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## PROPERTIES OF T\*-PHASE CUPRATE MATERIALS

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### Summary

Properties of the hole-type, single-layer cuprate T\*-phase superconductors are discussed. There is a strong variation of  $T_c$  with rare-earth constituent and oxygenation pressure. The magnetic properties of these materials have not yet been well investigated, but some aspects of the rare-earth ordering appear to be different from other known cuprates.

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### 1. Introduction

Rare earth cuprates of the general formula  $R_2CuO_4$  form in three basic structure types, the so-called T-, T\*- and T'-phases. These are shown in Fig. 1. Lanthanum forms the distorted T-phase; praeodymium through gadolinium form the T'-phase. The T\*-phase forms only with a combination of two rare earths, usually, but not always, lanthanum being one of them, and, with the exceptions of  $La_{1.3}Tb_{0.7}CuO_4$  and  $La_{1.35}Dy_{0.65}CuO_4$ , strontium is required to stabilize the compound. The T\*-phase can be seen to be built from a combination of T and T' structural elements, and it is easy to hypothesize that a combination of a large and smaller radius rare earth are necessary to form the T\* material.

From the standpoint of research in cuprate superconductivity, the interest in T\*-phase material derives from the much extended materials phase space provided by this structure. The copper environment combines features of the T- and T'-

phases, as well as having similarities to the Y123 copper environment. A broad range of rare earths from this T\*-structure, and this fact allows much latitude in the investigation of those parameters relevant to high  $T_c$ .

The T\*-phase in cuprates was first evident in the work of Kenjo and Yajima [1], although the structure ultimately determined by Takayama-Muromachi *et al.* [2] was identified much earlier in phosphor work on  $RNaTiO_4$  [3]. Superconductivity in T\*-cuprates was first reported by Akimitsu *et al.* [4] in  $(Nd_{0.66}Ce_{0.135}Sr_{0.205})_2CuO_4$ . Subsequently, Tokura *et al.* [5] and Cheong *et al.* [6] greatly extended the range of known T\*-phase cuprates and their superconductivity.

## 2. Crystal chemistry

The T\*-crystal structure, as it is now understood, appears as shown in Fig. 1. The phase seems to form most easily with approximately equiatomic mixtures of rare earths, such as  $La_{0.9}Sm_{0.9}Sr_{0.2}CuO_4$ . There is essentially complete separation of the large and small rare earths into their respective T- and T'-type rare-earth sites shown in Fig. 1 [7]. When non-equiatomic ratios of rare earths form the compound, there is clearly some "wrong site" occupation. Crystallographic

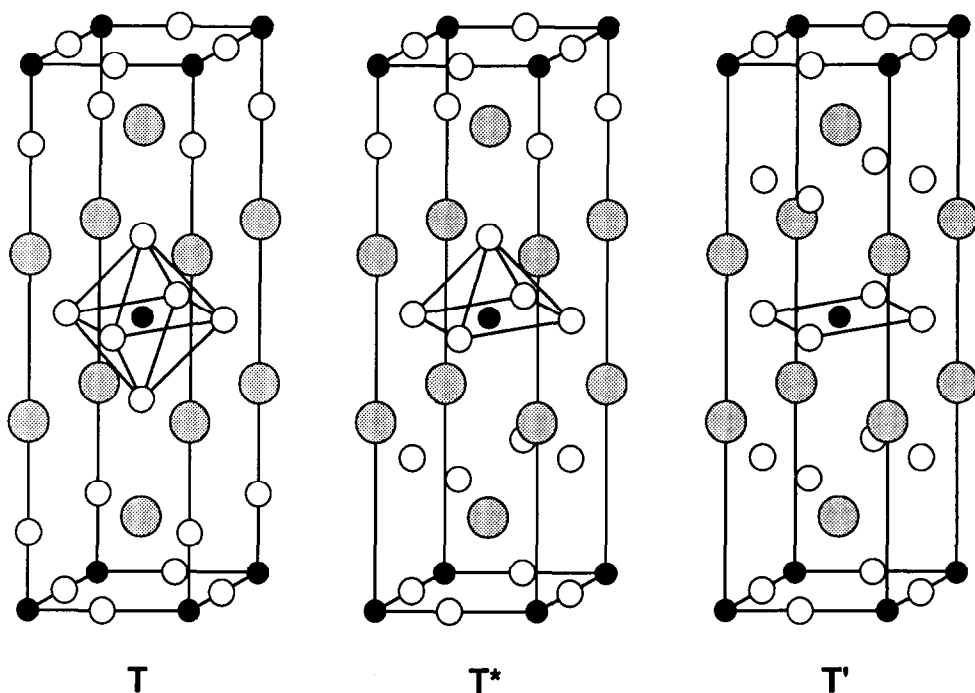


Fig. 1. T-, T\*- and T'-structures of  $R_2CuO_4$  rare earth cuprates. Small full circles represent copper atoms, small open circles oxygen and large shaded circles rare earths.

refinement appears consistent with the central  $\text{CuO}_2$ -plane being displaced from  $z = \frac{1}{2}$ , in contrast with the T- and T'-phases.

