TEM and EELS studies of \( \text{Sr}_2\text{CuO}_3+\delta \) (nominal \( \delta = 0.1–0.4 \)): Effect of apical oxygen ordering on \( T_C \) of cuprate superconductors

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Abstract

In this paper, transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) techniques are utilized to study the as prepared superconducting samples of \( \text{Sr}_2\text{CuO}_3+\delta \) with different nominal \( \delta \) to reveal the origin of superconductivity. The 60, 68 and 75 K superconductivities observed in these samples are revealed to arise, respectively, from the \( \text{Pmmm} \) (\( a = \sqrt{2}a_p, b = \sqrt{2}a_p \) and \( c = c_p \)), \( \text{Cmmm} \) (\( a = \sqrt{2}a_p, b = \sqrt{3}a_p \) and \( c = 2\sqrt{2}a_p \)) and \( \text{C}_2/\text{m} \) (\( a = \sqrt{2}a_p, b = c_p, c = \sqrt{2}a_p \) and \( \beta = 101.3^\circ \)) modulated phases. These superconducting modulated phases are suggested to be formed by the ordering of apical oxygen, and each of them is associated with a distinct type of the ordering. Oxygen K absorption edge measured by EELS indicates that these modulated phases have a similar hole doping level. Our experimental results suggest that the superconductivity differences in the \( \text{Sr}_2\text{CuO}_3+\delta \) system are mainly caused by the reordering of apical oxygen.

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1. Introduction

Crystallographically hole doped high-\( T_C \) cuprate superconductor (HTS) is built up from alternating stackings of charge reservoir blocks and the \( \text{CuO}_2 \) conducting planes. Chemical substitution and tuning the oxygen content in the charge reservoir blocks are the fundamental chemical doping mechanics of HTS. In most cases, chemical disorder is created in the charge reservoir blocks as doping is made. Besides the doping level [1] and the number of \( \text{CuO}_2 \) planes (\( n \)) in a unit-cell [2], the disorder induced by doping has been shown to be another important parameter influencing the superconducting transition temperature of HTS [3]. On the other hand, the oxygen atoms above or below the \( \text{CuO}_2 \) plane(s), usually called “apical oxygen”, form the nearest-neighbor charge reservoir block [2,4,5], and the apical oxygen serves as the connection between the charge reservoir blocks and the \( \text{CuO}_2 \) conducting planes in terms of electron exchange interaction [6]. Therefore, the apical oxygen doping (i.e., tuning the oxygen content in the nearest-neighbor charge reservoir block) and its ordering is expected to have an appreciable effect on the electronic structures of the \( \text{CuO}_2 \) planes and hence on high-\( T_C \) superconductivity. The \( \text{Sr}_2\text{CuO}_3+\delta \) superconducting system crystallizing into a highly apical oxygen-deficient \( \text{K}_2\text{NiF}_4 \)-type tetragonal structure supplies us a good example to study the effect of apical oxygen ordering on the high-\( T_C \) superconductivity. Recently, by studying the \( \text{Sr}_2\text{CuO}_3+\delta \) (nominal \( \delta = 0.4 \)) superconductor post-annealed at different temperatures, we found that the reordering of apical oxygen has dramatic effects on \( T_C \) [7,8].

