a weak and highly disordered magnetism is identified near the sample surface. Figure 33(e) shows ZF- μ SR time spectra at 5 K obtained with a variety of mean implantation depth d_p , where the amplitude of a strongly damped oscillation exhibits a monotonic decrease with increasing d_p . A similar observation of surface magnetism has recently been reported in ZF- μ SR measurements on $\text{T}'\text{-La}_{2-x}\text{Ce}_x\text{CuO}_4$ films by Saadaoui et al. [115].

The observations in LYCO, i.e., the bulk superconductivity and the near-surface magnetism, can be explained as follows. According to the experimental results, there are nonmagnetic and magnetic domains in LYCO. The nonmagnetic fraction (f_p) increases with d_p whereas the magnetic fraction ($1-f_p$) decreases with d_p , namely, approaching to surface. The superconductivity is assumed to occur in the nonmagnetic domain whereas the magnetism occurs near surface and destroys superconductivity. This surface magnetism is induced by oxygen adsorption at O_{ap} in the surface region. It is demonstrated from our early UPS/XPS studies on MBE-grown $(\text{Nd,Ce})_2\text{CuO}_4$ films that oxygen is adsorbed at O_{ap} immediately after taking films out from UHV chamber to air [116]. In order to suppress this oxygen adsorption, Ag was deposited on LYCO films but did not work perfectly. We know

from a long-term experience that oxygen atoms penetrate deeply from surface into films in La-based T' cuprates especially with low Ce doping. This is in accord with what we observed in μ SR experiments.

5.4. Experiments on undoped superconductors (2) optics

The μ SR experiments indicated that Cu^{2+} is nonmagnetic except near surface. It has to be borne in mind that “nonmagnetic” defined by μ SR is either that Cu^{2+} indeed has no magnetic moment or that Cu^{2+} has a magnetic moment but fluctuating very rapidly in the time scale of the precession period of muon, $2\pi/\gamma_\mu B$. It requires much faster experimental probes such as optics, neutron diffraction, electron transport, etc. to distinguish these two cases. Hence as the second experiment, we present the optical studies conducted by Chanda et al. on two-step annealed Pr_2CuO_4 films ($T_c = 27$ K) grown by MBE [117]. The measurements were carried out by various optical methods in a wide frequency ($7\text{--}55000\text{cm}^{-1}$) and temperature (2–300 K) range. The reflectivity at low frequencies is quite high and increases with decreasing temperature, typical for metals. By applying a thin-film fitting procedure, the film's complex optical conductivity, $\sigma = \sigma_1 + i\sigma_2$, is extracted from the reflectivity spectra. The real part of the Pr_2CuO_4 optical conductivity obtained by this modeling is shown in Fig. 34(a). The normal-state optical conductivity of Pr_2CuO_4 above T_c can be decomposed into a Drude component, a broad far-infrared (FIR) band, narrow FIR peaks, a mid-infrared (MIR) band, and interband-transition bands at the highest frequencies:

$$\sigma(\omega) = \text{Drude} + \text{FIR peaks} + \text{FIR band} + \text{MIR band} + \text{interband transitions}.$$

The decomposition of the optical conductivity into these components are shown in Fig. 34(b) for 30 K and 300 K. Each component can be interpreted as follows.

The Drude and the MIR band are used to mimic the free-carrier response, which can be alternatively described by the generalized Drude model with frequency-dependent scattering [118]

The FIR peaks (130 cm^{-1} , 304 cm^{-1} , 343 cm^{-1} , and 500 cm^{-1}) can be attributed to infrared active phonon modes. These frequencies are in good agreement with the values in the previous optical studies by Homes and Li on non-superconducting Pr_2CuO_4 [119]. However, it is worth noting here that in the studies by Homes and Li, in addition to the phonons characteristic to the T' structure, other modes which are not allowed by the crystal structure in the T' phase have been observed. The authors concluded as the possible origin of these additional modes that some impurities and/or contributions from different phases may play a role. Taking into account that the FIR spectra of **our** superconducting Pr_2CuO_4 **films** **did** not demonstrate any obvious signs of spurious phases, non-superconducting Pr_2CuO_4 appears to be contaminated by excess O_{ap} ions. This observation suggests the possibility that vibrational spectra may be used to assess the issue of how completely impurity O_{ap} ions are removed.

The FIR band (bump at about $300\text{ cm}^{-1} = 37.2\text{ meV}$) can be attributed to electron localization due to strong electron correlation. It has been demonstrated by Mutou and Kontani [120] using the dynamical mean-field theory and iterated perturbation theory that in a strongly correlated metallic state, realized by a large on-site repulsion energy, the optical conductivity exhibits a Drude peak centered at $\omega = 0$ at low temperatures and a shift of this peak to finite frequencies above the Ioffe-Regel-limit temperature T_{IR} .

The two highest-frequency absorption peaks at around $30\,000\text{--}40\,000\text{ cm}^{-1}$ ($4\text{--}5\text{ eV}$) are typical for cuprates and represent the interband transitions to the bands derived from oxygen p orbital [108]. The peak slightly below $20\,000\text{ cm}^{-1}$ ($1.5\text{--}2\text{ eV}$) is the one that has previously been assigned as the charge-transfer transition from the $\text{O}2p$ to the $\text{Cu}3d$ upper Hubbard band. However, it is important to realize that the presence of such a transition does not necessarily require a charge-transfer gap. The recent LDA + DFT calculations [108] demonstrated that such a band may coexist with a quasiparticle absorption peak with a metallic state in the case of undoped Pr_2CuO_4 with the perfect T' structure.

One of the most important observations in the optical studies of superconducting Pr_2CuO_4 films is the absence of a pseudogap. A well-known characteristic feature of underdoped cuprates is the occurrence of a pseudogap, i.e., a partial normal-state gap in the electronic density of states [121]. According to the previous reports, a suppression of the real-part MIR optical conductivity below the pseudogap is observed in underdoped T' cuprates [122, 123]. With Ce doping, the pseudogap is monotonically reduced in size together with the Neel temperature, and disappears at higher doping, where the AF order is completely suppressed. The pseudogap is definitely related to the development of the AF order. The origin is now understood as the new energy gap created by the magnetic Bragg reflection due to the AF order that changes the lattice periodicity. In the conductivity data of superconducting Pr_2CuO_4 presented in Fig. 34(a), however, such a normal-state gap is not evident. Thus, it can be concluded that a pseudogap is absent in the superconducting Pr_2CuO_4 films, implying a strong suppression or even absence of the AF correlation.

The optical studies on superconducting Pr_2CuO_4 sheds new light on the magnetic status of Cu^{2+} . The μSR experiment could not distinguish whether Cu^{2+} in the “nonmagnetic” domain has no moment or rapidly fluctuating moment. Now the above optics results appear to support the former. If it is the case, Cu^{2+} in the superconducting ground state of Pr_2CuO_4 is nonmagnetic. On the other hand, a different conclusion is reached by very recent studies [124] by Breznay et al. of Shubnikov-de Haas oscillations in superconducting Pr_2CuO_4 . The magnetic quantum oscillations observed are consistent with the presence of small hole-like Fermi surface pockets. These small Fermi surface pockets are the reconstructed Fermi surface resulted from the magnetic Bragg reflections truncating the original large Fermi surface (Fig. 32(c)). The result indicates that transport carriers feel the modified lattice periodicity due to AF spin fluctuations during cyclotron motion. In this case, AF spin fluctuations, either static or dynamic, still exist and plays a role in superconducting Pr_2CuO_4 , at least in the samples used for measurements of quantum oscillations. Hence it is

controversial, at present, whether Cu^{2+} in the superconducting ground state of $\text{T}'\text{-RE}_2\text{CuO}_4$ is magnetic or nonmagnetic

