INTRODUCTION

In recent decades, high-temperature superconductors have shown great potential in various applications due to their unique physical structures and electric and magnetic properties. In particular, high-temperature copper oxide superconductor is an alternating array consisting of \([\text{CuO}_2]\) conducting planes with charge reservoir blocks where holes or electrons are introduced by dopants. In most cases, the dopant atoms reside in the blocks and are randomly distributed. On the one hand, the superconducting transition temperature \((T_c)\) has been found to have a parabolic relationship with...
respect to the carrier density, attaining a maximum at an optimal doping level.\textsuperscript{1-3} On the other hand, apical oxygen atoms above or below the [CuO\textsubscript{2}] plane form the nearest-neighbor charge reservoir block and connect the charge reservoir blocks and the [CuO\textsubscript{2}] conducting planes through electron exchange interaction (Figure 1).\textsuperscript{4-7} Therefore, the apical oxygen doping concentration, which affects the nearest-neighbor charge reservoir block and its ordering, is expected to have an appreciable effect on the electronic structures of the [CuO\textsubscript{2}] planes and subsequently on high-$T_c$ superconductivity.

In previous studies, Hiroi et al. and Laffez et al. independently reported $4\sqrt{2}a_p \times 4\sqrt{2}a_p \times c_p$ and $5\sqrt{2}/2a_p \times 5\sqrt{2}/2a_p \times c_p$ modulated structures in as-prepared Sr\textsubscript{2}CuO\textsubscript{3+δ} and suggested that the latter structure could be responsible for the superconductivity.\textsuperscript{8,9} This was also confirmed by Wang et al. and Zhang et al. in their as-prepared and annealed samples.\textsuperscript{10,11} While, Shimakawa et al. studied the oxygen-deficient Sr\textsubscript{2}CuO\textsubscript{3+δ} system using neutron diffraction and suggested that oxygen vacancy was located in the Cu-O planes instead of the Sr-O layers.\textsuperscript{12} These contrasting results challenge the current understanding of superconductivity in high-$T_c$ copper oxide superconductors, which is based on oxygen vacancy-free Cu-O planes. In agreement with the results reported in Refs. 10,11, Liu et al. and Yang et al. observed the modulated phase with a space group of $Fmmm$ in high-pressure synthesized Sr\textsubscript{2}CuO\textsubscript{3+δ}.\textsuperscript{13-16} In addition, Liu et al. and Yang et al. reported another modulated phase with a space group of $C2/m$ in the as-prepared sample and proposed the possibility of this phase being responsible for the superconductivity at 75 K. With increasing annealing temperature in a N\textsubscript{2} atmosphere, they observed that phase transitions occurred from $C2/m$ (room pressure) to $Cmamm$ (150°C), then to $Pmmm$ (250°C), and finally to an unmodulated orthorhombic phase above 350°C. The $T_c$ increased from 75 K to 89 K, then to 95 K, and disappeared above 250°C. Hence, they deduced that the different modulated phases were responsible for the different transition temperatures of superconductivity and attributed the origin of the modulated phases to the ordering of apical oxygen. According to the above results, the mechanism of superconductivity in the high-pressure synthesized Sr\textsubscript{2}CuO\textsubscript{3+δ} ($\delta = 0.1 - 0.4$) system has not been fully understood yet.

If the position of oxygen vacancy can be directly observed, it will be of great significance for studying the mechanism of Sr\textsubscript{2}CuO\textsubscript{3+δ} superconductivity and can provide a deeper understanding of the doping/order effect on high-$T_c$ superconductivity. To this end, the aberration-corrected transmission electron microscopy (TEM) technique can be used to obtain structural information at an atomic scale. Okunishi et al. showed that the O contrast can be obtained as mid-tone spots in the annular bright-field (ABF) image, although the O columns are invisible in high-angle annular dark-field (HAADF) and conventional bright-field (BF) images for SrTiO\textsubscript{3} [001] zone-axis.\textsuperscript{17,18} Recently, Ishikawa et al. reported the direct observation of hydrogen atom columns in an YH\textsubscript{2} crystal using the ABF technique.\textsuperscript{19} Therefore, obtaining atomic scale structural data with an aberration-corrected electron transmission microscope (HAADF and ABF imaging techniques in scanning transmission electron microscopy (STEM) mode as well as TEM mode is crucial for understanding the above mechanism.