At ambient-pressure, the \( \text{Sr}_2\text{CuO}_3 \) composition forms as an orthorhombic structure with Cu-O chains along the...
a-axis [9–11]. Introducing extra O leads to the formation of a K$_2$NiF$_4$-type tetragonal structure of Sr$_2$CuO$_{3+\delta}$, and at the same time holes are doped in this cuprate due to the introduction of extra O; however, superconductivity is displayed only in the samples synthesized using high-pressure techniques [12–18]. Although high-pressure technique is a very effective method in searching for new HTS materials [19–23], preparation of a single-phase sample is generally difficult, and sometimes it is hard to identify the superconducting phase in the sample. Using KClO$_4$ as an oxidizer, Hiroi et al. [12] first succeeded in fabricating the tetragonal Sr$_2$CuO$_{3+\delta}$ showing superconductivity at $T_C = 70$ K. They suggested that the main phase in this material is a highly apical oxygen-deficient K$_2$NiF$_4$-type tetragonal structure and the superconductivity results from this tetragonal phase. Later, several groups also repeatedly synthesized the Sr$_2$CuO$_3$ superconductors using high-pressure technique [13–15], and $T_C$ was enhanced up to 94 K by post annealing [15]. In all these high-pressure samples both as prepared and post-annealed, however, modulated structures that have the K$_2$NiF$_4$-type tetragonal structure of Sr$_2$CuO$_{3+\delta}$ as their basic sub-structure were observed. For example, Hiroi et al. [12] and Lafleze et al. [13] observed, separately, a $4\sqrt{2}a_p \times 4\sqrt{2}a_p \times c_p$ and a $5\sqrt{2}a_p \times 5\sqrt{2}a_p \times c_p$ modulated structure in their as prepared samples, and the latter one was also found by Wang and Zhang et al. [24,25] in their as prepared and annealed samples. Contrary to the idea suggested in Refs. [12,13,15] that the non-modulated tetragonal form of Sr$_2$CuO$_{3+\delta}$ is the superconducting phase, Wang and Zhang et al. [24,25] suggested that the $5\sqrt{2}a_p \times 5\sqrt{2}a_p \times c_p$ modulated phase is actually responsible for the superconductivity. However, no convincing experimental results were given in all their works since those superconducting samples were multiphase mixtures and superconducting volume fraction was very small. In addition, the tetragonal form of Sr$_2$CuO$_{3+\delta}$ synthesized at ambient pressure has been shown to be isostructural with that obtained at high pressure on the basis of powder X-ray diffraction (XRD) analysis, but no superconductivity was observed in the ambient-pressure samples [16,17]. The above works seem not to support the predication that the tetragonal form of Sr$_2$CuO$_{3+\delta}$ is responsible for the superconductivity. At the same time, Shimakawa et al. [14] studied the compounds of Sr$_2$CuO$_{3+\delta}$ synthesized at high-pressure and ambient-pressure separately by means of neutron diffraction, and suggested that the compounds prepared at different pressures both have an oxygen-deficient K$_2$NiF$_4$-type tetragonal structure with oxygen vacancies located in the Cu–O planes instead of in the Sr–O layers, which indicates that the main phase in the samples is possibly non-superconducting in terms of our current understanding of superconductivity in the cuprates, which relies on oxygen vacancy-free in the Cu–O plane. Furthermore, Kawashima et al. [26] reported that the superconducting phase with $T_C = 70$ K prepared from the nominal starting powders of Sr$_2$CuO$_3$ with KClO$_4$ oxidizer was not of the 0201-type but of 0212-type Sr–Cu–O compound.

Up to now, despite extensive studies on the Sr$_2$CuO$_{3+\delta}$ system, it is still not clear what phase in the high-pressure material of this system can lead to the superconductivity. In order to find the answer, preparation of high-quality samples and the characterization of their detailed structures by means of transmission electron microscopy (TEM) are needed. To make the phase as pure as possible, recently we synthesized the Sr$_2$CuO$_{3+\delta}$ samples under high pressure using SrO$_2$ as an oxidizer. A series of superconducting samples of Sr$_2$CuO$_{3+\delta}$ for various values of $\delta$, commonly displaying different values of $T_C$, were prepared by changing the initial amount of SrO$_2$, and a single-phase one detected to be a K$_2$NiF$_4$-type tetragonal structure from XRD data was formed when nominal $\delta = 0.4$. We annealed the tetragonal single-phase sample in N$_2$ atmosphere, and found that with increasing the annealing temperature the value of $T_C$ increased from 75 K (as prepared), in turn, to 89 K (heat treatment at 150°C), 95 K (heat treatment at 250°C), and then disappeared when further increasing the annealing temperature above 250°C [7]. This is in consistent with the observation in Ref. [15]. However, our TEM investigations suggest that the enhancement of $T_C$ is mainly caused by the apical oxygen reordering [7,8]. In this paper, TEM and electron energy-loss spectroscopy (EELS) techniques are utilized to study the as prepared superconducting samples of Sr$_2$CuO$_{3+\delta}$ with different nominal $\delta$, further suggesting that the ordering of apical oxygen has effects on $T_C$.

