Superconductivity in a unique type of copper oxide

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Edited by T. H. Geballe, Stanford University, Stanford, CA, and approved April 18, 2019 (received for review January 18, 2019)

The mechanism of superconductivity in cuprates remains one of the big challenges of condensed matter physics. High-\textit{T}\textsubscript{c} cuprates crystallize into a layered perovskite structure featuring copper oxygen octahedral coordination. Due to the Jahn Teller effect in combination with the strong static Coulomb interaction, the octahedra in high-\textit{T}\textsubscript{c} cuprates are elongated along the c axis, leading to a 3\textit{dx}^2\textit{y}^2 orbital at the top of the band structure wherein the doped holes reside. This scenario gives rise to 2D characteristics in high-\textit{T}\textsubscript{c} cuprates that favor d-wave pairing symmetry. Here, we report superconductivity in a cuprate Ba\textsubscript{2}CuO\textsubscript{2}Sr\textsubscript{2}. This discovery provides a direction to further understand the pairing mechanism of high \textit{T}\textsubscript{c} in cuprate materials.

significance

Superconductivity is one of the most mysterious phenomena in nature in that the materials can conduct electrical current without any resistance. The cuprates hold the record high superconducting temperature at room pressure so far, but understanding their superconducting mechanism remains one of the big challenges. Here, we report high-\textit{T}\textsubscript{c} superconductivity in Ba\textsubscript{2}CuO\textsubscript{2}\textit{p} with two unique features: an exceptionally compressed local octahedron and heavily overdoped hole carriers. These two features are in sharp contrast to the favorable crystal structures of high-\textit{T}\textsubscript{c} cuprates that favor d-wave pairing symmetry.


The authors declare no conflict of interest.

This is a PNAS Direct Submission.

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See Commentary on page 12129.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1900908116/-/DCSupplemental.

Published online May 20, 2019.

12156-12160 | PNAS | June 18, 2019 | vol. 116 | no. 25
www.pnas.org/cgi/doi/10.1073/pnas.1900908116
this cuprate has quite unexpected features: (i) the apical oxygen distance can be extraordinarily shorter than that known for all other cuprate superconductors so far; (ii) a unique compressed version of the local octahedron becomes available; and (iii) HTS is realized at very high-hole doping level, contrary to the value of $p \sim 0.15$ discussed above for the previously known high-$T_c$ cuprates. All three characteristics have been thought to be unfavorable for high-$T_c$ in the previously discovered cuprates (8–19). Therefore, this material is a distinct kind of high-$T_c$ cuprate and challenges the established wisdom of HTS.

Polycrystalline Ba$_{2}$Cu$_{4}$ samples are synthesized at high pressure ($\sim$18 GPa), much higher than usually used ($\sim$6 GPa) for the high-pressure synthesis of oxide materials (15, 18, 19), and at high temperature ($\sim$1,000 °C) under a highly oxidizing atmosphere. High-$T_c$ superconducting samples were produced in the narrow range of the nominal oxygen deficiency $y \sim 0.8$ (excess oxygen content $\delta \sim 0.2$). Shown in Fig. 1A is the magnetization $M/H$ of a Ba$_{2}$Cu$_{4}$ polycrystalline sample measured in both zero field-cooled (ZFC; shielding) and field-cooled (FC; Meissner) modes in a magnetic field of 30 Oe. The sample exhibits a clear superconducting transition at the onset temperature 73 K. The large superconducting volume fraction estimated from dc magnetic susceptibility measurements as high as 30% indicated the bulk superconductivity behavior. The conclusion is further supported by muon spin rotation ($\mu$SR) and the specific heat measurements.

All three measurements guarantee that the bulk superconducting phenomenon of the samples. This is fairly large for samples synthesized under high pressure. A high pressure-synthesized Ba$_{2}$Cu$_{4}$ polycrystalline sample is generally composed of very fine grains with submicrometer size. This results in significant flux penetration at the grain surface, which dramatically reduces the Meissner signal (20). Therefore, the Meissner volume fraction should be regarded as a lower bound of the superconducting volume fraction. This evidence for bulk superconductivity, also confirmed by the $\mu$SR showing $\sim$40% superfluid volume and the specific heat measurements as shown in Fig. 1B and C, respectively, guarantees that the structure measured corresponds to the superconducting phase.

