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SYSTEMATICS OF NEW T*-PHASE SUPERCONDUCTIVITY

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A systematic study of the phase stability of $\text{La}(\text{Pr})_{2-x-y}\text{R}_x\text{Sr}(\text{Ba}, \text{Ca})_y\text{CuO}_4$ (R=rare earth) compounds reveals a broad composition range for T*-phase formation. Several members of this series of compounds show bulk superconducting transition temperatures up to $T_c \sim 20$ K. These superconducting cuprates raise further questions about the relationship between structural stability and high temperature superconductivity in oxides.

Lanthanides (R) are known to form compounds at the stoichiometry R_2CuO_4 [1] in three different, but closely related, I4/mmm tetragonal structures or variants thereof: the T-, T'- and T*-phases. All three phases contain square planar CuO_2 planes. In the T-phase, each copper is further coordinated by two out-of-plane oxygens, the six near-neighbor oxygens forming an elongated octahedron. La_2CuO_4 forms in an orthorhombic distortion of the T-phase. Lanthanum ions in this phase are coordinated by nine oxygens. The rare earths Pr through Gd form the T'-phase at 214 stoichiometry. Here the Cu-atoms are only four-fold coordinated oxygen: the 4e 0, 0, z out-of-plane octahedral oxygen of the T-phase moves to 4d 0, $\frac{1}{2}$, $\frac{1}{4}$ in the T'-phase, coordinating now only the rare earth atom. R ions in the T'-phase are coordinated by eight oxygens. Cerium and the rare earths beyond Gd form no phase at this stoichiometry, although they can be substituted into the above phases. Nedil'ko [2] reported the preparation of the T'-phase with two rare earths in a one-to-one ratio. He found the T'-phase for LaRCuO_4 (R=Pr through Gd) and for $\text{RR}'\text{CuO}_4$ (R=Pr through Gd and R'=Pr through Dy). The T*-phase appears to have oxygens in both the 0, 0, z and 0, $\frac{1}{2}$, $\frac{1}{4}$ positions. This structure was first suggested by Takayama-Muromachi et al. [3] in a single phase T*-sample of nominal composition $\text{Nd}_{1.32}\text{Ce}_{0.27}\text{Sr}_{0.41}\text{CuO}_4$. However, they were unable to clarify the ordering of the rare earth ions

in the structure or the oxygen coordination about copper. Some properties of $\text{La}_{2-x}\text{Tb}_x\text{CuO}_4$ in this structure had already been measured by Kenjo and Yajima [4].

Superconductivity is now known to occur in all three phases. T' superconductivity [5] appears to involve n-type carriers, in contrast to p-type carriers in the T[1] and T*[3] cases. In the course of studying T*-phase stability, we discovered superconductivity in several new T*-phase compounds $\text{La}_{1.8-x}\text{R}_x\text{Sr}_{0.2}\text{CuO}_4$, with R=Sm, Eu and Gd. We will discuss the region of T*-phase stability and the systematics of its superconductivity.

The samples used in this study were prepared by firing powders of the metal oxides (carbonates in the case of alkaline earths) at 950°C for 12 h, with one regrinding. These powders were then reground, pelletized and fired at 1050°C for 12 h, again reground, pelletized and fired at 1100°C for 12 h. All firings were done in air, and the samples were generally, but not always, over cooled. T*-phase samples annealed in 1 atm O_2 were found to have no, or at most a trace of, superconductivity. We, therefore, oxygenated all of these samples in a pressure cell at 150 atm and 550°C for 12 h minimum, followed by slow cooling. This final oxygenation was essential for producing bulk superconductivity. Samples were characterized by SQUID magnetometry, four-probe resistance and X-ray powder diffractometry.

