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T*-PHASE SUPERCONDUCTIVITY

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The T*-phase is a mixed rare earth oxide phase forming at the composition R_2CuO_4. Its crystal structure is intermediate between the La_2CuO_4 and Nd_2CuO_4 structures. Sr-doped samples have T_c onsets as high as 37 K. We discuss the systematics of T_c of T*-phases as a function of Sr doping, rare earth mixture and oxygenation. Structural and transport data will also be presented.

1. INTRODUCTION

Single layer rare earth cuprates at stoichiometry R_2CuO_4 form in three known structures: for R-La in the T-phase, orthorhombically distorted K_2NiF_4 structure type; for R-Pr through Gd in the T'-phase, tetragonal Nd_2CuO_4 structure type; and for R a mixture of early and later rare earths, the tetragonal T*-phase. Superconductivity is now known to occur in all three of these phases, and a comparison of the superconductivity in them is interesting from the standpoint of trying to determine what are the essential structural characteristics relevant to high T_c oxide superconductivity. We summarize here our work on T*-phase powders prepared by repeated grinding of rare earth and copper oxides and alkaline earth carbonates, sintered in air at temperatures progressing to 1100C, with subsequent oxygen anneals to be described.

2. PHASE STABILITY AND CRYSTAL STRUCTURE

The T*-phase was first identified by Takayama-Muromachi et al. [1] in superconducting $Nd_{1.32}Ce_{0.27}Sr_{0.41}CuO_4$. They suggested that this structure was intermediate between the T- and T'-types, having the out-of-plane oxygens in both the $(0,0,z)$ and $(0,1/2,1/4)$ positions of the respective T- and T'-structures (see fig. 1). They also suggested that partial ordering of the rare earth and Sr atoms might occur.
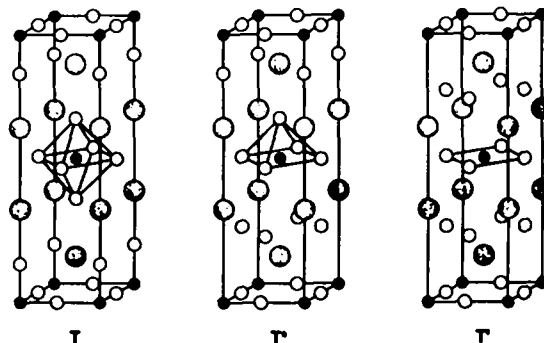

Fig. 1 R_2CuO_4 Compounds (R=rare earths) form in these three structures: T-, T*- and T'-structures.

A difficulty which appeared in the initial reports on the T*-phase was that of preparing single phase material [1,2]. If atomic ordering of the rare earth atoms occurs, a reasonable approach would be to choose the two rare earths with rather disparate ionic radii, and make preparations with a concentration of the two rare earths roughly equal. It has proved in our experience very difficult to make single phase T* in binary rare earth R_2CuO_4 preparations: addition of Sr greatly enhances the range of phase stability [3]. Some of our results on range of stability are tabulated in the Table. We note that Ca and Ba also stabilize T* but are not nearly as effective. The T*-phase can tolerate as much as $Sr_{0.4}$ in the La-Sm preparations. It is interesting that the T*-phase is evident in the much earlier work of Kenjo and Yajima [5] in the binary alloy $La_{1.33}Tb_{0.67}CuO_4$. T*-phase exists here in a very narrow ratio of La/Tb, as we have also confirmed.

Ordering among the rare earth atoms in T* should be evident in the presence of x-ray reflections forbidden in the I4/mmm tetragonal space group of undistorted T and T'. We have undertaken a Rietfeld analysis of anomalous x-ray diffraction data on $La_{0.9}Gd_{0.9}Sr_{0.2}CuO_4$ to refine the atomic positions and occupancies [6]. Nearly complete ordering is found between the large and small rare earth ions, with Sr choosing the large positions. What is found, then, is that the central CuO_2 plane of the unit cell is shifted away from z=1/2 by roughly 0.07 Å. The large (La) ions have a T-type oxygen environment, and the smaller ions (Gd) a T'-type. The Cu-Cu spacing is also intermediate, at 3.85 Å.

In fig. 2 we show the lattice parameter variations for T and T* alloys in the vicinity of the compositions where both

Table 1. X-ray and superconductivity data on $La(Pr,Nd)_{2-x-y}R_xSr(Ba,Ca)_yCuO_4$ with T*-phase.

