Received: 23 April 2019 | Revised: 18 June 2019 | Accepted: 20 June 2019

DOI: 10.1111/jace.16662

RAPID COMMUNICATION

Journal of the American Ceramic Society

The origin of the modulated structure in $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$): [CuO_2] in-plane oxygen vacancy or apical oxygen vacancy?

Xi Shen[1] | Li-Peng Cao[1] | Jian-Fa Zhao[1,2] | Wei-Peng Wang[1] | Qing-Qing Liu[1] | Yuan Yao[1] | Jun-Jie Li[1] | Chang-Zhi Gu[1,2] | Ming-Wei Chen[3] | Chang-Qing Jin[1,2] | Ri-Cheng Yu[1,2]

[1]Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, People's Republic of China

[2]School of Physical Sciences, University of Chinese Academy of Sciences, Beijing, People's Republic of China

[3]Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland

Correspondence

Chang-Qing Jin and Ri-Cheng Yu, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, People's Republic of China.

Email: Jin@iphy.ac.cn (C. -Q. J); rcyu@iphy.ac.cn (R. -C. Y)

Ming-Wei Chen, Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD, USA.

Email: mwchen@jhu.edu

Funding information

National key research program of China, Grant/Award Number: 2016YFA0300701, 2017YFA0206200 and 2018YFA0208402; National Natural Science Foundation of China, Grant/Award Number: 11374343, 11574376, 61504166 and 11874413; Youth Innovation Promotion Association of CAS, Grant/Award Number: 2019009

Abstract

We propose the question of the modulated structures of copper oxide is caused by the [CuO_2] in-plane oxygen vacancy or apical oxygen vacancy. $Sr_2CuO_{3+\delta}$ single-crystal samples were prepared using high-temperature and high-pressure methods. The major phase of $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$) single-crystal system is found to be constituted by the $5\sqrt{2}$ a modulated structure with the *Fmmm* space group, which originates from the [CuO_2] in-plane oxygen vacancy appearing in octahedral Cu-O. Besides, the presence of the [CuO_2] in-plane oxygen vacancy may obliterate the superconductivity of the system. Experimental results deduce that the oxygen vacancy may appear in the apical oxygen sites in high-temperature copper oxide superconductors.

KEYWORDS

copper oxide, high-temperature superconductor, modulated structure, oxygen vacancy

1 | 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 [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.[1–3] On the other hand, apical oxygen atoms above or below the [CuO_2] plane form the nearest-neighbor charge reservoir block and connect the charge reservoir blocks and the [CuO_2] conducting planes through electron exchange interaction (Figure 1).[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_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 $Sr_2CuO_{3+\delta}$ and suggested that the latter structure could be responsible for the superconductivity.[8,9] This was also confirmed by Wang et al. and Zhang et al. in their as-prepared and annealed samples.[10,11] While, Shimakawa et al. studied the oxygen-deficient $Sr_2CuO_{3+\delta}$ system using neutron diffraction and suggested that oxygen vacancy was located in the Cu-O planes instead of the Sr-O layers.[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 $Sr_2CuO_{3.4}$.[13–16] In addition, Liu et al. and Yang et al. reported another modulated phase with a space group of *C*2/*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_2 atmosphere, they observed that phase transitions occurred from *C*2/*m* (room pressure) to *Cmmm* (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 $Sr_2CuO_{3+\delta}$ ($\delta = 0.1 - 0.4$) system has not been fully understood yet.

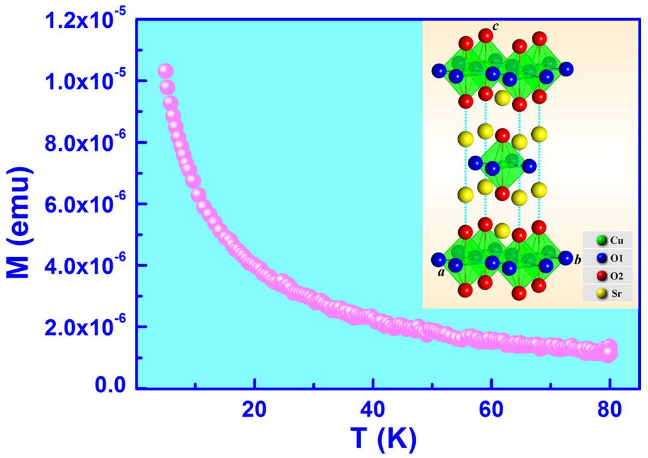

FIGURE 1 The temperature dependence of magnetization (M) curve after cooling in a 50 Oe magnetic field. The inset indicates the schematic view of the crystal structure of $Sr_2CuO_{3+\delta}$ with the K_2NiF_4 type tetragonal structure containing [CuO_2] planes (O1) and the apical oxygen sites (O2)

