High pressure studies of high $T_c$ superconductors in A–Cu–O system: The role of apical oxygen

C.Q. Jin *, Q.Q. Liu, H. Yang, L.X. Yang, R.C. Yu, F.Y. Li

National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, PR China

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Abstract

We address the role of apical oxygen that plays the bridges linking charge reservoir and CuO$_2$ conducting layers for high $T_c$ superconductors (HTS). The presentation will introduce our recent work on high pressure synthesis of novel superconductors in the A–Cu–O simple system by tuning apical oxygen content and arrangement (A represents alkaline earth element). The topic will focus on 214 type compounds highlighting apical oxygen as a novel doping mechanism in oxychloride HTS, or dopant at a partially occupied apex, especially the unusual enhancement of $T_c$ up to 95 K in a monolayered HTS by improving ordering state.

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1. Introduction

Since the historical discovery of high $T_c$ superconductors (HTS) of cuprate oxide in 1986 by Bednorz and Muller [1], a lot of HTS compounds have been synthesized [2–18]. Crystallographically HTS consists of periodic stacking of charge reservoir and [CuO$_2$] conducting layers, respectively. They are usually bridged via apical oxygen as shown in Fig. 1 [1–6]. Charge reservoir is responsible for generating carriers to the [CuO$_2$] superconducting plane through an appropriate doping. According to the geometric relationship with the [CuO$_2$] plane, the charge reservoir block can be further classified into two sub blocks: the nearest neighbor to [CuO$_2$] plane; and the next nearest neighbor to [CuO$_2$] plane as shown in Fig. 2. The oxygen which connects the nearest neighbor charge reservoir layer in turn is named “apical oxygen” since it is located at the apical position relative to the [CuO$_2$] plane (this is validate to p type HTS). Tuning the oxygen content at the charge reservoir layer is the most fundamental chemical doping mechanism of HTSs [2].

It is noted that most of oxygen doping are taking place at the next nearest neighbor charge reservoir block. One can expect that $T_c$ will be even more sensitive to the oxygen evolution at the nearest charge reservoir block via the apical bonding nature [3,6,11]. It was found that the distance of apical oxygen with the [CuO$_2$] plane has an essential effect on the hopping integral $t_0$ between the second nearest Cu–Cu within the [CuO$_2$] plane [6], and consequently it is crucial to modify $T_c$ value of p-type HTS. However almost all typical HTSs have a fully occupied oxygen site, leaving the apical oxygen amount stoichiometrically unchanged. Searching compounds with tunable apical oxygen content is thus of fundamental physical interests in terms of deeply understanding the unknown doping effects of oxygen at the nearest charge reservoir block.

Since HTS is of perovskite crystal nature [2,3], high pressure is thus thermodynamically favorable to stabilize novel HTSs [11]. High oxygen pressure can effectively modulate the copper valence. The obvious merit of high pressure is to build up novel HTS, which otherwise will be hard to approach in ambient conditions. On the other hand, the positive pressure effect on $T_c$, such as the record 160 K $T_c$ of Hg-1223 above 20 GPa will shed lights on pursuing new HTS with higher $T_c$ as well as solving mechanism puzzle. Here we will briefly introduce our recent
research progress on the high pressure studies of high $T_c$ superconductors in A–Cu–O system (A is alkaline earth element) highlighting the role apical oxygen as a dopant mechanism in 0201 type Sr$_2$CuO$_{2+d}$Cl$_2$/$\text{O}_x$ series, the ordering effects to enhance $T_c$ up to 95 K in Sr$_2$CuO$_3+d$.

3. The Sr$_2$CuO$_{2+d}$Cl$_{2-x}$ superconductor induced by “apical oxygen doping”

Using apical oxygen doping, we recently have been able to get the new Sr$_2$CuO$_{2+d}$Cl$_{2-x}$ superconductors using high pressure synthesis [13]. Bulk superconductivity was realized with $T_c$ up to 30 K.

The sample was synthesized under high pressure high temperature at 5 GPa and 1000°C. Fig. 4 shows the temperature dependence of the DC magnetic susceptibility of Sr$_2$CuO$_{2+d}$Cl$_{2-x}$.
Sr$_2$CuO$_2$:Cl$_{1.2}$ sample, indicating the bulk superconducting nature. The inset of Fig. 4 presents the temperature dependence of the resistivity of the sample.

Fig. 5 shows the lattice parameters versus apical oxygen content in Sr$_2$CuO$_{2+y}$Cl$_{2-x}$. The a axis shrunk with the increase of apical oxygen amount, indicating the hole doping nature. The inset of Fig. 4 presents the temperature dependence of the resistivity of the sample.

4. The enhanced superconductivity up to 95 K in 214 type Sr$_2$CuO$_3$ by apical oxygen ordering

Sr$_2$CuO$_{3+\delta}$ was synthesized under high pressure high temperature crystallizing into La$_2$CuO$_4$ structure. More interestingly as a dopant mechanism its apical oxygen site is partially occupied and the amount is adjustable as shown in Fig. 6.

Previously Hiroi et al. [7] synthesized a tetragonal form of Sr$_2$CuO$_3$ superconductor in 1993. They suggested that the main phase in this material is a highly apical oxygen-deficient K$_2$NiF$_4$-type tetragonal structure. Later, some Sr$_2$CuO$_{3+\delta}$ type superconductors were subsequently synthesized and the superconducting transition can be enhanced above 90 K after post annealing [8]. But there are uncertainty on which phase is real responsible for the superconducting transition [3,8,12,14,15].