Recent work [8] on single crystals of  $\text{La}_{1.3}\text{Tb}_{0.7}\text{CuO}_4$  grown with CuO-PbO flux finds that the tetragonal T\*-structure distorts below approximately 150 °C to orthorhombic or lower symmetry. However, on examination of T\* crystals of strontium-doped  $(\text{La}, \text{Sm})_2\text{CuO}_4$  from CuO flux they were found to be tetragonal at room temperature.

The T\*-phase of the form  $\text{La}_{2-x-y}\text{R}_x\text{Sr}_y\text{CuO}_4$ , has now been found to be formed by most R. For the heavy rare earths or yttrium, namely the small ionic size rare earths, fairly large  $y$  appears to be necessary to stabilize the phase. For example, Takayama *et al.* [3] report  $\text{La}_{0.9}\text{Y}_{0.8}\text{Sr}_{0.3}\text{CuO}_4$  in T\*. We also note that Xue *et al.* [9] report  $\text{Pr}_{1.2}\text{Ce}_{0.35}\text{Sr}_{0.45}\text{CuO}_4$  and  $\text{Gd}_{1.2}\text{Ce}_{0.35}\text{Sr}_{0.45}\text{CuO}_4$  in T\*. None of these last three formulations are superconducting. We note that X-ray data are consistent with the presence of stacking faults involving planes of square-pyramidal coordinated copper and that there are substantial changes in the transport and superconducting properties with accompanying oxygen loading: as prepared materials are semiconductor-like but with increased oxygenation pressure the transport becomes metallic in character and superconductivity appears.

### 3. Magnetic properties

There has so far been no report on magnetic ordering in copper in T\*-phase material. Such ordering seems likely, but there may be some difference from the T- and T'-cases due to the loss of centering of the  $\text{CuO}_2$ -planes in T\*.

We have examined the low temperature specific heat of 150 bar oxygenated  $\text{La}_{0.7}\text{Gd}_{1.1}\text{Sr}_{0.2}\text{CuO}_4$  and  $\text{La}_{0.9}\text{Gd}_{0.9}\text{Sr}_{0.2}\text{CuO}_4$  from 1.8 to 20 K. The data are shown in Fig. 2. There is a broad, large upturn in  $C/T$  below approximately 10 K. This behavior is somewhat more pronounced in the more gadolinium-rich sample. We tentatively interpret the data as showing the onset of a very broad magnetic ordering of the gadolinium moments. The broadened feature of this transition makes it quite different from the cleanly ordered antiferromagnetic transitions in  $\text{Gd}_2\text{CuO}_4$  and  $\text{GdBa}_2\text{Cu}_3\text{O}_7$  which occur at 6.5 [10] and 2.2 K [11] respectively. This difference is possibly associated with the large separation of T-slabs of gadolinium along the  $c$ -axis.

We also show magnetic susceptibility data taken on single crystals of unoxxygenated  $\text{La}_{0.9}\text{Eu}_{0.9}\text{Sr}_{0.2}\text{CuO}_4$  (nominal composition) in Fig. 3. The overall magnitude of the susceptibility per mole europium is very comparable with that of T'-phase  $\text{Eu}_2\text{CuO}_4$  [12]. We also find that the  $\chi$  perpendicular to the  $\text{CuO}_2$ -planes goes through a weak maximum. The value of  $\chi$  at low temperature is determined by the behavior of the  $J = 1$  first excited  $J$ -multiplet of europium. The crystal field splitting of the  $J = 1$  multiplet in T\* must be approximately the same as in T'. The susceptibility is larger for the field perpendicular compared with that parallel to the  $\text{CuO}_2$ -planes and this is also found above  $T_c$  in superconducting  $\text{La}_{0.9}\text{Sm}_{0.9}\text{Sr}_{0.2}\text{CuO}_4$ .