2. Experimental

To make the phase as pure as possible, we synthesized the Sr$_2$CuO$_{3+\delta}$ samples under high pressure using SrO$_2$ as an oxidizer. The starting material, Sr$_2$CuO$_3$, was prepared from high purity SrCO$_3$ and CuO raw materials mixed at a molar ratio of 2:1. The powder mixture was calcined at 950°C for 24 h with several intermediate grindings. Then, Sr$_2$CuO$_3$, SrO$_2$ and CuO were mixed to yield the nominal composition Sr$_2$CuO$_{3+\delta}$ at various molar ratios and subjected to high-pressure synthesis (6 GPa and 1100°C for 1 h) using a cubic-anvil-type apparatus. More detailed process and discussion of the sample preparation are given in Ref. [7].

A series of superconducting samples of Sr$_2$CuO$_{3+\delta}$ with different nominal $\delta$ were prepared by changing the initial amount of SrO$_2$. The sample structures detected from XRD using Cu K$_{α}$ radiation gradually transform to tetragonal form from orthorhombic structure with increasing nominal $\delta$, and a single-phase tetragonal form is formed when nominal $\delta = 0.4$. Superconductivity of these samples was examined by dc magnetic susceptibility measurements using a SQUID magnetometer in an external magnetic field of 20 Oe, and the results reveal that the samples for nominal $\delta = 0.1$ and 0.2 display a 60 K superconductivity, while the samples for nominal $\delta = 0.3$ and 0.4 exhibit, respectively, a 68 K and a 75 K superconductivity. In order to further identify the superconducting phase and reveal
the mechanics resulting in the superconductivity differences, in the following work we focus on the studies of these samples by means of TEM and EELS.

TEM thin foils were prepared by crushing the samples in an agate mortar filled with alcohol, and then dispersing the fine fragments suspended in alcohol on a microgrid. A Tecnai F20 electron microscope with a field emission gun, operated at an acceleration voltage of 200 keV, was used for TEM observations and EELS measurements. Our previous TEM work on the “apical oxygen doped” Sr$_2$CuO$_{2+\delta}$Cl$_{2-\delta}$ superconductor has suggested that an electron beam with high intensity could cause the superconductor to lose oxygen, and consequently result in the formation of modulated superstructure [27]. Therefore, during the TEM experiments, we tried our best not to expose the Sr$_2$CuO$_{3+\delta}$ samples to the intense electron beam, so as to avoid the electron-irradiation effects on the samples. For example, selected area electron diffraction (SAED) instead of convergent beam electron diffraction (CBED) has been used to search for and tilt grains. In fact, the Sr$_2$CuO$_{3+\delta}$ samples appeared to be stable under illumination with a weak electron beam. Even when the samples were exposed to the electron beam with high intensity, a short irradiation duration was not found to cause a structure change, either.

3. Results and discussion

3.1. Basic structure identification

Fig. 1 shows the XRD patterns of Sr$_2$CuO$_{3+\delta}$ samples for different values of $\delta$, revealing that with increasing $\delta$ the sample structures gradually transform from orthorhombic structure to tetragonal form, and a single-phase tetragonal structure is formed when nominal $\delta = 0.4$. In the samples for nominal $\delta \leq 0.3$, the orthorhombic structure coexists with the tetragonal form. The orthorhombic structure in these high-pressure samples has a low-oxidized form of Sr$_2$CuO$_{3+y}$ (where the “$y$” represents the real oxygen content doped in the orthorhombic structure), which can be suggested from oxygen K EELS spectra (shown in the following). Previous work [13] has also suggested that the low-oxidized form of Sr$_2$CuO$_{3+y}$ crystallizes mainly as an orthorhombic structure nearly same as that of the ambient-pressure orthorhombic phase of Sr$_2$CuO$_3$.

