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Enhanced two-dimensional behavior of metastable T'-La_2CuO_4, the parent compound of electron-doped cuprate superconductors

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We synthesized crystalline bulk samples of lanthanum cuprate in the metastable T' phase using cesium hydroxide flux. Its crystal structure was determined as space group $I4/mmm$, no. 139, $a=401.02$ pm, $c=1252.66$ pm. Muon spin rotation reveals a gradual slowing down of magnetic fluctuations below $T_{N1}\approx 200$ K, and static magnetic order below $T_{N2}=115$ K, in sharp contrast to La_2CuO_4 in the T structure where $T_{N1}\approx T_{N2}\approx 300$ K. Our result shows that the strikingly different magnetic behavior of the two parent compounds has its origin in the two crystal structure modifications. In addition, we find that T'-La_2CuO_4 has strongly reduced magnetic interactions compared to the other T' materials Nd_2CuO_4 and Pr_2CuO_4, where Nd^{3+} and Pr^{3+} are magnetic ions in contrast to the nonmagnetic La^{3+}.

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La_2CuO_4 is the parent compound of hole- and electron-doped high-temperature superconductors of the form $La_{2-x}A_xCuO_4$, e.g., with $A=Ba$ for hole doping and Ce for electron doping. Since all hole-doped cuprates crystallize in the so-called T phase, T-La_2CuO_4 is their parent compound. In contrast, all electron-doped cuprates crystallize in the so-called T' phase, which means that lanthanum cuprate in its metastable T' modification is their true parent compound. Most studies of electron-doped cuprates have been restricted to nonlanthanum based systems such as Nd_2CuO_4 or Pr_2CuO_4—materials which have no equivalent on the hole-doped side of the phase diagram.[1,2] Revealing the intrinsic magnetic and superconducting properties of hole- and electron-doped cuprates requires therefore also a comparison of T-La_2CuO_4 and T'-La_2CuO_4. The structure of T-La_2CuO_4 is similar to the tetragonal K_2NiF_4-structure type but reported to be orthorhombically [space group (s.g.), *Bmab*, no. 64] (Refs. 3 and 4) or even monoclinically distorted (s.g., *Bm*11, no. 8) as observed by neutron scattering in almost untwinned single crystals.[5] It exhibits static antiferromagnetism with reported Néel temperatures between 296 K (Ref. 6) and 316 K.[5] In the T'- or Nd_2CuO_4 structure ($I4/mmm$, no. 139), copper ions are not coordinated octahedrally but form layers consisting of CuO_4 squares. The magnetic properties of T'-La_2CuO_4 have not been investigated in detail so far, simply due to the lack of available bulk samples of this metastable compound. Magnetic studies of Nd_2CuO_4 and Pr_2CuO_4 have been performed[7] but are complicated by the presence of the additional magnetic ions Nd^{3+} and Pr^{3+}.

Using conventional bulk methods, only $Pr_{1-x}LaCe_xCuO_4$ could be synthesized with maximally half of the Pr sites occupied by La ions.[8] The parent compound T'-La_2CuO_4 itself is difficult to access because of the higher stability of the T modification. Only recently, Kato *et al.*[9] reported soft-chemical techniques to synthesize oxide superconductors and mentioned a successful preparation of T'-La_2CuO_4 as bulk material with lattice parameters $a=402$ pm and $c=1249$ pm employing NaOH/KOH melts at 350 °C.[10] Here we describe a cesium hydroxide flux based synthesis route to high-quality bulk samples of T'-La_2CuO_4, and determine its basic magnetic properties using the muon spin rotation technique.