5.5. Nature of superconductivity (1): hole-doped or electron-doped or truly undoped

The key issue is the nature of superconductivity in the nominally undoped $\text{T}'\text{-RE}_2\text{CuO}_4$. Are these materials (a) hole-doped or (b) electron-doped or (c) truly undoped? At first, it is safe to exclude hole-doped superconductivity because it is well-known that excess oxygen makes T' parent compounds more insulating, which is in contrast to the $\text{T-La}_2\text{CuO}_4$ case [14]. Electron-doped superconductivity due to oxygen deficiencies has been most frequently raised as a possibility to our first discovery of $\text{T}'\text{-La}_{2-x}\text{RE}_x\text{CuO}_4$. The groups of University of Maryland in US [125] and Hefei National Laboratory in China [126] claimed, based on their results of transport measurements (resistivity, Hall effect, Nernst effect), that nominally undoped $\text{T}'\text{-La}_{2-x}\text{RE}_x\text{CuO}_4$ may be, in reality, electron-doped due to oxygen deficiencies in the fluorite layers or in the CuO_2 layers. But it has to be kept in mind that these transport parameters are dependent not only on the subtle features ($d\varepsilon(\mathbf{k})/d\mathbf{k}$) of energy bands but also on the anisotropic relaxation time at Fermi surface in metals, which makes the interpretation not straightforward in contrast to semiconductors [127, 128]. Hence one cannot address the origin of the carriers unambiguously only from transport measurements. As mentioned in §3.5, from a solid-state chemistry point of view, the oxygen deficiencies in the CuO_2 planes may occur. But the substantial loss of oxygen ions at O1 kills the superconductivity (see Fig. 19 and 20), and eventually makes films insulating and even transparent with the T' structure preserved [footnote. This was demonstrated by the very detailed early work on the effect of oxygen nonstoichiometry to superconductivity performed almost two decade ago by Maryland group [129] and has also been confirmed by our recent work [17]]. The oxygen deficiencies at O2 in the fluorite RE_2O_2 layers is unlikely to occur since solid-state chemistry tells us that the RE-O bond is much stronger than the Cu-O bond

as mentioned in §3.5. $T\text{-La}_2\text{CuO}_4$ and $T'\text{-RE}_2\text{CuO}_4$ can be regarded as a stack of strongly bonded La_2O_2 or RE_2O_2 layers and weakly bonded CuO_2 layers. Hence, at present, the most likely is undoped superconductivity. This should be confirmed in future by unambiguous experiments such as the determination of the site-specific occupancies by neutron diffraction on well-qualified oxygen-homogeneous samples. Furthermore the answer for undoped or doped can be gained also from the probes to the electronic state such as photoemission spectroscopy, X-ray absorption spectroscopy, Fermiology based on quantum oscillations in high magnetic fields, etc.

5.6. Nature of superconductivity (2): spin-mediated or charge-mediated pairing

The scenario of undoped superconductivity in T' parent compounds argues sharply against the currently accepted “doped Mott-insulator scenario” for high- T_c superconductivity. However, another spin model, i.e., the itinerant weak-coupling spin model may still be possible. The itinerant spin model was initially proposed by Monthoux-Balatsky-Pines [130] and also Moriya et al [131]. The model is based on the idea that the retarded interaction between quasiparticles on a two dimensional square lattice induced by the exchange of AF paramagnons (no well-defined low-frequency magnetic excitations, but rather relaxation modes) causes the pairing of quasiparticles and leads uniquely to a transition to a superconducting state with $d_{x^2-y^2}$ symmetry. A similar model was previously proposed to heavy Fermion superconductors. In heavy Fermion superconductors, the fluctuations of $4f$ spins of rare-earth elements play a role of glue whereas in cuprates, those of $3d$ spins of Cu^{2+} do the same role. The schematic picture of this model is illustrated in Fig. 35. The strong AF fluctuation in cuprates can be attributed to large super-exchange coupling, $J_{\text{ex}}^{\text{super}}$, of Cu^{2+} . The $J_{\text{ex}}^{\text{super}}$ of Cu^{2+} is 0.13-0.15 eV, and the largest among divalent $3d$ transition metal ions. For example, the $J_{\text{ex}}^{\text{super}}$ of neighboring Ni^{2+} in La_2NiO_4 is ~ 0.03 eV, i.e., 5 times smaller than $J_{\text{ex}}^{\text{super}}$ of Cu^{2+} . In insulating magnets, $J_{\text{ex}}^{\text{super}}$ can be expressed as follows,

$$J_{\text{ex}}^{\text{super}} \approx \frac{t_{pd}^4}{\Delta^2} \left(\frac{4}{2\Delta + U_p} + \frac{4}{U_d} \right) \quad (4)$$

where t_{pd} is the transfer matrix element between Cu3d and O2p orbitals, Δ the charge transfer energy, U_d and U_p are the on-site Coulomb repulsion in Cu3d and O2p orbitals [132]. In cuprates, $J_{\text{ex}}^{\text{super}}$ is exceptionally large due to small Δ and large t_{pd} .

Since, in 1993, the pairing symmetry in hole-doped high- T_c superconductors has been identified as $d_{x^2-y^2}$, models for high- T_c superconductivity based on spin fluctuations have predominated in this field over two decades. As discussed in §5.4, however, it is controversial at present whether the ground state of superconducting $T'-RE_2\text{CuO}_4$ is magnetic or nonmagnetic as discussed in §5.4. In this situation, the possibility of non-spin mechanisms should not be discarded. Especially high- T_c superconductivity remains confined, at least at present, only to cuprates, and has not spread to neighboring transition-metal oxides whereas strong-correlated electron physics prevails in 3d transition-metal oxides. Therefore we should pay more attention not to features common to transition-metal oxides but to features unique to cuprates not shared by other transition-metal oxides. As such unique features in cuprates, we list the following key words:

(1) strong covalency and strong O2p character at the Fermi level that are exceptional as oxides.

(2) half-filled antibonding bands (d^9) that makes compounds thermodynamically unstable.

These features were stressed at the beginning of high- T_c research, three decades ago, but may have been forgotten in time.

6. Summary

The high- T_c cuprates were discovered in 1986. Before this discovery, there were 13-year struggle to higher T_c in late 1970's and early 1980's since Nb₃Ge recorded $T_c = 23$ K in 1973. During this era, there was a rumor of the “BCS limit” that T_c based on the BCS

mechanism would be limited by 30 K, which should now be withdrawn by the discovery of conventional superconductivity in H_3S with $T_c = 203$ K [133]. In such situations in 1986, the research for the high- T_c mechanism started with a bias for “non-BCS”. The identification of the $d_{x^2-y^2}$ pairing symmetry in hole-doped high- T_c superconductors in 1993 pushed forward the models for high- T_c superconductivity based on spin fluctuations. This direction has not been unchanged over two decades. We showed that $\text{T}'\text{-(La,RE)}_2\text{CuO}_4$ is superconducting with $T_c = 25$ K in 2003 [7] and that $\text{T}'\text{-RE}_2\text{CuO}_4$ is superconducting with $T_c \geq 30$ K in 2007 [8]. Our finding that the parent compounds of T' cuprates are not a charge-transfer insulator but a superconductor may provide a chance to change the direction of high- T_c research. It is a time to reassess the electronic state, magnetism, and superconductivity in not only T' cuprates but also all high- T_c cuprates on the basis of robust experimental results derived by precise measurements on well-qualified samples.

There has also been significant progress in the band calculation techniques. Thirty years ago, it was possible by no band calculation to predict that $\text{T-La}_2\text{CuO}_4$ is an antiferromagnetic insulator [105]. This failure at the beginning of high- T_c research resulted in a great skepticism to the reliability of band calculations for cuprates. But now it is possible to predict the different ground state for T- and $\text{T}'\text{-La}_2\text{CuO}_4$ [106-109]. High- T_c superconductivity, the fascinating phenomenon, remains confined, at least at present, only to cuprates. The reassessment of the electronic state by the state-of-the-art band calculations may unveil unique features of cuprates not shared by other transition-metal oxides.