Properties of samples forming the T*-phase are summarized in table I. There are no known examples of T*-phase material being formed by a single rare earth element, or one doped with Sr. For binary mixtures of rare earth elements, the T*-phase has in general a very narrow homogeneity range, or none at all. We did not see any indication of T*-phase formation in the La-Gd or La-Y binary rare earth systems: however, T*-phase forms as the dominant phase in $\text{La}_{1.34}\text{Tb}_{0.66}\text{CuO}_4$ and $\text{La}_{1.35}\text{Dy}_{0.65}\text{CuO}_4$. Some T-phase was detected in these samples. The average rare earth ionic radius, $\langle r \rangle$, seems to be an important criterion here, the T*-phase occurring near $\langle r \rangle = 1.135 \text{ \AA}$, using the 8-fold coordination radii of Shannon and Prewett [6]. For example, $\langle r \rangle = 1.137 \text{ \AA}$ in $\text{La}_{1.35}\text{Dy}_{0.65}\text{CuO}_4$. The interesting fact is that a remarkable extension of the homogeneity range is achieved with Sr additions. This extension is smaller for Ca and Ba additions. In the series emphasized in our work, we find that the T*-phase in $\text{La}_{1.8-x}\text{Sm}_x\text{Sr}_{0.2}\text{CuO}_4$ occurs between $0.6 < x < 1.4$, the T-phase occurring for smaller x , the T'-phase for

larger x . In the case of $\text{La}_{1.8-x}\text{Gd}_x\text{Sr}_{0.2}\text{CuO}_4$ we observed the formation of the T*-phase for $0.5 < x < 1.3$, consistent with Gd having a smaller ionic radius than Sm. We also find that the T*-phase in the series $\text{La}_{1-x}\text{SmSr}_x\text{CuO}_4$ exists between $0.1 < x < 0.5$ as the main phase. Samples with composition close to the phase boundary are multiphase; however, a compound such as $\text{La}_{0.75}\text{SmSr}_{0.25}\text{CuO}_4$ is extremely clean T*.

The T- and T'-phases have largely different c/a ratios: for the T-phase, $c/3a \approx 1.15$ while for the T'-phase, $c/3a \approx 1.02$. This difference allows the phases to be easily distinguished by X-ray diffraction. The $c/3a$ ratio in the T*-phase, ≈ 1.08 , is intermediate to that of the T- and T'-phases [4]. Takayama-Murumachi et al. [3] have suggested that the T*-phase consists of alternating stackings of half unit cells of the T- and T'-phases. This unusual situation results in a non-centrosymmetric tetragonal unit cell which should give rise to many X-ray reflections not found in the T- and T'-phases. We have observed these reflections in $\text{La}_{0.75}\text{SmSr}_{0.25}\text{CuO}_4$ and the results are

Table I
X-ray and superconductivity data on $\text{La}(\text{Pr})_{2-x-y}\text{R}_x\text{Sr}(\text{Ba}, \text{Ca})_y\text{CuO}_4$ with T* phase.

Compound	Phase	T_c (Onset) ^{a)}	Remarks
$\text{La}_{1.34}\text{Tb}_{0.66}$	T* + [T]	-	b)
$\text{La}_{1.35}\text{Dy}_{0.65}$	T* + [T]	-	
$\text{La}_{0.37}\text{Nd}_{1.43}\text{Sr}_{0.2}$	T' + T*	< 5 K	
$\text{La}_{0.84}\text{Sm}_{0.96}\text{Sr}_{0.2}$	T*	21 K	$-4\pi\chi_M(5 \text{ K}) = 0.29$ ^{c,d)}
$\text{La}_{0.9}\text{Eu}_{0.9}\text{Sr}_{0.2}$	T*	13.5 K	$-4\pi\chi_M(5 \text{ K}) = 0.13$
$\text{La}_{0.9}\text{Gd}_{0.9}\text{Sr}_{0.2}$	T*	13 K	$-4\pi\chi_M(5 \text{ K}) = 0.12$
$\text{La}_1\text{Tb}_{0.8}\text{Sr}_{0.2}$	T*	< 5 K	
$\text{La}_{1.08}\text{Dy}_{0.72}\text{Sr}_{0.2}$	T*	< 5 K	
$\text{La}_{1.1}\text{Ho}_{0.7}\text{Sr}_{0.2}$	T*	< 5 K	
$\text{La}_{1.13}\text{Y}_{0.67}\text{Sr}_{0.2}$	T* + [T]	-	
$\text{La}_{1.06}\text{Y}_{0.67}\text{Sr}_{0.27}$	T* + [T]	-	
$\text{La}_{0.62}\text{Gd}_{1.18}\text{Ba}_{0.2}$	T* + [T']	-	
$\text{La}_{1.19}\text{Tb}_{0.67}\text{Ba}_{0.14}$	T*	< 5 K	
$\text{La}_{0.9}\text{Dy}_{0.9}\text{Ba}_{0.2}$	T* + [T']	< 5 K	
$\text{La}_{0.9}\text{Sm}_{0.9}\text{Ca}_{0.2}$	T' + [T*]	< 5 K	
$\text{La}_{1.14}\text{Eu}_{0.67}\text{Ca}_{0.19}$	T* + [T]	< 5 K	
$\text{Pr}_1\text{Sm}_{0.75}\text{Sr}_{0.25}$	T' + [T*]	< 5 K	
$\text{Pr}_1\text{Gd}_{0.75}\text{Sr}_{0.25}$	T* + [T']	< 5 K	
$\text{Pr}_1\text{Tb}_{0.75}\text{Sr}_{0.25}$	T* + [T']	< 5 K	
$\text{Pr}_1\text{Dy}_{0.75}\text{Sr}_{0.25}$	T* + [T']	< 5 K	

