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Electron Doping of the Parent Cuprate La_2CuO_4 without Cation Substitution

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In the cuprates, carrier doping of the Mott insulating parent state is necessary to realize superconductivity as well as a number of other exotic states involving charge or spin density waves. Cation substitution is the primary method for doping carriers into these compounds, and is the only known method for electron doping in these materials. Here, we report electron doping *without* cation substitution in epitaxially stabilized thin films of La_2CuO_4 grown via molecular-beam epitaxy. We use angle-resolved photoemission spectroscopy to directly measure their electronic structure and conclusively determine that these compounds are electron doped with a carrier concentration of $0.09 \pm 0.02 e^-/\text{Cu}$. We propose that intrinsic defects, most likely oxygen vacancies, are the sources of doped electrons in these materials. Our results suggest a new approach to electron doping in the cuprates, one which could lead to a more detailed experimental understanding of their properties.

In quantum many-body systems, exotic phenomena are typically realized through carrier doping. One example is in the cuprates, where high- T_c superconductivity arises via doping of a Mott insulating parent state [1]. Carrier doping in the cuprates, as in many other strongly correlated systems, is typically achieved through cation substitution, e.g. divalent Sr^{2+} cations for trivalent La^{3+} cations in p -type $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [2] or tetravalent Ce^{4+} cations for trivalent cations in n -type $\text{R}_{2-x}\text{Ce}_x\text{CuO}_4$ ($R=\text{La}, \text{Nd}, \text{Pr}, \text{Sm}, \text{Eu}$) [3–5]. Cation substitution doping, however, introduces disorder at the dopant site which can reduce T_c [6, 7] and prevent the use of disorder-sensitive techniques such as measurements of magnetic quantum oscillations in studying these compounds. In hole-doped cuprates, this limitation can be overcome by doping through control of oxygen stoichiometry rather than cation substitution, which can result in less disordered samples that allow the use of quantum oscillations to study compounds such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [8, 9], $\text{YBa}_2\text{Cu}_4\text{O}_8$ [10, 11], $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [12], and $\text{HgBa}_2\text{CuO}_{4+\delta}$ [13] to achieve a deeper understanding of the cuprate phase diagram. In the electron-doped cuprates, however, cation substitution remains the only reported pathway to carrier doping.

The necessity of doping in achieving superconductivity and the validity of the doped Mott insulator paradigm in the n -type cuprates has recently been called into question by work on epitaxial thin films of nominally undoped RE_2CuO_4 ($\text{RE} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$) synthesized in the so-called T' phase [14–16]. The authors have observed metallic and even superconducting behavior in the absence of cation doping, a scenario which may be consistent with dynamical mean field theory (DMFT) studies

showing that the parent T' compounds may be better described as weakly correlated Slater insulators rather than strongly correlated charge transfer insulators [17, 18].

Here, we report electron doping without cation substitution in epitaxially stabilized thin films of La_2CuO_4 grown by reactive oxide molecular-beam epitaxy (MBE). We employ angle-resolved photoemission spectroscopy (ARPES) to measure the electronic structure and directly determine the carrier concentration of these thin films, confirming their electron doped nature. We also demonstrate that the carrier concentration can be controlled by compensating electron carriers with doped holes by substituting Sr^{2+} for La^{3+} , driving the system back into a Mott insulating state. We propose that intrinsic defects, most likely oxygen vacancies, are sources of the as-grown electron carriers. This work rules out the possibility of intrinsic metallic behavior in seemingly undoped thin films due to the collapse of the Mott gap in the T' structure.

Bulk La_2CuO_4 typically crystallizes in a body-centered tetragonal structure, also called the T phase, shown in Fig. 1e. In this structure, the Cu atoms are six-fold coordinated with oxygen atoms – four in-plane and two in the out-of-plane apical positions. This T -phase compound is the parent of p -type cuprates such as $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ [1] and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [2]. Via epitaxy, it is also possible to stabilize another polymorph of La_2CuO_4 in which the Cu atoms are only four-fold coordinated with in-plane oxygens, without any apical oxygens [15, 19]. This structure, shown in Fig. 1a, is also called the T' phase and is the parent structure for virtually all of the known n -type cuprate superconductors, with $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ being the canonical example [3, 4].

