Emerging superconductivity hidden beneath charge-transfer insulators

Yoshiharu Krockenberger¹, Hiroshi Irie¹, Osamu Matsumoto², Keitaro Yamagami¹*, Masaya Mitsuhashi¹*, Akio Tsukada¹†, Michio Naito² & Hideki Yamamoto¹

¹NIT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato-Wakamiya, Atsugi, Kanagawa 243-0198, Japan,
²Department of Applied Physics, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan.

In many of today’s most interesting materials, strong interactions prevail upon the magnetic moments, the electrons, and the crystal lattice, forming strong links between these different aspects of the system. Particularly, in two-dimensional cuprates, where copper is either five- or six-fold coordinated, superconductivity is commonly induced by chemical doping which is deemed to be mandatory by destruction of long-range antiferromagnetic order of 3d⁹ Cu²⁺ moments. Here we show that superconductivity can be induced in Pr₂CuO₄ where copper is four-fold coordinated. We induced this novel quantum state of Pr₂CuO₄ by realizing pristine square-planar coordinated copper in the copper-oxygen planes, thus, resulting in critical superconducting temperatures even higher than by chemical doping. Our results demonstrate new degrees of freedom, i.e., coordination of copper, for the manipulation of magnetic and superconducting order parameters in quantum materials.

While the issue of the mechanism of high temperature superconductivity continues to be controversial, one can clearly state that there have been many experimental results demonstrating that the lattices make a strong impact on the behavior of electrons. First principle methods predict that square planar coordinated cuprates, e.g., Pr₂CuO₄ are expected to be metals, unlike octahedral-coordinated cuprates. Square planar coordinated cuprates are those which, upon electron doping, become eventually high temperature superconductors subject to an annealing treatment. The purpose of the annealing process is not related to an improved crystal quality but an adjusted oxygen stoichiometry irrespective of the Ce concentration x. A rich interplay of magnetic and electronic phases are reported for electron doped cuprates in relation to the doping concentration x. In particular, the vicinity of the insulating antiferromagnetic ground state to the superconducting ground state has been investigated and it was found that both phases, superconducting and insulating, are in competition with each other. Moreover, the boundary between the superconducting and antiferromagnetic-insulating phases in the electronic phase diagram of electron doped cuprate superconductors is not associated to a definite value x, but rather varies. Li et al. and Charpentier et al. reported a critical doping concentration x_c = 0.12, Krockenberger et al. reported x_c = 0.10 and Brinkmann et al. reported a x_c = 0.04 for superconducting Pr₂-xCeₓCuO₄. Furthermore, Matsumoto et al. reported superconductivity even for x_c = 0.00 in Nd₂-xCeₓCuO₄. Although each group applies its unique annealing recipe, it is common to all five reports that the annealing conditions themselves have been kept almost constant over the entire doping range. The wide range of x_c between 0.00 and 0.12 suggests that the annealing recipe affects the competition between the antiferromagnetic insulating and superconducting states, severely. Additionally, the wide range of x_c may reflect that the appropriate annealing conditions for the induction of superconductivity themselves are doping dependent.

Electron-doped cuprate superconductors adopt the T’-structure (Nd₂CuO₄ structure) where two primary sites are occupied by oxygen: O(1) in the CuO₂ planes and O(2) in the rare-earth (RE) oxide layers. Apical oxygen should not exist in the ideal T’ structure though they are clearly observed by Raman and far-infrared crystal-field spectroscopy, Mössbauer spectroscopy, extended X-ray absorption fine structure spectroscopy and neutron scattering. An ideal annealing recipe would solely evacuate apical oxygen atoms while keeping regular oxygen sites at the O(1) and O(2) sites occupied.

Results
In this study, we used thin film Pr₂CuO₄ samples (1000 Å thick) synthesized by state-of-the-art molecular beam epitaxy (MBE). In contrast to bulk samples, the large surface-to-volume ratio of thin films along with their tenuity...
Superconductivity is induced by the standard annealing process with a maximum $T_{c}$.