Stoichiometric amounts of copper oxide CuO (Fluka >99%) and lanthanum oxide La_2O_3 (Merck KGaA Darmstadt 99.5%) were mixed using a ball mill at 15 Hz for 18 min, ground and put in an open silver crucible together with cesium hydroxide CsOH (monohydrate, Fluka >95%), the oxides/hydroxide molar ratio being approximately 1:3. The crucible was placed in a furnace and heated under purified argon flow to 653 K for 24 h. After cooling to room temperature, the reaction cake was ground in an argon glove box, and then, under flowing argon, washed with distilled (deionized) water to dissolve the hydroxide. A black powder was filtered off and dried at 343 K in vacuum over night. The absence of elements (particularly Cs) other than La, Cu, and O in the samples was shown by energy dispersive x-ray spectroscopy. X-ray diffraction patterns of the products on flat plate holders were collected at room temperature, using a powder-diffraction system STOE STADI P with monochromatized cobalt radiation ($\lambda=178.896$ pm) in transmission geometry. A Rietveld refinement [program GSAS (Ref. 11)] was performed using structure data from Nd_2CuO_4 (Ref. 12) as starting parameters. Powder patterns, both experimental and calculated, are shown in Fig. 1. Table I gives the results of the structure determination of T'-La_2CuO_4. Figure 2 shows the evolution of the a and c axes of T'-Ln_2CuO_4 following the lanthanide (Ln) contraction.

We have derived the site occupancies of oxygen in T'-La_2CuO_4 including the defect site O(3) of apical oxygen on an identically fabricated sample. We have found in-plane

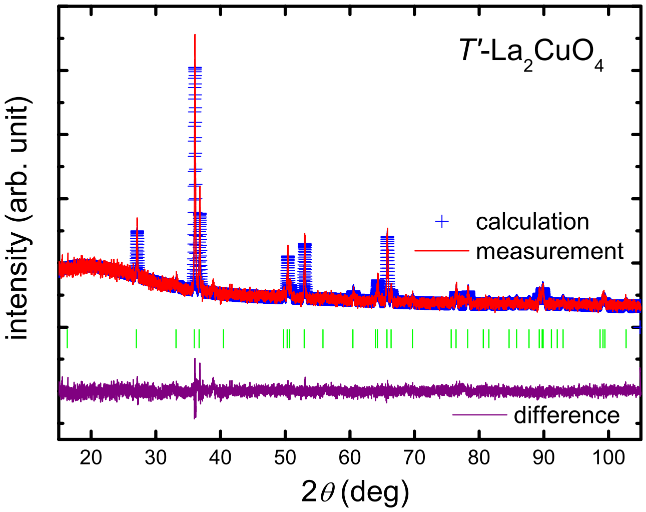

FIG. 1. (Color online) Observed, calculated powder pattern, and difference curve (bottom) for T'-La$_2$CuO$_4$. Vertical dashes indicate the positions of the reflections.

oxygen O(1) 2.000(12), out-of-plane O(2) 1.938(11), and apical oxygen O(3) 0.018(5). Comparing this result to literature values,[15] our samples are close to the reported values of the best reduced samples. This shows that the low-temperature synthesis yields about stoichiometric compounds without additional reduction step. While it is difficult to tell whether the small O(3) value is significant without having large single crystals, it is interesting to note that there seem to be vacancies on the O(2) site. Again, this has been also found in Nd$_2$CuO$_4$.[15]

TABLE I. Details on the structure refinement of T'-La$_2$CuO$_4$. Numbers in brackets are standard deviations that refer to the last digit. $U_{\rm iso}$ values (in picometer square) are defined as one third of track of the orthogonalized tensor U_{ij}. Wyckoff sites for La, Cu, O(1), and O(2), respectively, are 4e, 2a, 4c, and 4d (Ref. 13).