X-ray diffraction (XRD) was measured for different batches of Ba$_{2}$Cu$_{4}$ samples to examine the phase purity (a representative XRD pattern is shown in Fig. 2) and is consistent with the La$_{2}$CuO$_{4}$-type structure with space group ${}\bar{4}mm$. The intensities and shapes of diffraction peaks agree with the previously well-characterized high-$T_c$ cuprates, and the statistics of the pattern are good enough for a detailed structural refinement. Rietveld refinement yields the lattice parameters of the compound with $a = 4.003$ Å and $c = 12.94$ Å at room temperature. The summary of the structure based on Rietveld refinements from powder X-ray diffraction patterns is shown in SI Appendix, Table S1. It yields the apical oxygen distance $d_{o} = 1.86$ Å. The Cu–O bond lengths for Ba$_{2}$Cu$_{4}$ at room temperature are estimated to be 2.00 Å in the plane and 1.86 Å along the $c$ axis (corresponding to the apical oxygen distance $d_{o}$). These values should be taken as average values of the bond lengths. The 2.00 Å in-plane Cu–O bond length of Ba$_{2}$Cu$_{4}$ is the record for the longest among hole-doped cuprates, normally ranging from 1.88 to 1.96 Å (Fig. 3) (21–23). By contrast, the apical oxygen distance $d_{o} = 1.86$ Å is the shortest known among the cuprates: about 25% shorter than the typical value of 2.42 Å in La$_{2}$CuO$_{4}$. The large ionic radius of Ba$^{2+}$ without any other nearby spacer layers in Ba$_{2}$Cu$_{4}$ expands the in-plane Cu–O bond dramatically. Also, it is inferred that the short apical oxygen distance might arise from the electroneutral [Ba$_{2}$O$_{3}$] spacer layer. This neutral [Ba$_{2}$O$_{3}$] layer, without other charge reservoir layers, would allow the apical oxygen to come near the plane, thus realizing the heretofore unprecedented situation that the apical oxygen to Cu bond length is appreciably shorter than the in-plane Cu–O bond length.

As in the case of ordinary high-$T_c$ cuprates, useful information on the distribution of holes in Cu$3d$ and O$2p$ states can be
dependent on the specific arrangement of the Cu–O network (28). For the corner O shared networks (180° Cu–O–Cu bond), such as those in LSCO and LaCuO$_3$, the intensity of B is strongly reduced due to the strong hybridization between neighboring Cu$3d^x$-$p_y$ and O$2p_x$ orbitals, which act to screen the Cu core holes. Because of this effect, the feature B is hard to see in the spectrum of LSCO with $x = 0.15$ and is only seen as a weak high-energy tail for overdoped $x = 0.34$ (25, 26). It appears as a subdominant peak even for “all-Cu$^{2+}$” LaCuO$_3$ ($p = 1$) (27). In the Cu–L$_3$ XAS spectrum of Ba$_2$Cu$_4$, the B peak is also subdominant as in the case of LaCuO$_3$ (where the copper is in the extreme high valence of Cu$^{3+}$), but its intensity is significantly stronger than that for heavily overdoped LSCO ($x = 0.34$) in ref. 25. This further demonstrates a heavily doped phase for the Ba$_2$Cu$_4$ sample. The result is not only indicative of the presence of a strong Cu–O–Cu bond with bond angle of nearly 180°, but also, it gives support for a very high doping level in Ba$_2$Cu$_4$, consistent with the estimated $y$ values. The combined results of the O–K and Cu–L$_2$, XAS indicate not only that the hole density is fairly high but also, that the doped holes are predominantly on the strongly hybridized Cu–O orbitals, like the Z–R singlet also in this cuprate.

The longer apical oxygen distance (i.e., an elongated octahedron) generically seen in high-$T_c$ cuprates pushes the 3$d^x$-$p_y$ orbital level above the 3$d^z$ orbital level. Hence, the doped holes reside primarily on the 3$d^z$-$p_y$ orbital (or in the Z–R singlet states) that causes the carriers to have predominantly in-plane orbital character. To the contrary, a consequence of a shorter $d_{xy}$ is that the 3$d^x$ orbital level moves above the 3$d^x$-$p_y$ level as schematically illustrated in Fig. 3. This makes the 3$d^z$ orbital character equally present in the electronic states near the Fermi level with enhanced interlayer coupling and thereby, renders this HTS cuprate a multiband system, like the iron-based superconductors as preliminarily presented in SI Appendix, Fig. S1. Two cuprate superconducting systems have been reported, both characterized as heavily overdoped. One is Cu$_{0.75}$Mo$_{0.25}$Sr$_2$YCu$_2$O$_{7.54}$, which is