If the position of oxygen vacancy can be directly observed, it will be of great significance for studying the mechanism of $Sr_2CuO_{3+\delta}$ 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 $SrTiO_3$ [001] zone-axis.[17,18] Recently, Ishikawa et al. reported the direct observation of hydrogen atom columns in an YH_2 crystal using the ABF technique.[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 $Sr_2CuO_{3+\delta}$ system, it still needs to be ascertained if the origin of its modulated structures is caused by the [CuO_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 $Sr_2CuO_{3+\delta}$ samples. A series of single-crystal $Sr_2CuO_{3+\delta}$ 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 $Sr_2CuO_{3+\delta}$ system.

2 | EXPERIMENT PROCEDURE

$Sr_2CuO_{3+\delta}$ samples were synthesized by a high-temperature and high-pressure method. $SrCO_3$ and CuO were used as raw materials and sintered at 980°C by solid-phase reaction in order to obtain the Sr_2CuO_3 precursor. Then, Sr_2CuO_3, CuO, and SrO_2 were used with the stoichiometric ratio of $Sr_2CuO_{3.4}$:SrO_2 = 1:1 and loaded in a glove box. They were mixed well and pressed into a 4-mm diameter disc, then put into the MgO crucible with a platinum cylinder. Meanwhile,

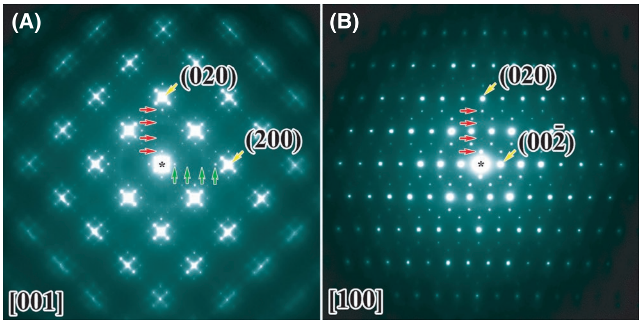

FIGURE 2 The SAED patterns of $Sr_2CuO_{3+\delta}$ sample with $5\sqrt{2}\,a$ modulated structure along [001] (A) and [100] (B) zone-axes, respectively. All basic diffraction spots and satellite diffraction spots have been indexed, respectively

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 × 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 $Sr_2CuO_{3+\delta}$ 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 $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$) single-crystal sample was probed by X-ray diffraction and indexed to a typical body-centered tetragonal structure with a space group of *I*4/*mmm*, with lattice parameters of $a = b = 3.7631$ Å and $c = 12.5601$ Å, consistent with the results in Ref. [13]. $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$) has a typical K_2NiF_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_2] 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_2] 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 $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$) 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 $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$) single crystal did not exhibit any superconductivity in the measured temperature range.

In our TEM experiments, it was observed that the $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$) single crystal shows a commensurately modulated structure with a fivefold periodicity. Figure 2A and 2 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 K_2NiF_4-type tetragonal structure. Red and green arrows indicate satellite diffraction spots. Systemic tilting experiments suggest that the modulation plane for the modulated structure lies in the *ab*-plane, and the space group of the modulated structure can be approximately described as *Fmmm* considering that the substructure of the modulated phase has a K_2NiF_4-type tetragonal structure with the space group *I*4/*mmm*. The lattice parameters are $a_s = b_s = 5\sqrt{2}\,a$ and $c_s = c$ (where the subscript "s" stands for the modulated superstructure), which are consistent with the results of polycrystalline samples in Refs. 13–16. Therefore, it can be deduced that the $5\sqrt{2}\,a$ modulated structure corresponds to a nonsuperconducting phase. It should be noted that, no other phases were observed in our single-crystal samples.

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 3, 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.[13–16] Therefore, it can be deduced that the oxygen vacancy in the Cu-O octahedron may induce nonsuperconductivity 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 $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$) 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.[12] 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.[13–16] 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 $Sr_2CuO_{3+\delta}$ 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.[20] Therefore, high pressure can alter the number of the carriers and result in different T_cs 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 $Sr_2CuO_{3.4}$ superconductor can give rise to different orderings of apical oxygen which are related to different T_cs.[13,15] Besides, in the $Sr_2CuO_{3+\delta}$ with different stoichiometry (δ = 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.[21,22] Further, the distance between charge reservoir layers and outermost $[CuO_2]$ planes results in a non-monotonic behavior of T_c. Besides, in the