Compound	Phase	Tc (onset)[1]
$La_{1.34}Tb_{0.66}$	T* + [T]	--[2]
$La_{1.35}Dy_{0.65}$	T* + [T]	--
$Pr_{1.6}Sr_{0.4}$	T*	--
$Nd_{1.4}Ce_{0.2}Sr_{0.4}$	T*	~30 K[3]
$La_{0.5}Pr_{1.3}Sr_{0.2}$	T*+[T,T']	< 5 K
$La_{0.37}Nd_{1.43}Sr_{0.2}$	T' + T*	< 5 K
$La_{0.82}Sm_1Sr_{0.18}$	T*	37 K [4]
$La_{0.84}Sm_{0.96}Sr_{0.2}$	T*	35 K [4]
$La_{0.9}Eu_{0.9}Sr_{0.2}$	T*	34 K [4]
$La_{0.9}Gd_{0.9}Sr_{0.2}$	T*	33 K [4]
$La_1Tb_{0.8}Sr_{0.2}$	T*	< 5 K
$La_{1.08}Dy_{0.72}Sr_{0.2}$	T*	< 5 K
$La_{1.1}Ho_{0.7}Sr_{0.2}$	T*	< 5 K
$La_{1.13}Y_{0.67}Sr_{0.2}$	T* + [T]	--
$La_{1.06}Y_{0.67}Sr_{0.27}$	T* + [T]	--
$La_{0.62}Gd_{1.18}Ba_{0.2}$	T* + [T']	--
$La_{1.19}Tb_{0.67}Ba_{0.14}$	T*	< 5 K
$La_{0.9}Dy_{0.9}Ba_{0.2}$	T* + [T']	< 5 K
$La_{0.9}Sm_{0.9}Ca_{0.2}$	T' + [T*]	< 5 K
$La_{1.14}Eu_{0.67}Ca_{0.19}$	T* + [T]	< 5 K
$La_{0.9}Sm_{0.65}Sr_{0.15}Ce_{0.3}$	T*	< 5 K[5]
$Pr_1Sm_{0.75}Sr_{0.25}$	T'+ [T*]	< 5 K
$Pr_1Gd_{0.75}Sr_{0.25}$	T* + [T']	< 5 K
$Pr_1Tb_{0.75}Sr_{0.25}$	T* + [T']	< 5 K
$Pr_1Dy_{0.75}Sr_{0.25}$	T* + [T']	< 5 K

[1] T_c (onset) is determined by the temperature at which the susceptibility deviates diamagnetically from the normal state paramagnetism

[2] The phase in brackets is second phase (more that 5%). Values of x and y are starting compositions.

[3] After Ref. 4.

[4] Samples are oxygenated under 3kbar pressure.

[5] T_c is measured on samples with various heat treatments (high pressure oxygenation or inert gas annealing).
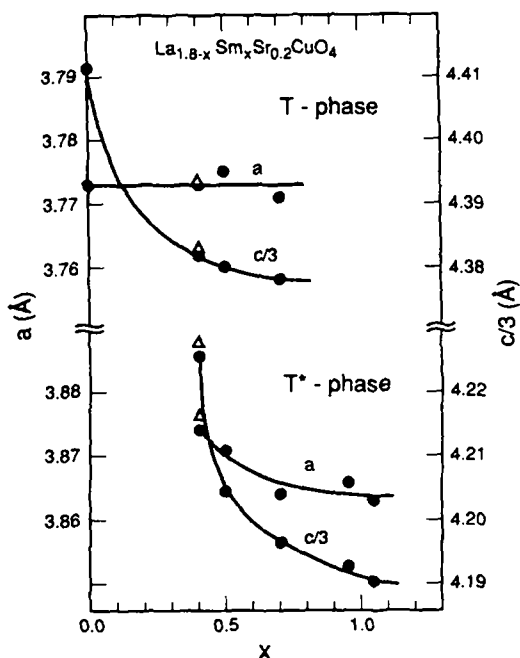
Fig. 2 Variation of a and c lattice constants with x of $La_{1.8-x}Sm_xSr_{0.2}CuO_4$. Upper and bottom curves are for T- and T^*-phases, respectively. The open triangles denote data on an oxygenated sample under 150bar pressure. Note that T- and T^*-phases coexist in the range of $0.4 \leq x \leq 0.7$.

