

Superconductivity of a cuprate with compressed local octahedron

WenMin Li^{1,2}, LiPeng Cao¹, JianFa Zhao^{1,2}, XianCheng Wang¹, RunZe Yu¹, YouWen Long^{1,2,3},
QingQing Liu¹, and ChangQing Jin^{1,2,3*}

¹ Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China;

² School of Physics, University of Chinese Academy of Sciences, Beijing 100049, China;

³ Collaborative Innovation Center of Quantum Matter, Beijing 100190, China

Received December 11, 2018; accepted December 18, 2018; published online January 21, 2019

Citation: W. M. Li, L. P. Cao, J. F. Zhao, X. C. Wang, R. Z. Yu, Y. W. Long, Q. Q. Liu, and C. Q. Jin, Superconductivity of a cuprate with compressed local octahedron, *Sci. China-Phys. Mech. Astron.* **62**, 037421 (2019), <https://doi.org/10.1007/s11433-018-9346-8>

Since the historical discovery of high T_c superconductivity (HTS) of La_2CuO_4 in 1986 [1], the superconductivity mechanism of copper oxides remains one of the biggest mysteries in the field of condensed matter physics [2-10]. High- T_c cuprates crystallize into layered perovskite structure, as well as copper oxygen octahedron coordination. In octahedron symmetry, the 3d orbitals of Cu^{2+} with a $3d^9$ configuration degenerate into two top e_g and three lower t_{2g} orbitals. Given that the octahedron is distorted owing to the strong Jahn Teller effects of Cu^{2+} ion, the two e_g orbitals further split into a higher x^2-y^2 orbital vs a lower $3z^2-r^2$ orbital based on the electrostatic interactions of the layered structure [6]. This gives rise to the universal elongated octahedron in high- T_c cuprates, leading to the scenario wherein the doped holes primarily reside at the x^2-y^2 orbital strongly hybridized with oxygen 2p orbital. The configuration is consistent with the d-wave pairing symmetry that lay the foundation for the mechanism studies of HTS [7,8]. This study aims to report the discovery of a new type of copper oxide superconductor, $\text{Ba}_2\text{CuO}_{3+\delta}$, with La_2CuO_4 -type structure synthesized at high pressure and high temperature. The $\text{Ba}_2\text{CuO}_{3+\delta}$ compound shows superconductivity with T_c of more than 70 K, which is approximately 30 K higher than that of the isostructural counterpart based on La_2CuO_4 [1]. However, the new superconductor exhibits the compressed local octahedron co-

ordination, which is remarkably different from the elongated version identified in other cuprate superconductors, as shown in Figure 1

The $\text{Ba}_2\text{CuO}_{3+\delta}$ samples are synthesized through high pressure and high temperature. The precursor materials of the nominal composition Ba_2CuO_3 are prepared via the solid-state reaction of BaO, BaO_2 , and CuO powders with purity of more than 99.9% in an oxygen atmosphere at 800°C for 60 h with one intermediate grinding. Then, the obtained precursor is thoroughly mixed with an appropriate ratio of BaO_2 and CuO powder before subjected to synthesis at a pressure of 18 GPa and temperature of 1000°C or 1 h using the self-oxidizing mechanism [9,10]. Given that the sample is highly hygroscopic, most of the processing is performed in a glove box protected with flowing Ar. The sample quality and crystal structure are characterized by powder X-ray diffraction (XRD) using a Huber diffractometer (Cu $K\alpha_1$ radiation, 40 kV, 300 mA). The diffraction data are collected in the angle (2θ) range from 20° to 100° with steps of 0.01° at room temperature. The crystallographic parameters are analyzed via the Rietveld full-profile refinement using the GSAS program. The DC magnetic susceptibility is measured using a vibrating sample magnetometer (Quantum Design) at a magnetic field of 30 Oe.