In general the annealing process in oxide materials is a diffusion process. In particular, regular O(1) and O(2), as well as apical O(3) sites are occupied or evacuated in the $T'$-cuprates. Here, we use a high precision partial oxygen pressure monitoring and control system (POPMCS) combined with X-ray diffraction and transport data of Pr$_2$CuO$_4$ for the analysis of the annealing process. A commercial quartz tube furnace equipped with a turbo molecular pump and POPMCS was used. The Pr$_2$CuO$_4$ film was mounted on the tip of a SSA-S alumina tube placed at the center of the quartz tube.

Starting from the standard annealing process (Fig. 1) typically applied to electron doped cuprates, we split the annealing procedure, thus a two-step annealing process. Our systematic investigation on this new two-step annealing scheme reveals that only certain annealing conditions are suitable to preserve the $T'$-structure and induce superconductivity into Pr$_2$CuO$_4$. In Fig. 1b, we plot the electronic phase diagram of Pr$_{2-x}$Ce$_x$CuO$_4$ (standard annealed), where the superconducting transition temperatures of 273 $T_{c}$-axis oriented, single phase thin films of Pr$_{2-x}$Ce$_x$CuO$_4$ on (001) SrTiO$_3$ ($a = 3.905$ Å) substrates are shown for $0.00 < x < 0.25$. In contrast to the phase diagram for standard annealed Pr$_{2-x}$Ce$_x$CuO$_4$, the ex-situ two-step annealing process allows superconductivity even without cerium. The phase diagram shown in Fig. 1c shows that superconductivity appears at all doping levels up to $x = 0.22$ and the highest $T_c$ is not at $x = 0.15$ but 0.00, in stark contrast to the commonly observed phase diagram (Fig. 1b). The newly obtained superconducting phase diagram indicates that the apparent symmetry of electronic phases for hole and electron doped cuprate superconductors with respect to the antiferromagnetic-insulating ground state might be an artifact of commonly used annealing treatments, thus, not representative. Instead, it appears that for zero doping, only the $T$-phase is an antiferromagnetic Mott insulator whereas the $T'$-phase is a superconductor, in agreement with the first principle methods’ predictions.

**Discussion**

Comparing the influence of doping to the influence of annealing to Pr$_2$CuO$_4$ reveals that a hidden, hole-like Fermi surface may be present. The Ce doping dependence of the evolution of the Fermi surface of Nd$_{2-x}$Ce$_x$CuO$_4$ has been reported by Armitage et al. for $x = 0.04$, with $T_c = 0.10$ and $x = 0.15$. Traces of a hole-like Fermi surface can be detected even for $x = 0.04$. However, such a sample is neither metallic nor superconducting owing to the annealing conditions applied. The hidden Fermi surface suggests that the applied annealing conditions were not optimal. Commonly, the observed Hall coefficient is negative for $x = 0.04$. The negative Hall coefficient can be attributed to “hot spots” located at $(\pi, 0)$ and $(0, \pi)$. The overall contribution to the Hall coefficient of those hot-spots is significant for Pr$_{2-x}$Ce$_x$CuO$_4$ as the Hall coefficient is negative up to $x = 0.17$ (Fig. 2b). The Hall coefficients $R_H$ taken on superconducting Pr$_2$CuO$_4$ show unambiguously that the origin of metallic conduction and superconductivity itself is not electron doping but points towards a redistribution of spectral weight from those anti-ferromagnetic “hot-spots” into the hole-like Fermi-surface.

Figure 2(c) shows the temperature dependence of $R_H$ for superconducting Pr$_2$CuO$_4$, and the Hall coefficient of standard annealed Pr$_2$CuO$_4$.