Fig. 3 T_C (•) defined 5% of $-1/4\pi$ shielding temperature and true Meissner effect (▲) at 5 K versus x in $La_{1-x}Sm_lSr_xCuO_4$ oxygenated under 150bar pressure. Multiphases form in the range of ~0.03 < x < ~0.15 and x > 0.4; however, clean T^*-phase forms for ~0.15 < x < 0.4.

phases occur in sintered samples of $La_{1.8-x}Sm_xSr_{0.2}CuO_4$. A strong variation in the T^* parameters is evident in the region where T becomes the dominant phase. We note that, as one might expect from the ordering among the rare earth ions, compositions near equiatomic for the rare earths are found to be favorable for T^* formation.

3. SUPERCONDUCTIVITY AND RELATED PROPERTIES

We first turn to data on $La_{1-x}SmSr_xCuO_4$ alloys (fig. 3). We see that evidence for T^* formation is found for x=0.03, but that clean T^* is found only above X~0.15. Samples annealed at 1bar oxygen are not superconducting. The data in fig. 3 are for
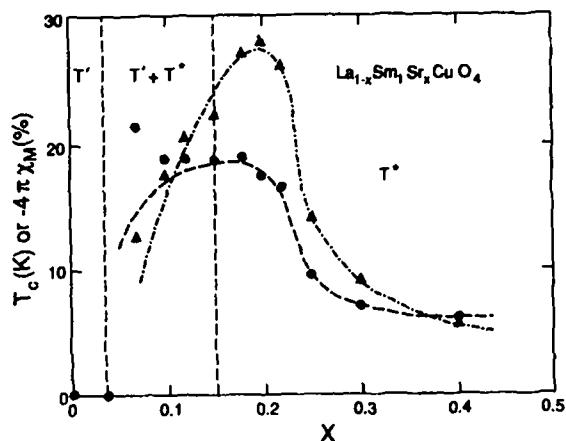
oxygenation at 150bar and 550C. Clear evidence for bulk superconductivity is found. It is interesting that T_c as a function of x is very similar to that found for Sr-doped La_2CuO_4. Oxygenation at higher pressure (3 kbar) increases T_c substantially, as seen for the x~0.18 sample in fig. 4. The sample is already diamagnetic at 37 K [7]. This is very close to the maximum T_c observed in the Sr-doped La_2CuO_4 system.

This last result is surprising in view of the T_c dependence with Sm concentration in 150bar-oxygentated $La_{1.8-x}Sm_xSr_{0.2}CuO_4$ samples shown in fig. 5. There is a strong depression of T_c with x in the T-phase, but when the T^*-phase is cleanly established at higher Sm concentrations the value of T_c is essentially unchanged from the x~0 T-phase value. We also show in fig. 6 similar data for samples with Gd and Eu in place of Sm, the data being for 150bar oxygenated samples. In these cases it is interesting that the
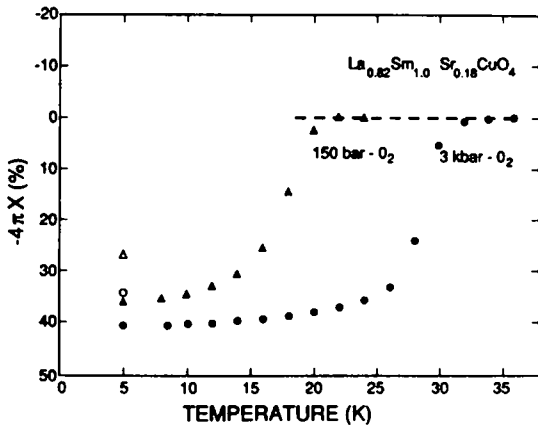
Fig. 4 Magnetization measurements on 150bar (▲)- and 3kbar (●) -oxygenated $La_{0.82}Sm_{1.0}Sr_{0.18}CuO_k$ powders. Solid symbols represent zero-field cooled results. Whereas the open symbols are for field cooling from above T_c.

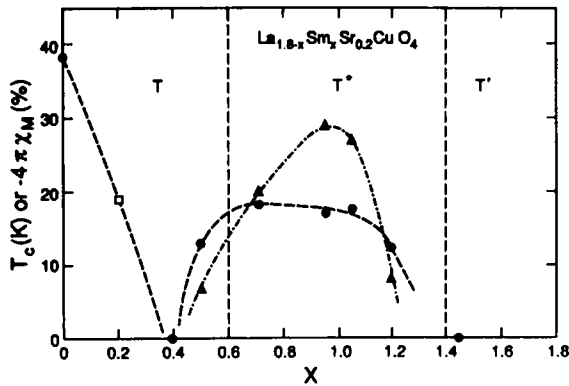superconductivity is in a narrow region near x=0.9 and cleanly away from the T/T^* and T^*/T' phase boundaries. This narrow region of superconductivity needs further investigation. It should be further noted that samples made with Tb in place of Sm have not become superconducting even with 3kbar oxygenation.