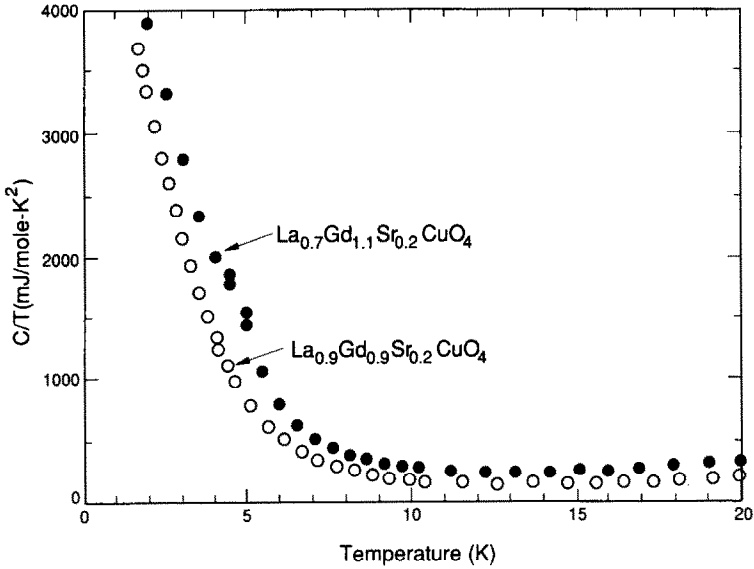


Fig. 2. Low temperature specific heat of polycrystalline gadolinium-based  $T^*$ -phases. Specific heat divided by  $T$  is plotted against  $T$ . The feature in the  $Gd_{1.1}$  sample near 4.5 K is believed due to a small amount of  $Gd_2CuO_4$   $T'$ -phase impurity which orders magnetically near this temperature.

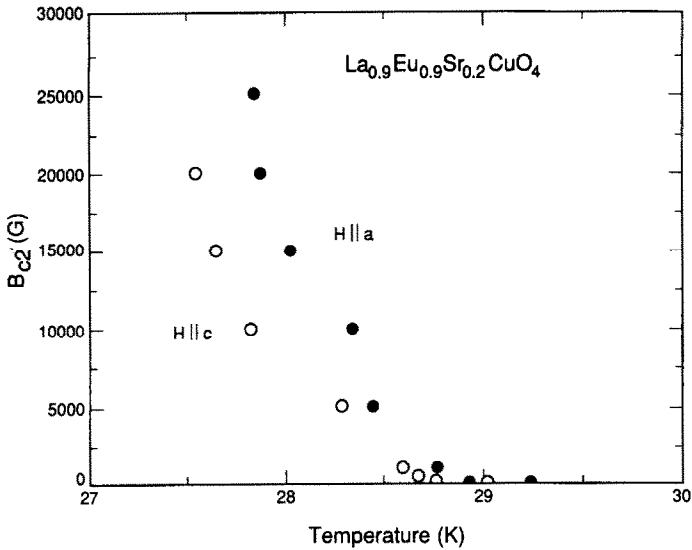


Fig. 3. Magnetic susceptibility data parallel and perpendicular to the  $CuO_2$  planes of single crystals of nominal  $La_{0.9}Eu_{0.9}Sr_{0.2}CuO_4$ .

#### 4. Superconducting properties

T\*-based superconductors have hole-type conductivity.  $T_c$  as a function of strontium-doping peaks near Sr<sub>0.2</sub>, just as in strontium-doped La<sub>2</sub>CuO<sub>4</sub>.  $T_c$  also peaks near equiatomic rare earth mixtures in T\*, with the peaking becoming more pronounced as the rare earth becomes heavier (Fig. 4). To date, (La, Tb, Sr)<sub>2</sub>CuO<sub>4</sub> materials have not shown any superconductivity. We have made polycrystalline samples of La<sub>0.9</sub>Sm<sub>0.7</sub>Tb<sub>0.2</sub>Sr<sub>0.2</sub>CuO<sub>4</sub> and La<sub>0.9</sub>Sm<sub>0.7</sub>Dy<sub>0.2</sub>Sr<sub>0.2</sub>CuO<sub>4</sub> and find that they are not superconducting above 2 K after 150 bar oxygenation at 650 °C. This most likely points to some subtle undetected structural effect accompanying the introduction of the small rare earths into the T\*-structure. We have found that attempts to n-dope T\* with cerium has not led to superconductivity, nor has fluorine-doping for oxygen, as reported in ref. 13.