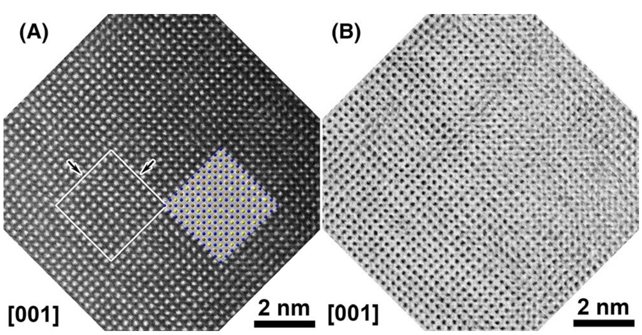

FIGURE 3 The HAADF (A) and ABF (B) images of $Sr_2CuO_{3+\delta}$ sample with $5\sqrt{2}\,a$ modulated structure along [001] zone-axis. The white frame and crystal model projection indicates the super-unit of modulated structure in (A)

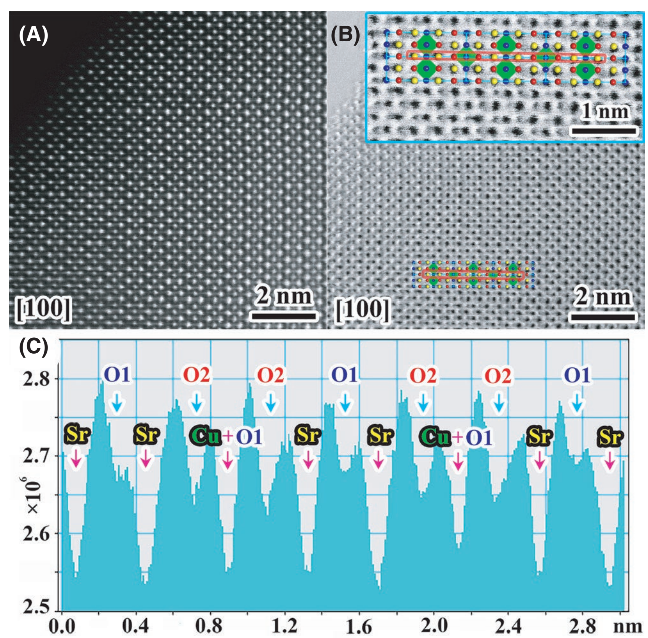

FIGURE 4 The HAADF (A) and ABF (B) images of $Sr_2CuO_{3+\delta}$ sample with $5\sqrt{2}\,a$ modulated structure along [100] zone-axis. The inset of (B) is an enlarged image of red line scan region. C shows the line scan intensity profile along the red frames in (B)

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_cs.[23] In a word, the [CuO_2] 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_cs of cuprate superconductors. In this study, oxygen vacancies were observed in the [CuO_2] plane of the non-superconductivity $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$) 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 $Sr_2CuO_{3+\delta}$ samples. The presence of [CuO_2] in-plane oxygen vacancy was found to obliterate the superconductivity of the $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$) 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.

ACKNOWLEDGMENTS

This work was supported by the National key research program of China (Grant Nos. 2017YFA0206200, 2016YFA0300701, 2018YFA0208402) and the National Natural Science Foundation of China (Grant Nos. 11374343, 11574376, 61504166, 11874413). X. Shen is grateful for the support from the Youth Innovation Promotion Association of CAS (2019009). The authors thank Prof. S. Uchida at University of Tokyo for the very helpful and valuable discussion.