**Figure 1** | Annealing paths of Pr$_2$CuO$_4$ and the resulting electronic phase diagrams. In (a), the thermodynamic phase diagram is plotted where logarithmic and reciprocal scaling is used for the oxygen pressure and the absolute temperature, respectively. Thermodynamic stability lines for the copper-oxygen system and Pr$_2$CuO$_4$ are shown. Pr$_2$CuO$_4$ films were grown using a radio-frequency activated oxygen plasma (O$^+$) by molecular beam epitaxy. The oxygen pressure during the synthesis is $2 \times 10^5$ Torr, corresponding to an equilibrium molecular oxygen pressure of $10^5$ Torr. The synthesis temperature of Pr$_2$CuO$_4$ is 650–750 °C. Standard annealing is carried out at temperatures between 550 and 650 °C under $10^{-5}$ Torr. In the two-step annealing process, Pr$_{2-x}$Ce$_x$CuO$_4$ is annealed ex-situ first at 750–850 °C and 7.6 $\times 10^{-4}$ Torr O$_2$ and subsequently annealed at temperatures between 450 and 700 °C under high vacuum. In (b), the doping dependence of the superconducting phase diagram of Pr$_{2-x}$Ce$_x$CuO$_4$ is shown for 273 different samples obtained by the standard annealing process. For $0.00 < x < 0.10$, Pr$_{2-x}$Ce$_x$CuO$_4$ is an antiferromagnetic insulator (AFI). For $0.11 < x < 0.23$, superconductivity is induced by the standard annealing process with a maximum $T_c$ of 25 K at $x = 0.14$. In (c), the doping dependence of the superconducting phase diagram of Pr$_{2-x}$Ce$_x$CuO$_4$ is shown. Data points (black triangle) have been taken from. At $x = 0.00$, results of 84 samples are summarized (star). Dashed lines represent the phase diagram as obtained in Fig. 1(b).
Pr2-xCexCuO4 with x = 0.15 at μH = 14 T and in (b) R_H is plotted as a function of T and x (data taken from Refs. 35-36). Additionally, T_N and T_c are plotted as a function of x (T_N taken from Ref. 37 and T_c from Ref. 38). The "+" and "−" marks indicate the sign of the Hall coefficient R_H and are separated by the dashed line. The cross-over from "+" to "−" is at x ≈ 0.165 and coincides with the quantum critical-point14. In case of conventionally annealed Pr2-xCexCuO4 the Hall coefficient develops monotonically upon electron doping (Ce doping) up to x = 0.165. For the 2-step annealing process (c) and (d), the highest T_c is observed at x = 0.00 (star). In (c) R_H (black line) and the resistivity at μH=14 T are plotted as a function of T for Pr2CuO4 treated by a 2-step annealing process at μH = 14 T and in (d) as a function of T and x (T_c data taken from Ref. 39). The "+" and "−" marks indicate the sign of the Hall coefficient R_H and are separated (R_H = 0) by the dashed line. In case of 2-step annealed Pr2CuO4 the Hall coefficient is positive at 300 K, and at 150 K and 120 K, a sign change appears. Below 120 K, the Hall coefficient is positive down to 1.7 K. Upon electron doping (Ce doping) the low temperature Hall coefficient stays positive irrespective of the Ce concentration level. The contour-plots (b) and (d) were made from linear interpolation of R_H(T) curves for x = 0.05, 0.075, 0.09, 0.10, 0.12, 0.14, 0.15, 0.17, 0.19 and x = 0.00, 0.06, 0.08, 0.10, 0.15, 0.17 in (b) and (d), respectively.