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Reference

- [1] Y. Tokura, H. Takagi, S. Uchida, A superconducting copper oxide compound with electrons as the charge carriers, *Nature*, 337 (1989) 345-347.
- [2] H. Takagi, S. Uchida, Y. Tokura, Superconductivity produced by electron doping in CuO_2 -layered compounds, *Physical Review Letters*, 62 (1989) 1197-1200.
- [3] J.B. Torrance, Y. Tokura, A.I. Nazzari, A. Bezing, T.C. Huang, S.S.P. Parkin, Anomalous disappearance of high- T_c superconductivity at high hole concentration in metallic $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, *Physical Review Letters*, 61 (1988) 1127-1130.
- [4] M.B. Maple, High T_c oxide superconductors, *MRS Bulletin*, 14 (1989) 20-24.
- [5] H. Sato, M. Naito, Increase in the superconducting transition temperature by anisotropic strain effect in (001) $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ thin films on LaSrAlO_4 substrates, *Physica C: Superconductivity*, 274 (1997) 221-226.
- [6] H. Yamamoto, M. Naito, H. Sato, Surface and interface study on MBE-grown $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ thin films by photoemission spectroscopy and tunnel spectroscopy, *Physical Review B*, 56 (1997) 2852-2859.
- [7] A. Tsukada, Y. Krockenberger, M. Noda, H. Yamamoto, D. Manske, L. Alff, M. Naito, New class of T'-structure cuprate superconductors, *Solid State Communications*, 133 (2005) 427-431.
- [8] M. Naito, O. Matsumoto, A. Utsuki, A. Tsukada, H. Yamamoto, T. Manabe, Undoped cuprate superconductors — band superconductors or oxygen-doped Mott-Hubbard superconductors?, *Journal of Physics: Conference Series*, 108 (2008) 012037.
- [9] M. Naito, M. Hepp, Superconducting T'- $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ films grown by molecular beam epitaxy, *Japanese Journal of Applied Physics*, 39 (2000) L485.
- [10] M. Naito, H. Sato, H. Yamamoto, MBE growth of $(\text{La,Sr})_2\text{CuO}_4$ and $(\text{Nd,Ce})_2\text{CuO}_4$ thin films, *Physica C: Superconductivity*, 293 (1997) 36-43.
- [11] M. Naito, M. Hepp, Superconducting T'- $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ films grown by molecular beam epitaxy, *Physica C: Superconductivity*, 357–360, Part 1 (2001) 333-336.
- [12] M. Naito, S. Karimoto, A. Tsukada, Epitaxy-stabilized *n*-type superconducting cuprates, *Superconductor Science and Technology*, 15 (2002) 1663.
- [13] Y. Krockenberger, J. Kurian, A. Winkler, A. Tsukada, M. Naito, L. Alff, Superconductivity phase diagrams for the electron-doped cuprates $R_{2-x}\text{Ce}_x\text{CuO}_4$ ($R = \text{La, Nd, Sm, and Eu}$), *Physical Review B*, 77 (2008) 060505.
- [14] A. Tsukada, T. Greibe, M. Naito, Phase control of La_2CuO_4 in thin film synthesis, *Physical Review B*, 66 (2002) 184515.
- [15] Y. Krockenberger, B. Eleazer, H. Irie, H. Yamamoto, Superconducting- and insulating-ground states in La_2CuO_4 structural isomers, *Journal of the Physical Society of Japan*, 83 (2014) 114602.
- [16] M. Noda, A. Tsukada, H. Yamamoto, M. Naito, Origin of superconducting carriers in “non-doped” T'- $(\text{La,RE})_2\text{CuO}_4$ ($\text{RE} = \text{Sm, Eu, Gd, Tb, Lu, and Y}$) prepared by molecular beam epitaxy, *Physica C: Superconductivity*, 426–431, Part 1 (2005) 220-224.
- [17] A. Tsukada, M. Noda, H. Yamamoto, M. Naito, Role of impurity oxygen in superconductivity of “non-doped” T'- $(\text{La, RE})_2\text{CuO}_4$, *Physica C: Superconductivity*, 426–431, Part 1 (2005) 459-463.
- [18] O. Matsumoto, A. Tsukada, H. Yamamoto, T. Manabe, M. Naito, Material characterization of

superconducting T'-Nd₂CuO₄ films synthesized by metal organic decomposition, *Physica C: Superconductivity*, 470 (2010) 1029-1032.

[19] G.M. Luke, L.P. Le, B.J. Sternlieb, Y.J. Uemura, J.H. Brewer, R. Kadono, R.F. Kiefl, S.R. Kreitzman, T.M. Riseman, C.E. Stronach, M.R. Davis, S. Uchida, H. Takagi, Y. Tokura, Y. Hidaka, T. Murakami, J. Gopalakrishnan, A.W. Sleight, M.A. Subramanian, E.A. Early, J.T. Markert, M.B. Maple, C.L. Seaman, Magnetic order and electronic phase diagrams of electron-doped copper oxide materials, *Physical Review B*, 42 (1990) 7981-7988.

[20] M. Matsuda, K. Yamada, K. Kakurai, H. Kadowaki, T.R. Thurston, Y. Endoh, Y. Hidaka, R.J. Birgeneau, M.A. Kastner, P.M. Gehring, A.H. Moudden, G. Shirane, Three-dimensional magnetic structures and rare-earth magnetic ordering in Nd₂CuO₄ and Pr₂CuO₄, *Physical Review B*, 42 (1990) 10098-10107.

[21] M. Matsuda, Y. Endoh, K. Yamada, H. Kojima, I. Tanaka, R.J. Birgeneau, M.A. Kastner, G. Shirane, Magnetic order, spin correlations, and superconductivity in single-crystal Nd_{1.85}Ce_{0.15}CuO_{4+δ}, *Physical Review B*, 45 (1992) 12548-12555.

[22] M. Brinkmann, T. Rex, H. Bach, K. Westerholt, Extended superconducting concentration range observed in Pr_{2-x}Ce_xCuO_{4-δ}, *Physical Review Letters*, 74 (1995) 4927-4930.

[23] M. Brinkmann, T. Rex, M. Stief, H. Bach, K. Westerholt, Residual resistivity and oxygen stoichiometry in Pr_{2-x}Ce_xCuO_{4+δ} single crystals, *Physica C: Superconductivity*, 269 (1996) 76-82.

[24] M. Brinkmann, H. Bach, K. Westerholt, Electrical resistivity study of metallic Pr_{2-x}Ce_xCuO_{4+δ}-single crystals over a broad concentration and temperature range, *Physica C: Superconductivity*, 292 (1997) 104-116.

[25] H. Sato, A. Tsukada, Y. Krockenberger, H. Yamamoto, M. Naito, Comprehending high temperature superconductivity: a study on 214-type cuprate superconductor thin films, in: T. Das (Ed.) *Magnetic Mechanism of Superconductivity in Copper-Oxide*, Nova Science Publishers, New York, 2011, pp. 235.

[26] O. Matsumoto, A. Utsuki, A. Tsukada, H. Yamamoto, T. Manabe, M. Naito, Synthesis and properties of superconducting T'-R₂CuO₄ (R = Pr, Nd, Sm, Eu, Gd), *Physical Review B*, 79 (2009) 100508.

[27] O. Matsumoto, A. Utsuki, A. Tsukada, H. Yamamoto, T. Manabe, M. Naito, Reduction dependence of superconductivity in the end-member T' cuprates, *Physica C: Superconductivity*, 469 (2009) 940-943.

[28] O. Matsumoto, A. Utsuki, A. Tsukada, H. Yamamoto, T. Manabe, M. Naito, Generic phase diagram of "electron-doped" T' cuprates, *Physica C: Superconductivity*, 469 (2009) 924-927.

[29] H. Okada, M. Takano, Y. Takeda, Synthesis of Nd₂CuO₄-type R₂CuO₄ (R = Y, Dy, Ho, Er, Tm) under high pressure, *Physica C: Superconductivity*, 166 (1990) 111-114.

[30] P. Bordet, J.J. Capponi, C. Chaillout, D. Chateigner, J. Chenavas, T. Fournier, J.L. Hodeau, M. Marezio, M. Perroux, G. Thomas, A. Varela, High pressure synthesis and structural study of R₂CuO₄ compounds with R = Y, Tb, Dy, Ho, Er, Tm, *Physica C: Superconductivity*, 193 (1992) 178-188.

[31] H. Sawa, S. Suzuki, M. Watanabe, J. Akimitsu, H. Matsubara, H. Watabe, S.-i. Uchida, K. Kokusho, H. Asano, F. Izumi, E. Takayama-Muromachi, Unusually simple crystal structure of an Nd-Ce-Sr-Cu-O superconductor, *Nature*, 337 (1989) 347-348.

[32] J.F. Bringley, S.S. Trail, B.A. Scott, An ionic model of the crystal chemistry in the superconducting copper oxides of stoichiometry (RE)₂CuO₄, *Journal of Solid State Chemistry*, 86 (1990) 310-322.