The powder XRD profile of $\text{Ba}_2\text{CuO}_{3+\delta}$ apparently matches with the 214 type structure with space group $I4/mmm$. No crystal structure transition is detected until 6 K. The re-

*Corresponding author (email: jin@iphy.ac.cn)

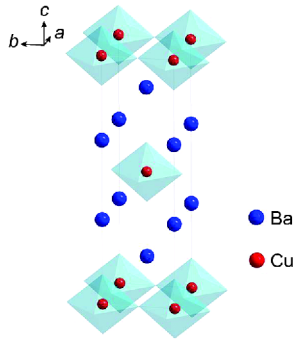


Figure 1 (Color online) Schematic crystal structure of $\text{Ba}_2\text{CuO}_{3+\delta}$ that is isostructural to La_2CuO_4 but with a compressed copper oxygen octahedron (the blue ball is Ba, the red ball is copper, and oxygen is at the ligand site).

finement produces R_{wp} , R_p , and χ^2 as 4.52%, 3.71%, and 1.618, respectively, indicating the reasonable of the structure model. Based on the refinement result, the lattice parameters of the compound are $a = 4.0030(3)$ Å and $c = 12.942(1)$ Å at room temperature. The extra oxygen amount (δ) is estimated to be approximately 0.2 based on the structure refinement calculation, suggesting that the oxygen sites are partially occupied; more details of the oxygen distribution will be systematically investigated via neutron diffraction but will not change the conclusion related to the primary structure framework. The copper valence is calculated to be +2.4, corresponding to 0.4 holes/Cu-doping level. This is well in the heavily overdoped region according to the phase relation for high T_c cuprates [11]. The copper oxygen bond length for $\text{Ba}_2\text{CuO}_{3+\delta}$ is 2.00 Å within the copper oxygen plane vs 1.86 Å along the c axis, based on the Rietveld refinements. The in-plane bond length of $\text{Ba}_2\text{CuO}_{3+\delta}$ refers to the record long for copper oxide superconductors. The extremely large A site ion dramatically expands the in plane dimension to the unprecedented long ever known for high T_c superconductors [12-17], while the reduced electron affinity of Ba relative to La further pushes the apical oxygen toward the transition metal element similar to that found in the BaRuO_3 perovskite [18]. Hence, the local octahedron of $\text{Ba}_2\text{CuO}_{3+\delta}$ exceptionally becomes compressed instead of elongated, which is remarkably opposite to the previously studied cuprates with 214 structure as shown in Figure 2 [19-21].

Figure 3 shows the magnetic susceptibility of $\text{Ba}_2\text{CuO}_{3+\delta}$ polycrystals measured both in ZFC and FC (Meissner) modes at an applied magnetic field of 30 Oe. The volume fraction estimated from the Meissner effect is high enough. The measurements evidently indicate the bulk superconducting nature of the sample. However, owing to a very hygroscopic surface, measuring resistance and temperature is difficult.

The elongated copper-oxygen local octahedron in high- T_c cuprates lifts the x^2-y^2 orbital above the $3z^2-r^2$ orbital. Thus, the doped holes are primarily at the x^2-y^2 orbital that intends

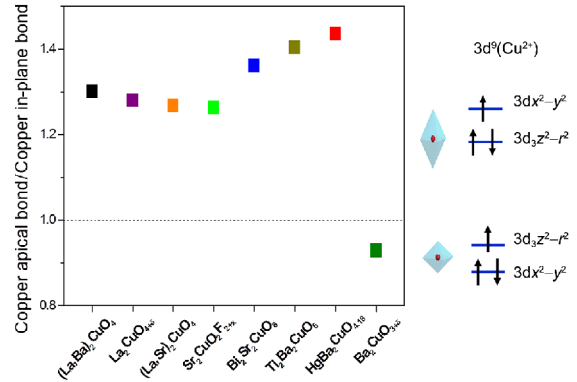


Figure 2 (Color online) The ratio between the bond lengths of copper apical oxygen and that of the in plane copper oxygen for various cuprate superconductors. The octahedron, among others, is elongated wherein the x^2-y^2 orbital is above the $3z^2-r^2$, whereas the octahedron in $\text{Ba}_2\text{CuO}_{3+\delta}$ compound is compressed wherein the $3z^2-r^2$ is lifted above the x^2-y^2 orbital. The dashed line corresponds to the distortion free octahedron.