The temperature dependence of the Hall coefficient is not that of a simple metal but rather demonstrates the competition between a hole-like metal and an antiferromagnetic insulator. This asymmetric scenario15,34-36 between square- and octahedral coordinated cuprates also shows that their electronic correlations are entirely different15. The absence of a doping mechanism in our elaborate annealing process is independently supported by the fact that the in-plane lattice constants of as-grown and annealed Pr2CuO4 films are constant upon annealing as it is well known that electron-doping stretches and hole-doping shrinks the Cu-O bonds in the CuO2 planes due to accumulation or depletion of electrons to/from the Cu-O d̄b anti-bonding bands39. The presence of additional oxygen in as-grown Pr2CuO4 is well established15,34 as is its removal by annealing. We visualized our annealing scenario in Fig. 3a. The as-grown crystal contains more than the stoichiometric amount of oxygen which are randomly distributed at apical sites (Fig. 3a). After the first annealing step we find that the lattice parameters are nearly unchanged (Fig. 3f) when compared to the as-grown sample (Fig. 3e). However, its resistivity value is significantly higher (Fig. 3c). We explain such behavior by the introduction of oxygen vacancies in the CuO2 plane since such defects would disturb electronic conduction severely. The second annealing step does repair those in-plane defects by relocating apical oxygen atoms to the planes and consequently the resistivity is lowered significantly (Fig. 3d). This final step creates a situation similar to what has been observed after an annealing treatment40 for the cerium doped superconductors36. Overall we do observe that the c-axis lengths decreases upon annealing (Fig. 3 e–g) and that has been unambiguously proven to be associated to the removal of apical oxygen by neutron scattering32,34. A typical value of the oxygen off-stoichiometry estimated from neutron scattering experiments of as-grown Nd2CuO4 + δ single crystals is δ ≈ 0.05, which indicates that one Cu ion out of ten unit cells is pyramidal coordinated. Experimentally, this is a sufficient condition to stabilize a long-range antiferromagnetic order even at Ce doping levels of x = 0.1540. In Ref. 39 it was shown that even for x = 0.15 the as-grown cuprate is an antiferromagnetic insulator with a T_N = 150 K. After annealing, however, the cuprate system goes into the superconducting state. The only chemical difference is that occupied apical oxygen sites have been evacuated during that annealing process. Those occupied apical oxygen sites break the symmetry for all nearest and next-nearest-neighbor Cu plaquettes. Such a locally broken symmetry localizes electrons primarily on one Cu site and induce a gap in the Fermi surface. Therefore, the doping process in electron doped cuprates might be considered as a band filling process, as its ground state is already a metal40.

It is worth mentioning that the entire annealing process is a diffusion process as long as thermodynamic limits are not violated. Certainly, those limits have been violated considering earlier reports41. In contrast to the standard annealing process applied for bulk specimens, thermodynamic constraints, e.g., the Pr2CuO4 ↔ Pr2O3 + Cu2O stability line, may not be crossed in our 2-step annealing process. As for the standard annealing process, reduction conditions below the thermodynamic stability regions may harm the T’ phase, therefore RE2O3 oxides are often observed and consequently cause an increase of the absolute resistivity value. The annealing conditions applied in the first annealing step of our experiments are above the thermodynamic stability lines of Pr2CuO4 and CuO, thus, decomposition products, i.e., Pr2O3, can be ruled out in contrast to other experiments as we do not see indication of their presence either by transmission electron microscopy or X-ray diffraction. Besides the influence of the annealing conditions on the electronic transport properties (Fig. 4a,b), the crystallite dimensions of the thin film are also affected. Low annealing temperatures result in larger (A/q) values (Fig. 4c and 4d), though the superconducting transition temperatures are constant (Fig. 4a, 4b). Both of the annealing steps of our two-step annealing process are independent and...
their correlation to superconductivity is visualized in Fig. 4e where the superconducting transition temperature (T_c) is plotted as a function of the first- (T_a) and second- (T_red) annealing temperatures. For optimal superconducting transition temperatures, a low T_red requires a low T_a and a high T_a requires a high T_red. Consequently, when the annealing time and the oxygen partial pressures are kept constant, optimal superconducting transition temperatures are associated to T_a and T_red in an arc shaped relation.

Finally, we compare our data to results reported from first principle calculations mentioned earlier. The contrasting ground states in square-planar and octahedral coordinated cuprates, i.e., T' and T, are consequences of the difference in the charge-transfer gap Δ_0, originating primarily from the different oxygen coordination. Vacant apical sites substantially reduce the electrostatic potential at the copper site, thus, the 3d^9 Cu energy levels of the T'-phase are lower than in the T-phase, whereas the 2p^6 O energy levels remain almost constant. A simple evaluation of the unscreened Δ_0 from Madelung potential calculations show that the difference in Δ_0 between T'- and T-phases is in the range of several eV – therefore, the charge transfer gap might be very small or may even vanish in the T'-cuprates. Under such circumstances, the model of ionic binding, which is tacitly assumed in the discussion of the charge-transfer energy, loses its vindicability. Instead, hybridization effects between Cu 3d_{x^2-y^2} and O 2p_π orbitals may dominate electronic correlations, though they are not taken into account in the commonly used t-J model. A superconducting ground state in square planar coordinated cuprates, where doping is not a prerequisite but an option, may promote a deep understanding of the rich variety of electronic phases of cuprates as they depend on coordination, doping and diluted impurities. Moreover, the new phase diagram of square-planar coordinated cuprates implies the following question: Does T'_c further increase upon hole-doping? A recent article by Takamatsu et al. indeed observed superconductivity in hole doped square-planar coordinated cuprates. Answering may provide a fundamental understanding of the mechanism of high temperature superconductivity. Certainly, the induction of a long range commensurate 3D antiferromagnetic order by a tiny amount of apical oxygen in T'-cuprates may provide a fundamental understanding of the mechanism of high temperature superconductivity. Answering may provide a fundamental understanding of the mechanism of high temperature superconductivity.

