Journal of Superconductivity and Novel Magnetism (2020) 33:81–85
https://doi.org/10.1007/s10948-019-05302-6

ORIGINAL PAPER

The Unconventional Copper Oxide Superconductor with Conventional Constitution

W. M. Li [1,2,3] · J. F. Zhao [1,2] · L. P. Cao [1,2] · Z. Hu [4] · Q. Z. Huang [5] · X. C. Wang [1,2,3] · R. Z. Yu [1,2,3] · Y. W. Long [1,2,3] · H. Wu [5] · H. J. Lin [6] · C. T. Chen [6] · Z. Z. Gong [7] · Z. Guguchia [7] · J. S. Kim [8] · G. R. Stewart [8] · Y. J. Uemura [7] · S. Uchida [1,9] · C. Q. Jin [1,2,3]

Received: 3 August 2019 / Accepted: 10 September 2019 / Published online: 30 November 2019

Abstract

A new Ba_2CuO_{4-y} superconductor with critical temperature (T_c) exceeding 70 K was discovered. The X-ray absorption measurement gives evidence that this cuprate resembles La_2CuO_4 but is doped with a fairly large amount of holes, while in contrast to the so far known hole-doped high-T_c cuprates, the new cuprate possesses a much shorter local apical oxygen distance as well as much expanded in-plane Cu–O bond, leading to unprecedented compressed local octahedron. In compressed local octahedron, the Cu3$d3z^2$–r^2 orbital level will be lifted above the Cu3dx^2-y^2 orbital level with more three-dimensional features, implying that pairing symmetry may carry admixtures from more than one gap, suggesting that Ba_2CuO_{4-y} composed of alkaline earth copper oxides that are the essential elements to form cuprate superconductors may belong to a new branch of cuprate superconductors.

Keywords Unconventional cuprates · Compressed octahedron · High pressure

1 Introduction

Searching for superconductors with higher T_c has attracted great interest since cuprate superconductors was discovered [1–9]. It is widely accepted that the superconducting critical temperature (T_c) is a function of carrier doping level, i.e., T_c becomes maximum at optimal doping while gradually diminishing at both sides of underdoped or overdoped regions [10, 11]. Consensus is currently that a T_c dome in the low p region (optimum doping around $p \sim 0.15$) is born out of the Mott insulator with antiferromagnetic (AF) order [12, 13], and high T_c superconductivity (HTS) emerges from around $p \sim 0.08$ [14]. In the overdoping region, T_c vanishes again when the doping level is larger than a critical value $p_{\max} \sim 0.27$ [11]. The material is deemed a Fermi-liquid-like metal in which electronic correlations become weak in heavily overdoped regions. But a growing number of researches in recent years suggest that it shows not a simply Fermi liquid behavior even in very highly overdoped copper oxides [15, 16].

Prof. T. H. Geballe is the pioneer who paid much attention to the unusual phenomenon in the heavily doped region of cuprates [1, 17, 18]. Some cuprates synthesized at a high pressure show very high T_c in the strongly overdoped region well beyond the normal superconducting phase diagram for the established cuprate superconductors [18–20]. This raised the question to the paradigm where the high T_c of cuprates actually originates from [17]. One typical system is $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7.54}$ with double CuO layers in the unit cell similar to YBCO123 phase which is in the heavily overdoped regime ($p \sim 0.46$) but shows a T_c up to 87 K [19, 21]. Another system is a monolayer CuO_2 deposited on a single crystal of $Bi_2Sr_2CaCu_2O_{8+\delta}$ which is thought to be heavily overdoped ($p \sim 0.9$) due to charge transfer at the interface [22, 23]. Besides, a very important system is $Sr_2CuO_{3+\delta}$

✉ C. Q. Jin
Jin@iphy.ac.cn

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

2 School of Physics, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100190, China

3 Materials Research Lab, Songshan Lake, Dongguan 523808, China

4 Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Straβe 40, 01187 Dresden, Germany