For the tetragonal form of Sr$_2$CuO$_{3+x}$ in these high-pressure samples (where the “$x$” represents the real oxygen content doped in the tetragonal form), a complex picture was observed. TEM investigations showed that almost all the grains of the tetragonal form in the samples for nominal $\delta = 0.3$ and $0.4$ exhibit modulated structures, and most grains of the tetragonal form in the samples for nominal $\delta = 0.1$ and $0.2$ show up modulated structures. In the following studies by oxygen K EELS spectra, we can see that these modulated phases have obviously higher oxygen content than the unmodulated tetragonal structure. In addition, we should point out that no any other layered copper oxide such as copper-rich phases including the infinite-layer phase SrCuO$_2$ ($n = \infty$) and the double Cu–O planes phase Sr$_3$Cu$_2$O$_5$ ($n = 2$) was detected by TEM in all the samples.

3.2. Superstructure modulation of the Sr$_2$CuO$_{3+x}$ tetragonal form

The K$_2$NiF$_4$-type tetragonal form of Sr$_2$CuO$_{3+x}$ was revealed by TEM to prefer to form modulated superstructures. Systemic tilting experiments suggested that the modulation plane for all the modulated structures lies in the a$_p$-p-plane, where the subscript “$p$” stands for the basic K$_2$NiF$_4$-type tetragonal structure.

In the sample for nominal $\delta = 0.4$, two types of superstructure modulation of the Sr$_2$CuO$_{3+x}$ tetragonal form were found. One exhibits a superlattice with a constant of $\sim 5\sqrt{2}a_p \times 5\sqrt{2}a_p \times c_p$ same as reported in Ref. [13]. Fig. 2 presents a typical [001]$_p$ zone-axis ED pattern of this modulated structure. Based on the consideration that the superstructure spots do not construct an exact tetragonal array but an orthorhombic one, and according to the extinction rule (hkl are all odd or all even), this modulated phase is identified to be a face-centered orthorhombic superstructure. Its space group can be approximately described as Fmmm in consideration of the sub-structure of the modulated phase being the K$_2$NiF$_4$-type tetragonal structure with the space group I4/mmm. The lattice parameters are $a \approx b = 5\sqrt{2}a_p$ and $c = c_p$. Fig. 3 shows the [001]$_p$ zone-axis ED pattern of the other modulated structure. By systemic tilting experiments this superstructure modulation is determined to be one-dimensional and the superstructure...
peaks are characterized by a unique modulation wave vector $q = (2\pi/a_p)(\frac{2}{3}, \frac{1}{3}, 0)$. It is clear that the superlattice spots construct a base-centered monoclinic space array and the conditions for reflection are:

$$hk l : h + k = 2n$$
$$h0 l : h = 2n$$
$$0k 0 : k = 2n$$

Since its sub-structure is the K$_2$NiF$_4$-type tetragonal structure with the space group $I4/mmm$, this monoclinic modulated phase has approximately a space group $C2/m$. The unit-cell parameters are determined to be: $a = 5\sqrt{2}a_p$, $b = c_p$, $c = \sqrt{26}\sqrt{2}/2a_p$ and $\beta = 101.3^\circ$. We noted that the $C2/m$ modulated phase exists only in the sample for nominal $\delta = 0.4$, while the $Fmmm$ one exists in all the samples with various nominal values of $\delta$.

For the Sr$_2$CuO$_{3+x}$ tetragonal form in the sample for nominal $\delta = 0.3$, besides the $Fmmm$ superstructure modulation as described above, we found another new superstructure modulation. Fig. 4a shows the ED pattern along [001]$_p$ zone-axis of this modulated structure. The schematic representation of the diffraction pattern along this direction is shown in Fig. 4b. The superlattice spots were determined by systemic tilting experiments to construct base-centered orthorhombic space arrays and the reflection conditions are:

$$hkl : h + k = 2n$$
$$hk0 : h + k = 2n$$
$$h00 : h = 2n$$
$$0k0 : k = 2n$$

Therefore, this modulated structure has a $Cmmm$ symmetry with the unit-cell parameters $a = c_p$, $b = 3\sqrt{2}a_p$ and $c = 4\sqrt{2}a_p$. The $Cmmm$ modulated phase was found to exist only in the sample with nominal $\delta = 0.3$.