- [33] A. Manthiram, J.B. Goodenough, Crystal chemistry of the $\text{La}_{2-y}\text{Ln}_y\text{CuO}_4$ ($\text{Ln} = \text{Pr}, \text{Nd}$) systems, *Journal of Solid State Chemistry*, 87 (1990) 402-407.
- [34] V.M. Goldschmidt, Die Gesetze der Krystallochemie, *Naturwissenschaften*, 14 (1926) 477-485.
- [35] A. Manthiram, J.B. Goodenough, Thermal-expansion mismatch and intergrowth types in the system $\text{La}_{2-y}\text{Nd}_y\text{CuO}_4$, *Journal of Solid State Chemistry*, 92 (1991) 231-236.
- [36] F.C. Chou, J.H. Cho, L.L. Miller, D.C. Johnston, New phases induced by hydrogen reduction and by subsequent oxidation of L_2CuO_4 ($\text{L} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$), *Physical Review B*, 42 (1990) 6172-6180.
- [37] Y. Idemoto, K. Fueki, T. Shinbo, T -log P_{O_2} diagram and copper valence of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$, *Physica C: Superconductivity*, 166 (1990) 513-517.
- [38] T. Yamada, K. Kinoshita, H. Shibata, Synthesis of superconducting $\text{T}'\text{-(La}_{1-x}\text{Ce}_x)_2\text{CuO}_4$, *Japanese Journal of Applied Physics*, 33 (1994) L168.
- [39] J.T. Markert, J. Beille, J.J. Neumeier, E.A. Early, C.L. Seaman, T. Moran, M.B. Maple, Pressure dependence of T_c in $\text{L}_{2-y}\text{M}_x\text{CuO}_{4-y}$ ($\text{L} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$; $\text{M} = \text{Ce}, \text{Th}$): Antisymmetric behavior of electron- versus hole-doped copper-oxide superconductors, *Physical Review Letters*, 64 (1990) 80-83.
- [40] M. Matsuda, Y. Endoh, Y. Hidaka, Crystal growth and characterization of $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$, *Physica C: Superconductivity*, 179 (1991) 347-352.
- [41] T. Uzumaki, K. Hashimoto, N. Kamehara, Raman scattering and X-ray diffraction study in layered cuprates, *Physica C: Superconductivity*, 202 (1992) 175-187.
- [42] J.S. Zhou, J. Chan, J.B. Goodenough, Copper-oxygen bond length and self-doping in R_2CuO_4 ($\text{R} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$), *Physical Review B*, 47 (1993) 5477-5480.
- [43] T. Kawashima, E. Takayama-Muromachi, Oxygen deficiency and superconductivity in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, *Physica C: Superconductivity*, 219 (1994) 389-394.
- [44] T.C. Huang, E. Moran, A.I. Nazzari, J.B. Torrance, Synthesis and x-ray characterization of superconducting and related $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($\text{Ln} = \text{Nd}$ and Gd) compounds, *Physica C: Superconductivity*, 158 (1989) 148-152.
- [45] T.C. Huang, E. Moran, A.I. Nazzari, J.B. Torrance, P.W. Wang, Determination of the average ionic radius and effective valence of Ce in the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ electron superconductor system by X-ray diffraction, *Physica C: Superconductivity*, 159 (1989) 625-628.
- [46] Y. Hidaka, M. Suzuki, Growth and anisotropic superconducting properties of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ single crystals, *Nature*, 338 (1989) 635-637.
- [47] H. Ishii, T. Koshizawa, T. Hanyu, S. Yamaguchi, Effects of Ce doping on electronic structures of $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$) studied by core-level photoemission spectroscopy, *Japanese Journal of Applied Physics*, 32 (1993) 1070.
- [48] E. Takayama-Muromachi, Y. Uchida, K. Kato, Electron-doped system $(\text{La}, \text{Nd}, \text{Ce})_2\text{CuO}_4$ and preparation of T' -type $(\text{La}, \text{Ln})\text{CuO}_4$ ($\text{Ln} = \text{Ce}, \text{Y}$), *Physica C: Superconductivity*, 165 (1990) 147-151.
- [49] Y.D. Tretyakov, A.R. Kaul, N.V. Makukhin, An electrochemical study of high-temperature stability of compounds between the rare earths and copper oxide, *Journal of Solid State Chemistry*, 17 (1976) 183-189.
- [50] Y. Idemoto, I. Oyagi, K. Fueki, Determination of thermodynamic data of $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ and Ln_2CuO_4 ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}$) by the EMF method, *Physica C: Superconductivity*, 195 (1992) 269-276.

- [51] H. Kanai, J. Mizusaki, H. Tagawa, S. Hoshiyama, K. Hirano, K. Fujita, M. Tezuka, T. Hashimoto, Defect chemistry of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$: oxygen nonstoichiometry and thermodynamic stability, *Journal of Solid State Chemistry*, 131 (1997) 150-159.
- [52] A.N. Petrov, A.Y. Zuev, V.A. Cherepanov, Thermodynamic stability of the lanthanide cuprates Ln_2CuO_4 and LnCuO_2 , where $\text{Ln} = \text{La, Pr, Nd, Sm, Eu, or Gd}$, *Russian Journal of Physical Chemistry*, 62 (1988) 1613-1615.
- [53] A.N. Petrov, V.A. Cherepanov, A.Y. Zuyev, V.M. Zhukovsky, Thermodynamic stability of ternary oxides in $\text{Ln}\cdot\text{M}\cdot\text{O}$ ($\text{Ln} = \text{La, Pr, Nd}$; $\text{M} = \text{Co, Ni, Cu}$) systems, *Journal of Solid State Chemistry*, 77 (1988) 1-14.
- [54] J.S. Kim, D.R. Gaskell, The phase stability diagrams for the systems $\text{Nd}_2\text{CuO}_{4-\delta}$ and $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$, *Physica C: Superconductivity*, 209 (1993) 381-388.
- [55] P.G. Radaelli, J.D. Jorgensen, A.J. Schultz, J.L. Peng, R.L. Greene, Evidence of apical oxygen in Nd_2CuO_y , determined by single-crystal neutron diffraction, *Physical Review B*, 49 (1994) 15322-15326.
- [56] A.J. Schultz, J.D. Jorgensen, J.L. Peng, R.L. Greene, Single-crystal neutron-diffraction structures of reduced and oxygenated $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_y$, *Physical Review B*, 53 (1996) 5157-5159.
- [57] C. Marin, J.Y. Henry, J.X. Boucherle, Structural neutron diffraction study of a $\text{Nd}_2\text{CuO}_{4-\delta}$ single crystal, *Solid State Communications*, 86 (1993) 425-430.
- [58] I. Magelschots, N.H. Andersen, B. Lebech, A. Wisniewski, C.S. Jacobsen, Crystal structure, magnetic susceptibility and thermopower of superconducting and non-superconducting $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4+y}$, *Physica C*, 203 (1992) 369-377.
- [59] G.H. Kwei, S.W. Cheong, Z. Fisk, F.H. Garzon, J.A. Goldstone, J.D. Thompson, Structure and oxygen stoichiometry for the electron-doped cuprate superconductor $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$, *Physical Review B*, 40 (1989) 9370-9373.
- [60] F. Izumi, Y. Matsui, H. Takagi, S. Uchida, Y. Tokura, H. Asano, Neutron and electron diffraction study of the electron-doped superconductor $\text{Nd}_{1.845}\text{Ce}_{0.155}\text{CuO}_{4-y}$, *Physica C: Superconductivity*, 158 (1989) 433-439.
- [61] H.J. Kang, P. Dai, B.J. Campbell, P.J. Chupas, S. Rosenkranz, P.L. Lee, Q. Huang, S. Li, S. Komiya, Y. Ando, Microscopic annealing process and its impact on superconductivity in T'-structure electron-doped copper oxides, *Nat Mater*, 6 (2007) 224-229.
- [62] A.N. Petrov, A.Y. Zuev, T.P. Rodionova, V.I. Voronin, Crystal and defect structure of $\text{Nd}_{1.9}\text{Ce}_{0.1}\text{CuO}_{4\pm y}$, *Journal of the American Ceramic Society*, 82 (1999) 1037-1044.
- [63] E. Takayama-Muromachi, F. Izumi, Y. Uchida, K. Kato, H. Asano, Oxygen deficiency in the electron-doped superconductor $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$, *Physica C*, 159 (1989) 634-638.
- [64] E. Moran, A.I. Nazzari, T.C. Huang, J.B. Torrance, Extra oxygen in electron superconductors: Ce and Th doped $\text{Nd}_2\text{CuO}_{4+\delta}$ and $\text{Gd}_2\text{CuO}_{4+\delta}$, *Physica C*, 160 (1989) 30-34.
- [65] E. Wang, J.M. Tarascon, L.H. Greene, G.W. Hull, W.R. McKinnon, Cationic substitution and role of oxygen in the n-type superconducting T' system $\text{Nd}_{2-y}\text{Ce}_y\text{CuO}_2$, *Physical Review B*, 41 (1990) 6582-6590.
- [66] Y. Idemoto, K. Fueki, Defect Thermodynamics of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$, *Japanese Journal of Applied Physics*, 30 (1991) 2471.
- [67] K. Suzuki, K. Kishio, T. Hasegawa, K. Kitazawa, Oxygen nonstoichiometry of the $(\text{Nd, Ce})_2\text{CuO}_{4-\delta}$ system, *Physica C: Superconductivity*, 166 (1990) 357-360.