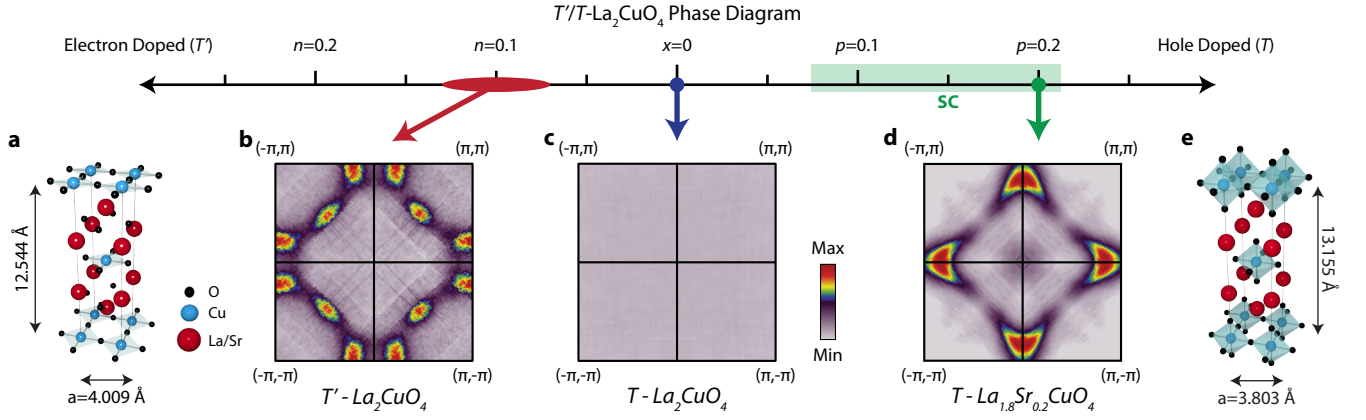


FIG. 1. Structure of (a) T' - La_2CuO_4 and (e) T - La_2CuO_4 . (b)-(d) Fermi surface maps of (b) as-grown T' - La_2CuO_4 , (c) undoped T - La_2CuO_4 , and (d) T - $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ ($T_c=27\text{K}$). All maps show integrated spectral weight within $E_F \pm 25$ meV, with (b) and (d) measured at 30 K and (c) at 180 K.

We have synthesized $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in both the T and T' phases using a Veeco GEN10 MBE system, using *in situ* reflection high energy electron diffraction (RHEED) to monitor the growths. The large difference in the in-plane lattice constants of the T (3.803 Å) and T' (4.009 Å [20]) phases enables control of the phase during growth via epitaxial stabilization[21, 22]. (001) oriented T - La_2CuO_4 films were grown on (001) LaSrAlO_4 ($a=3.75$ Å), and (001) oriented T' - La_2CuO_4 films were grown on (001)_p PrScO_3 ($a_p=4.021$ Å), where p indicates pseudocubic indices [(110) oriented with respect to orthorhombic indices]. All samples were terminated with a single LaO layer to mimic the termination of a cleaved single crystal surface. Shuttered layer-by-layer deposition was performed in distilled ($\approx 80\%$) O_3 at a background pressure of 1×10^{-6} torr for the T phase and in the range of 1×10^{-7} torr to 2×10^{-6} torr for the T' phase. Immediately following growth, samples were transferred within 300 s under ultra-high vacuum ($< 5 \times 10^{-10}$ torr) into the ARPES measurement chamber. ARPES measurements were performed with a VG Scienta R4000 electron spectrometer and a VUV5000 helium plasma discharge lamp and monochromator. He-I α (21.2 eV) photons were used for the T phase and infinite-layer $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ and He-II α (40.8 eV) photons were used for the T' phase samples. The base pressure of the ARPES system is 5×10^{-11} torr. Following ARPES measurements, samples were characterized via x-ray diffraction, resistivity, and x-ray photoelectron spectroscopy, whose results, along with the *in situ* RHEED measurements, are shown in the Supplemental Materials [23].