^{a)} T_c (onset) is determined by the temperature at which the susceptibility deviates diamagnetically from the normal state paramagnetism.

^{b)} The phase in brackets is second phase (more than 5%). Values of x and y are starting compositions.

^{c)} The whole series of La-Sm-Sr samples are shown in figs. 2 and 3.

^{d)} Meissner effect (field cooled diamagnetism) at 5 K.

Table II

X-ray diffraction intensities of $\text{La}_{0.75}\text{SmSr}_{0.25}\text{CuO}_4$ at 300 K measured with Mo-K α radiation. The structure is tetragonal with $a=3.853 \text{ \AA}$ and $c=12.55 \text{ \AA}$.

	hkl	$d(\text{\AA})$	Int.
	101	3.689	27
*	102	3.280	3
	004	3.133	17
	103	2.834	100
	110	2.723	80
	112	2.500	1
*	104	2.432	5
	105,006	2.095	33
	114	2.055	40
	200	1.927	60
*	115	1.847	1
	211	1.706	7
	116,212	1.659	21
	107	1.625	21
	213	1.594	54
	008	1.570	3
*	214	1.514	1
*	117	1.503	1
*	108	1.455	1
	215,206	1.419	26
	220	1.361	16
*	207	1.312	2

tabulated in table II. The absence of reflections corresponding to either T- or T'-phases indicates our T* material is single phase. Furthermore, simple structure-factor calculations show that if our sample had the T- or T'-structures, then the reflections indicated by asterisks would have been absent. These extra reflections appear consistent with the T*-structure being formed by some form of alternate stacking of T and T' units. We have calculated the X-ray intensities for such a hypothetical lattice and find that the extra reflections should be much more intense than observed. We have also calculated the intensities assuming that only the oxygens change positions so as to form locally the T- and T'-structures, but then the extra reflections are too weak. This suggests that the cations at the R sites are neither randomly distributed nor completely ordered. It is likely that larger cations are located preferentially at T-type positions, whereas the smaller ones are at T'-type positions, and that these two positions tend to alternate along the z-direction. A further peculiarity of the T*-phase is

that the separation between consecutive CuO_2 (001) planes may change by as much as 8%.

High pressure oxygenation produces bulk superconductivity in some Sr-doped T*-phases. Two examples of single T*-phase exhibiting bulk superconductivity are shown in fig. 1. Plotted are both shielding and Meissner (field-cooled) effect results. The Meissner effect is $\sim 30\%$ of $-1/4\pi$ in $\text{La}_{0.84}\text{Sm}_{0.96}\text{Sr}_{0.2}\text{CuO}_4$. This results suggest that annealing at higher oxygen pressures will increase the superconducting volume fraction, especially since we find no superconductivity or trace thereof in samples annealed at 1 atm O_2 . Magnetization measurements as a function of temperature in various fields on $\text{La}_{0.84}\text{Sm}_{0.96}\text{Sr}_{0.2}\text{CuO}_4$ find that near T_c the temperature derivative of the upper critical field is $\sim -3.9 \text{ kG/K}$. We note that the corresponding value for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ is -16 kG/K [1]. For all temperatures we observed that the normal state susceptibility of high pressure oxygenated $\text{La}_{0.84}\text{Sm}_{0.96}\text{Sr}_{0.2}\text{CuO}_4$ is higher by a constant amount than that of a deoxygenated sample, indicating the presence of a Pauli-like term in the former. This constant shift is $\sim 2.7 \times 10^{-4} \text{ emu/mol-Cu}$ for $100 \text{ K} < T < 300 \text{ K}$. In a free electron picture with 0.2 holes/Cu, this implies a mass-enhancement factor of ~ 10 .

