

Superconducting phases of $\text{La}_2\text{CuO}_{4+\delta}$ prepared by electrochemical oxidation at ambient temperature

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Superconducting phases in $\text{La}_2\text{CuO}_{4+\delta}$ prepared at ambient temperature by electrochemical oxidation have been investigated for the nominal composition range $0 < \delta < 0.1$. Consistent with previous reports, a stable superconducting phase with $T_c \sim 32\text{--}34$ K is observed for $\delta \leq 0.05$. In contrast, samples with $\delta > 0.05$ are found to be unstable either at room temperature or upon annealing between 25 °C and 110 °C. All phases with T_c higher than 34 K, such as $T_c \sim 45$ K phase, are metastable and only accessible under highly nonequilibrium intercalation conditions. A phase with $T_c = 15$ K is also observed at a nominal hole concentration of $p \sim 0.125$, indicating that all of the observed T_c depressions in the cation substituted $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4$ and anion doped $\text{La}_2\text{CuO}_{4+\delta}$ at $p \sim 0.125$ are electronically driven and are of a common origin.

Excess interstitial oxygen can be incorporated into insulating La_2CuO_4 by high-pressure oxygenation,¹ electrochemical intercalation,² and chemical oxidation.³ Bulk superconductivity is observed in samples of $\text{La}_2\text{CuO}_{4+\delta}$ prepared by electrochemical oxidation at ambient temperature with superconducting transition temperatures as high as 45 K. Excess interstitial oxygen atoms in $\text{La}_2\text{CuO}_{4+\delta}$ are found to be mobile down to 200 K with profound effects on the electronic and structural properties. For example, a macroscopic phase separation into a metallic superconducting oxygen-rich ($\delta \sim 0.055$) and an insulating antiferromagnetic oxygen-poor ($\delta \sim 0.012$) phases, a miscibility gap, was observed.^{4,5} A dependence of T_c on cooling-rate, subtleties associated with intrinsic electronic responses due to doped holes, and microscopic segregation of doped holes have been reported for the $\text{La}_2\text{CuO}_{4+\delta}$ system.⁶⁻⁹

Although the electronic and structural properties of electrochemically doped $\text{La}_2\text{CuO}_{4+\delta}$ have been extensively studied and are relatively clear for $\delta < 0.05$,^{5,10,11} the region beyond the miscibility gap is much less understood in spite of the occurrence of the highest value of T_c (~ 45 K) in this region.^{2,10,11} In this paper, we report the studies of superconducting phases in $\text{La}_2\text{CuO}_{4+\delta}$ prepared at ambient temperature by three electrochemical intercalation techniques. Depending on the δ value and the technique used, stable, metastable and unstable superconducting transitions are observed. We show that samples close to equilibrium with a stable $T_c \sim 32\text{--}34$ K can be obtained for $0 < \delta < 0.05$, but high intercalation rates produced nonequilibrium samples. For $\delta > 0.05$, the reaction rates of the three techniques used are too fast and the samples are nonequilibrium. Phases with transitions greater than 34 K in samples with $\delta < 0.1$ are found to be metastable and accessible only at high intercalation rates at a significant overpotential. A 15-K phase is observed when the samples are made under conditions approaching equilibrium by thermal annealing at temperatures between 25 and 110 °C.

The starting material, $\text{La}_2\text{CuO}_{4+\delta'}$, was prepared by calcining thoroughly mixed stoichiometric amounts of La_2O_3 (99.99%) (preheated at 850 °C) and CuO (99.9%) in air at 925 °C for 12 h followed by heating for 12 h at 1000 °C and 1050 °C with intermediate grindings. The powder was pressed into pellets and sintered at 1100 °C for 4 h. Sintered pellets, typically at $\sim 75\%$ of the theoretical density, have an excess oxygen content of $\delta' \sim 0.0035$ estimated from electrochemical deintercalation (reduction). Both electrochemically deintercalated and nitrogen annealed pellets exhibit a clear antiferromagnetic transition at 310 K and a normal state magnetic susceptibility $\chi \sim 2 \times 10^{-7}$ emu/g at 340 K. Powder x-ray diffraction pattern collected at 25 ± 0.5 °C indicates the sample is phase pure with orthorhombic lattice parameters $a = 5.3553(1)$ Å, $b = 5.4051(1)$ Å, and $c = 13.1431(3)$ Å. A three-electrode electrochemical cell was used for the electrochemical synthesis with $\text{La}_2\text{CuO}_{4+\delta'}$ as the working electrode, a platinum wire or gold foil as the counter electrode, Ag/AgCl or Hg/HgO as the reference electrode, and 1M KOH aqueous solution as the electrolyte. All the intercalated samples reported in this work were prepared at ambient temperature by one of the following three methods: (I) a constant potential, 450 mV vs Ag/AgCl , is applied to the sample; (II) a constant current density, $50 \mu\text{A}/\text{cm}^2$ calculated using the external geometric surface area, is applied to the sample; (III) a potential step technique in which the potential is increased in 5 mV steps using a cutoff current of $10 \mu\text{A}$, as described previously.¹² The typical sample dimensions were $2 \times 6 \times 0.3$ mm³ slabs and 8 mm diameter, 0.3 mm thick disks for methods (I), (II) and (III), respectively. To intercalate two identical pellets to the same excess oxygen level, $\delta = 0.08$ for instance, method (III) takes about twice the time required for method (II). Therefore, qualitatively, method (III) is a more "gentle" process compared to method (II). All intercalations were performed below the oxygen evolution potential (~ 0.55 V vs Ag/AgCl) which limits δ to be less than 0.1. The values of δ are determined by $\delta = Q/2$ where Q

