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A new modulated structure in $Sr_2CuO_{3+\delta}$ superconductor synthesized under high pressure

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ABSTRACT

A $Sr_2CuO_{3+\delta}$ superconductor with a new modulated structure has been synthesized using high pressure technique. Two superconducting transitions with $Tc \sim 75$ K and ~ 48 K respectively were found in $Sr_2CuO_{3+\delta}$ superconductor. The superconducting volume fraction is calculated to be 85% at 2 K, which is much higher than anyone else reported before. A new type of modulated phase with a periodicity of $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times c_p$ of *Pmmm* symmetry is found in the sample by using transmission electron microscopy. Our experimental results suggest that the new *Pmmm* modulated phase is responsible for superconductivity with *Tc* at 48 K, while *C2/m* modulated phase for that with *Tc* at 75 K found previously.

1. Introduction

High-temperature cuprate superconductor (HTS) is an alternating array consisting of $[CuO_2]$ conducting planes with charge reservoir blocks. The hole or electron type carriers are introduced into the $[CuO_2]$ planes by dopants at the charge reservoir blocks and in most cases dopants are disordered since dopant atoms reside in the blocks and are randomly distributed. The superconducting transition temperature (*Tc*) was found to be a function of carrier density following a parabolic relation, becoming maximum at optimal doping level [1]. However it was further found that the disorder caused by dopants plays significant role in tuning *Tc* [2]. The hole doped $Sr_2CuO_{3+\delta}$ superconductor synthesized under high pressure and high temperature is such an ideal system that crystallizes into an oxygen deficient K_2NiF_4 structure with partially occupied apical sites as shown in Fig. 1. The oxygen atoms at the apical sites of a CuO_5 pyramid or a CuO_6 octahedron is called "apical oxygen" relative to the $[CuO_2]$ plane [3]. Pressure tuning is a very powerful tool to search for novel HTS materials or to improve their physical properties [4–11]. The recent study of $Sr_2CuO_{3+\delta}$ synthesized under high pressure has shown that different *Tc* in this superconductor is much associated with the ordering of apical oxygen atoms [12]. Modulated superstructures commonly exist in this system [13,14]. Hiroi et al. [5] first reported the occurrence of superconductivity at 70 K in tetragonal $Sr_2CuO_{3+\delta}$. They suggested that the main phase in this material is a highly apical oxygen-deficient K_2NiF_4 structure. Several groups also observed the superconductivity in this material [6,7]. In all these samples, the presence of modulated structures based on the K_2NiF_4-type tetragonal primary unit cell of $Sr_2CuO_{3+\delta}$ was reported. For example, Hiroi et al. [5] and Laffez et al. [6] observed, separately, a $4\sqrt{2}a_p \times 4\sqrt{2}a_p \times c_p$ and a $5\sqrt{2}/2a_p \times 5\sqrt{2}/2a_p \times c_p$ modulated structure in their own samples, while Wang et al. [15] and Zhang et al. [16] reported a $5\sqrt{2}a_p \times 5\sqrt{2}a_p \times c_p$ structure. In our previous work, two types of modulated structures are found in the single-phase $Sr_2CuO_{3.4}$ superconductor with $Tc = 75$ K, one is face-centered orthorhombic modulated structure (space group *Fmmm*) with a periodicity of $5\sqrt{2}a_p \times 5\sqrt{2}a_p \times c_p$ same as reported in [14,15], and the other is a new base-centered monoclinic modulated phase with approximately a space group *C2/m* whose unit-cell parameters are $a = 5\sqrt{2}a_p$, $b = c_p$, $c = \sqrt{26}\sqrt{2}/2a_p$, and $\beta = 101.3°$. Our experimental results strongly suggest that the *C2/m* modulated phase is responsible for the superconductivity at 75 K [12–14]. Study of $Sr_2CuO_{3+\delta}$ with partially occupied apical oxygen sites is thus of fundamental physical interest for a deeper understanding of the yet unresolved doping/order effect on high-*Tc* superconductivity [17,18]. In this paper, we report the discovery of a new superconducting phase with *Tc* at 48 K in $Sr_2CuO_{3.4}$ superconductor synthesized at high pressures. The superconducting volume fraction of the sample is rather large comparing to those reported before, which provides a good opportunity to study the relationship between the modulated structure and superconductivity.