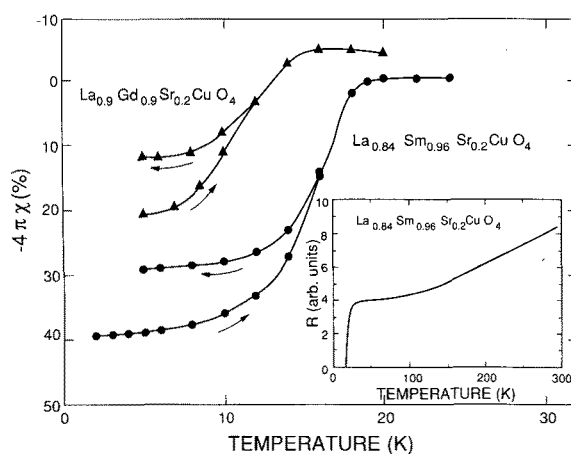


Fig. 1. Shielding effect and Meissner effect measured with 20 G versus temperature in $\text{La}_{0.84}\text{Sm}_{0.96}\text{Sr}_{0.2}\text{CuO}_4$ (●) and $\text{La}_{0.9}\text{Gd}_{0.9}\text{Sr}_{0.2}\text{CuO}_4$ (▲). Demagnetizing effects due to sample geometry have been taken into account. The inset displays the temperature dependent resistance of a $\text{La}_{0.84}\text{Sm}_{0.96}\text{Sr}_{0.2}\text{CuO}_4$ pellet.

We have found further that $\text{LaTb}_{0.8}\text{Sr}_{0.2}\text{CuO}_{0.4}$, $\text{La}_{1.08}\text{Dy}_{0.72}\text{Sr}_{0.2}\text{CuO}_4$, $\text{La}_{1.1}\text{Ho}_{0.7}\text{Sr}_{0.2}\text{CuO}_4$, and $\text{La}_{1.19}\text{Tb}_{0.67}\text{Ba}_{0.14}\text{CuO}_4$ are clean T*-phase but do not become superconducting above 5 K. The multiphase (including T*) $\text{La}_{1.14}\text{Eu}_{0.67}\text{Ca}_{0.19}\text{CuO}_4$ also does not become superconducting above 5 K; however, $\text{La}_{0.9}\text{Eu}_{0.9}\text{Sr}_{0.2}\text{CuO}_4$ with the T* structure does become superconducting below ~ 13.5 K. As shown in table I, some Sr-doped Pr-R samples (e.g. $\text{PrGd}_{0.75}\text{Sr}_{0.25}\text{CuO}_4$) are dominantly T* but not superconducting.

Shown in the inset of fig. 1 is the temperature dependence of the resistance for a Sm sample. The behavior is typical of that for a dirty metal: we do not find a linear dependence down to T_c as has been observed in many other oxide superconductors. It is possible that a balance between a semiconducting tail at low T and a linear T -dependence is causing the flat portion above T_c , and experiments on samples oxygenated in the kbar region could address this possibility. As expected, the thermoelectric power is positive at room temperature, indicating conduction by hole-like carriers.

The principal result of this paper is the T_c variation with x in $\text{La}_{1.8-x}\text{Sm}_x\text{Sr}_{0.2}\text{CuO}_4$, shown in fig. 2. For $x=0.2$, T_c is depressed by ~ 20 K in the T-phase, as originally observed by Tarascon et al. [7]. Clean materials in the range between $x=0.4$ and $x=0.8$ are very difficult to prepare, and the samples in this range contain in general both T- and T*-phases. What is

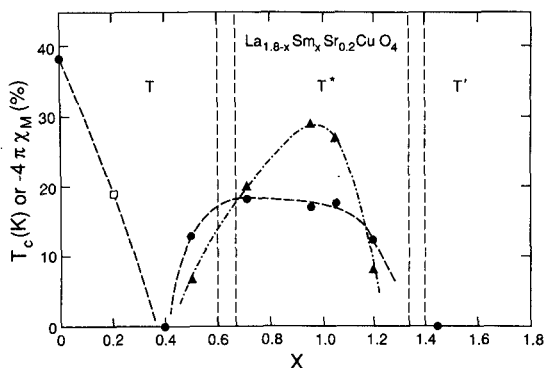


Fig. 2. T_c (\bullet) defined by 5% of $-1/4\pi$ shielding temperature and true Meissner effect (\blacktriangle) at 5 K as function of x in $\text{La}_{1.8-x}\text{Sm}_x\text{Sr}_{0.2}\text{CuO}_4$. (\square) is T_c from ref. [7]. Phase boundaries (dashed vertical lines) are defined by compositions at which the second phase becomes comparable to the primary phase.