In Fig. 1b-1d we present Fermi surface maps of both T and T' phase cuprates measured using *in situ* ARPES, with spectral weight integrated within $E_F \pm 25$ meV and four-fold symmetrized. In Fig. 1c, we see that undoped T - La_2CuO_4 , the canonical parent cuprate Mott insulator, exhibits no appreciable spectral weight near E_F ,

while Fig. 1d shows that hole-doped T - $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ ($T_c=27$ K) has a large Fermi surface centered at $k = (0, 0)$, both consistent with earlier ARPES data from single crystals at similar Sr concentrations [24–26]. In Fig. 1b, we show the Fermi surface of as-grown T' - La_2CuO_4 synthesized in 1×10^{-7} torr of distilled O_3 , which shows clear weight at E_F and a well-defined Fermi surface, unexpected for a nominally undoped Mott insulator. In contrast, ARPES measurements on single crystals of undoped T' - Nd_2CuO_4 [27] as well as thin films of SrCuO_2 [28] show the expected insulating behavior qualitatively consistent with their T -phase counterparts, with no appreciable spectral weight near E_F and well-defined lower Hubbard bands.

More careful examination of the Fermi surface of as-grown T' - La_2CuO_4 reveals distinctive variations in spectral weight around the Fermi surface, as shown in Fig. 2. This intensity modulation is a hallmark of the electron-doped cuprates, widely reported in numerous single crystal doped T' cuprates [30–32] as well as MBE-synthesized thin film samples of $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ [29], shown in Fig. 2b for comparison. The modulation is understood to be a result of (π, π) antiferromagnetic ordering or fluctuations in the CuO_2 plane which cause a doubling of the unit cell and a subsequent reconstruction of the Fermi surface [31–33], shown schematically in Fig. 2d. The reconstruction creates folded electron-like (blue) and hole-like (red) bands, causing the observed intensity modulation. The reconstructed electronic structure is better seen in Fig. 3a, represented by the contour lines based on the ARPES image data shown. In the case of T' - La_2CuO_4 , we note that the hole-like band lies fully below the Fermi level, as can be seen in Fig. 3b and presented in more detail in the Supplemental Materials [34]. The intensity near $(\pi/2, \pi/2)$ is due to residual spectral weight of the broad hole-like band rather than a true Fermi crossing. We find the maximum of the hole-like band to be at 50

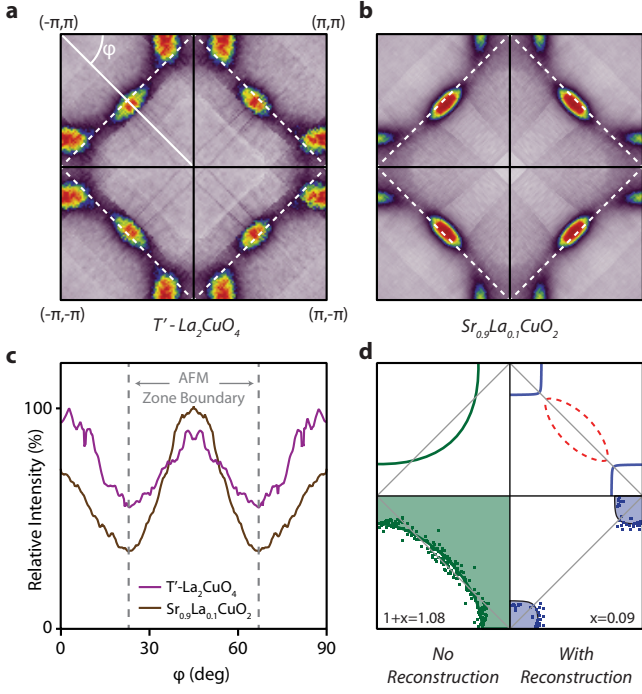


FIG. 2. (Color Online) Fermi surface maps of (a) T' - La_2CuO_4 and (b) $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ (spectral weight integrated within $E_F \pm 30$ meV, measured at 10 K) [29]. (c) Variation of spectral weight intensity along the Fermi surfaces as a function of ϕ . (d) Schematic of the Fermi surface before (left) and after (right) the (π, π) reconstruction, showing the extracted k_F s used to calculate the Luttinger count assuming an unreconstructed (lower left) or reconstructed (lower right) Fermi surface.