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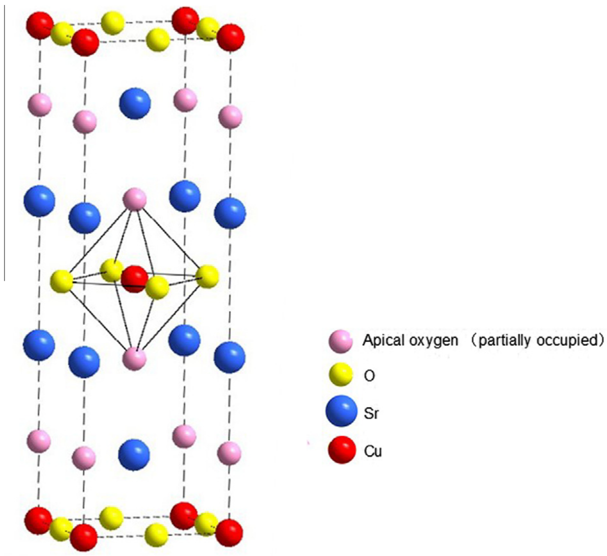

Fig. 1. Schematic view of the crystal structure of $Sr_2CuO_{3+\delta}$ with K_2NiF_4 type tetragonal structure containing the [CuO_2] plane, but the apical oxygen sites are partially occupied.

2. Experimental

Polycrystalline samples with nominal compositions of $Sr_2CuO_{3.4}$ were synthesized from SrO_2, CuO and the precursor of Sr_2CuO_3 under high pressure and high temperature. The precursor Sr_2CuO_3 was prepared by solid-state reaction with high pure $SrCO_3$ and CuO mixed at a molar ratio of 2:1 and was sintered at 950 °C for 12 h with several intermediate grindings. To obtain high quality of the sample (i.e., much higher superconducting volume fraction), we change the synthesis condition which is different from reported previously [9]. At first, the sample was synthesized at the pressure of 5.5 GPa and temperature of 850 °C for 30 min, followed by keeping at the same pressure but temperature at 450 °C for 60 min. This high pressure low temperature annealing is expected to enhance the apical oxygen ordering. The DC magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer in an external magnetic field of 30 Oe for both zero-field-cooling (ZFC) and field-cooling (FC) modes. The resistivity was measured using standard four-probe method with a MAGLAB system. A Tecnai F20 electron microscope with a field emission gun was used for electron diffraction experiments.

3. Results and discussion

The superconducting properties of the sample were measured by DC susceptibility using a SQUID magnetometer and electrical resistance by the standard four-probe resistance method. Fig. 2a presents the temperature dependence of magnetic susceptibility in both modes of zero-field-cooling (ZFC) and field-cooling (FC) in the applied field of 30 Oe. The two superconducting transitions of $Tc \sim 75$ K and ~ 48 K were clearly observed in the sample. The FC data which corresponds to the Meissner signal revealed a total superconducting volume fraction ~85% at 2 K, which is much higher than that of reported previously [12,19]. Hereinto, the superconducting phase of 75 K accounts for ~46% as calculated by extrapolation the FC curve from 50 K to 2 K. In the context the volume fraction of the superconducting phase with *Tc* 48 K is approximately to be 39%. Fig. 2b shows the temperature dependence of electrical resistance of the $Sr_2CuO_{3.4}$ superconductor. The much higher superconducting volume fraction will benefit to studying the structural features and to identify the superconducting phase definitely by the transmission electron microscopy (TEM). In our previous work, we have reported two types of modulated structures in the single-phase $Sr_2CuO_{3.4}$ ($Tc = 75$ K) as-prepared sample. One is *Fmmm* modulated, the other is *C2/m* modulated. By systematic study of $Sr_2CuO_{3.4}$ superconductor, it was strongly suggested that the *C2/m* modulated phase is responsible for the superconductivity at 75 K while the *Fmmm* modulated phase is non-superconducting. To further confirm the relationship between superconducting phases and modulated structures, we also carried out the high resolution TEM studies in $Sr_2CuO_{3.4}$ sample with two superconducting transition phase of *Tc* 75 K and 48 K. The results of the electron diffraction (ED) and high resolution TEM investigations show that almost all grains in the $Sr_2CuO_{3.4}$ sample exhibit modulated structure having the K_2NiF_4-type tetragonal structure in the basal *a*–*b* plane, which is strongly suggested that superconductivity with 75 K and 48 K in the material is associated with the modulated phases. Three types of modulated structures having different primitive cell were found, which included the *Fmmm*, *C2/m* and *Pmmm* modulated structures. The two types of *Fmmm* and *C2/m* modulated structures were reported in our previous study [11], while a new type of modulated structure was found in this sample at first time. Since its sub-structure is the K_2NiF_4-type tetragonal structure with the space group *I4/mmm*, the new modulated structure has approximately a space group *Pmmm*. Fig. 3a exhibits a typical $[001]_p$ zone-axis selected area electron diffraction pattern of the modulated structure with a periodicity of $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times c_p$. Since all modulated structures lies in the a_pb_p-plane, we use the