is the amount of charge transferred per formula unit. The excess oxygen content, as determined by measuring weight loss after the sample was washed, dried, and annealed at 550 °C for 6 hours in N_2 is identical to that determined by the formula $\delta=Q/2$ within our experimental resolution of $\Delta\delta=\pm 0.002$. No obvious electrochemical side reactions were detected under our preparation conditions consistent with the result that $\delta=Q/2$. The hole concentration was determined by iodometric titration as described in Refs. 13 and 14. All magnetic measurements were done by using a Quantum Design superconducting quantum interference device (SQUID) magnetometer at 5 G upon warming under field cooled (Meissner signal) or zero field cooled conditions.

Both superconducting transition onset temperatures (T_c 's) and the Meissner signal sizes (χ_m 's) from this work and from various groups are summarized in Figs. 1(a) and 1(b).^{10,11,15} For T_c 's of our as-charged samples (closed triangles and squares), a phase, we call it 32 K phase hereafter, with a stable $T_c\sim 32\text{--}34$ K is observed for $\delta<0.05$. This is identical to that observed by every group in spite of the wide differences in oxidation techniques and the initial sample preparations. This indicates that the phase separation proceeds extremely fast and samples are close to equilibrium. This is consistent with a previous neutron diffraction study.⁵ Although the 32-K phase is readily achieved, it is noted that a sample oxidized to $\delta=0.03$ using a constant current density of 1 mA/cm² can produce a T_c at ~ 40 K shown in the inset of Fig. 1(a). The coexistence of two T_c 's at ~ 40 K and ~ 26 K instead of the common stable $T_c\sim 32$ K indicates the sample is not in equilibrium. Those two superconducting phases are metastable and thermal annealing of the sample at 110 °C results in a single $T_c\sim 32$ K (solid line) similar to that (dotted line) of sample charged to $\delta=0.03$ by method (II) as seen in the inset of Fig. 1(a). These results demonstrated that, even for $\delta<0.05$, caution should still be exercised to avoid using too rapid reaction rates and thermal annealing can bring the sample close to equilibrium. For $\delta>0.05$, different T_c 's and/or coexistence of two T_c 's can be observed at different δ values depending on the technique used. The inconsistent occurrences of two coexisting T_c 's and the variations in T_c 's with synthesis techniques indicate that the reaction rates of methods (I), (II), and (III) are already too fast for preparing samples with $\delta>0.05$. Those samples in the composition range $0.05<\delta<0.1$ are not in thermal equilibrium. This is consistent with a previous electrochemistry study of intercalated $\text{La}_2\text{CuO}_{4+\delta}$ charged to $\delta\sim 0.085$.¹² From a plot of the χ_m versus δ , Fig. 1(b), a larger scatter in χ_m 's than in the T_c values is apparent. The Meissner signal of a high-temperature superconductor is a complicated property which depends sensitively on extrinsic sample properties (such as particle size and grain connectivity) and measuring conditions (such as applied field).^{16–18} A detailed study of χ_m 's of $\text{La}_2\text{CuO}_{4+\delta}$ will be reported later.