The Sr$_2$CuO$_{3+x}$ tetragonal form in the samples for both nominal $\delta = 0.1$ and 0.2 exhibits also two types of superstructure modulation. One is the $Fmmm$ superstructure modulation, but the other is a new one. Fig. 5a and b displays, respectively, the [001]$_p$ zone-axis ED pattern and its schematic representation of this new modulated structure. Unlike those modulated structures described above, this one bears no extinction conditions, indicating that it belongs to primary (P) space group. So this modulated phase has reasonably a space group of $Pmmm$, and the unit-cell parameters are obtained to be: $a = 5\sqrt{2}a_p$, $b = \sqrt{2}a_p$ and $c = c_p$.

Table 1 summarizes the properties of the Sr$_2$CuO$_{3+x}$ tetragonal form in the high-pressure samples for different nominal values of $\delta$ together with the sample superconductivity. The primitive-cell volume of each modulated phase, obtained from reference to that of the $Fmmm$ modulated phase assumed to be $V_p$, is also listed in the table. The primitive-cell volume of modulated phase directly reflects the periodicity of superlattice, and may be related to the total amount of oxygen in the structure as suggested in Ref. [13].

### 3.3. Oxygen K absorption edge

For the hole doped cuprate compounds, the oxygen K edge fine structure can provide important information about the charge carriers and their crystallographic confinement [28–30], and the presence of pre-peak in the low-energy part (usually $E < 531$ eV) of the O–K edge is related to the unoccupied O 2$p$ states. The intensity of the pre-peak is proportional to the number of holes introduced by doping and directly related to metallic behavior for cuprates [31]. Therefore, it is interesting to see how the pre-peak changes for different phases in the samples. In our EELS experiments, image mode was used to acquire the O–K absorption edge in order to avoid the anisotropy on the hole-related pre-peak intensity.

First we noted that a defined phase has a similar O–K absorption edge albeit it can exist in different samples. Tak-
ing the \textit{Fmmm} modulated phase for example, no obvious difference was observed between the O–K edges acquired from that in different samples. This phenomenon is different from that reported previously \cite{24}. Fig. 6a and b show O–K absorption edges obtained, respectively, from the ambient-pressure orthorhombic phase and the high-pressure orthorhombic phase in the sample for nominal $\delta = 0.1$. A hole-related pre-peak at $\sim 528$ eV is clearly seen for the latter orthorhombic phase, while the pre-peak disappeared for the former one, indicating that the high-pressure orthorhombic phase has obviously a low-oxidized form of Sr$_2$CuO$_{3+x}$ as shown in Fig. 6c–g.

Fig. 6c corresponds to O–K edge from the unmodulated Sr$_2$CuO$_{3+x}$ tetragonal structure (in the sample for nominal $\delta = 0.1$), while Fig. 6d–g correspond to O–K edge, respectively, from the \textit{Pmmm} modulated phase (in the sample for nominal $\delta = 0.1$), the \textit{Cnmm} modulated phase (in the sample for nominal $\delta = 0.3$), the \textit{C2/m} modulated phase (in the sample for nominal $\delta = 0.4$), and the \textit{Fmmm} modulated phase (in the sample for nominal $\delta = 0.4$). It can be seen that for the Sr$_2$CuO$_{3+x}$ tetragonal form the unmodulated phase has a lower hole-related pre-peak than those modulated phases; while between those modulated phases a similar pre-peak is observed, indicating a close hole density doped in them. As the primitive-cells of these modulated phases are very similar in volume (see Table 1), the total amount of oxygen doped in their structures, which directly determine the hole intensity, would be very close. The slight differences of the doped oxygen content for the modulated phases cannot be clearly detected by the hole-related pre-peak in O–K absorption edge.