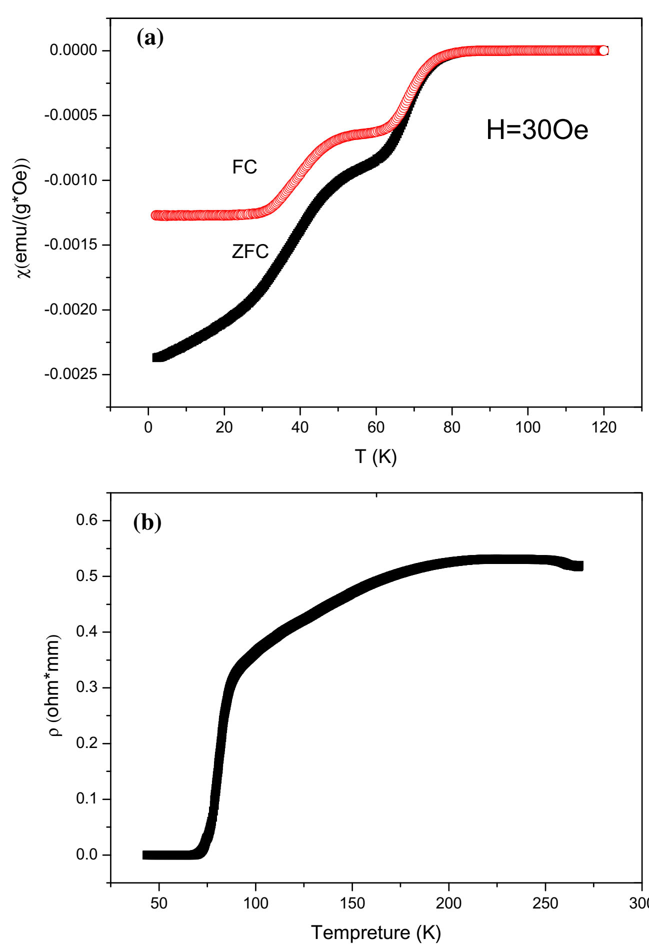

Fig. 2. (a) *T* dependence of χ in $H = 30$ Oe (two superconducting phases are shown in both ZFC and FC modes) and (b) is temperature dependence of resistivity.