ORCID

Xi Shen https://orcid.org/0000-0003-4677-2455

REFERENCES

1. Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y, Akimitsu J. Superconductivity at 39 K in magnesium diboride. Nature. 2001;410(6824):63–4.
2. Tranquada JM, Sternlieb BJ, Axe JD, Nakamura Y, Uchida S. Evidence for stripe correlations of spins and holes in copper oxide superconductors. Nature. 1995;375(6532):561–3.
3. Dagotto E. Correlated electrons in high-temperature superconductors. Rev Mod Phys. 1994;66(3):763–840.
4. Karppinen M, Yamauchi H. Control of the charge inhomogeneity and high-T_c superconducting properties in homologous series of multi-layered copper oxides. Mater Sci Eng R-Rep. 1999;26(3):51–96.
5. Müller KA. On the oxygen isotope effect and apex anharmonicity in high-T_c cuprates. Z Phys B: Condens Matter. 1990;80(2):193–201.
6. Conradson SD, Raistrick ID. The axial oxygen atom and superconductivity in $YBa_2Cu_3O_7$. Science. 1989;243(4896):1340–3.
7. Pavarini E, Dasgupta I, Saha-Dasgupta T, Jepsen O, Andersen OK. Band-structure trend in hole-doped cuprates and correlation with $T_{c\ max}$. Phys Rev Lett. 2001;87(4):047003.
8. Hiroi Z, Takano M, Azuma M, Takeda Y. A new family of copper oxide superconductors $Sr_{n+1}Cu_nO_{2n+1+\delta}$ stabilized at high pressure. Nature. 1993;364(6435):315–7.
9. Laffez P, Wu XJ, Adachi S, Yamauchi H, Môri N. Synthesis of superconducting $Sr_2CuO_{3+\delta}$ using-high pressure techniques. Physica C. 1994;222(3–4):303–9.
10. Wang YY, Zhang H, Dravid VP, Marks LD, Han PD, Payne DA. A TEM study of the incommensurate modulated structure in $Sr_2CuO_{3+\delta}$ superconductor synthesized under high pressure A. Evolution of the incommensurate modulated structure and the electronic structure with post-heat treatment. Physica C. 1995;255(3–4):247–56.
11. Zhang H, Wang YY, Marks LD, Dravid VP, Han PD, Payne DA. A TEM study of the incommensurate modulated structure in Sr_2CuO_{3+x} superconductors synthesized under high pressure B. Structural model. Physica C. 1995;255(3–4):257–65.
12. Shimakawa Y, Jorgensen Jd, Mitchell Jf, Hunter Ba, Shaked H, Hinks Dg, et al. Structural study of $Sr_2CuO_{3+\delta}$ by neutron powder diffraction. Physica C. 1994;228(1–2):73–80.
13. Liu QQ, Yang H, Qin XM, Yu Y, Yang LX, Li FY, et al. Enhancement of the superconducting critical temperature of $Sr_2CuO_{3+\delta}$ up to 95 K by ordering dopant atoms. Phys Rev B. 2006;74(10):100506.
14. Yang H, Liu QQ, Li FY, Jin CQ, Yu RC. Structure and microstructure of superconductor $Sr_2CuO_{3+\delta}$ (nominal $\delta = 0.4$) prepared under high pressure. Supercond Sci Technol. 2006;19(9):934–40.
15. Yang H, Liu QQ, Li FY, Jin CQ, Yu RC. TEM and EELS characterization of a $Sr_2CuO_{3+\delta}$ superconductor post-annealed at different temperatures: enhancement of T_c by apical oxygen reordering. Supercond Sci Technol. 2007;20(10):904–10.
16. Yang H, Liu QQ, Li FY, Jin CQ, Yu RC. TEM and EELS studies of $Sr_2CuO_{3+\delta}$ (nominal $\delta = 0.1$–0.4): Effect of apical oxygen ordering on T_c of cuprate superconductors. Physica C. 2007;467(1–2):59–66.
17. Okunishi E, Ishikawa I, Sawada H, Hosokawa F, Hori M, Kondo Y. Visualization of light elements at ultrahigh resolution by STEM annular bright field microscopy. Microsc Microanal. 2009;15(2):164–5.
18. Okunishi E, Sawada H, Kondo Y. Experimental study of annular bright field (ABF) imaging using aberration-corrected scanning transmission electron microscopy (STEM). Micron. 2012;43(4):538–44.
19. Ishikawa R, Okunishi E, Sawada H, Kondo Y, Hosokawa F, Abe E. Direct imaging of hydrogen-atom columns in a crystal by annular bright-field electron microscopy. Nature Mater. 2011;10(4):278–81.

20. Takayama-Muromachi E. High-pressure synthesis of homologous series of high critical temperature (T_c) Superconductors. Chem Mater. 1998;10(10):2686–98.
21. Balestrino G, Martellucci S, Medaglia PG, Paoletti A, Petrocelli G, Varlamov AA. Dependence of the critical temperature on n in $(BaCuO_2)_2/(CaCuO_2)_n$ superlattices. Phys Rev B. 1998;58(14):R8925–R8928.
22. Raghu S, Thomale R, Geballe TH. Optimal T_c of cuprates: role of screening and reservoir layers. Phys Rev B. 2012;86(9):094506.
23. Chmaissem O, Jorgensen JD, Short S, Knizhnik A, Eckstein Y, Shaked H. Scaling of transition temperature and CuO_2 plane buckling in a high-temperature superconductor. Nature. 1999;397(6714):45–8.

How to cite this article: Shen X, Cao L-P, Zhao J-F, et al. The origin of the modulated structure in $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$): $[CuO_2]$ in-plane oxygen vacancy or apical oxygen vacancy? *J Am Ceram Soc*. 2019;00:1–6. https://doi.org/10.1111/jace.16662