5 NIST Center for Neutron Research, Gaithersburg, MD 20899, USA

6 National Synchrotron Radiation Research Center, 30076 Hsinchu, Taiwan

7 Department of Physics, Columbia University, New York, NY 10027, USA

8 Department of Physics, University of Florida, Gainesville, FL 32611, USA

9 Department of Physics, University of Tokyo, Tokyo 113-0033, Japan

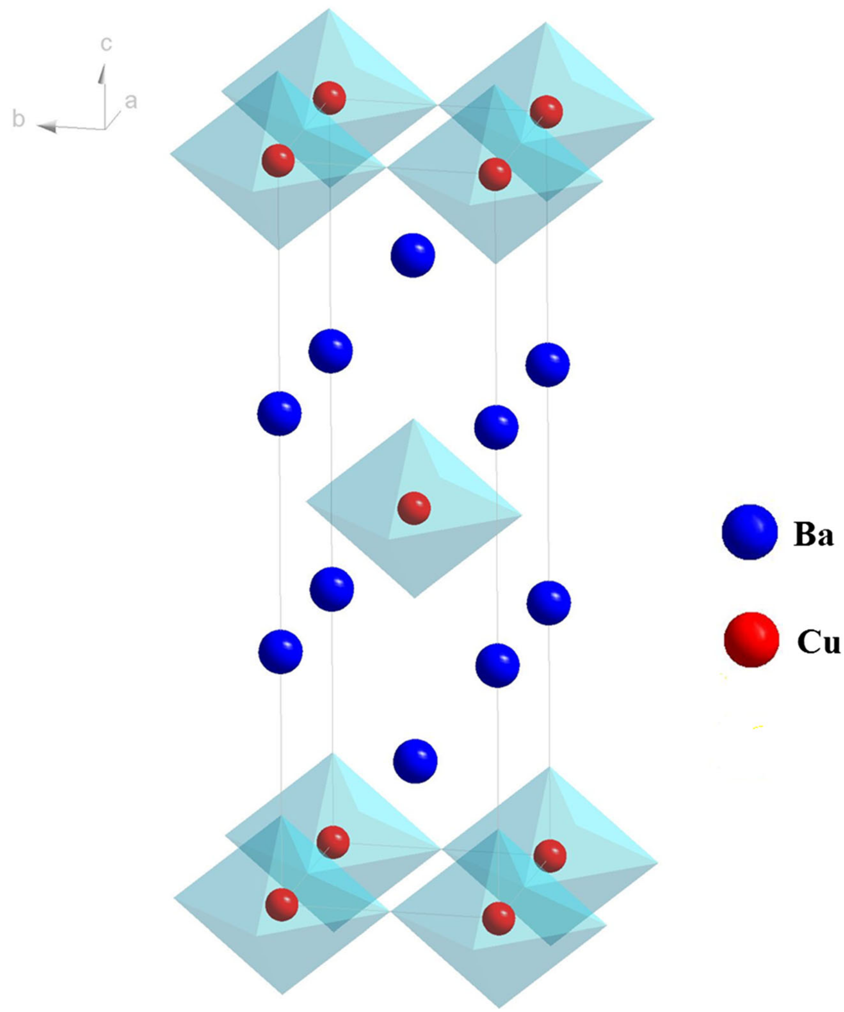

Fig. 1 Schematic crystal structure of the Ba_2CuO_{4-y} that is isostructural to La_2CuO_4 but with a compressed copper oxygen octahedron (the blue ball is Ba and the red ball is copper, while oxygen is at the ligand site)

[20, 24, 25]. The hole-doped $Sr_2CuO_{3+\delta}$ superconductor crystallizes into an oxygen-deficient La_2CuO_4 (i.e., K_2NiF_4) structure. Our previous studies show that the maximum T_c of $Sr_2CuO_{3+\delta}$ can reach 95 K with a nominal $\delta \sim 0.4$ ($p \sim 0.8$) which will be located in the very heavily overdoped region [20, 25]. Further, $T_c^{max} = 98$ K is achieved in the Ba-substituted material $Sr_{2-x}Ba_xCuO_{3+\delta}$ ($0 \leq x \leq 0.6$) with $x =$ 0.6 that reaches the record value among the single-layer copper oxide superconductors—even higher than that of Hg1201 [26]. These materials are all synthesized at high oxygen pressure and characterized as heavily overdoping cuprates.