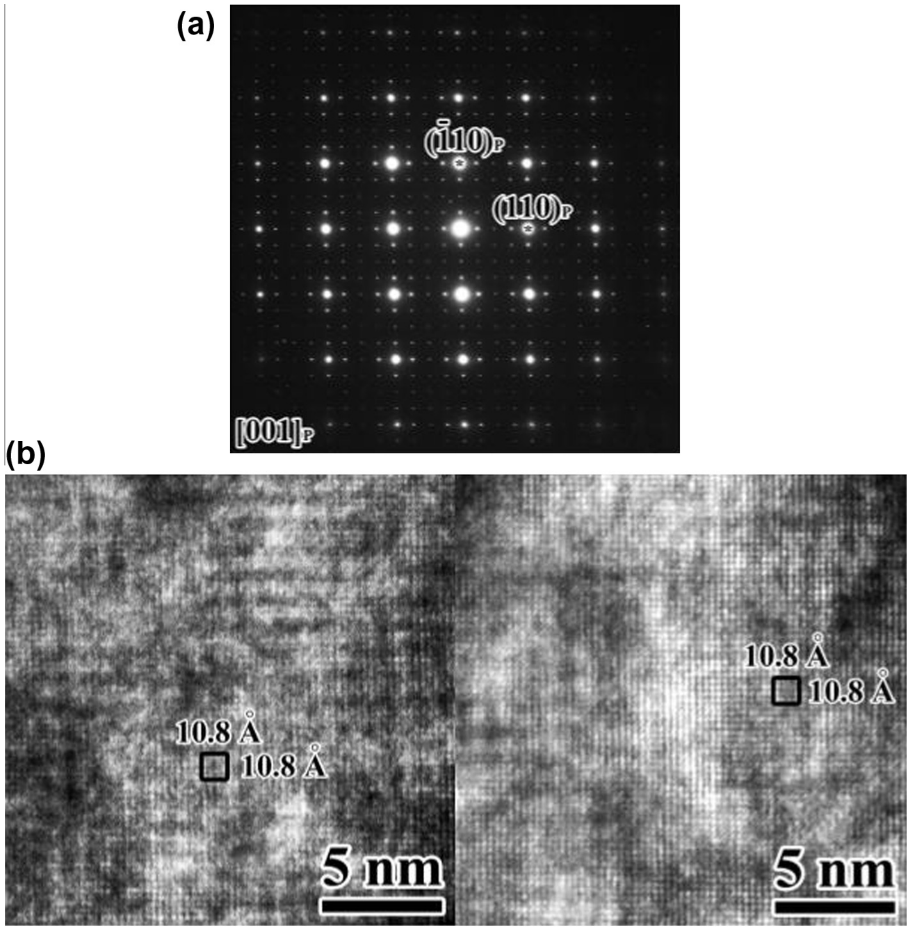

Fig. 3. (a) $[001]_p$ zone-axis selected area electron diffraction pattern of the $2\sqrt{2}a_p$ modulated phase. (b) Corresponding high resolution TEM images along the $[001]_p$ zone-axis direction, one super cell is indicated in the black square.

Table 1
Relationship between modulated structures and superconducting phases in $Sr_2CuO_{3.4}$.

Superconducting transition temperature Tc (K)	Modulated structures		Remark
	Space group	Lattices	
48	*Pmmm*	$a \approx b = 2\sqrt{2}a_p$ $c = c_p$	This work
75	*C2/m*	$a = 5\sqrt{2}a_p$ $b = c_p$ $c = \sqrt{26}\sqrt{2}/2a_p$ $\beta = 101.3°$	Ref. [12]
89	*Cmmm*	$a = c_p$ $b = 5\sqrt{2}a_p$ $c = 5\sqrt{2}a_p$	Ref. [12]
95	*Pmmm*	$a \approx b = 4\sqrt{2}a_p$ $c = c_p$	Ref. [12]

subscript "p" to stand for the basic K_2NiF_4 type tetragonal structure of $Sr_2CuO_{3.4}$ sample. Fig. 3b presents corresponding high resolution TEM images along the $[001]_p$ zone-axis direction, showing clearly its modulated periodicity 10.8 Å. One super cell is indicated in the black square. Considering our previous works [12], it is consequently inferable that the new *Pmmm* modulated structure with the unit cell parameters $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times c_p$ is responsible for superconductivity at 48 K, while *C2/m* modulated structures for superconductivity at 75 K. Table 1 lists the relationship between superconducting transition temperature Tc and modulated structure with different unit cell parameters. The experimental results suggest that our samples are primarily bulk materials with tens of micrometers grains size which are different from nanomaterials [20,21]. In addition, we found that the formation of modulated structures is strongly associated with the high pressure synthesizing conditions, such as pressure, temperature, composition and reaction time, in this system. The apical oxygen relocation by optimizing the synthesis condition may have such a significant effect on forming modulated structures. Thus the mechanism resulting in the new modulated phase and the effect of synthesis conditions on modulated structure need to be investigated by further experiments.

4. In summary

We have synthesized the $Sr_2CuO_{3.4}$ superconductor with two superconducting transition of Tc at 75 K and 48 K, respectively. The results of TEM investigations indicated that 75 K superconducting phase corresponds to the $C2/m$ modulated structure while 48 K superconducting phase corresponds to a new *Pmmm* modulated structure.

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