± 10 meV binding energy, as determined by the position of the peak in the energy distribution curve (EDC). As a result, the only states which cross E_F are the electron pockets around the $(\pi, 0)$ and $(0, \pi)$ points (Fig. 3c), suggesting the sample must be electron doped. A similar gapping of the hole pocket has also been reported in other electron-doped cuprates such as T' - $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_4$ [32], T' - $\text{Eu}_{2-x}\text{Ce}_x\text{CuO}_4$ [35], and $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ [29].

In order to quantitatively estimate the carrier concentration, we have determined the Luttinger count using the measured Fermi surface, as shown in Fig. 2d (more details in Supplemental Materials [36]). In the reconstructed Fermi surface, whose volume scales as the doping x , the hole pocket lies completely below E_F , so only the electron pockets contribute carriers, giving a doping of $0.09 \pm 0.02 e^-/\text{Cu}$. We also consider the case of an unreconstructed Fermi surface in the absence of (π, π) folding, where now the Fermi surface volume scales as $(1+x)$. We use maxima in the momentum distribution cuts (MDC) taken across the Fermi surface to determine k_F , ignoring the fact that the hole pocket around $(\pi/2, \pi/2)$ does not cross E_F . This method gives a similar doping of $0.08 \pm 0.02 e^-/\text{Cu}$, leading us to conclude

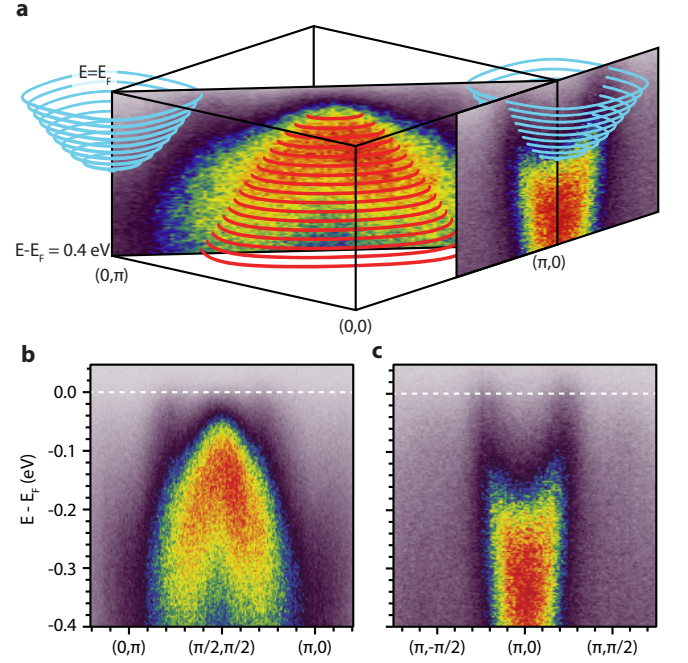


FIG. 3. (Color Online) (a) Schematic of the electronic structure of T' - La_2CuO_4 , with the contour plots showing the shape of the electron-like (blue) and hole-like (red) bands. Image plots show ARPES data along (b) $(0, \pi)$ - $(\pi, 0)$ and (c) $(0, 0)$ - $(\pi, 0)$. The difference in intensity of the electron pocket along different cut directions is due to changes in the photoelectron matrix elements with sample rotation.

that as-grown T' - La_2CuO_4 is in fact non-stoichiometric and clearly electron-doped.