- [68] S. Yamaguchi, K. Yasui, F. Matsumoto, K. Terabe, T. Sukigara, Y. Iguchi, Defect chemical study of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$, *Solid State Ionics*, 49 (1991) 63-70.
- [69] P.W. Klamut, Evidence for interstitial oxygen and possible role of reduction in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4+y}$, *Journal of Alloys and Compounds*, 194 (1993) L5-L7.
- [70] Y.T. Zhu, A. Manthiram, Role of bond-length mismatch in $L_{2-x}\text{Ce}_x\text{CuO}_4$ (L =lanthanide), *Physical Review B*, 49 (1994) 6293-6298.
- [71] Y.T. Zhu, A. Manthiram, Role of oxygen in $L_{2-x}\text{Ce}_x\text{CuO}_4$ superconductors, *Physica C: Superconductivity*, 224 (1994) 256-262.
- [72] Y.T. Zhu, A. Manthiram, A thermogravimetric study of the influence of internal stresses on oxygen variations in $L_{2-x}\text{Ce}_x\text{CuO}_4$, *Journal of Solid State Chemistry*, 114 (1995) 491-498.
- [73] F. Prado, A. Caneiro, A. Serquis, J. Briatico, Thermogravimetric study of the reduction step in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1.01}\text{O}_y$ as a function of the oxygen partial pressure, *Solid State Communications*, 94 (1995) 75-80.
- [74] A. Serquis, F. Prado, A. Caneiro, On the role of the reduction step in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1\pm\delta}\text{O}_y$: a study of thermodynamic properties and electrical resistivity at high temperature, *Physica C: Superconductivity*, 313 (1999) 271-280.
- [75] Y. Tanaka, T. Motohashi, M. Karppinen, H. Yamauchi, Conditions for superconductivity in the electron-doped copper-oxide system, $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{CuO}_{4+\delta}$, *Journal of Solid State Chemistry*, 181 (2008) 365-372.
- [76] T. Sekitani, M. Naito, N. Miura, K. Uchida, Kondo effect in the normal state of T' - $L_{2-x}\text{Ce}_x\text{CuO}_4$ (L =La, Pr, Nd), *Journal of Physics and Chemistry of Solids*, 63 (2002) 1089-1092.
- [77] T. Sekitani, M. Naito, N. Miura, Kondo effect in underdoped n -type superconductors, *Physical Review B*, 67 (2003) 174503.
- [78] P. Fournier, P. Mohanty, E. Maiser, S. Darzens, T. Venkatesan, C.J. Lobb, G. Czjzek, R.A. Webb, R.L. Greene, Insulator-metal crossover near optimal doping in $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$: anomalous normal-state low temperature resistivity, *Physical Review Letters*, 81 (1998) 4720-4723.
- [79] P. Fournier, J. Higgins, H. Balci, E. Maiser, C.J. Lobb, R.L. Greene, Anomalous saturation of the phase coherence length in underdoped $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ thin films, *Physical Review B*, 62 (2000) R11993-R11996.
- [80] S.J. Hagen, X.Q. Xu, W. Jiang, J.L. Peng, Z.Y. Li, R.L. Greene, Transport and localization in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ crystals at low doping, *Physical Review B*, 45 (1992) 515-518.
- [81] Y. Hidaka, Y. Tajima, K. Sugiyama, F. Tomiyama, A. Yamagishi, M. Date, M. Hikita, Two-dimensional weak localization in electron high- T_c superconductor $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_y$ under high magnetic field, *Journal of the Physical Society of Japan*, 60 (1991) 1185-1188.
- [82] R. Kadono, K. Ohishi, A. Koda, W. Higemoto, K. M. Kojima, S.-i. Kuroshima, M. Fujita, K. Yamada, Magnetic ground state of $\text{Pr}_{0.89}\text{LaCe}_{0.11}\text{CuO}_{4+\alpha-\delta}$ with varied oxygen depletion probed by muon spin relaxation, *Journal of the Physical Society of Japan*, 72 (2003) 2955-2958.
- [83] M. Fujita, T. Kubo, S. Kuroshima, T. Uefuji, K. Kawashima, K. Yamada, I. Watanabe, K. Nagamine, Magnetic and superconducting phase diagram of electron-doped $\text{Pr}_{1-x}\text{LaCe}_x\text{CuO}_4$, *Physical Review B*, 67 (2003) 014514.
- [84] S. Li, S. Chi, J. Zhao, H.H. Wen, M.B. Stone, J.W. Lynn, P. Dai, Impact of oxygen annealing on the heat

capacity and magnetic resonance of superconducting $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$, *Physical Review B*, 78 (2008) 014520.

[85] A. Ikeda, O. Matsumoto, H. Yamamoto, T. Manabe, M. Naito, *RE* dependence of superconductivity in parent $\text{T}'\text{-RE}_2\text{CuO}_4$, *Physica C: Superconductivity*, 471 (2011) 686-689.

[86] H. Yamamoto, A. Tsukada, O. Matsumoto, M. Naito, Preparation of superconducting parent compounds $\text{T}'\text{-RE}_2\text{CuO}_4$ by molecular beam epitaxy, *Physica C: Superconductivity*, 470, Supplement 1 (2010) S88-S89.

[87] H. Yamamoto, O. Matsumoto, Y. Krockenberger, K. Yamagami, M. Naito, Molecular beam epitaxy of superconducting Pr_2CuO_4 films, *Solid State Communications*, 151 (2011) 771-774.

[88] Y. Krockenberger, M. Horio, H. Irie, A. Fujimori, H. Yamamoto, As-grown superconducting Pr_2CuO_4 under thermodynamic constraints, *Applied Physics Express*, 8 (2015) 053101.

[89] S. Ueda, S. Asai, M. Naito, Low temperature synthesis and superconducting properties of polycrystalline $\text{T}'\text{-(La,Sm)}_2\text{CuO}_4$, *Physica C: Superconductivity*, 470 (2010) 1173-1176.

[90] S. Asai, S. Ueda, M. Naito, Superconductivity in bulk $\text{T}'\text{-(La,Sm)}_2\text{CuO}_4$ prepared via a molten alkaline hydroxide route, *Physica C: Superconductivity*, 471 (2011) 682-685.

[91] Y. Imai, M. Kato, Y. Takarabe, T. Noji, Y. Koike, Low-temperature synthesis of La_2CuO_4 with the T' -structure from molten hydroxides, *Chemistry of Materials*, 19 (2007) 3584-3585.

[92] W.K. Ham, G.F. Holland, A.M. Stacy, Low-temperature synthesis of superconducting $\text{La}_{2-x}\text{M}_x\text{CuO}_4$: direct precipitation from NaOH/KOH melts, *Journal of the American Chemical Society*, 110 (1988) 5214-5215.

[93] W. Günther, R. Schöllhorn, Low temperature synthesis and properties of superconducting alkali substituted La_2CuO_4 phases, *Physica C: Superconductivity*, 203 (1992) 115-120.

[94] D. Sandford, L.N. Marquez, A.M. Stacy, Precipitation of superconducting, single phase $\text{EuBa}_2\text{Cu}_4\text{O}_8$ from molten hydroxide at 475 °C, *Applied Physics Letters*, 67 (1995) 422-423.

[95] J.L. Luce, A.M. Stacy, Crystallization of LnCu_2O_4 ($\text{Ln} = \text{La, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er}$) from hydroxide melts: synthesis and structure, *Chemistry of Materials*, 9 (1997) 1508-1515.

[96] W. Günther, W. Paulus, R. Schöllhorn, Correlation between synthesis, stoichiometry, structure and superconductivity of $\text{La}_{2-x}\text{K}_x\text{CuO}_{4-\delta}$, *Physica C: Superconductivity*, 312 (1999) 61-70.

[97] T. Takamatsu, M. Kato, T. Noji, Y. Koike, Low-temperature synthesis of $\text{T}'\text{-La}_2\text{CuO}_4$ using CaH_2 as reductant, *Physica C: Superconductivity*, 471 (2011) 679-681.

[98] M.I. Houchati, M. Ceretti, C. Ritter, W. Paulus, From T to $\text{T}'\text{-La}_2\text{CuO}_4$ via oxygen vacancy ordered $\text{La}_2\text{CuO}_{3.5}$, *Chemistry of Materials*, 24 (2012) 3811-3815.

[99] T. Takamatsu, M. Kato, T. Noji, Y. Koike, Undoped and hole-doped superconductors $\text{T}'\text{-La}_{1.8-x}\text{Eu}_{0.2}\text{Sr}_x\text{CuO}_4$ ($x = 0$ and 0.05) prepared by solid-state reaction, *Applied Physics Express*, 5 (2012) 073101.

[100] T. Takamatsu, M. Kato, T. Noji, Y. Koike, Superconductivity in hole-doped $\text{La}_{1.8-x}\text{Eu}_{0.2}\text{Ca}_x\text{CuO}_4$ with the Nd_2CuO_4 -type structure, *Physics Procedia*, 58 (2014) 46-49.

[101] J. Zaanen, G.A. Sawatzky, J.W. Allen, Band gaps and electronic structure of transition-metal compounds, *Physical Review Letters*, 55 (1985) 418-421.

[102] J.B. Torrance, P. Lacorre, C. Asavaroengchai, R.M. Metzger, Why are some oxides metallic, while most are insulating?, *Physica C: Superconductivity*, 182 (1991) 351-364.