Despite the extensive studies on the Sr\textsubscript{2}CuO\textsubscript{3+δ} system, it still needs to be ascertained if the origin of its modulated structures is caused by the [CuO\textsubscript{2}] in-plane oxygen vacancy or apical oxygen vacancy. In order to probe this, we investigate the position of the oxygen vacancy in our high-pressure synthesized Sr\textsubscript{2}CuO\textsubscript{3+δ} samples. A series of single-crystal Sr\textsubscript{2}CuO\textsubscript{3+δ} samples was prepared using a high-temperature and high-pressure synthesis route and atomic scale microstructural analyses were performed using an aberration-corrected transmission electron microscope. This research will help us in understanding the mechanism of superconductivity in the Sr\textsubscript{2}CuO\textsubscript{3+δ} system.

![Figure 1](image.png)  
**Figure 1** The temperature dependence of magnetization (M) curve after cooling in a 50 Oe magnetic field. The inset indicates the schematic view of the crystal structure of Sr\textsubscript{2}CuO\textsubscript{3+δ} with the K\textsubscript{2}NiF\textsubscript{4} type tetragonal structure containing [CuO\textsubscript{2}] planes (O1) and the apical oxygen sites (O2).
FIGURE 2 The SAED patterns of Sr$_2$CuO$_{3+\delta}$ sample with $5\sqrt{2}a$ modulated structure along [001] (A) and [100] (B) zone-axes, respectively. All basic diffraction spots and satellite diffraction spots have been indexed, respectively.

a six-face pressing equipment was used for holding them at about 1350°C for 30 minutes under the pressure of 5.5 GPa, then 2 hours for dropping to about 1100°C, and finally dropping to room temperature. In the end, the pressure was released and single-crystal samples were synthesized.

Single sheet-like crystals could be obtained as the crystal sample was easily dissociated in the vertical axial direction. Using a focused ion beam (FIB) equipment, the Omni Probe mechanical arm was used to extract ~5 x 4 μm sheets in the axial and vertical axial directions (along the [100] and [001] zone-axes, respectively) of the single crystal. The sheets were fixed on a copper chip with several columns using Pt deposition. The electron microscopy specimen with a thickness of ~50 nm was cut and milled on the copper chip by the FIB machine and the damage layer on the surface of the specimen was cleaned by a weak Ga ion beam. The magnetic properties of the sample were measured using a superconducting quantum interference device (SQUID).

Thereafter, the atomic scale structure of Sr$_2$CuO$_{3+\delta}$ samples was studied using a combination of selected area electron diffraction (SAED), HAADF, and ABF imaging methods. Aberration-corrected TEM and STEM studies were performed on a JEOL ARM200F transmission electron microscope equipped with double Cs correctors (CEOS) for the condenser lens and objective lens. ABF and HAADF images were acquired at acceptance angles of 11.5-23.0 and 90-370 mrad, respectively. The available spatial resolution of the STEM images is better than 78 pm at 200 kV.