To deal with the topic, we have been focusing for long time on the alkaline earth and copper oxide system that is the simplest composition to build up cuprate superconductors [18, 20, 25–29]. However, high pressure is usually required in order to get the structure by design. Recently, we discovered a new type of superconductor Ba_2CuO_{4-y} (briefly coined Ba214) with the oxygen-deficient La_2CuO_4 (La214) structure [18]. It has so far the only compressed local octahedron, in sharp contrast to the elongated octahedron for all previously known cuprate superconductors. Moreover, it is in an extremely overdoped state as well. The new superconductor shows superconductivity with T_c up to 73 K. It is generally believed that orbital reversal and extreme overdoping will suppress superconductivity in cuprates [11]. These suggest that Ba214 is a member of a new branch of high T_c cuprate superconducting materials with unconventional features that challenge the established wisdom of HTS [30].

2 Experiments

The polycrystalline sample of Ba214 was synthesized at high pressure (~ 18 GPa) and high temperature (~ 1000 °C) conditions with a highly self-oxidizing atmosphere [27–29] using a 6 over 8 double-stage type multianvil high-pressure facility. Phase purity of the obtained high-pressure products was examined by both powder X-ray diffraction (XRD) at room temperature and neutron at low temperature. Rietveld refinements were performed using the GSAS software package. The direct-current magnetic susceptibility was measured using a commercial SQUID-VSM (Quantum Design). Soft X-ray

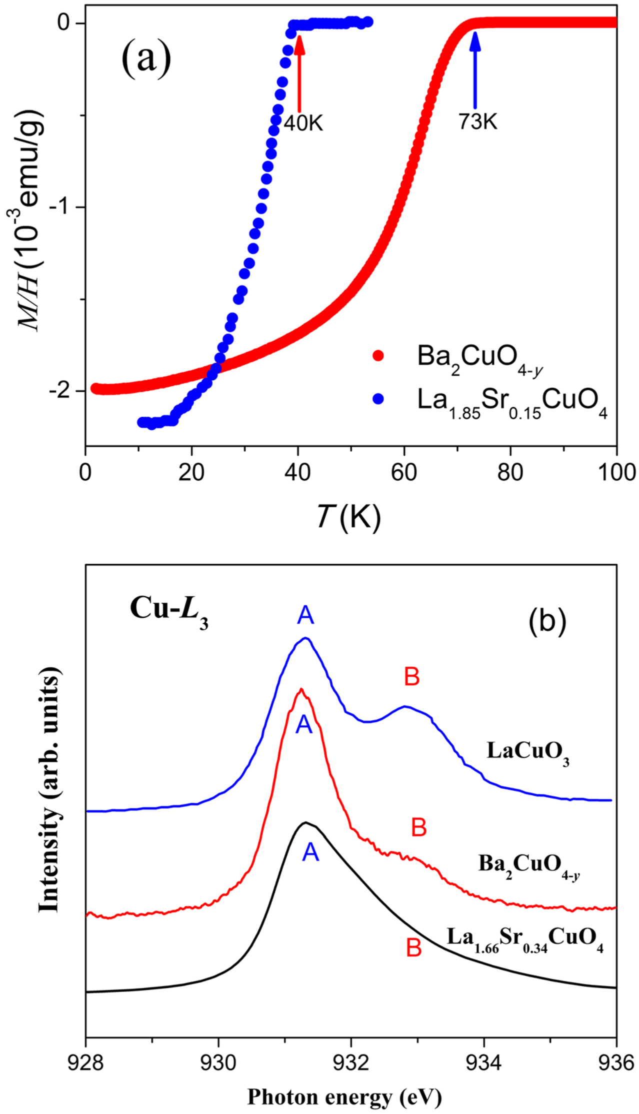

Fig. 2 **a** Temperature dependence of field-cooling (FC) *dc* magnetic susceptibility of Ba214 and optimum doped $La_{1.85}Sr_{0.15}CuO_4$ taken from ref. 32. **b** The Cu-L_3 edge XAS spectrum of Ba_2CuO_{4-y}, $La_{1.66}Sr_{0.34}CuO_4$, and $LaCuO_3$

absorption spectroscopy (XAS) at the Cu $L_{2,3}$ edges and O-*K* edge was measured at beamline BL11A of the NSRRC in Taiwan.