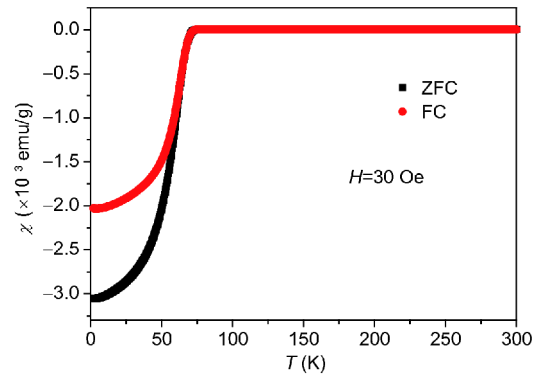


Figure 3 (Color online) Temperature dependence of magnetic susceptibility measured in a magnetic field of 30 Oe with ZFC and FC modes that indicate the bulk superconducting nature.

to confine carriers within the CuO_2 plane, i.e., the system is highly two dimensional. The cuprate superconductors are preferred for the d-wave pairing symmetry in the x^2-y^2 scenario [9]. However, in present study the local copper oxygen octahedron becomes compressed with the $3z^2-r^2$ orbital above the x^2-y^2 . This switch of relative position of the two e_g orbitals will increase the contribution of the doped holes with $3z^2-r^2$ characters. Given that the $3z^2-r^2$ orbital is bonded to apical oxygen along the c axis, the interlayer coupling will be consequently enhanced in $\text{Ba}_2\text{CuO}_{3+\delta}$. Therefore, the materials become more three dimensional in the cuprate superconductors with compressed local octahedron [22]. Interestingly a possible s-wave pairing symmetry signature is recently reported in one layer thin film of the cuprate superconductor [23-26]. More systematic studies, including polarization and microstructure characterization [27,28], are necessary for an in-depth understanding of the new superconductor when single crystals are available.

The work was supported by the National Natural Science Foundation of China (Grant No. 11820101003), and the Ministry of Science & Technology (Grant Nos. 2018YFA0305701, 2017YFA0302901, and 2016YFA0300301). We thank QingZhen Huang, ZhiWei Hu, Yasutomo Uemura, Gregory R. Stewart, JiangPing Hu, ShiPing Feng, S. Uchida, FuChun Zhang for the helpful discussions. ChangQing Jin is grateful to Tao Xiang, Lu Yu, ZhongXian Zhao for consistent encouragements.