- [103] W.A. Harrison, *Electronic Structure and the Properties of Solids*, W.H. Freeman and Company, 1979.
- [104] J.B. Goodenough, J. Zhou, Correlation bag and high- T_c superconductivity, *Physical Review B*, 42 (1990) 4276-4287.
- [105] S. Massidda, N. Hamada, J. Yu, A.J. Freeman, Electronic structure of Nd-Ce-Cu-O, a Fermi liquid superconductor, *Physica C: Superconductivity*, 157 (1989) 571-574.
- [106] C. Weber, K. Haule, G. Kotliar, Optical weights and waterfalls in doped charge-transfer insulators: A local density approximation and dynamical mean-field theory study of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, *Physical Review B*, 78 (2008) 134519.
- [107] C. Weber, K. Haule, G. Kotliar, Apical oxygens and correlation strength in electron- and hole-doped copper oxides, *Physical Review B*, 82 (2010) 125107.
- [108] C. Weber, K. Haule, G. Kotliar, Strength of correlations in electron- and hole-doped cuprates, *Nat Phys*, 6 (2010) 574-578.
- [109] H. Das, T. Saha-Dasgupta, Electronic structure of La_2CuO_4 in the T and T' crystal structures using dynamical mean field theory, *Physical Review B*, 79 (2009) 134522.
- [110] K.M. Kojima, Y. Krockenberger, I. Yamauchi, M. Miyazaki, M. Hiraishi, A. Koda, R. Kadono, R. Kumai, H. Yamamoto, A. Ikeda, M. Naito, Bulk superconductivity in undoped T'- $\text{La}_{1.9}\text{Y}_{0.1}\text{CuO}_4$ probed by muon spin rotation, *Physical Review B*, 89 (2014) 180508.
- [111] E. Morenzoni, T. Prokscha, A. Suter, H. Luetkens, R. Khasanov, Nano-scale thin film investigations with slow polarized muons, *Journal of Physics: Condensed Matter*, 16 (2004) S4583.
- [112] T. Prokscha, E. Morenzoni, K. Deiters, F. Foroughi, D. George, R. Kobler, A. Suter, V. Vrankovic, The new beam at PSI: A hybrid-type large acceptance channel for the generation of a high intensity surface-muon beam, *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 595 (2008) 317-331.
- [113] J.A. Skinta, M.-S. Kim, T.R. Lemberger, T. Greibe, M. Naito, Evidence for a transition in the pairing symmetry of the electron-doped cuprates $\text{La}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ and $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$, *Physical Review Letters*, 88 (2002) 207005.
- [114] T.R. Lemberger, *et al.*, unpublished.
- [115] H. Saadaoui, Z. Salman, H. Luetkens, T. Prokscha, A. Suter, W.A. MacFarlane, Y. Jiang, K. Jin, R.L. Greene, E. Morenzoni, R.F. Kiefl, The phase diagram of electron-doped $\text{La}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$, *Nat Commun*, 6 (2015).
- [116] H. Yamamoto, M. Naito, H. Sato, Surface stability of MBE-grown $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ thin films in air investigated by RHEED, XPS, and UPS, *Physica C: Superconductivity*, 291 (1997) 67-72.
- [117] G. Chanda, R.P.S.M. Lobo, E. Schachinger, J. Wosnitza, M. Naito, A.V. Pronin, Optical study of superconducting Pr_2CuO_x with $x \approx 4$, *Physical Review B*, 90 (2014) 024503.
- [118] A.V. Puchkov, D.N. Basov, T. Timusk, The pseudogap state in high- T_c superconductors: an infrared study, *Journal of Physics: Condensed Matter*, 8 (1996) 10049.
- [119] C.C. Homes, Q. Li, P. Fournier, R.L. Greene, Infrared optical properties of Pr_2CuO_4 , *Physical Review B*, 66 (2002) 144511.

- [120] T. Mutou, H. Kontani, Optical conductivity of bad metals: Shift of the Drude peak, *Physical Review B*, 74 (2006) 115107.
- [121] T. Timusk, B. Statt, The pseudogap in high-temperature superconductors: an experimental survey, *Reports on Progress in Physics*, 62 (1999) 61.
- [122] Y. Onose, Y. Taguchi, K. Ishizaka, Y. Tokura, Charge dynamics in underdoped $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$: Pseudogap and related phenomena, *Physical Review B*, 69 (2004) 024504.
- [123] A. Zimmers, J.M. Tomczak, R.P.S.M. Lobo, N. Bontemps, C.P. Hill, M.C. Barr, Y. Dagan, R.L. Greene, A.J. Millis, C.C. Homes, Infrared properties of electron-doped cuprates: Tracking normal-state gaps and quantum critical behavior in $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$, *EPL (Europhysics Letters)*, 70 (2005) 225.
- [124] N.P. Breznay, R.D. McDonald, Y. Krockenberger, K.A. Modic, Z. Zhu, I.M. Hayes, N.L. Nair, T. Helm, H. Irie, H. Yamamoto, J.G. Analytis, Quantum oscillations suggest hidden quantum phase transition in the cuprate superconductor $\text{Pr}_2\text{CuO}_{4\pm\delta}$, *arXiv:1510.04268*, (2015).
- [125] W. Yu, B. Liang, P. Li, S. Fujino, T. Murakami, I. Takeuchi, R.L. Greene, Oxygen-doped Mott-Hubbard cuprate superconductor $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_{4-\delta}$ from transport measurements, *Physical Review B*, 75 (2007) 020503.
- [126] L. Zhao, G. Wu, R.H. Liu, X.H. Chen, Intrinsic electron doping in nominal “nondoped” superconducting $(\text{La},\text{Y})_2\text{CuO}_4$ thin films grown by magnetron sputtering, *Applied Physics Letters*, 90 (2007) 072503.
- [127] C. Kittel, *Quantum Theory of Solids*, 1963.
- [128] J.M. Ziman, *Electrons and Phonons*, (1960).
- [129] W. Jiang, S.N. Mao, X.X. Xi, X. Jiang, J.L. Peng, T. Venkatesan, C.J. Lobb, R.L. Greene, Anomalous Transport Properties in Superconducting $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4\pm\delta}$, *Physical Review Letters*, 73 (1994) 1291-1294.
- [130] P. Monthoux, A.V. Balatsky, D. Pines, Weak-coupling theory of high-temperature superconductivity in the antiferromagnetically correlated copper oxides, *Physical Review B*, 46 (1992) 14803-14817.
- [131] T. Moriya, Y. Takahashi, K. Ueda, Antiferromagnetic spin fluctuations and superconductivity in two-dimensional metals -a possible model for high T_c oxides, *Journal of the Physical Society of Japan*, 59 (1990) 2905-2915.
- [132] F.C. Zhang, T.M. Rice, Effective Hamiltonian for the superconducting Cu oxides, *Physical Review B*, 37 (1988) 3759-3761.
- [133] A.P. Drozdov, M.I. Eremets, I.A. Troyan, V. Ksenofontov, S.I. Shylin, Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system, *Nature*, 525 (2015) 73-76.

Figure captions

Fig. 1. Early electronic phase diagram, the T_c -vs- x and T_N -vs- x curves, for $T\text{-La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $T'\text{-Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. SC: superconducting phase, AFM: antiferromagnetic phase, and SG: spin glass phase. It was believed that the parent compounds, $T\text{-La}_2\text{CuO}_4$ and $T'\text{-Nd}_2\text{CuO}_4$, are an antiferromagnetic insulator and the superconductivity develops by the doping of holes (Sr) or electrons (Ce). The T_c -vs- x curves in both of the hole- and electron-doped sides show a well-known ‘dome’ shape with maximal superconductivity at a doping level of about 0.15 and are roughly symmetrical. The T_N -vs- x in $T'\text{-Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ is plotted for both of “reduced” (solid line) and “as-grown” (broken line) samples. Adapted from Ref. [4].

Fig. 2. Comparison of the resistivity between $T\text{-La}_2\text{CuO}_4$ and $T'\text{-La}_2\text{CuO}_4$.

Fig. 3. Oxygen defects in T' cuprates: (a) excess oxygen ions residing at the apical site, (b) no defect, and (c) oxygen vacancies created in the CuO_2 plane.

Fig. 4 Ce doping dependence of T_c in $T'\text{-Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ obtained by Brinkmann *et al.* The T_c -vs- x by the improved (solid line) and standard (broken line) reduction are compared. With the improved reduction, the superconducting window expands down to $x = 0.04$ and there is a clear tendency of an increasing T_c with decreasing x . Adapted from Ref. [22].

Fig. 5 Summary of T_c -vs- x for MBE-grown $T'\text{-RE}_{2-x}\text{Ce}_x\text{CuO}_4$ films with various RE . The symbols represent T_c^{zero} , and the dashed lines T_c^{onset} .

Fig. 6 Superconductivity in $T'\text{-La}_{2-x}\text{RE}_x\text{CuO}_4$ films grown by MBE: (a) temperature dependence of resistivity and diamagnetic signal (inset), (b) RE concentration dependence of T_c for $T'\text{-La}_{2-x}\text{RE}_x\text{CuO}_4$ films. The T_c is defined as the zero resistance temperature. Symbols denote RE 's as follows: Sm (◆), Eu (●), Gd (■),

Tb (▲), Lu (▼), and Y (□).