remarkable is that as soon as x is solidly in the T*-phase, T_c (defined by the temperature at which the diamagnetism reaches 5% of $-1/4\pi$) appears near 20 K and is only weakly dependent on x until $x > 1$. The variation of T_c with Sr content in $\text{La}_{1-x}\text{SmSr}_x\text{CuO}_4$ shown in fig. 3 peaks at $x=0.18$, essentially the same value of x for which T_c peaks with Sr additions to La_2CuO_4 in the distorted T-phase, [1] and with Ce additions to Nd_2CuO_4 in the T'-phase [5]. T_c in the T'-phase is very close to that found here. In the two phase T'/T* region shown in fig. 3 we sometimes find a small amount of T-phase and that T_c is not a smooth function of x , suggesting that superconductivity in this region depends sensitively on sample processing conditions and/or oxygenation.

Our findings on T*-material are additional evidence for the irrelevance of the out-of-plane oxygen atoms to high T_c : the out-of-plane chemistry merely adjusts the electron count off half-filling of the highest band, a deviation of more than 0.1 being required to achieve the metallic state. The value of this deviation is essentially the same for the three different 214 phases, while T_c changes little. This suggests to us that the mechanism is to be sought in the CuO_2 planes, not in the oxygens bridging CuO_2 layers. The substantial variation in the Cu-O-Cu spacing in the plane between the different superconducting phases (3.77 Å in T, ~ 3.85 Å in T* and ≤ 3.96 Å in T') puts further boundary conditions on ones thinking.

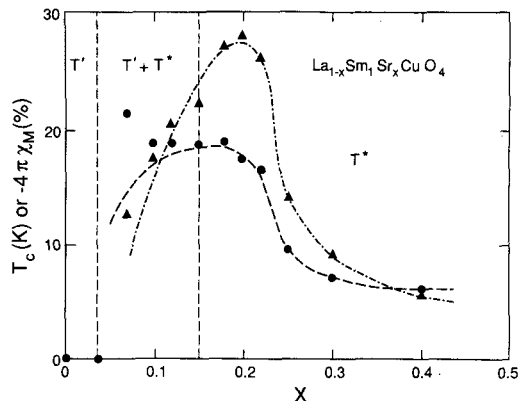


Fig. 3. T_c (\bullet) defined by 5% of $-1/4\pi$ shielding temperature and true Meissner effect (\blacktriangle) at 5 K versus x in $\text{La}_{1-x}\text{Sm}_1\text{Sr}_x\text{CuO}_4$. Multiphases form in the range of $\sim 0.03 < x < \sim 0.15$ and $x > 0.4$. Clean T*-phase forms for $\sim 0.15 < x < 0.4$.

The significant drop in T_c in the T-phase with Sm substitution remains without explanation. The nearness of the T/T* phase boundary to $T_c=0$ in the T-phase is suggestive of reduction of T_c by, perhaps, rare-earth site disorder or incipient structural instability. It is also interesting that resistance measurements on rare earth doped T-phase material $\text{La}_{1.6}\text{R}_{0.2}\text{Sr}_{0.2}\text{CuO}_4$ show a growing low temperature semiconductor-like characteristic as R is varied from Pr to Gd [7]. One approaches the T* boundary more closely as R is varied towards Gd, and it may be that the metal-semiconductor transition is more delicate near Gd. In this context, the lack of superconductivity in some samples of clean T*-phase material (e.g. $\text{LaTb}_{0.8}\text{Sr}_{0.2}\text{CuO}_4$) needs to be clarified. A further remark is that the presence of both T- and T'-type structural units in the T*-phase leads one to wonder about the possibility of n-type doping of the T*-phase for producing superconductivity, a possibility we are investigating.

After completing our work, we became aware that Tokura et al. [8] have also prepared T*-phase material in the $(\text{La-Sm-Sr})_2\text{CuO}_4$ system but apparently have not observed bulk superconductivity.

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