3 Results and Discussion

High-T_c superconducting Ba214 samples can be synthesized only in a narrow range of the nominal oxygen deficiency $y \sim 0.8$. Powder Ba214 compound crystallizes into the La_2CuO_4-type structure with space group *I4/mmm* and gives rise to the lattice parameters $a = 4.0030(3)$ Å and $c = 12.942(1)$ Å. The Cu–O bond lengths for Ba214 are estimated to be 2.0015(2) Å in the plane and 1.861(8) Å along the *c*-axis (corresponding to the apical O distance d_A). It yields both records of the longest

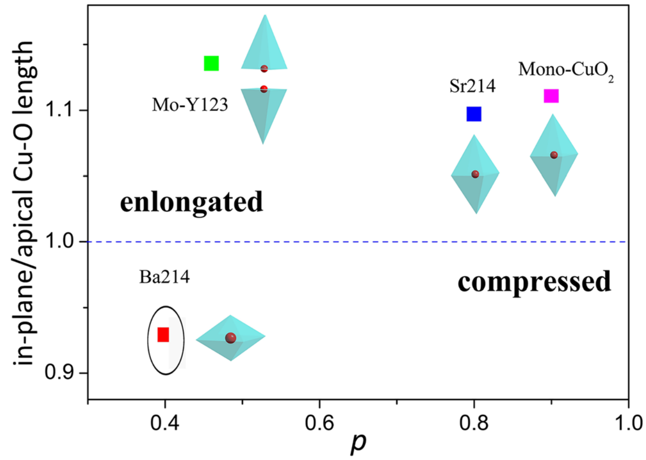

Fig. 3 The ratio between the bond lengths of in-plane Cu–O and copper apical oxygen of heavily overdoped cuprates $Cu_{0.s75}Mo_{0.25}Sr_2YCu_2O_{7.54}$ (Mo-Y123), monolayer CuO_2 (Mono-CuO_2), and $Sr_2CuO_{3+\delta}$ (Sr214), compared with Ba214

in-plane Cu–O bond length and shortest apical-O distance among hole-doped cuprates as known so far. This may be attributed to the extremely large A site cation Ba^{2+} dramatically expanding the in-plane Cu–O bond to the unprecedented length ever reported. As a consequence, the octahedron in turn becomes compressed instead of elongated as shown in Fig. 1. The locally compressed octahedron of Ba214 is exceptionally opposite to the previously "conventional" cuprates [31], which strongly suggests Ba214 may belong to a new type of "non-conventional" high-T_c cuprate superconductor.

Temperature dependence of field-cooling (FC) *dc* magnetic susceptibility of the Ba214 compound is shown in Fig. 2a together with optimum doped isostructural $La_{1.85}Sr_{0.15}CuO_4$ taken from ref. 32. The Ba214 sample shows a $T_c^{max} \sim 73$ K after post annealing under O_2 flow. The bulk superconductivity behavior of the Ba214 sample was also confirmed by the muon-spin-rotation (μSR) and the specific heat measurements.

X-Ray absorption spectroscopy (XAS) is a very useful tool to detect the doped hole numbers and the distribution in cuprate superconductors [33]. The result obtained from both the study of the Cu-L_3 edge and O-*K* edge spectrum indicated a very high doping level in the Ba214 sample, consistent with the estimated δ values and the XRD spectrum Rietveld refinements. We take the bulk-sensitive fluorescence-yield (FY) mode measurement results. Figure 2b shows the Cu-L_3 spectra of Ba_2CuO_{4-y} together with spectra for the overdoped $La_{1.66}Sr_{0.34}CuO_4$ [33] and perovskite $LaCuO_3$ [34] as references. Two peaks are observed in Ba214. Peak A around 931.3 eV, assigned to a $2p^53d^{10}$ final state (upper Hubbard band) coming from a $2p^63d^9$ initial state, and peak B at the high-energy side of peak A, around 932.9 eV, are assigned to a $2p^53d^{10}L$ (L refers to a hole in the O2*p* ligand state) coming from a $2p^63d^9$ L initial state and strongly related to the Cu^{3+} state. In the Cu-L_3 XAS spectrum, the intensity of B peak for