Formula unit		La$_2$CuO$_4$
Temperature (K)		293(2)
Crystal system		Tetragonal
Space group		$I4/mmm$
a,b (pm)		401.02(2)
c (pm)		1252.66(9)
$V/10^{-6}$ (pm^3)		201.45(3)
Calculated density (g/cm^3)		6.683
No. of reflections (measured)		70
No. of parameters (refined)		10
$\rho_{\rm min/max}$		−3.256/4.458
$R_{\rm p}$		0.0741
$R_{\rm wp}$		0.0945
$\chi 2$		0.9468
Atom	$x\ y\ z$	$U_{\rm iso}$ or U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{23}
La	0 0 0.3528(4)	0.024(2), 0.024(2), 0.037(3), 0, 0, 0
Cu	0 0 0	0.023(6), 0.023(6), 0.048(9), 0, 0, 0
O(1)	0 0.5 0	0.025
O(2)	0 0.5 0.25	0.05(2)

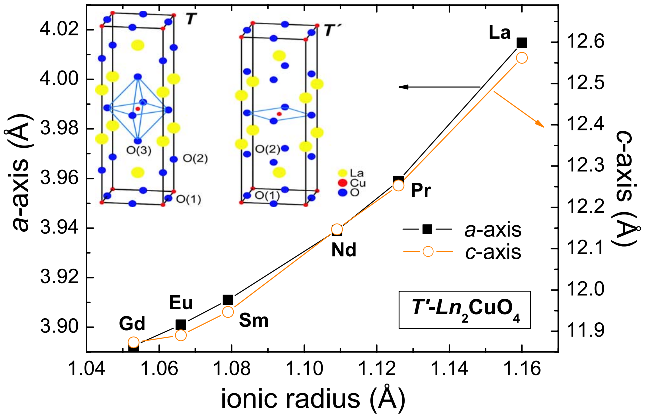

FIG. 2. (Color online) Lattice constants for T'-Ln_2CuO$_4$. The data points for $Ln \neq$ La are taken from literature (Ref. 14). Inset: comparison of the T and the (tetragonally idealized) T' structures of La$_2$CuO$_4$.

The choice of CsOH as flux medium is important to ensure an *undoped* compound T'-La$_2$CuO$_4$. Since the La position is eightfold coordinated, the ionic radius of La^{3+} is about 116 pm. Sodium with an ionic radius of 118 pm therefore is a good substitution and (hole) dopant. In T-La$_2$CuO$_4$ sodium doping leads to similar superconducting critical temperatures of up to 40 K as the classical doping by Sr^{2+}.[16] Doping with potassium (ionic radius of 151 pm) is more difficult and superconducting T-structure samples were not reported.[16] For Cs$^+$ with an even larger ionic radius of 174 pm doping in both the T and T' structures can be excluded due to the huge difference in size between Cs$^+$ and La^{3+}.

T'-La$_2$CuO$_4$ is an electrical insulator, i.e., in pressed bulk pellets the resistivity in a standard four-probe setup was too high to be measured. We investigated the magnetic properties of T'-La$_2$CuO$_4$ by muon spin rotation and relaxation (μSR).[17]

In the inset of Fig. 3 we show representative zero-field μSR data at 10, 130, 180, and 220 K. At the highest

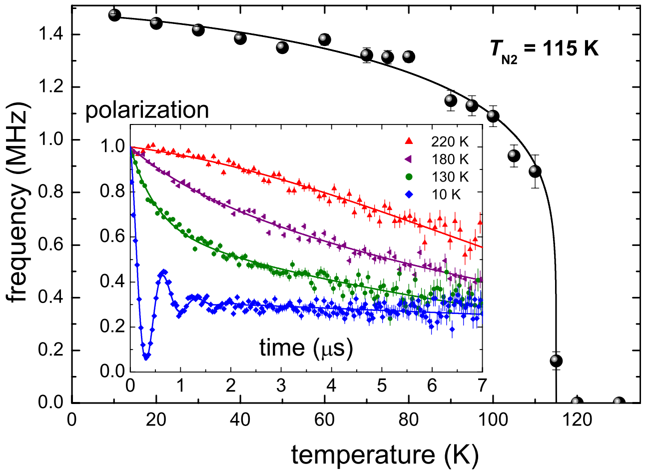

FIG. 3. (Color online) Temperature dependence of the magnetic order parameter as measured by the μSR precession frequency (the solid line is a guide to the eyes). Inset: representative zero-field μSR spectra for 10, 130, 180, and 220 K.