We also demonstrate control over the carrier density in T' - La_2CuO_4 by substituting Sr^{2+} for La^{3+} to compensate the as-grown mobile electron carriers in order to drive the material back into a Mott insulator. Figures 4b and 4c show background-subtracted [37] representative EDCs taken at $(\pi/2, \pi/2)$ of T' - $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ (c) compared to that of T' - La_2CuO_4 (b). In the Sr-substituted sample, the near- E_F spectral weight has been almost entirely suppressed compared to the unsubstituted sample. In addition, a lower Hubbard band (LHB) peak is recovered around 1.7 eV binding energy, in contrast to the unsubstituted sample where there is no such feature (the rising tail below 1.5 eV is attributed to the oxygen 2p valence band). The suppression of the LHB is also consistent with what has been observed in single crystals of the T' cuprates such as $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ as a function of doping [27]. Furthermore, the chemical potential of the Sr-substituted sample is shifted towards lower binding energy by 180 meV relative to the unsubstituted sample, as seen in both the O 2p valence band as well as the Cu 2p core level spectra (see Supplemental Material [38]). This indicates that the suppression of spectral weight does not arise from disorder, but rather from a reduction in the carrier concentration in the Sr-

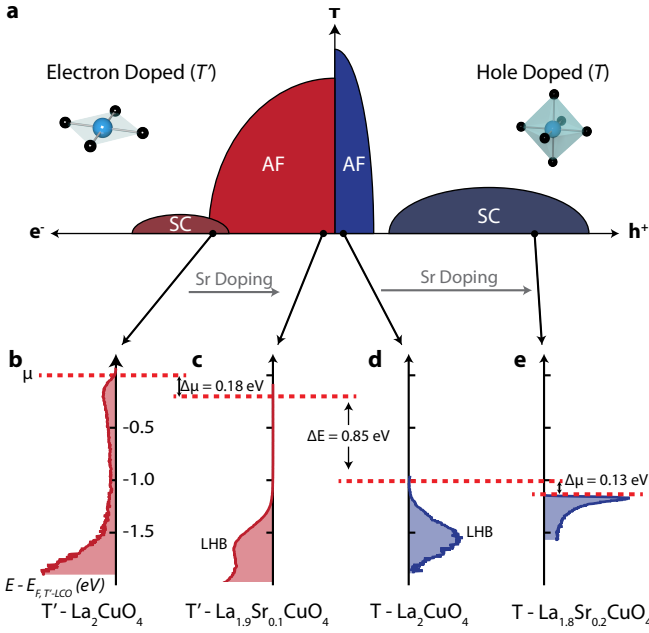


FIG. 4. (a) Schematic phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$. (b)-(e) Representative EDCs after background subtraction at $(\pi/2, \pi/2)$ for (b)-(d) and $(\pi, 0)$ for (e). LHB indicates the lower Hubbard bands and $\Delta\mu$ the relative shift of the chemical potential between different compounds. ΔE indicates the difference in locations of the chemical potential of the T' and T Mott insulating phases when the energies of the lower Hubbard bands are aligned.

substituted samples. These observations, taken together, clearly demonstrate the recovery of the parent Mott insulating state following Sr substitution, indicating the presence of doped electrons in the as-grown T' - La_2CuO_4 samples. By comparing to the representative EDC of Mott insulating T - La_2CuO_4 , we also see that the chemical potential is pinned to the bottom of the upper Hubbard band for T' - $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ and to the top of the lower Hubbard band in T - La_2CuO_4 , as expected for their respective n - and p -type dopants. Utilizing a combination of structural and doping control, we have been able to reach the entire phase diagram of both hole-doped as well as electron-doped La_2CuO_4 , as illustrated in Fig. 4.

Finally, we discuss possible origins for the doped electrons in as-grown T' - La_2CuO_4 . In earlier studies of nominally undoped thin films of T' - R_2CuO_4 [14, 16, 39], it was speculated that the observed metallic and superconducting behaviors may originate from the collapse of the Mott gap, possibly caused by weakened correlations in the T' phase. It has been suggested by DMFT calculations [17, 18] that due to the lack of apical oxygens, the T' -phase parent cuprates may exhibit weaker correlations and might be better described as Slater rather than Mott or charge-transfer insulators. Our measurements, however, indicate that these compounds are electron doped with $x = 0.09 \pm 0.02$, and that the parent half-filled Mott

insulating state ($x = 0$) can be recovered by Sr doping. This result precludes a collapse of the insulating gap from weakened correlations as the origin for our observed low energy spectral weight.