**Methods**

Thin films of c-axis oriented, single phase Pr_2CuO_4 were epitaxially grown on SrTiO_3 substrates by molecular beam epitaxy (MBE). The growth of the T'-Pr_2CuO_4 films was performed in a custom-designed MBE chamber (base pressure ~ 10^-10 Torr) from metal sources by using multiple e-gun evaporators and an atomic oxygen source (0.5 sccm, radio-frequency (RF) power of 250 W) as an oxidizing agent. The cation stoichiometry was adjusted by controlling the evaporation beam flux of each constituent element by electron impact emission spectrometry (EIES) (Guardian IV, Inficon, USA) via feedback loops to the e-guns. Ultra-fine tuning of the evaporation beam fluxes (< 0.005 Å/s) was done by reflection high-energy electron diffraction (RHEED) monitoring. Typically, the substrate temperature for the growth of T'-Pr_2CuO_4 thin films was T_s = 600–650 °C. The film thickness is 1000 Å. For comparison purpose, some of the films were reduced in-situ after the growth under the ultra-high vacuum (UHV) environment.
Pr$_2$CuO$_4$ to the (001) SrTiO$_3$ diffraction spot shows that Pr$_2$CuO$_4$ films are epitaxial but relaxed grown on (001) SrTiO$_3$. The in-plane lattice constant of the Pr$_2$CuO$_4$ films is 3.96 Å. The influence of the annealing steps were kept constant and are 7.6 Å.

The in-plane lattice constant of the Pr$_2$CuO$_4$ films is 3.96 Å. (Δq$_{\perp}$) | 3 : 2235 | DOI: 10.1038/srep02235

Using the MBE-grown films, we investigated the reduction condition dependence of the properties of T$	extsubscript{c}$ Pr$_2$CuO$_4$. A commercial quartz tube furnace of 60 cm length and 30 mm diameter was used. The furnace is equipped with a turbo molecular pump (TMP) and a commercial (SIOC-200, STLAB, Japan) high precision partial oxygen pressure monitoring and control system (POPMCS). The POPMCS allows a precise control of the oxygen partial pressure between 10$^{-2}$ to 10$^{-6}$ atm by mixing an inert gas, e.g., N$_2$, and oxygen at an electrochemically controlled oxygen diffuser (yttrium stabilized zirconium oxide). The Pr$_2$CuO$_4$ film was mounted on the tip of a SSA-S alumina tube placed at the center of the quartz tube in longitudinal direction. Prior to its first usage the quartz tube was cleaned in boiling piranha clean whereas the alumina tube was rinsed by deionized water. The cleaned quartz tube and SSA-S aluminia tube were prebaked at 1000°C for 10 h under ultra-high vacuum. Prior to the first annealing step, the partial pressure of oxygen was adjusted to a defined value. The N$_2$/O$_2$ gas mixture was kept at a constant flow rate of 500 sccm throughout all experiments. The second annealing step is performed in the same tubular furnace evacuated in 10$^{-2}$ Torr residual gas pressure.

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Author contributions
All the MBE samples for ex-situ annealing experiments were prepared by H.Y. or Y.K. O.M., K.Y. and M.M. performed the ex-situ post-annealing experiments as well as most of the XRD, AFM, and ρ(T) measurements. In-situ annealing experiments were done by A.T. Y.K. carried out XRD experiments as well as characterization of magnetic properties by using a SQUID magnetometer. H.I. prepared the Hall bars and H.I. and Y.K. performed measurements of the Hall coefficient. M.N. along with other authors discussed the results and commented on the paper. All work was coordinated and overseen by H.Y. and M.N.

Additional information
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