temperature the muon spin polarization $P(t)$ is well described by the Gaussian Kubo-Toyabe (GKT) function $P(t)=\frac{1}{3}+\frac{2}{3}[1-(\sigma t)^2]\exp(-\frac{1}{2}\sigma^2 t^2)$.[18] The small relaxation rate σ and the functional form are typical for static and randomly oriented magnetic fields originating from nuclear moments only. This means that at 220 K, T'-La$_2$CuO$_4$ is in the paramagnetic state and that the electronic Cu 3d moments are rapidly fluctuating so that the resulting depolarization, given by the field averaged over the muon lifetime (2.2 μs), is small compared with the nuclear contribution. Below temperatures of $T_{\mathrm{N}1}\approx 200$ K an additional exponential depolarization gradually develops with decreasing temperature on the cost of the paramagnetic GKT signal which can be fitted to $P(t)=\exp(-\lambda t)$ with a relaxation rate λ. In principle this relaxation could stem from static or slowly (in the megahertz region) fluctuating electronic moments. Longitudinal field (LF) μSR experiments can distinguish between these two scenarios.[18] Our LF-μSR measurements prove the predominantly dynamic character of the depolarization. With decreasing temperature the fluctuation slows down, thereby bringing the fluctuation rate into the time window of the muon ($10^{-6}-10^{-11}$ s), which increases the observable depolarization. Below $T_{\mathrm{N}2}=115$ K, the electronic moments become static on the scale of the muon lifetime, causing the muon spins to precess in the static local fields B_{loc} produced by the Cu moments.

A translationally invariant antiferromagnet possesses a well-defined local field B_{loc} at the muon site. Correspondingly a single Larmor precession frequency $2\pi f=\gamma_\mu B_{\mathrm{loc}}$ (muon gyromagnetic ratio $\gamma_\mu=8.531\times 10^8$ rad s^{-1} T^{-1}) is found which in an insulator is proportional to the staggered magnetization, i.e., the magnetic order parameter. The observed damped oscillation is indicative of long-range order with a moderate degree of magnetic disorder.[17] At lowest temperatures the μSR data of T'-La$_2$CuO$_4$ can be well described by $P(t)=\frac{2}{3}e^{-\lambda_T t}\cos(2\pi f t)+\frac{1}{3}e^{-\lambda_L t}$ with λ_T and λ_L being the transverse and longitudinal relaxation rate. Interestingly, in the temperature interval of 40 to 115 K the low-temperature fit function does not describe the data well. This might indicate some more complicated magnetic state in this temperature range. The temperature dependence of the μSR precession frequency is shown in Fig. 3. The observation of a 1/3 nonoscillating μSR signal fraction proves that 100% of our sample orders since in a fully magnetic powder 1/3 of the local fields are parallel to the initial muon spin direction and do not cause a precession. This information is only obtainable with a local probe like μSR and is indispensable for the absolute determination of the Cu magnetic moment by subsequent neutron-diffraction studies. However, since μSR is a *local* probe, the Cu spin structure cannot be determined directly by our measurements and awaits neutron scattering. The observed μSR frequency is a bit smaller than, but of the same order as, that in other members of the T'-Ln_2CuO$_4$ family.[8,19]