Ba_2CuO_{4-y} is stronger than that for highly overdoped $La_{1.66}Sr_{0.34}CuO_4$ even if it is still weaker than that for "all-Cu^{3+}" $LaCuO_3$ ($p = 1$) while they all have a nearly 180° Cu–O–Cu bond with bond angle. The result explicitly indicates a very high doping level in Ba214, consistent with the estimated δ values.

In copper oxides, the octahedrons are generically elongated due to both Jahn–Teller effect and strong interlayer Coulomb interactions which push the $3dx^2$-y^2 orbital topmost and the doped holes to reside primarily on the $3dx^2$-y^2 orbital, forming the so-called Zhang–Rice (Z–R) singlet [35] via strong hybridization with oxygen 2p orbital. It is very fascinating that the overdoped cuprates synthesized at high-pressure and high-oxidizing atmosphere as mentioned before usually possess a short apical oxygen distance d_A compared with the normal or "conventional" cuprates (the typical value of 2.42 Å in La_2CuO_4): $d_A = 2.165$ Å for double-layered $Cu_{0.s75}Mo_{0.25}Sr_2YCu_2O_{7.54}$ (Mo-Y123), $d_A = 2.11$ Å for monolayer CuO_2 (Mono-CuO_2), and $d_A = 2.085$ Å for $Sr_2CuO_{3+\delta}$ (Sr214), respectively [19, 20, 22]. Figure 3 shows the ratio of the bond lengths of in-plane Cu–O and copper apical oxygen of Mo-Y123 (double layered), Mono-CuO_2, and Sr214, compared with Ba214. Nonetheless, the octahedrons (pyramid for Mo-Y123) of all above non-conventional-like cuprates are still elongated which result in an ordinary degenerate of Cu e_g orbitals split into a higher $3dx^2$–y^2 orbital vs a lower $3dz^2$–r^2 orbital except Ba214.

The Ba214 sample possesses a compressed octahedron which is completely different from the conventional cuprates. In a compressed octahedron, the Cu3$d3z^2$–r^2 orbital will be pushed higher than the Cu3dx^2-y^2 orbital level. This suggests that the doped holes may reside preferentially in the $3dz^2$-r^2 orbital and considerable $d3z^2$–r^2 orbital character might be mixed up in the states near the Fermi level that has been thought to be harmful for high-T_c superconductivity. It also means pairing symmetry of Ba214 may carry admixtures from more than one gap, and the system becomes more three-dimensional. It renders this new HTS cuprate a multi-band system like the iron-based superconductors [36–38]. K. Liu et al. suggested that the AFM fluctuations in one-dimensional Cu–O chains may play an important role in the superconducting pairing of electrons [36]. T. Maier et al. found two domes of pairing strength while one corresponds to the extremely overdoped regime and there is significant pairing strength in both the d-wave and $s^{\pm}$ channels in the overdoped regime [37]. M. Jiang et al. provided a new model featuring in a Cu-3d multiplet structure that only the ligand O-2p orbitals play an essential role [38].

The unique structure features of compressed octahedron in extremely overdoped Ba_2CuO_{4-y} with conventional constitution of alkaline earth copper oxides kindled keen interest in a deeper understanding of the unconventional copper oxide superconductor.

Funding information The work was supported by Ministry of Science and Technology(MOST) and Natural Science Foundation (NSF) of China, Max Planck Institute (MPI), US NSF, and US Department of Energy, Bureau of Energy Sciences.