The highest T_c at 45 K can only be obtained for $\delta>0.06$ prepared by methods (I) or (II). The reaction rate used in constant potential technique [identical to method (I)] in Ref. 11 is even faster than method (II). For instance, to charge a sample to $\delta=0.05$ by method (I), the initial current density (~ 1 mA/cm²) is much larger than 50 $\mu\text{A}/\text{cm}^2$ used in method (II) and the time taken is about half of that in method (II). The most "gentle" process [method (III)] can

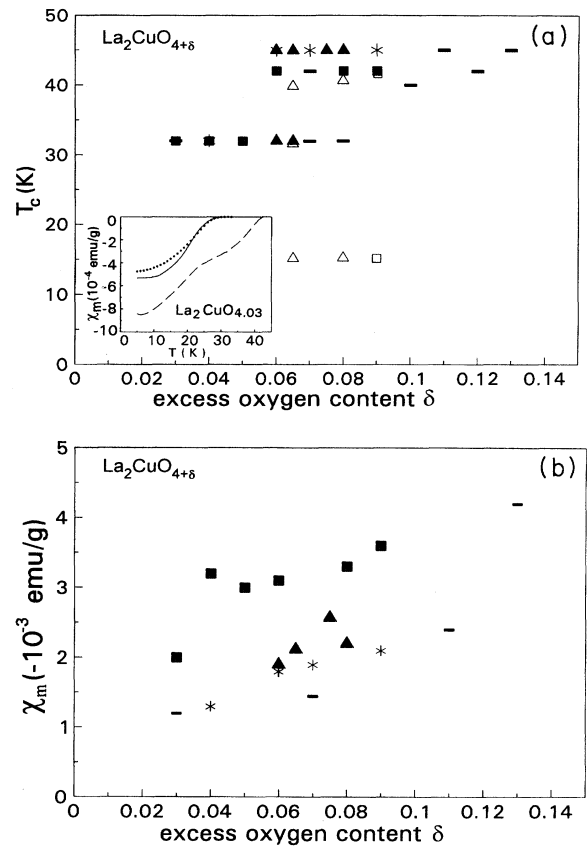


FIG. 1. (a) T_c 's of room temperature electrochemically intercalated $\text{La}_2\text{CuO}_{4+\delta}$ from literatures and this work. *: J.-C. Grenier *et al.* (constant potential) (Ref. 11), —: F. C. Chou *et al.* and P. G. Radaelli *et al.* (constant current and potential) (Refs. 10 and 15), ■: this work (potential step, as charged), □: this work (potential step, after ~ 6 months), ▲: this work (constant current, as charged), △: this work (constant current, after ~ 6 months). The inset: Meissner signals of two samples, $\delta=0.03$, charged by 1 mA/cm² (dashed line: as charged, solid line: annealed at 110 °C for 48 hours) and 50 $\mu\text{A}/\text{cm}^2$ (dotted line). (b) χ_m 's of room temperature electrochemically intercalated $\text{La}_2\text{CuO}_{4+\delta}$ from literatures and this work. *: J.-C. Grenier *et al.* (constant potential) (Ref. 11), —: F. C. Chou *et al.* (constant current) (Ref. 10), ■: this work (potential step, as charged), ▲: this work (constant current, as charged).

only produce a T_c at ~ 42 K. This indicates that the high T_c at 45 K, similar to the 40-K transition observed in $\delta=0.03$, is a nonequilibrium metastable state created by electrochemical processes with high reaction rates. In fact, for all samples with $\delta>0.05$, superconducting properties continue to develop either at room temperature or upon thermal annealing between 25 and 110 °C. In Fig. 2, we show the time evolution of the Meissner signal of a typical unstable sample, $\text{La}_2\text{CuO}_{4.064}$. The curve is obtained immediately after the sample was oxidized by method (II). The transitions at 45 and 32 K are clearly visible. The sample was then stored at room temperature in a desiccator, T_c and χ_m were periodically measured over a six months period. Both the T_c and χ_m of the 45-K phase decrease with time and the χ_m of the 32-K phase, with a stable T_c , increases continuously. A weak T_c anomaly, indicative of a phase at 15 K, also

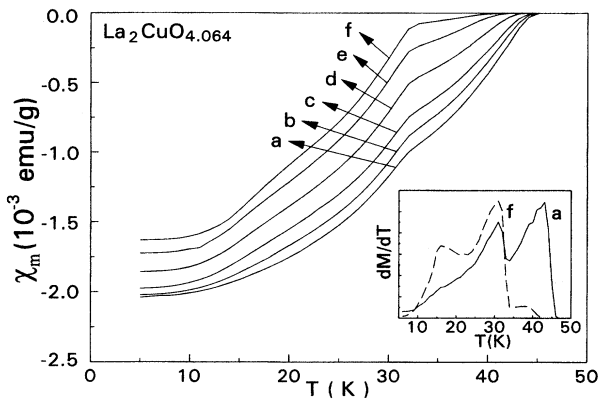


FIG. 2. Time evolution of Meissner signals of room temperature electrochemically (constant current) intercalated $\text{La}_2\text{CuO}_{4.064}$, the sample was stored in dessicator at room temperature between measurements. a: as charged, b: 2 days later, c: 5 days later, d: 15 days later; e: 40 days later, f: 6 months later. The inset: the derivative of χ_m (a: as charged, f: 6 months later).