3 | RESULTS AND DISCUSSION

A sample with $\delta = 0.4$ was chosen for the current study, of which crystallization and phase purity are the best in the series samples. The purity of the synthesized Sr$_2$CuO$_{3+\delta}$ ($\delta = 0.4$) single-crystal sample was probed by X-ray diffraction and indexed to a typical body-centered tetragonal structure with a space group of I4/mmm, with lattice parameters of $a = b = 3.7631$ Å and $c = 12.5601$ Å, consistent with the results in Ref. 13. Sr$_2$CuO$_{3+\delta}$ ($\delta = 0.4$) has a typical K$_2$NiF$_4$-type tetragonal structure, which is evident from the inset of Figure 1. Copper atoms (green balls) occupy the body-centered positions in the Cu-O octahedron, which is constituted by four [CuO$_3$] in-plane oxygen atoms (blue balls) and two apical oxygen atoms (red balls). Sr atoms (yellow balls) occupy the corner sites of a quasi-cube including the Cu-O octahedron. Since there is no overlap between (among) Sr, Cu, or (and) O atomic columns along [100] zone-axis direction, direct evidence regarding the positions of the [CuO$_3$] in-plane oxygen sites (O1) and the apical oxygen sites (O2) can be obtained at atomic resolution. Figure 1 also shows the magnetic susceptibility measured for the Sr$_2$CuO$_{3+\delta}$ ($\delta = 0.4$) single-crystal sample in the Meissner (field cooling) mode in a 50 Oe magnetic field. The samples did not show any evidence of the Meissner effect during the measured temperature range (80 K to 5 K). This implied that perfect diamagnetism was not observed in the sample and the Sr$_2$CuO$_{3+\delta}$ ($\delta = 0.4$) single crystal did not exhibit any superconductivity in the measured temperature range.

In our TEM experiments, it was observed that the Sr$_2$CuO$_{3+\delta}$ ($\delta = 0.4$) single crystal shows a commensurately modulated structure with a fivefold periodicity. Figure 2A and 2B show the SAED patterns of the fivefold modulated structure along [001] and [100] zone-axes, respectively. We have indexed basic diffraction spots according to the basic structure along [001] and [100] zone-axes, respectively. The magnetic susceptibility measured for the Sr$_2$CuO$_{3+\delta}$ ($\delta = 0.4$) single-crystal sample in the Meissner (field cooling) mode in a 50 Oe magnetic field. The samples did not show any evidence of the Meissner effect during the measured temperature range (80 K to 5 K). This implied that perfect diamagnetism was not observed in the sample and the Sr$_2$CuO$_{3+\delta}$ ($\delta = 0.4$) single crystal did not exhibit any superconductivity in the measured temperature range.

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To confirm the existence of modulated structure, STEM studies were performed for the sample. The corresponding HAADF and ABF images along [001] zone-axis are shown in Figure 3A and 3B, respectively, showing clearly its modulated periodicity. One super-unit is outlined in the white frame in Figure 3A. In order to probe the origin of the modulated structure in this sample, we focus on the contrast characterization of Cu-O octahedron in the ABF image. A slight distortion and rotation of Cu-O octahedron is observed, which may be induced by the oxygen vacancy in Cu-O octahedra, leading to ordering structural fluctuations which form the
modulated structure finally. In previous reports, SAED and high-resolution TEM measurements were used to investigate the evolution of the structural modulation associated with the oxygen vacancy ordering under different annealing temperatures. Liu et al. and Yang et al. suggested that oxygen vacancy ordering affected the resulting superconductivity of the modulated structure. Therefore, it can be deduced that the oxygen vacancy in the Cu-O octahedron may induce non-superconductivity in our modulated structure.