References

1. Geballe, T.H.: Paths to higher temperature superconductors. Science. **259**, 1550 (1993)
2. Bednorz, J.G., Müller, K.A.: Possible high T_c superconductivity in the Ba-La-Cu-O system. Z. Phys. B. Condens. Matter. **64**, 189–193 (1986)
3. Wu, M.K., et al.: Superconductivity at 93 K in a new mixed-phase Yb-Ba-Cu-O compound system at ambient pressure. Phys. Rev. Lett. **58**, 908–910 (1987)
4. Zhao, Z.X., et al.: High T_c superconductivity of Sr(Ba)-La-Cu oxides. Chin. Sci. Bull. **8**, 522–525 (1987)
5. Logvenov, G., Gozar, A., Bozovic, I.: High-temperature superconductivity in a single copper-oxygen plane. Science. **326**, 699–702 (2009)
6. Geballe, T.H.: The never-ending search for high-temperature superconductivity. J. Supercond. Nov. Magn. **19**, 261–276 (2006)
7. Kivelson, S.A., Lederer, S.: Linking the pseudogap in the cuprates with local symmetry breaking: a commentary. Proc. Natl. Acad. Sci. **116**, 14395–14397 (2019)
8. Geballe, T.H., Hammond, R.H., Wu, P.M.: What T_c tells. Phys. C. **514**, 9–16 (2015)
9. Jin, C.Q., et al.: Superconductivity at 80 K in $(Sr,Ca)_3Cu_2O_{2+\delta}Cl_{2-y}$ induced by apical oxygen doping. Nature. **375**, 301 (1995)
10. Zhang, H., Sato, H.: Universal relationship between T_c and the hole content in p-type cuprate superconductors. Phys. Rev. Lett. **70**, 1697 (1993)
11. Keimer, B., Kivelson, S.A., Norman, M.R., Uchida, S., Zaanen, J.: From quantum matter to high-temperature superconductivity in copper oxides. Nature. **518**, 179–186 (2015)
12. Lee, P.A., Nagaosa, N., Wen, X.G.: Doping a Mott insulator: physics of high-temperature superconductivity. Rev. Mod. Phys. **78**, 17–85 (2006)
13. Scalapino, D.J.: A common thread: the pairing interactions for unconventional superconductors. Rev. Mod. Phys. **84**, 1383–1417 (2012)
14. Emery, V.J., Kivelson, S.A.: Importance of phase fluctuations in superconductors with small superfluid density. Nature. **374**, 434 (1995)
15. Le Tacon, M., et al.: Dispersive spin excitations in highly overdoped cuprates revealed by resonant inelastic X-ray scattering. Phys. Rev. B. **88**, 020501 (2013)
16. Bozovic, I., He, X., Wu, J., Bollinger, A.T.: Dependence of the critical temperature in overdoped copper oxides on superfluid density. Nature. **536**, 309–311 (2016)
17. Geballe, T.H., Marezio, M.: Enhanced superconductivity in Sr_2CuO_{4-v}. Phys. C. **469**, 680 (2009)
18. Li, W.M., Zhao, J.F., Cao, L.P., Hu, Z., Huang, Q.Z., Wang, X.C., Liu, Y., Zhao, G.Q., Zhang, J., Liu, Q.Q., Yu, R.Z., Long, Y.W., Wu, H., Lin, H.J., Chen, C.T., Li, Z., Gong, Z.Z., Guguchia, Z.,