### 3.4. Discussion

The sample structures of Sr$_2$CuO$_{3+x}$ were revealed by XRD to transform gradually from orthorhombic structure to tetragonal form with increasing nominal $\delta$, and a single-phase tetragonal structure is formed when nominal $\delta = 0.4$.
Although the orthorhombic phase in these high-pressure samples has a low-oxidized form of Sr$_2$CuO$_{3+y}$ and a number of holes were doped in its structure, this phase can be said to be non-superconducting because the CuO$_2$ planes, which is one of the requirements for occurrence of superconductivity, are missing in the orthorhombic phase, instead Cu–O chains are formed in its structure. The absence of superconductivity in the low-oxidized orthorhombic phase of Sr$_2$CuO$_{3+y}$ formed under high-pressure was also discussed by Laffez et al. [13]. In addition, no trace of other layered copper oxide, such as SrCuO$_2$ and Sr$_3$Cu$_2$O$_5$ copper-rich phases, was detected in the samples by careful TEM investigations. Therefore, the observed bulk superconductivity in the high-pressure samples must result from the tetragonal form of Sr$_2$CuO$_{3+x}$. Preferring to form modulated superstructures is one of the main characteristics of the tetragonal form. TEM investigations reveal that of the tetragonal form almost all the grains in the samples for nominal $d = 0.3$ and 0.4, and most grains in the samples for nominal $d = 0.1$ and 0.2 exhibit modulated structures, which strongly suggests that the superconductivity is associated with the modulated phases. It should be noted that the Fmmm modulated phase always exists as major phase in all the samples. This means that, if the Fmmm modulated phase were superconducting, nearly a same $T_C$ could have been observed for all the samples. Therefore, the Fmmm modulated phase is not superconducting. Thus the $T_{Cs}$ can be definitely correlated with the modulated phases based on the data shown in Table 1, i.e. the Pmmm modulated phase is responsible for $T_C$ at 60 K, the Cmmm modulated phase for $T_C$ at 68 K, and the C$2/m$ modulated phase for $T_C$ at 75 K.

Now one of the questions that arise is why the Fmmm modulated phase, distinct from the Pmmm, Cmmm and C$2/m$ modulated phases, is not superconducting? A possi-

<table>
<thead>
<tr>
<th>Samples with different nominal $d$</th>
<th>$T_C$ (K)</th>
<th>Unmodulated tetragonal phase</th>
<th>Modulated phases</th>
<th>Space group</th>
<th>Lattices</th>
<th>Primitive-cell volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d = 0.4$</td>
<td>75</td>
<td>No</td>
<td>Fmmm</td>
<td>$a \approx b = 5\sqrt{2}a_p$</td>
<td>$V_o$</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>$c = c_p$</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>$b = c_p$</td>
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<td></td>
<td></td>
<td></td>
<td>$e = \sqrt{26}/2a_p$</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta = 101.3^\circ$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d = 0.3$</td>
<td>68</td>
<td>No</td>
<td>Fmmm</td>
<td>$a \approx b = 5\sqrt{2}a_p$</td>
<td>$V_o$</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$c = c_p$</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$b = 3\sqrt{2}a_p$</td>
<td></td>
<td></td>
<td>0.96 $V_o$</td>
</tr>
<tr>
<td>$d = 0.2$</td>
<td>60</td>
<td>Some grains</td>
<td>Fmmm</td>
<td>$a \approx b = 5\sqrt{2}a_p$</td>
<td>$V_o$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$c = c_p$</td>
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<td></td>
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<td></td>
<td>$b = \sqrt{2}a_p$</td>
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<td></td>
<td>0.8 $V_o$</td>
</tr>
<tr>
<td>$d = 0.1$</td>
<td>60</td>
<td>Some grains</td>
<td>Fmmm</td>
<td>$a \approx b = 5\sqrt{2}a_p$</td>
<td>$V_o$</td>
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<td></td>
<td>$b = \sqrt{2}a_p$</td>
<td></td>
<td></td>
<td>0.8 $V_o$</td>
</tr>
</tbody>
</table>

The primitive-cell volume of each modulated phase is obtained from reference to that of the Fmmm modulated phase assumed to be $V_o$.