To make the phase as pure as possible, we synthesized the Sr$_2$CuO$_3$. sample under high pressure high temperature using an improved approach with Sr$_2$CuO$_3$ + SrCuO$_2$ + SrO as the starting materials for high pressure synthesis. The role of SrO peroxide is to create an oxygen atmosphere during the high-pressure synthesis that will not introduce third element or other phases containing chlorine [12].

In order to further “optimize” the superconducting phase through tuning the apical oxygen distribution, the high pressure synthesized Sr$_2$CuO$_{3+\delta}$ sample of optimally doping with $\delta = 0.4$ was post heat treated in the temperatures range of 150 °C to 300 °C for 12 h in 1 atm N$_2$ atmosphere. X-ray diffraction shows that the sample keeps the tetragonal single phase unchanged up to 300 °C heat treatment, before becoming mixture of tetragonal and the ambient orthorhombic phase at 350 °C.

Fig. 7 illustrates the magnetic susceptibility measurement at a Meissner mode for the high pressure as-prepared and those after different heat treatments of Sr$_2$CuO$_{3+\delta}$ superconductors. It is shown as increasing the annealing temperature, $T_c$ increases monotonically up to 95 K which is the highest $T_c$ observed in the single-layer copper oxide superconductors.

ED and HRTEM investigations showed that almost all grains in the superconducting samples exhibited modulated structures at $a$–$b$ plane based on the K$_2$NiF$_4$ structure. In the as-prepared sample, two types of modulated structures were found. One is the already reported face-centered orthorhombic modulated structure (space group Fmmm) with the lattice constants of about $5\sqrt{2}a_p \times 5\sqrt{2}a_p \times c_p$ [12].

The other is a new base-centered monocline modulated structure (space group C2/m) with the unit-cell parameters $a = 5\sqrt{2}a_p$, $b = c_p$, $c = \sqrt{26}/2a_p$ and $\beta = 101.3^\circ$. Fig. 8a shows the ED patterns taken along [001]$_p$ zone-axis of the C2/m modulated phase. After heat treatment at 150 °C, parts of C2/m modulated phase was found to convert to another new modulated phase as shown in Fig. 8b (space group Cmmm) with the unit-cell parameters $a = c_p$, $b = 5\sqrt{2}a_p$ and $c = 5\sqrt{2}a_p$, while the Fmmm modulated structure almost remains the same. As the post annealed temperature was increased to 250 °C, all the C2/m and Cmmm modulated phases converted to another modulated phase as shown in Fig. 8c (space group Pmmm) with the unit-cell parameters $a \approx b = 4\sqrt{2}a_p$ and $c = c_p$ which was previously reported.

Fig. 8. The TEM images of Sr$_2$CuO$_{3+\delta}$ samples, (a) the C2/m superlattice for the as prepared sample with $T_c$ 75 K, (b) the Cmmm superlattice appeared in the sample with $T_c$ 89 K, (c) the Pmmm superlattice observed in the sample with $T_c$ 95 K.
The results of our experiments strongly suggest that the observed superconductivities in Sr$_2$CuO$_{3+x}$ samples are related to these modulated phases. The as-prepared sample with an onset $T_c$ at 75 K contained two types of modulated phases (Fmmm and C2/m), respectively. Therefore, it is likely that the Fmmm or/and the C2/m modulated phase is responsible for $T_c$ at 75 K. However, the Fmmm modulated phase has always existed in the as-prepared and heat treated superconducting samples. This means if the Fmmm modulated phase is responsible for the $T_c$ at 75 K, the same $T_c$ (75 K) could be observed in the heat-treated samples either, but it did not. Therefore only the C2/m modulated phase is responsible for the $T_c$ at 75 K. The evolution route of superconductivity and the relation with modulation structure of the Sr$_2$CuO$_{3+x}$ superconductor are thus following the rationale: starting from the 75 K original superconducting transition with C2/m modulation structure in the high pressure as prepared sample →95 K superconducting transition with Cmmm modulation structure in the 150 °C post annealed sample →89 K superconducting transition with Pmmm modulation structure in the 300 °C post annealed sample, respectively. The Fmmm modulated phase was in fact the optimally ordered phase associated with the highest $T_c$ (95 K) for the optimally doped Sr$_2$CuO$_{3+x}$ superconductor.

The TG-DTA experiments of Sr$_2$CuO$_{3+x}$ superconductor indicate little weight evolution below 300 °C. Since the modulation is taking place at a–b plane, assuming a perfect [CuO$_2$] plane as it is a very well established consensus, the oxygen vacancy should be on the rock salt type [SrO] layer, i.e., the apical oxygen layer. It is in fact found that oxygen can even migrate at room temperature. Thus the modulation is reasonably related to the apical oxygen rearrangement at the low annealing temperature. It is consequently inferred that the modulation structure related to the apical oxygen ordering state has an additional contribution to enhance superconducting transition temperature for an optimally doped sample. These further support the recent research that the quenched order disorder of dopant atom has sufficient effects on the superconductivity [16,17]. The results indicate that $T_c$ might be significantly enhanced by ordering dopant such as the apical oxygen [18].

5. Summary

The high pressure synthesized 214 type superconductors with partially occupied oxygen at the nearest charge reservoir provide opportunities to understand the role of apical oxygen atoms and to further identify the intrinsic feature of ordering effects on superconducting transition temperature in the high $T_c$ cuprate superconductors.

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References

P.D. Han, L. Chang, D.A. Payne, Physica C 228 (1994) 129.