It is not known why the T\*-phase is so difficult to oxygenate, but the transport data clearly reflect substantial changes with oxygenation pressure changing from 150 to  $3 \times 10^3$  bar [14]. The maximum  $T_c$  for 3 kbar oxygenated La<sub>0.9</sub>Sm<sub>0.9</sub>Sr<sub>0.2</sub>CuO<sub>4</sub> pre in the mid thirties. Owing to the various preparation conditions used by different authors, and the extreme sensitivity to oxygenation pressure, it is not clear how  $T_c$  varies with rare earth. What data exist suggest that  $T_c$  is depressed sharply with the size of the smaller rare earth constituent.

Our  $H_{c2}$  critical field data obtained from magnetization measurements on aligned powders of La<sub>0.9</sub>Sm<sub>0.9</sub>Sr<sub>0.2</sub>CuO<sub>4</sub> are shown in Fig. 5. This alignment has been verified by X-ray analysis. What is most surprising is the small anisotropy ( $H_{c2}^{\parallel}/H_{c2}^{\perp} \approx 2.4$ ) in  $H_{c2}$ . A simple analysis of these critical field data in terms of a weak coupling model [15] gives coherence lengths at  $T=0$  K of  $\xi_{\parallel} \approx 21$  Å and  $\xi_{\perp} \approx 14$  Å, and a ratio of effective masses  $m_c/m_{ab} \approx 2.4$ . This makes the T\*-phase material somewhat different from other reported cuprates [16]. An explanation for this will await measurements of transport anisotropies.

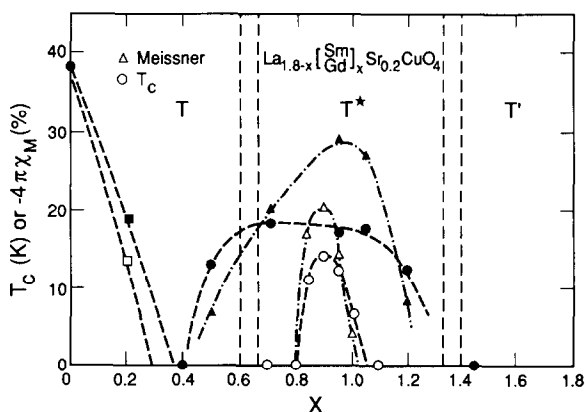


Fig. 4. Rare earth composition dependence of  $T_c$  of Sr<sub>0.2</sub>-doped T\*-phases. The squares are taken from ref. 17.

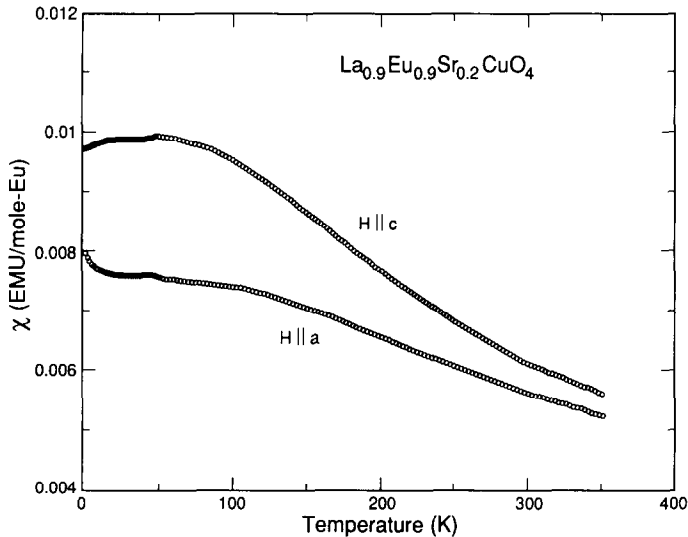


Fig. 5. Anisotropy of the upper critical field  $H_{c2}$  of aligned polycrystalline  $\text{La}_{0.9}\text{Eu}_{0.9}\text{Sr}_{0.2}\text{CuO}_4$ . The degree of alignment is approximately  $2^\circ$ .  $\parallel$  and  $\perp$  refers to parallel and perpendicular to the  $\text{CuO}_2$ -planes, respectively.

## 5. Concluding remarks

The normal state and superconducting properties of  $T^*$ -phase material bear many close resemblances to those of strontium-doped  $\text{La}_2\text{CuO}_4$ . We note the sensitivity of  $T_c$  to the rare earths in  $T^*$ , and the reduced symmetry of  $T^*$  and a number of effects possibly associated with this: broadened or absent rare earth magnetic transitions and reduced upper critical field anisotropy. The difficulty of obtaining fully oxygenated samples has not been overcome, and even now it is unlikely that this oxygen parameter has been optimized. Single crystals are now becoming available, so it is to be hoped that the data base for these materials will be substantially enlarged in the near future.

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