The evolution of the electrical resistivity with oxygenation treatment is shown for $La_{0.82}SmSr_{0.18}CuO_4$ in fig. 7. What is remarkable here is the rapid evolution from semiconductor-like to metallic to approaching linear in T dependence of the electrical resistivity. In view of the broad onset of T_c in the 3kbar oxygenated sample, we speculate that the resistivity of a fully oxygenated sample would indeed be strictly linear to T_c with T=0K intercept near zero. We suggest that this characteristic, often remarked upon in connection with other high T_c oxide superconductors, can be used as a
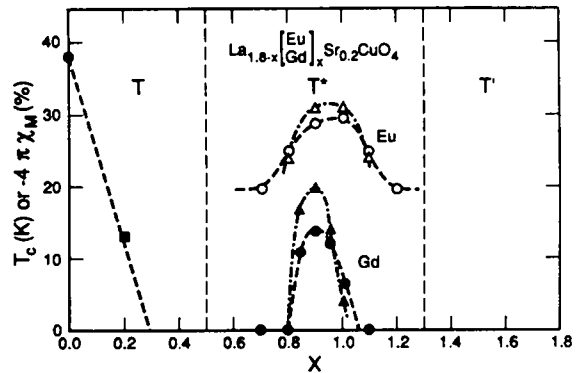

Fig. 5 T_c (●) and Meissner effect (▲), defined as those in Fig. 3, as functions of x in $La_{1.8-x}Sm_xSr_{0.2}CuO_4$ oxygenated under 150bar pressure. (□) is T_c from Ref. 8. Phase boundaries (dashed vertical lines) are defined by compositions at which the second phase becomes comparable to the primary phase.

Fig. 6 T_c (○ and ●) and Meissner effect (Δ and ▲), defined as those in Fig. 3, versus x in $La_{1.8-x}$ (Eu and Gd)$_x$$Sr_{0.2}CuO_4$ oxygenated under 150bar pressure, respectively. (■) is T_c of $La_{1.8-x}Gd_xSr_{0.2}$ from Ref. 8. Phase boundaries for $La_{1.8-x}Gd_xSr_{0.2}CuO_4$ (dashed vertical lines) are defined as those in Fig. 4. Data for Eu-based samples are shifted up by 20 units.

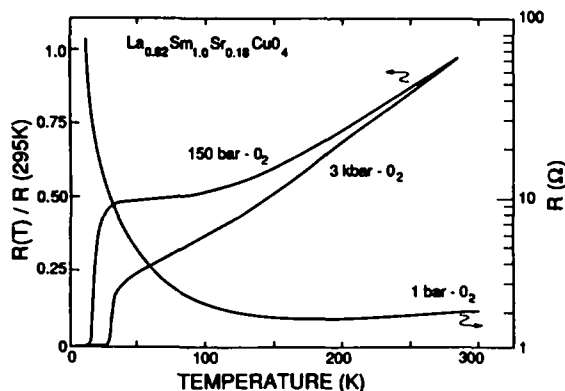Fig. 7 Resistance versus temperature for a singly T*-phase sample of $La_{0.82}Sm_{1.0}Sr_{0.18}CuO_4$ subjected to anneals in O_2 at 1bar, 150bar and 3kbar. In the latter two cases the resistance has been normalized to its value at 295 K.

diagnostic for sample quality, especially as regards oxygen stoichiometry. Our thermopower data (not shown [7]) has a corresponding evolution with oxygenation and is positive in sign, indicating the probability of hole-type superconductivity here. Attempts to n-dope T*-phase material via Ce substitution did not produce n-type superconducting material (see Table).

4. CONCLUSIONS

The variation of T_C with rare earth substitution in T-phase coupled with the high T_C found in T* in a narrow composition range prompts the speculation that rare earths, such as Sm, when dissolved in T-material actually have a T′ environment. The T_C of such substituted T-material might then be depressed by these "unfavorable" T′ regions. Within the T*-phase, the high degree of ordering of the rare earths atoms might then

lead to p-type superconductivity in the La dominant T-regions, with unchanged T_C from pure T-phase. The range of composition in which T* is superconducting could narrow then with smaller rare earth ionic radius because the degree of ordering is higher for larger ionic radii difference.

Independent of such speculations, our results re-emphasize that the primary physics in the cuprates is confined to the CuO_2 planes.

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