![Fig. 2. Structural analysis. Typical X-ray (l = 1.54056 Å) powder diffraction pattern of a Ba$_2$Cu$_4$ sample measured at room temperature (open circles). The high background in the low-angle range is from a covering organic material of Mylar thin film to prevent exposure of the sample to air, since the sample is highly hygroscopic. Vertical purple lines indicate the possible Bragg peak positions for the La$_2$CuO$_4$-type structure with tetragonal symmetry, which fit very well to the data as shown by the red solid line. The difference between the observed and calculated patterns is shown by the blue curve at the bottom ($R_p$ = 3.41%, $R_w$ = 2.47%, and $\chi^2 = 1.114$, where the abbreviations mean weighted profile reliability factor, profile reliability factor, and match factor, respectively), evidencing the high quality of the refinement. The lattice parameters thus obtained are $a = 4.0030$ (3) Å and $c = 12.942$ (1) Å. Numbers in parentheses are SDs of the last significant digit.](Image)

![Fig. 3. In-plane Cu–O and apical Cu–O bond lengths. (Upper Left) In-plane Cu–O bond length for various single-layer cuprates: LSCO (21), Bi$_2$Sr$_2$CuO$_{6+x}$, Tl$_2$Ba$_2$CuO$_{6+x}$ (22), HgBa$_2$CuO$_{4+y}$ (23), and Ba$_2$Cu$_4$. (Lower Left) The same set of the data for Cu apical O bond length (apical O distance). In Ba$_2$Cu$_4$, the bond-length ratio is smaller than one, in which case the 3$d^z$ orbital level is expected to be located above the 3$d^x$-$p_y$ orbital level in contrast to the case where the ratio is significantly larger than one as in the case of conventional high-$T_c$ cuprates sketched in Right. A schematic crystal structure with a compressed “oxygen octahedron” is also shown (exact positions of oxygen vacancies in the plane are not known at present).](Image)
in the heavily overdoped regime ($p \approx 0.46$) with $d_L = 2.165$ Å (20, 29) (vs. the typical value of 2.42 Å in La$_2$CuO$_4$ and 1.86 Å for the Ba$_2$CuO$_{3.2}$ sample reported here). The other is a monolayer CuO$_2$ deposited on a single crystal of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (30). The monolayer CuO$_2$ is thought to be heavily overdoped due to charge transfer at the interface (31). Density functional theory gives a simulated hole density of $p \approx 0.9$ and an apical oxygen distance $d_L = 2.11$ Å with elongated octahedron (32). Both are supposed to be multiband systems with multiple Fermi surface pockets with $3d^x$-$3d^y$ and $3d^z$-$3d^x$ orbital character.

HTS in this cuprate emerges under apparently unique circumstances: short apical oxygen distance, compressed local octahedron version, and heavily hole overdoped. These properties were thought to be detrimental for high $T_c$ in the previously known cuprates but seem to cooperate to produce HTS in this type of cuprate. These unusual properties in this synthesized at high pressure bulk cuprate superconductor offer important input to theory for understanding of the mechanism of high $T_c$ in cuprate materials in general.

**Methods**

**Synthesis.** In this work, polycrystalline samples of Ba$_2$CuO$_{3.2}$ were synthesized using solid-state reaction at high pressure and high temperature. The precursors were prepared by the conventional solid-state reaction method from high-purity raw materials BaO and CuO in a molar ratio BaCuO = 2:1:3. The powder mixture in an appropriate ratio was ground thoroughly in an agate mortar before being calcined at 850 °C in an O$_2$ flow for 24 h with one intermediate grinding. Then, the precursors were mixed with BaO$_2$ and CuO with a molar ratio of 9:2:1 in a dry glove box to protect hygroscopic reagents. The role of BaO$_2$ is to create an oxygen atmosphere during the high-pressure synthesis of Cu$_{12-n}$In$_n$ homolog series cuprate superconductors as previously described (19). The samples are synthesized using a so-called self-oxidation method (33), where the oxidizer itself serves as both chemical composition as well as the atomic oxygen source. The advantage of the method is that it can reduce the unwanted impurity phases generated from other oxidizers (such as KClO$_3$). The materials are further subjected to high-pressure synthesis at 18-GPa pressure and at 1,000 °C temperature for 1 h with a Walker-type multiturn high-pressure apparatus and then quenched to room temperature immediately after releasing the pressure. The 18-GPa pressure was necessary to stabilize the 214 tetragonal phase. The Ba$_2$CuO$_{3.2}$ sample showing a superconductivity onset at $T_c$ of 73 K was obtained by annealing at 150 °C for 24 h under 1-atm O$_2$ gas flow in a tube furnace.