- 1 J. G. Bednorz, and K. A. Müller, *Zeitschrift Phys. B Condens. Matter.* **64**, 189 (1986).
- 2 M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, *Phys. Rev. Lett.* **58**, 908 (1987).
- 3 Z. X. Zhao, L. Q. Chen, Q. S. Yang, Y. Z. Huang, G. H. Chen, R. M. Tang, G. R. Liu, Y. M. Ni, C. G. Cui, L. Chen, L. Z. Wang, S. Q. Guo, S. L. Li, J. Q. Bi, and C. Q. Wang, *Chin. Sci. Bull.* **32**, 661 (1987).
- 4 H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, *Jpn. J. Appl. Phys.* **27**, L209 (1988).
- 5 A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott, *Nature* **363**, 56 (1993).
- 6 H. Keller, A. Bussmann-Holder, and K. A. Müller, *Mater. Today* **11**, 38 (2008).
- 7 Z. X. Shen, D. S. Dessau, B. O. Wells, D. M. King, W. E. Spicer, A. J. Arko, D. Marshall, L. W. Lombardo, A. Kapitulnik, P. Dickinson, S. Doniach, J. DiCarlo, T. Loeser, and C. H. Park, *Phys. Rev. Lett.* **70**, 1553 (1993).
- 8 C. C. Tsuei, J. R. Kirtley, C. C. Chi, L. S. Yu-Jahnes, A. Gupta, T. Shaw, J. Z. Sun, and M. B. Ketchen, *Phys. Rev. Lett.* **73**, 593 (1994).
- 9 C. Q. Jin, S. Adachi, X. J. Wu, and H. Yamauchi, *A New Superconducting Homologous Series of Compounds: Cu-12(n-1)n. Advances in Superconductivity VII*, edited by K. Yamafuji, and T. Morishita (Springer Verlag, Tokyo, 1995), pp. 249-254.
- 10 C. Q. Jin, S. Adachi, X. J. Wu, H. Yamauchi, and S. Tanaka, *Phys. C-Supercond.* **223**, 238 (1994).
- 11 B. Keimer, S. A. Kivelson, M. R. Norman, S. Uchida, and J. Zaanen, *Nature* **518**, 179 (2015).
- 12 S. L. Chaplot, W. Reichardt, L. Pintschovius, and N. Pyka, *Phys. Rev. B* **52**, 7230 (1995).
- 13 R. J. Cava, A. Santoro, D. W. Johnson Jr., and W. W. Rhodes, *Phys. Rev. B* **35**, 6716 (1987).
- 14 D. U. Gubser, R. A. Hein, S. H. Lawrence, M. S. Osofsky, D. J. Schrodt, L. E. Toth, and S. A. Wolf, *Phys. Rev. B* **35**, 5350 (1987).
- 15 M. Ai-Mamouri, P. P. Edwards, C. Greaves, and M. Slaski, *Nature* **369**, 382 (1994).
- 16 Q. Huang, J. W. Lynn, Q. Xiong, and C. W. Chu, *Phys. Rev. B* **52**, 462 (1995).
- 17 C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, E. M. McCarron, K. J. Morrissey, T. R. Askew, R. B. Flippin, U. Chowdhry, and A. W. Sleight, *Phys. Rev. B* **38**, 225 (1988).
- 18 C. Q. Jin, J. S. Zhou, J. B. Goodenough, Q. Q. Liu, J. G. Zhao, L. X. Yang, Y. Yu, R. C. Yu, T. Katsura, A. Shatskiy, and E. Ito, *Proc. Natl. Acad. Sci. USA* **105**, 7115 (2008).
- 19 C. Q. Jin, X. J. Wu, P. Laffez, T. Tatsuki, T. Tamura, S. Adachi, H. Yamauchi, N. Koshizuka, and S. Tanaka, *Nature* **375**, 301 (1995).
- 20 P. Chan, and R. Snyder, *J. Am. Ceram. Soc.* **78**, 3171 (1995).
- 21 S. Karimoto, H. Yamamoto, H. Sato, A. Tsukada, and M. Naito, *J. Low Temper. Phys.* **131**, 619 (2003).
- 22 T. Xiang, and J. M. Wheatley, *Phys. Rev. Lett.* **77**, 4632 (1996).
- 23 Y. Zhong, Y. Wang, S. Han, Y. F. Lv, W. L. Wang, D. Zhang, H. Ding, Y. M. Zhang, L. Wang, K. He, R. Zhong, J. A. Schneeloch, G. D. Gu, C. L. Song, X. C. Ma, and Q. K. Xue, *Sci. Bull.* **61**, 1239 (2016).
- 24 G. Y. Zhu, Z. Wang, and G. M. Zhang, *EPL* **118**, 37004 (2017), arXiv: 1610.08728.
- 25 F C Zhang, *Sci. Bull.* **61**, 1236 (2016).
- 26 K. Jiang, X. Wu, J. Hu, and Z. Wang, *Phys. Rev. Lett.* **121**, 227002 (2018).
- 27 M. Fratini, N. Poccia, A. Ricci, G. Campi, M. Burghammer, G. Aeppli, and A. Bianconi, *Nature* **466**, 841 (2010), arXiv: 1008.2015.
- 28 N. Poccia, M. Fratini, A. Ricci, G. Campi, L. Barba, A. Vittorini-Orgeas, G. Bianconi, G. Aeppli, and A. Bianconi, *Nat. Mater.* **10**, 733 (2011), arXiv: 1108.4120.