Fig. 7 Resistivity versus temperature of T'-Nd₂CuO₄ synthesized by MOD. The T_c^{onset} is higher than 30 K.

Fig. 8 T_c -versus- x of Nd_{2-x}Ce_xCuO₄ films prepared by MOD. For a comparison, the data of bulk samples (broken line) and MBE films (triangles) are also plotted. Open and filled symbols represent T_c^{onset} and T_c^{end} . The solid line is a guide for eye.

Fig. 9 Three crystal structures of rare-earth copper oxides: (a) K₂NiF₄ (abbreviated as T), (b) T*, and (c) Nd₂CuO₄ (abbreviated as T') structures.

Fig. 10 Phase relationships for the system La_{2-y}Nd_yCuO₄ obtained by Manthiram and Goodenough. The vertical axis is the firing temperature and the horizontal axis is y . The T' phase is stabilized to higher y with lowering a firing temperature, which is in accord with the prediction of “thermal expansion mismatch”. The T'' phase is slightly different from the T' phase and is a line phase, La₃NdCu₂O₈, at $y = 0.5$. The shaded area around 850-1050°C and $y \sim 0.5$ represents a non-equilibrated region consisting of T/O, T', and T''. Adapted from Ref. [35].

Fig. 11 Phase diagram of the selective stabilization of T versus T' for La₂CuO₄ films in the T_s - a_s plane. Symbols denote the phases as follows: T (◊), T' (□), and T* (Δ). The T' phase is stabilized in the grey area whereas the T* phase is stabilized in the hatched area ($a_s \sim 3.9$ Å, $T_s = 475$ -575°C).

Fig. 12 Overview of the Ce concentration dependence of the lattice constants (a_0 : lower and c_0 : upper) in T'-RE_{2-x}Ce_xCuO₄.

Fig. 13 Decomposition lines of K₂NiF₄-type or Nd₂CuO₄-type transition-metal (Co, Ni, and Cu) oxides in a comparison with simple transition-metal oxides in the p_{O_2} - $1/T$ plane.

Fig. 14 (a) Overview of the decomposition lines for T'-RE₂CuO₄ and T'-RE_{1.85}Ce_{0.15}CuO₄ (RE = Nd, Sm, and Eu). One can see two trends: (1) the T' phase is more stable

with larger RE^{3+} and (2) the T' phase is more stable with substitution of Ce^{4+} for RE^{3+} . The thermodynamic data are taken from Ref. [50, 54]. (b) Coordination of cations around oxygen ions in the CuO_2 plane, from which those trends can be understood qualitatively.

Fig. 15 Oxygen sites in T' cuprates: O1 in the CuO_2 layer, O2 in the fluorite layer, and interstitial O_{ap} at the apical site.

Fig. 16 Comparison of the ρ - T curves for optimally reduced and insufficiently reduced T'- $La_{1.9}Ce_{0.1}CuO_4$ films. Insufficient reduction results in higher resistivity with a low-temperature upturn and in reduced (or no) T_c , both of which seem to be caused by the Kondo effect. It is speculated that Cu^{2+} , which is otherwise nonmagnetic, is driven to be magnetic by the presence of an interstitial O_{ap} ion just above as shown in the inset.

Fig. 17 Behavior of the low-temperature resistivity under magnetic fields in underdoped T' cuprates: (a) nonsuperconducting $Pr_{1.902}Ce_{0.098}CuO_4$ and (b) superconducting $Nd_{1.869}Ce_{0.131}CuO_4$ grown by MBE. The resistivity upturn at low temperatures has a $\log$ - T dependence but saturates to a finite value toward lowest temperatures. In addition, the upturn is suppressed in magnetic fields ($\log$ - B -dependent negative magnetoresistance). From Ref. [77].

Fig. 18 Comparison of the ρ - T curves for two T'- Sm_2CuO_4 thin films. Nonsuperconducting film A was fired at 900°C for 1 h in $p_{O_2} = 1$ atm followed by at 750°C for 10 min whereas superconducting film B was fired at 850°C for 1 h in $p_{O_2} = 2.8 \times 10^{-3}$ atm followed by reduction at 440°C for 10 min. From Ref. [77].

Fig. 19 Reduction dependence of structural and transport properties of T'- Sm_2CuO_4 films: (a) c_0 as a function of T_{red} and (b) variation of ρ - T with T_{red} . The solid line in (a)

represents the c -axis length of bulk samples. From Ref. [86].

Fig. 20 Overview of the RE dependence of superconductivity in $T'-RE_2CuO_4$. The T_c and $\rho(300\text{ K})$ are plotted against c_0 for all RE_2CuO_4 films prepared by MOD. The filled and open symbols in the upper figure correspond to T_c^{end} and T_c^{onset} , respectively. The filled symbols, open symbols, and crosses in the lower figure represent films showing zero resistance, showing only an onset of superconductivity, and showing no trace of superconductivity, respectively. The shaded window represents the range of c_0 of films that showed a full superconducting transition for each RE . The dotted lines are a guide for the eye. From Ref. [86].

Fig. 21 Temperature dependence of resistivity for the best $T'-RE_2CuO_4$ films ($RE = \text{Pr, Nd, Sm, Eu, Gd, and Tb}$) synthesized by MOD. The inset is an enlarged view of superconducting transitions. From Ref. [86].

Fig. 22 Schematic two-step annealing path for superconducting RE_2CuO_4 ($RE = \text{Pr or Nd}$), which is compared with the standard annealing path for Ce-containing $RE_{2-x}Ce_xCuO_4$. The MBE growth temperature is $650\text{--}750^\circ\text{C}$. Our standard annealing for $RE_{2-x}Ce_xCuO_4$ is carried out at temperatures between 550 and 650°C under 10^{-9} Torr. In the two-step annealing process, RE_2CuO_4 is annealed *ex situ* first at $750\text{--}850^\circ\text{C}$ and $\sim 8 \times 10^{-2}$ Torr O_2 and subsequently annealed at temperatures between 450 and 700°C under high vacuum. In (b), the details of the temperature and p_{O_2} profiles are shown for the synthesis of superconducting $Nd_{1.85}Ce_{0.15}CuO_4$ (black) and Nd_2CuO_4 (red) thin films. $Nd_{1.85}Ce_{0.15}CuO_4$ was grown by O_3 and Nd_2CuO_4 by O^* (RF-activated atomic O). For $Nd_{1.85}Ce_{0.15}CuO_4$ the standard *in situ* annealing process is performed and for Nd_2CuO_4 a two-step annealing process is employed to induce superconductivity.

Fig. 23 (a) Speculated copper-oxygen configurations in the CuO_2 planes in RE_2CuO_4 ($\text{RE} = \text{Pr}$ or Nd) during our two-step annealing procedure. In the as-grown state, apical sites of copper are randomly occupied. During the first high- T annealing step, not apical but regular oxygen sites of the CuO_2 planes are being evacuated. During the second annealing step, the defective CuO_2 plane is being “healed” by an oxygen rearrangement from the apical sites to regular in-plane sites (shrinkage of c -axis). Evolution of the ρ - T curves are shown in (b)–(d) and lattice constants after each synthesis step in (e)–(g). The in-plane lattice constant (a_0) remains constant throughout the annealing process while that of c -axis (c_0) shows an abrupt drop after the second step.

Fig. 24 (a) Map of temperatures at which Pr_2CuO_4 thin films were synthesized on (001)(LaAlO_3)_{0.3}($\text{Sr}_2\text{AlTaO}_6$)_{0.7} (LSAT), (001) SrTiO_3 (STO), (110) DyScO_3 (DSO), (110) TbScO_3 (TSO), (110) GdScO_3 (GSO), (110) SmScO_3 (SSO), (110) NdScO_3 (NSO), and (110) PrScO_3 (PSO) substrates. In (b), the ρ - T curve of Pr_2CuO_4 grown coherently on (110) GdScO_3 is shown by a red line. For comparison, the ρ - T of Pr_2CuO_4 grown on (001) SrTiO_3 and treated by two-step annealing is also shown by a dashed line. The inset shows the resistivity as a function of temperature when the magnetic field is increased from 0 to 3.5 T in increments of 0.5 T.

Fig. 25 Comparison of electrical conductivity in T -, T' -, and T^* - La_2CuO_4 . T - and T^* - La_2CuO_4 are an insulator whereas T' - La_2CuO_4 is a superconductor.

Fig. 26 Zero-field-cooled magnetization for reduced $T'-La_{2-x}Sm_xCuO_4$ powder samples in applied field of 0.5 mT. $T'-La_{2-x}Sm_xCuO_4$ powder samples were synthesized via a molten-alkaline hydroxide route. From Ref. [91].