**Physics Properties Characterization.**

**Superconducting measurements.** The magnetization measurement is performed for the in-house characterization of the superconducting state using a Quantum Design VSM facility as shown in Fig. 1A. The advantage of the method is that it can reduce the unwanted impurity phases generated from other oxidizers (such as KClO$_3$). The materials are further subjected to high-pressure synthesis at 18-GPa pressure and at 1,000 °C temperature for 1 h with a Walker-type multiturn high-pressure apparatus and then quenched to room temperature immediately after releasing the pressure. The 18-GPa pressure was necessary to stabilize the 214 tetragonal phase. The Ba$_2$CuO$_{3.2}$ sample showing a superconductivity onset at $T_c$ of 73 K was obtained by annealing at 150 °C for 24 h under 1-atm O$_2$ gas flow in a tube furnace.

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**μSR measurements.** μSR measurements were performed at Tri-University Meson Facility (TRIUMF) in zero field (ZF) and transverse field (TF) with TF = 200 G. The ZF relaxation rate showed a modest increase from 0.1 to 0.35 $μ$s$^{-1}$ below $T_c$ ~ 10 K. This confirms the absence of strong magnetism background in the observed TF spectra, which exhibit the effect of the superfluid energy density (34). The temperature spectra in TF were fitted to a model based on the presence of two components, a portion of which exhibits a fast damping due to the magnetic penetration depth and the other component shows temperature-independent relaxation due to nonsuperconducting and paramagnetic volume. The fraction of the superconducting volume shown in Fig. 1B was estimated from the amplitude of the former component.

The superconducting volume fraction was estimated by μSR plotted as a function of temperature in terms of superfluid volume of ~40% at the lowest temperature.

**Specific heat measurements.** To avoid the air sensitivity of the sample, the sample was transported sealed in inert gas and coated with GE 7031 varnish in an inert atmosphere glove box before being exposed to air for less than 5 min while being transferred into the calorimeter (35). This sealing away of the sample below a cured GE 7031 varnish layer seemed to be effective in maintaining the intrinsic properties of the sample. The mass of the sample measured was 53.3 mg; the mass of the cured varnish was 0.54 mg. Note that the γ value at the lowest temperature is ~14 mJ mol$^{-1}$ K$^{-2}$, which is significantly larger than the value ~3 mJ mol$^{-1}$ K$^{-2}$ for optimally doped YBa$_2$Cu$_3$O$_{6.9}$ (YBCO) at $T_c = 4.2$ K and is comparable with the values reported for overdoped cuprates (36) that are ascribed to contribution of normal electrons not condensed into the superconducting state.

A characteristic jump-like feature is seen at $T_c = 73$ K in the temperature dependence of specific heat measured on a Ba$_2$CuO$_{3.2}$ sample, which provides additional evidence for bulk superconductivity (Fig. 1C). A crude estimate of the jump $ΔC$ divided by $T_c$ gives $ΔC/T_c = 33$ mJ mol$^{-1}$ K$^{-2}$, but the values are subject to uncertainty due to possible degradation of the sample during
shipping or loading. A jump-like feature is also identified at 66 K for an applied magnetic field of 12 T, and the upper critical magnetic field $H_{c2}$ is roughly estimated to be 80 T.

**Structural Measurements.** The powder X-ray diffraction is performed based on a Rigaku diffractometer with $\lambda = 1.54056$ Å at room temperature. The specimen is covered with transparent organic material (Mylar thin film) to prevent the highly hygroscopic sample from being exposed to air. The Rietveld refinement on the powder X-ray diffraction pattern was performed using the GSAS program. The crystallographic and structural parameters are shown in [Table S1](#).