Fig. 6. O–K absorption edges obtained from (a) the ambient-pressure orthorhombic phase, (b) the high-pressure orthorhombic phase in the sample for nominal $d = 0.1$, (c) the unmodulated tetragonal phase in the sample for nominal $d = 0.1$, (d)–(f) the Pmmm, Cmmm and C$2/m$ modulated phases, respectively, in the samples for nominal $d = 0.1$, 0.3 and 0.4, (g) the Fmmm modulated phase in the sample for nominal $d = 0.4$. (see Fig. 1).
ble reason is that the main mechanism resulting in the formation of the $Pmmm$ modulated phase is different from that for the latter three. Previous neutron powder diffraction suggested that the main phase in Sr$_2$CuO$_{3+\delta}$ samples formed as an oxygen-deficient K$_x$NiF$_4$-type tetragonal structure with oxygen vacancies located in the Cu–O planes, not in the Sr–O layers [14]. Zhang et al. [25] proposed an atomic model of the average commensurate lattice to explain the $Pmmm$ modulated structure. They suggested that the modulated structure results from metal ion shear displacements with half sine and half cosine waves along $<110>_T$ directions. According to this model, the Cu ions have a half cosine wave displacement while Sr ions have a half sine wave displacement, indicating that oxygen atoms are lost in the Cu–O planes instead of in the Sr–O layers. Therefore, the $Pmmm$ modulated phase, revealed to be the major phase in all our samples, results from the ordered oxygen deficiency in the Cu–O planes, and thus it is reasonable for it to be non-superconducting. For the $Pmmm$, $Cnmm$ and $C2/m$ superconducting modulated phases, the oxygen vacancies can only be located in the Sr–O layers (i.e., in the apical sites) due to the requirement of oxygen vacancy-free CuO$_2$ planes for superconductivity. Thus the formation of the superconducting modulated phases is naturally explained to be the ordering of apical oxygen vacancies.

Then another question that arises is why the $Pmmm$, $Cnmm$ and $C2/m$ modulated phases exhibit different $T_C$s. From Table 1, we can see that the primitive-cells of the three modulated phases are slightly different in volume from one another, indicating that the numbers of oxygen introduced in these modulated phases could be different. The correlation between the primitive-cell volume of the modulated phase and the total amount of doped oxygen has also been suggested by Laffez et al. [13]. This means that the three modulated phases could have different hole doping levels. However, the effect on $T_C$ by the doping level would be slight, and can be neglected to some extent, because the difference between the doping levels of the modulated phases is very slight and cannot be detected clearly by the hole-related pre-peak in O–K absorption edge. On the other hand, these superconducting modulated phases are induced by the ordering of apical oxygen, and exhibit clearly different symmetries from one another, in other words, each of the modulated phases has a distinct type of the apical oxygen ordering. It is consequently iner-

able that the apical oxygen ordering is the key factor influencing the superconducting transition temperature.

In cuprate superconductors, the apical oxygen is located at the first nearest layer of charge reservoir and serves as the direct connection between the charge reservoir blocks and the CuO$_2$ conducting planes in terms of electron exchange interaction [6]. Therefore, the reordering of apical oxygen, which can only be realized in a system with apical sites partially occupied by oxygen, is expected to have dramatic effects on the electronic structures of the CuO$_2$ planes and hence on high-$T_C$ superconductivity. Normally, the chemical doping introduces disorder into the charge reservoir blocks owing to random distribution of dopant atoms. It has been shown that the chemical disorder, which might be responsible for the observed electronic inhomogeneity on the nanometer scale in the CuO$_2$ plane [32–34], has a dramatic effect on $T_C$. The Sr$_2$CuO$_{3+\delta}$ superconducting system is an example showing the impact of apical oxygen ordering.

4. Conclusion

By systematic TEM investigations on the as prepared Sr$_2$CuO$_{3+\delta}$ samples for different nominal values of $\delta$, we find that the 60, 68 and 75 K superconductivities observed in these samples arise, respectively, from the $Pmmm$, $Cnmm$ and $C2/m$ modulated phases formed by the ordering of apical oxygen. Oxygen K EELS measurements have shown that a similar hole density is doped in these superconducting modulated phases. These experimental results suggest that the reordering of apical oxygen is the key factor resulting in the superconductivity differences in the Sr$_2$CuO$_{3+\delta}$ system.

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