Kim, J.S., Stewart, G.R., Uemura, Y.J., Uchida, S., Jin, C.Q.: Superconductivity in a unique type of copper oxide. Proc. Natl. Acad. Sci. **116**, 12156–12160 (2019)
19. Gauzzi, A., et al.: Bulk superconductivity at 84 K in the strongly overdoped regime of cuprates. Phys. Rev. B. **94**, 180509 (2016)
20. Liu, Q.Q., Yang, H., Qin, X.X., Yu, Y., Yang, L.X., Li, F.Y., Yu, R.C., Jin, C.Q., Uchida, S.: Enhancement of the superconducting critical temperature of $Sr_2CuO_{3+\delta}$ up to 95 K by ordering dopant atoms. Phys. Rev. B. **74**, 100506 (R) (2006)
21. Ono, A.: High-pressure synthesis of Mo-containing 1212 and 1222 compounds, (Cu, Mo)$Sr_2YCu_2O_z$ and (Cu, Mo)Sr_2(Y, Ce)$_2Cu_2O_z$. Jpn. J. Appl. Phys. **32**, 4517 (1993)
22. Zhong, Y., et al.: Nodeless pairing in superconducting copper-oxide monolayer films on $Bi_2Sr_2CaCu_2O_{8+\delta}$. Sci. Bull. **61**, 1239–1247 (2016)
23. Zhu, G.Y., Wang, Z.Q., Zhang, G.M.: Two-dimensional topological superconducting phases emerged from *d*-wave superconductors in proximity to antiferromagnets. EPL. **118**, 37004 (2017)
24. 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**. 364**(375), 315 (1993)
25. Yang, H., Liu, Q.Q., Li, F.Y., Jin, C.Q., Yu, R.C.: Structure and microstructure of superconductor $Sr_2CuO_{3+\delta}$ (nominal δ=0.4) prepared under high pressure. Supercond. Sci. Technol. **19**, 934–940 (2006)
26. Gao, W.B., Liu, Q.Q., Yang, L.X., Yu, Y., Li, F.Y., Jin, C.Q., Uchida, S.: Out-of-plane effect on the superconductivity of $Sr_{2-x}Ba_xCuO_{3+\delta}$ with T_c up to 98 K. Phys. Rev. B. **80**, 94523 (2009)
27. Jin, C.Q.: Using pressure effects to create new emergent materials by design. MRS Adv. **2**, 2587 (2017)
28. Jin, C.Q., Adachi, S., Wu, X.J., Yamauchi, H.: A new superconducting homologous series of compounds: Cu-12(n-1)n. Advances in superconductivity VII, p. P249. Springer-Verlag, Tokyo (1995)
29. Jin, C.Q., et al.: 117K superconductivity in the Ba-Ca-Cu-O system. Physica C. **223**, 238 (1994)
30. Scalapino, D.J.: A different branch of the high T_c family? Proc. Natl. Acad. Sci. **116**, 12129–12130 (2019)
31. Huang, Q., Lynn, J.W., Xiong, Q., Chu, C.W.: Oxygen dependence of the crystal structure of $HgBa_2CuO_{4+\delta}$ and its relation to superconductivity. Phys. Rev. B. **52**, 462–470 (1995)
32. Tarascon, J.M., Greene, L.H., Mckinnon, W.R., Hull, G.W., Geballe, T.H.: Superconductivity at 40 K in the oxygen-defect perovskites $La_{2-x}Sr_xCuO_{4-y}$. Science. **235**, 1373–1376 (1987)
33. Chen, C.T., Tjeng, L.H., Kwo, J., Kao, H.L., Rudolf, P., Sette, F., Fleming, R.M.: Out-of-plane orbital characters of intrinsic and doped holes in $La_{2-x}Sr_xCuO_4$. Phys. Rev. Lett. **68**, 2543–2546 (1992)
34. Mizokawa, T., Fujimori, A., Namatame, H., Takeda, Y., Takano, M.: Electronic structure of tetragonal $LaCuO_3$ studied by photoemission and X-ray absorption spectroscopy. Phys. Rev. B. **57**, 9550–9556 (1998)
35. Zhang, F.C., Rice, T.M.: Effective Hamiltonian for the superconducting Cu oxides. Phys. Rev. B. **37**, 3759–3761 (1988)
36. Liu, K., Lu, Z.Y., Xiang, T.: Electronic structures of quasi-one-dimensional cuprate superconductors $Ba_2CuO_{3+\delta}$. Phys. Rev. M. **3**, 044802 (2019)
37. Maier, T., Berlijn, T., Scalapino, D.J.: Two pairing domes as Cu^{2+} varies to Cu^{3+}. Phys. Rev. B. **99**, 224515 (2019)
38. Jiang, M., Moeller, M., Berciu, M., Sawatzky, G. A.: Relevance of Cu-3d multiplet structure in models of high T_c cuprates. arXiv: 1906.10254v2 (2019)