In the absence of cation substitution and given the need to synthesize these films at low ($\leq 10^{-6}$ torr) pressures, oxygen vacancies are the most likely source of electron doping in our samples. Oxygen non-stoichiometry is common in oxide thin films and plays an important role in the properties of many cuprates, such as oxygen ordering in the ortho phases of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and oxygen staging in $\text{La}_2\text{CuO}_{4+\delta}$ [40–43], as well as other oxides such as brownmillerites and SrTiO_3 [44, 45]. In T' cuprates, a reduction process has been seen to be essential to achieving superconductivity [3, 4], and it is believed that this annealing process may remove excess apical oxygen [46, 47] as well as possibly dope additional electron carriers [48, 49]. To explore the effect of oxygen pressure during growth on doping level, we have grown T' - La_2CuO_4 over a range of distilled ozone background pressures spanning a factor of 20, from 1×10^{-7} torr to 2×10^{-6} torr. Over this entire range, the electron doping level showed no significant dependence on oxygen pressure and was consistently measured to be within the range of $x = 0.10 \pm 0.03 e^-/\text{Cu}$. If oxygen vacancies are indeed responsible for electron doping in our samples, this result suggests that their formation is robust to growth conditions and that a fixed concentration of vacancies may be energetically favored in the growth of T' - La_2CuO_4 thin films, also suggested in work on T' - $\text{La}_{2-x}\text{Y}_x\text{CuO}_4$ thin films [50, 51].

The possibility of electron doping via oxygen vacancies in n -type cuprates opens up a new possible avenue of control of their properties using well-established techniques such as post-growth annealing and electrochemical intercalation or reduction to alter the defect content and structure, in close analogy to the hole-doped cuprates [52–55]. Previous reports by Yamamoto *et al.* [15] and Krockenberger *et al.* [16] on T' cuprates without cation doping suggest that T_c may be even higher in thin-film samples, which could arise from a reduction of disorder due to an ordering of defect dopants. This is analogous to the case of ortho-ordered $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, in which oxygen ordering, combined with the lack of cation dopants, has been critical in realizing quantum oscillations in the hole-doped cuprates and greatly enhancing understanding of their Fermiology [8–11, 56, 57]. In the electron-doped cuprates, similar quantum oscillations experiments have limited by the difficulty in achieving samples with low disorder, and existing measurements have been unable to probe the entire Fermi surface [58, 59]. Samples with lower disorder may lead to a more complete understanding of the Fermiology of the electron-doped cuprates by enabling more comprehensive experimental studies, particularly at high magnetic fields where charge and spin density wave orders could be enhanced.

We also demonstrated that traditional cation substitution can be employed in conjunction with this intrinsic defect doping, as shown by the growth of Mott insulating T' -La_{1.9}Sr_{0.1}CuO_{4- δ} . Rather than using cations to hole dope, it may also be possible to use a combination of tetravalent cation substitution together with defects to achieve higher electron doping levels, overcoming the threshold due to cation solubility limits and potentially enabling the study of compounds such as highly over-doped $R_{2-x}\text{Ce}_x\text{CuO}_4$.

We have employed MBE to epitaxially stabilize thin film samples of T' -La₂CuO_{4- δ} and measured its electronic structure using *in situ* ARPES for the first time. We find as-grown thin films of T' -La₂CuO₄ to be electron-doped at $x = 0.09 \pm 0.02 e^-/\text{Cu}$ despite the absence of cation doping. We propose intrinsic defects, most likely oxygen vacancies, as the source of these mobile electrons, and find that their formation in T' -La₂CuO₄ is robust to variations over a factor of 20 in the oxygen pressure during growth. Our results suggest a new avenue towards electron doping in cuprates which may be used instead of cation substitution to achieve lower disorder samples for experiments such as quantum oscillations, or which may be used in conjunction with cation substitution to achieve higher doping levels than previously possible to study the properties of highly over-doped n -type cuprates.

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