In order to obtain deeper insights into the structure of the samples, further observations were carried out along [100] zone-axis. Figure 4A and 4 show the HAADF and ABF images of the Sr$_2$CuO$_{3+\delta}$ (\(\delta = 0.4\)) single crystal, respectively. In the ABF image, light element O1 and O2 can be clearly distinguished from heavy elements Sr, Cu atomic columns through the difference in the contrast (as shown in the inset of Figure 4B). Figure 4C shows the line scan intensity profiles along the red frame in Figure 4B, which indicates the arrangement of atomic columns: Sr - O1 - Sr - O2 - Cu + O1 (overlap) - O2. Line scan intensity profiles indicate that the trough intensity of the oxygen in the [CuO$_2$] plane (O1 sites) is significantly lower than the apical oxygen (O2 sites). Whereas, the trough intensity of the apical oxygen (O2 sites) is identical, indicating that the oxygen vacancy appears in the [CuO$_2$] plane, which leads to the decreasing of trough intensity. Besides, we also carried out statistical analysis for line scan intensity profiles from other regions and the results are consistent. As mentioned above, the neutron diffraction result by Shimakawa et al. challenges the current understanding of superconductivity mechanism, which is based on oxygen vacancy-free Cu-O planes. Besides, Liu et al and Yang et al. reported different modulated structures, which are considered to be induced by oxygen vacancies, corresponding to different \(T_c\). Therefore, we propose that this nonsuperconducting modulated structure is induced by the [CuO$_2$] in-plane oxygen vacancy. As a result, the incomplete [CuO$_2$] plane may restrain the formation of Cooper electronic pairs and further obliterate the superconductivity in Sr$_2$CuO$_{3+\delta}$ system. We examined that the neutron diffraction data might come from this nonsuperconducting phase.

To explore the superconductivity mechanism of copper oxide high-temperature superconductors, previous researches revealed several factors affecting \(T_c\). For example, high pressure can affect \(T_c\) through varying the type of insertion period of a charge reservoir layer where carriers are created and doped into the [CuO$_2$] planes. Therefore, high pressure can alter the number of the carriers and result in different \(T_c\)s in copper oxides. Furthermore, different annealing temperatures also affect the \(T_c\) of superconductors. As mentioned earlier, using TEM technique, Liu et al. and Yang et al. reported that different annealing conditions for Sr$_2$CuO$_{3.4}$ superconductor can give rise to different orderings of apical oxygen which are related to different \(T_c\). Besides, in the Sr$_2$CuO$_{3+\delta}$ with different stoichiometry (\(\delta = 0.1-0.4\)), some modulated structures may come from the oxygen vacancy ordering at apical oxygen site, which are corresponding to different \(T_c\), while other nonsuperconducting modulated phases may be induced by oxygen vacancies in Cu-O planes. In addition, Raghu et al. and Balestrino et al. believed that the number of [CuO$_2$] planes may affect the coupling between charge reservoir layers and [CuO$_2$] planes. Further, the distance between charge reservoir layers and outermost [CuO$_2$] planes results in a non-monotonic behavior of \(T_c\). Besides, in the
123-type cuprate superconductors, different [CuO$_2$] plane bucklings can modify a peak in electronic density of states with the flat regions of Fermi surface, resulting in different $T_c$s. In a word, the [CuO$_3$] plane which plays an essential role in the formation of the Cooper electronic pairs and the carriers created in the charge reservoir layers determine $T_c$s of cuprate superconductors. In this study, oxygen vacancies were observed in the [CuO$_3$] plane of the non-superconductivity Sr$_2$CuO$_{3+\delta}$ ($\delta = 0.4$) single crystal, in consistent with the generally accepted viewpoint that copper oxide high-temperature superconductors must have complete [CuO$_2$] planes.

4 | CONCLUSIONS

Using a series of techniques based on aberration-corrected TEM and STEM, atomic scale structural analysis was performed for a series of Sr$_2$CuO$_{3+\delta}$ samples. The presence of [CuO$_2$] in-plane oxygen vacancy was found to obliterate the superconductivity of the Sr$_2$CuO$_{3+\delta}$ ($\delta = 0.4$) single-crystal system. It was deduced that the complete [CuO$_2$] planes (oxygen vacancy-free) may guarantee superconductivity in copper oxide high-temperature superconductors in which oxygen vacancy may appear in the apical oxygen sites. Results address the origin of the modulated structure in the copper oxide and present arguments in favor of [CuO$_2$] in-plane oxygen vacancy responsible for the loss of superconductivity for copper oxide samples. Therefore, our results pave the way to material designs and applications in copper oxide high-temperature superconductors.

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