develops over time and can be easily seen in the inset of Fig. 2 by taking the derivatives of the χ_m curves. The occurrence of the 15-K phase is particularly intriguing. Thermal annealing at the temperatures between 25 and 110 °C continuously promotes the development of the 15-K phase. For example, in Fig. 3, there is a single transition at 45 K for a sample charged to $\delta=0.065$. After annealing at 110 °C for 24 h in air, the 15- and 32-K transitions clearly develop and the Meissner signal of the 45-K phase disappears. The annealed sample represents a state approaching equilibrium and the 15-K phase is clearly a superconducting phase that coexists with the 32-K phase for that δ value. This coexistence of two T_c 's at ~ 15 and ~ 32 K is observed for all annealed samples for $0.05 < \delta < 0.1$, independent of the value and the stability of original T_c 's and preparation techniques. It is also noted that one sample charged to $\delta=0.12$, with a hole concentration $p \sim 0.16$ (holes per formula unit), and annealed at 110 °C exhibits two T_c 's at ~ 15 and ~ 34 K. The high oxy-

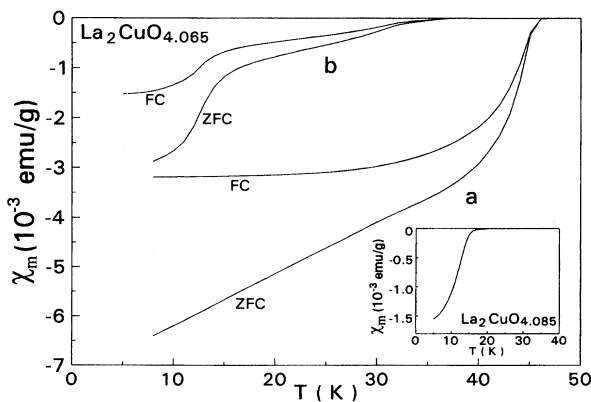


FIG. 3. Shielding (ZFC) and Meissner (FC) signals of constant potential intercalated $\text{La}_2\text{CuO}_{4.065}$. a: as charged, b: annealed at 110 °C for 24 hours. The inset: Meissner signals of the 15-K phase.

gen content of $\delta=0.12$ can be achieved by charging to above [method (II)] or below [method (I)] oxygen evolution potential at ambient temperature or 70 °C, respectively. The possible loss of oxygen due to prolonged annealing between 25 and 110 °C was checked by weighing samples using a microbalance. Within the experimental resolution, $\Delta\delta = \pm 0.0005$, samples annealed for 72 hours at 110 °C do not lose oxygen. The drastic reduction of the Meissner signal upon annealing is, therefore, an intrinsic effect. It seems to be related to the development of the 15-K phase and/or the disappearance of the 45-K phase, especially, when the size of superconducting domain becomes comparable to the penetration depth. Since no loss of oxygen is expected at room temperature, the continuous reduction of the χ_m in Fig. 2 while the 45-K phase disappears and the 15-K phase develops is consistent with the annealing results. Therefore, the changes in T_c 's and χ_m 's upon annealing are due to thermally activated rearrangements of interstitial oxygen atoms with the formation of different superconducting domains. The above results indicate that, for $0 < \delta < 0.1$, phases with T_c 's above 34 K in oxygen intercalated $\text{La}_2\text{CuO}_{4+\delta}$ are metastable. The measured T_c 's for different samples after six months are summarized in Fig. 1(a) by the open symbols.