The difference between $T_{\mathrm{N}1}$ and $T_{\mathrm{N}2}$ is most pronounced for the here reported parent compound T'-La$_2$CuO$_4$. However, qualitatively the same picture was also previously observed for other members of the T'-Ln_2CuO$_4$ family. For example, slow magnetic fluctuations below $T_{\mathrm{N}1}$ and the appearance of static magnetic order below $T_{\mathrm{N}2}$ has been also observed in Pr$_{1-x}$LaCe$_x$CuO$_4$ and Nd$_2$CuO$_4$.[8,20] It has been shown on identical samples that $T_{\mathrm{N}1}$ as sensed by muons corresponds to the temperature $T_{\mathrm{N}}^{\mathrm{neutron}}$, where the magnetic peak intensity starts to develop in elastic neutron-scattering experiments.[21] Taking into account the different time scales of μSR and neutron scattering a clear physical picture emerges from the complementary information of the two techniques: below $T_{\mathrm{N}1}\approx T_{\mathrm{N}}^{\mathrm{neutron}}$ long-range antiferromagnetic correlations build up in the systems which are quasistatic on the time scale of the neutron measurement but still slowly fluctuating in the longer μSR time window while below $T_{\mathrm{N}2}$ true static order develops on the time scale of the muon measurement. Please note that this scenario also naturally explains the unusually fast (almost first order) increase in the observed μSR frequency below $T_{\mathrm{N}2}$ (see Fig. 3).

The most interesting result is that T'-La$_2$CuO$_4$ has strongly reduced Néel temperatures $T_{\mathrm{N}1}\approx 200$ K and $T_{\mathrm{N}2}=115$ K (static order) compared to T-La$_2$CuO$_4$ with $T_{\mathrm{N}1}\approx T_{\mathrm{N}2}\approx 300$ K. Our result suggests that the octahedral copper environment stabilizes the antiferromagnetic order in the copper oxygen plane. It is likely that the energy cost of a copper spin flip in the rigid oxygen octahedra is enhanced compared to the planar coordination. This simple picture gives a first qualitative argument for a reduced T_{N} in T'-La$_2$CuO$_4$ compared to T-La$_2$CuO$_4$, which even has wider in-plane lattice spacings in the copper oxide plane.

Also compared to other T' cuprates such as Nd$_2$CuO$_4$ and Pr$_2$CuO$_4$ with $T_{\mathrm{N}1}\approx 250$ K,[19,22] T'-La$_2$CuO$_4$ has the lowest Néel temperatures $T_{\mathrm{N}1}$ and $T_{\mathrm{N}2}$ (the onset temperature of spontaneous muon spin precession indicating static magnetic order). Taking, e.g., the data of Fujita *et al.*[8] on Pr$_{1-x}$LaCe$_x$CuO$_4$ $T_{\mathrm{N}2}$ extrapolates for $x=0$ (corresponding to PrLaCuO$_4$) to approximately 170 K. In the following, we discuss a possible origin of this strong reduction in T_{N} in some detail. In principle, this can be anticipated from the increase in the lattice parameters along both the c and a axes as shown in Fig. 2 which should reduce both the in-plane coupling constant (J) as well as coupling between the CuO$_2$ planes (J'). Generally, the cuprates are characterized by small ratios of J'/J, therefore they can be regarded as nearly two-dimensional (2D) magnetic systems. The magnetic ground state of such a 2D system has been extensively studied since the discovery of high-T_{C} cuprates. It has been shown that the 2D Heisenberg model can be mapped onto a quantum nonlinear sigma model.[23] The three-dimensional (3D) magnetic ordering temperature is determined by the small interplanar coupling and T_{N} can be estimated from $J'(N_0/S)^2(\xi_{2\mathrm{D}}/a)^2\simeq k_{\mathrm{B}}T_{\mathrm{N}}$. $N_0/S\simeq 0.36$ denotes the reduced staggered magnetization at $T=0$ due to quantum fluctuations and $\xi_{2\mathrm{D}}$ is the magnetic correlation length. Within this model and in the so-called renormalized classical regime, for which experiments suggest applicability for the cuprates,[24,25] the magnetic correlation length can be written as $\xi_{2\mathrm{D}}\simeq 0.5a\exp(1/x)[1-x/2+O(x^2)]$ with the lattice constant a and $x=k_{\mathrm{B}}T/(1.13J)$. It has been shown experimentally[26,27] that the in-plane coupling J for T and T' cuprates depends only weakly on the lattice constant a. It follows a power-law dependence $J=J_0(a_0/a)^4$ with $J_0=0.13$ eV and $a_0=382$ pm. Therefore, in T'-La$_2$CuO$_4$ the coupling is reduced by approximately 5% compared to the Pr compound