Fig. 27 Superconducting properties of $T'-La_{2-x}Sm_xCuO_4$ samples: (a) superconducting volume fraction at 5 K and (b) T_c plotted as a function of x . The circles and squares represent the samples reduced for 48 h and 96 h, respectively. Most of samples were synthesized in flowing pure N_2 whereas one sample with $x = 0.05$ showing an improved superconducting volume fraction was synthesized in air. From Ref. [91].

Fig. 28 Ionic model for copper oxides. The Coulomb energy (U_0') is the energy required for transferring an electron at Cu^{2+} to the neighboring Cu^{2+} site whereas the charge transfer energy (Δ_0) is the energy required for transferring an electron at O^{2-} to the neighboring Cu^{2+} site.

Fig. 29 Schematic diagram of the relative energies of the oxygen and metal states in the ZSA framework. Five examples are shown with different relative values of Δ , U' , and W , which are defined in the figure. Adapted from Ref. [102].

Fig. 30 (a) Madelung potential energies, $-eV_M(Cu)$ and $-eV_M(O)$, and charge transfer energy, Δ_0 , for $T'-RE_2CuO_4$. The values for T- and $T^*-La_2CuO_4$ are also included. RE^{3+} is surrounded by eight O^{2-} in the T' structure and by nine O^{2-} in the T structure, so $r_i^{VIII}(RE^{3+})$ is used for T' and $r_i^{IX}(RE^{3+})$ is used for T in the horizontal axis. In $T^*-La_2CuO_4$, there are two La sites with eight and nine oxygen coordinations, and the

average of $r_i^{\text{VIII}}(\text{La}^{3+})$ and $r_i^{\text{IX}}(\text{La}^{3+})$ was used. (b) Comparison of the of the Cu and O energy levels in T'- and T-La₂CuO₄ based on (a). The Cu3 $d_{x^2-y^2}$ levels in T'-La₂CuO₄ are lowered relatively to those in T-La₂CuO₄.

Fig. 31 Semi-empirical variation of M^{2+} energy levels relative to the $M4s$ conduction and $O2p$ valence bands for the first-row transition-metal (M) oxides. Adapted from Ref. [104].

Fig. 32 (a) Schematic illustration for the hybridization of Cu3 $d_{x^2-y^2}$, $O2p_x$, and $O2p_y$ orbitals. (b) Energy bands for T'-Nd₂CuO₄ calculated using APW by Massidda et al. [106]. The Cu3 $d_{x^2-y^2}$ - $O2p_{x,y}$ bonding (σ) and antibonding (σ^*) bands are indicated by thick broken lines. (c) Resultant Fermi surface. The Fermi surface is hole-like and has a rounded square shape centered around the X point (see the notation of the symmetry points of the Brillouin zone of the body-centered tetragonal lattice in the upper of (c)). Adapted from Ref. [105] for (b) and (c).

Fig. 33 (a) Experimental configuration in TF- μ SR. An incident muon ($//z$) with an initial muon polarization $\mathbf{P}_\mu(0)$ ($//x$) stops in the films at some depth (d_p) depending on the implantation energy. The muon implantation depth, d_p , was evaluated as a function of the implantation energy from the muon depth distribution calculated by a Monte Carlo code. In TF- μ SR, a weak magnetic field ($B_0 = 7$ mT) ($//y$) is applied parallel to the T'-LYCO film surface and the field is attenuated inside the film by the Meissner effect. $\mathbf{P}_\mu(t)$ rotates around this local field by Larmor precession, whose angular frequency is proportional to the magnetic field at the position, where muon stopped. This situation, although somewhat exaggerated, is illustrated in the upper part in (a). (b) Typical examples of TF- μ SR time spectra observed in the superconducting state of Ag-coated T'-LYCO thin films (at 5 K) with $E_\mu = 10$ keV and 23 keV. (c) Mean local field B vs depth d_p in LYCO probed by μ SR under an external field $\mu_0 H \approx 7$ mT, where filled circles are data at 5 K ($< T_c$) and open squares are those at 25 K ($> T_c$). (d) Nonmagnetic volume fraction, f_p , determined by TF-(filled circles) and ZF- μ SR (filled squares) as a function of d_p in LYCO (open

circles denote the f_p value corrected by the presence of a coated Ag layer). The dashed line corresponds to the boundary between Ag coating and LYCO. (e) ZF- μ SR time spectra observed in LYCO at 5 K with various muon implantation depth (d_p). Adapted from Ref. [111].

Fig. 34 (a) Real part of the optical conductivity of a superconducting Pr_2CuO_4 film as a function of frequency for various temperatures listed in the legend. Dots on the left-hand axis of the main panel represent the DC-conductivity values. (b) Decomposition of the real part of the optical conductivity, $\sigma_1(\omega)$, at 30 K (left panel) and 300 K (right panel). Adapted from Ref. [117].

Fig. 35 Cartoon of spin-mediated pairing in the case of itinerant electrons.

Table I. RE dependence of the optimum doping level (x_{opt}) and the highest T_c (T_c^{max}) for MBE-grown $T'-RE_{2-x}\text{Ce}_x\text{CuO}_4$.

RE	x_{opt}	T_c^{max} [K]
La	0.08	31.0
Pr	0.135	27.0
Nd	0.140	25.5
Sm	0.150	19.0
Eu	0.155	12.0
Gd	—	0.0

Table II. RE dependence of T_c (T_c^{onset} and T_c^{end}) for $T'-RE_2\text{CuO}_4$ synthesized by MOD.

RE	T_c^{onset} [K]	T_c^{end} [K]
Pr	30.5	25.8
Nd	32.8	29.4
Sm	30.7	25.4
Eu	28.9	18.2
Gd	18.5	7.2
Tb	< 4.2	< 4.2

Table III. Tolerance factors for T stability calculated from Eq. (1).

RE^{3+}	$r_i^{\text{IX}}(RE^{3+}) [\text{\AA}]$	tolerance factor t_0
La ³⁺	1.216	0.8685
Ce ³⁺	1.196	0.8618
Pr ³⁺	1.179	0.8562
Nd ³⁺	1.163	0.8509
Pm ³⁺	1.144	0.8445
Sm ³⁺	1.132	0.8406
Eu ³⁺	1.120	0.8366
Gd ³⁺	1.107	0.8323
Tb ³⁺	1.095	0.8283
Dy ³⁺	1.083	0.8243
Ho ³⁺	1.072	0.8206
Er ³⁺	1.062	0.8173
Tm ³⁺	1.052	0.8140
Yb ³⁺	1.042	0.8107
Lu ³⁺	1.032	0.8074
Y ³⁺	1.075	0.8216

Table IV. Lattice parameters (a_0 and c_0) of $T'-RE_2CuO_4$ with different RE . The values for La are taken from Ref. [16] whereas those for other RE are from Ref. [31].

	$a_0[\text{\AA}]$	$c_0[\text{\AA}]$
La	4.026	12.496
Pr	3.958	12.288
Nd	3.943	12.163
Sm	3.905	11.929
Eu	3.894	11.882
Gd	3.888	11.859
Tb	3.880	11.815
Dy	3.869	11.771
Ho	3.861	11.721
Er	3.840	11.637
Tm	3.830	11.578
Y	3.861	11.721

Table V. Structural parameters (atomic position (z) and occupancy (n)) determined by the powder neutron diffraction [63] on oxygenated and reduced $\text{Nd}_{1.9}\text{Ce}_{0.1}\text{CuO}_{4+\delta}$. The atomic positions are: Nd $4e[0,0,z]$; Cu $2a[0,0,0]$; O1 $4c[1/2,0,0]$; O2 $4d[0,1/2,1/4]$; O_{ap}

atom	z/n	oxygenated	reduced
Nd	z	0.3513	0.3516
	n	2	2
Cu	n	1	1
O(1)	n	1.96	1.94
O(2)	n	1.91	1.91
O(3)	z	0.202	0.205
	n	0.10	0.04

Table VI. Process parameters to synthesize T' cuprate films by MOD.

MO	RE and Cu naphthenates
substrates	$\text{DyScO}_3(110)$ for $RE = \text{Pr, Nd}$
	$\text{SrTiO}_3(001)$ for $RE = \text{Nd, Sm, Eu, Gd}$
calcination	400°C/30 min/in air
firing	850-900°C/60 min/in N_2/O_2 mixture ($p_{\text{O}_2} = 10^{-4} \sim 10^{-2}$ atm)
reduction	400-450°C/10 min/in vacuum

Table VII. Synthesis and reduction conditions for T' - $\text{La}_{2-x}\text{Sm}_x\text{CuO}_4$ [91].

x	T_s ($^{\circ}\text{C}$)	T_{red} ($^{\circ}\text{C}$)
0.0	400	600
0.05	400	650
0.1	400	700
0.2	400	700
0.3	400	700
0.4	400	700
0.5	400	650
0.6	420	700
0.7	440	700
0.8	440	700
0.9	440	700
1.0	440	700
1.3	440	700
1.5	440	700
2.0	480	750

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