For $\delta=0.065$, after annealing at 110 °C for only 15 minutes, the sample is already very close to the final state. This indicates that the conversion to the 15-K phase corresponds to a very low activation energy and is possibly related to the local rearrangements of the interstitial oxygen atoms as reported in the literature.¹⁵ Iodometric titration of a close to pure 15-K (inset in Fig. 3) phase ($\delta \sim 0.085$) indicates a hole concentration of $p = 0.13 \pm 0.005$. Therefore, it is plausible that this 15-K phase is actually related to the reduction in T_c observed in $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4$ around $x = 0.125$.¹⁹⁻²¹ This coincidence strongly suggests that all the anomalies observed in cation substituted $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4$ at $p \sim 0.125$ are of a common electronic origin and that a single anomalous low T_c exists at this hole concentration. Hydrostatic pressure at ~ 6 Kbar can suppress the transition from high-temperature orthorhombic (HTO) to low-temperature tetragonal structure (LTT) in Ba-doped La214 and restore T_c .²² However, a characteristic decrease of T_c is still present at $p \sim 0.125$ at 20 Kbar.²³ In $\text{La}_{2-y-x}\text{Th}_y\text{Ba}_x\text{CuO}_4$, the sharp depression of T_c is found to be centered at $x-y = 0.125$ instead of $x = 0.125$.²⁴ Those are consistent with the suggestion that there is a common electronic origin for T_c suppression. After the LTT structure is completely suppressed by pressure, the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.125$) reaches an optimal T_c of ~ 15 K,²² which is identical to the T_c at $p = 0.125$ in doped La_2CuO_4 . Indeed, it is recently shown that carefully prepared $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_{4-\delta}$ samples exhibit full bulk superconductivity except in a very narrow composition range close to $x = 0.0625$.^{25,26} This is consistent with both the drastic reduction of the Meissner signal when the 15-K phase develops and a single $T_c \sim 15$ K phase at $p = 0.125$. The coexistence of two T_c 's seems to suggest another phase separation into two superconducting phases with $T_c \sim 32$ K and ~ 15 K for $0.05 < \delta < 0.085$. This suggestion is consistent with the fact that this two-phase region is only observable in oxygen intercalated samples where excess oxygen atoms are mobile. The absence of two T_c 's and the presence of a T_c minimum around $x = 0.125$ in $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4$ is, there-

fore, due to the frustration of the phase separation caused by doping with immobile cations. More detailed studies are required to clarify this point. It should also be noted that, a superconducting transition at ~ 15 K is apparent in some literature reports.^{27,28}

It is well known that nonequilibrium metastable alloys or compounds play an important role in the unusually high T_c values found in some systems. For example, the equilibrium A-15 phase of Nb_3Ge has a stoichiometry of 14 to 17 at. % Ge with a $T_c \sim 7$ K. A $T_c \sim 23$ K is achieved in a nonequilibrium, metastable, near stoichiometric Nb_3Ge which is stabilized by nonequilibrium techniques such as sputtering or evaporation. It seems that it is also true for whatever phase with a stable T_c higher than 34 K observed in $\text{La}_2\text{CuO}_{4+\delta}$ for $0 < \delta < 0.1$. Electrochemical intercalation at ambient temperature is inherently heterogeneous and nonequilibrium if the bulk chemical diffusion coefficient is low relative to the rate of the intercalation process used to synthesize the samples. Under these circumstances, a surface layer is oxidized to a much higher oxidation state with possible structural distortions may or may not be reversed by annealing at 110 °C. In general, samples with an inhomogeneous distribution of excess oxygen atoms will relax to a final state which is either in real thermodynamic equilibrium or only kinetically stable. For $\delta > 0.05$, due to the possible complications of oxygen-oxygen interaction and lattice distortion, it is conceivable that many metastable states can be

created as long as the reaction rate is faster than the bulk diffusion. It should be noted that the constant current ($50 \mu\text{A}/\text{cm}^2$) used in method (II) is already smaller than that ($100 \mu\text{A}/\text{cm}^2$) used in Ref. 10. Method (III) is even more "gentle" than method (II). However, it is shown that even method (III) is already too fast for preparing samples for $\delta > 0.05$. Therefore, practically, a stable equilibrium sample with $\delta > 0.05$ seems to be difficult to achieve by room temperature electrochemical oxidation alone.

In summary, we have investigated ambient temperature electrochemically doped $\text{La}_2\text{CuO}_{4+\delta}$ for $0 < \delta < 0.1$. For $0 < \delta < 0.05$, although subtle differences still exist in χ_m 's, a consistent stable 32-K phase is relatively easy to achieve. For $0.05 < \delta < 0.1$, all samples are nonequilibrium and phases with $T_c > 34$ K are metastable. A 15-K phase with hole concentration $p \sim 0.125$ is observed, indicating that all depressions in T_c in cation substituted $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4$ at $p \sim 0.125$ are electronically driven from a common origin. The 15-K phase provides a unique opportunity to further investigate all the anomalies at $p \sim 0.125$ observed in cation substituted $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4$.

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