($J_{\mathrm{La}}=0.95J_{\mathrm{Pr}}$) and amounts to $J\approx0.11$ eV. This means that if T_{N} would be determined by J like in a 3D Heisenberg magnet ($J\simeq k_{\mathrm{B}}T_{\mathrm{N}}$, which represents an upper limit for the influence of J on T_{N} in the 2D system), one would expect a reduction of maximally 5% which would be still much smaller than the observed difference ($T_{\mathrm{N1}}^{\mathrm{Pr}}\approx250$ K and $T_{\mathrm{N1}}^{\mathrm{La}}\approx200$ K). On the other hand, this estimate of J now allows us to determine the interplanar coupling from the combination of the above equations using the measured $T_{\mathrm{N}}=T_{\mathrm{N1}}\approx200$ K and $a=401$ pm. This means that such a low T_{N} results from an approximately ten times smaller J' compared to other T' cuprates ($J'_{\mathrm{La}}\approx0.08J'_{\mathrm{Pr}}$).

This effect seems to be large bearing in mind the increase in the c axis by only 2%. At least qualitatively this result can be understood in a different way. It is well established that in contrast to T-La$_2$CuO$_4$ the T'-Ln_2CuO$_4$ compounds possess a noncollinear magnetic structure, see, e.g. Ref. 28. In such a noncollinear structure the static and dynamic magnetic properties are governed by weak pseudodipolar interaction which derives from the slight polarization of the rare-earth angular momenta by the antiferromagnetic ordered Cu spins.[29] In contrast to other lanthanides in T'-Ln_2CuO$_4$ the La^{3+} is a closed-shell nonmagnetic ion which does not allow for such a polarization therefore leading to a reduced coupling of the CuO$_2$ planes. In other words, the substitution of La by, e.g., Pr or Nd is equivalent to taking out some of the magnetic "glue" between the 2D CuO$_2$ layers. As a result, only the direct comparison of T and T'-La$_2$CuO$_4$ (without the interference of additional magnetic ions) reveals the true structural effect on the *intrinsic* magnetic properties. One may speculate that the observed enhanced two dimensionality ($J'/J\approx2\times10^{-6}$) and the corresponding increase in magnetic fluctuations favors a faster transition into a superconducting phase upon doping. Indications of such behavior were found previously in bulk[30] and in molecular beam epitaxy grown thin films[31] of T'-La$_{2-x}$Ce$_x$CuO$_4$, where superconductivity occurred even at slightly lower doping values than on the hole-doped side of the phase diagram. Recent electronic-structure calculations also indicate a more metallic character of the T' structure.[32] Furthermore, the doping of maximal critical temperature in La$_{2-x}$Ce$_x$CuO$_4$ is about $x_{\mathrm{opt}}=0.09$, which is well reduced compared with the optimal doping concentration in La$_{2-x}$Sr$_x$CuO$_4$, where $x_{\mathrm{opt}}=0.15$.[31] However, these results have to be confirmed by bulk samples.

In conclusion, bulk material of crystalline T'-La$_2$CuO$_4$ was synthesized at moderate temperatures and its crystals structure was determined. Muon spin rotation measurements indicate a slowing down of weakly dynamic antiferromagnetism below $T_{\mathrm{N1}}\approx200$ K and static order below $T_{\mathrm{N2}}=115$ K, which is strongly reduced compared to T-La$_2$CuO$_4$ and the other members of the T'-Ln_2CuO$_4$ family. Within the T' compounds this reduction in T_{N} can be traced back to a ten times decrease in the interplanar coupling possibly due to the missing polarizable lanthanide ion in T'-La$_2$CuO$_4$. Our result can be used as test for a realistic theoretical modeling of the parent compounds of the electron- and hole-doped high-temperature superconductors, taking into account their different crystalline structure.

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