Superconductivity in a unique type of copper oxide

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Abstract

The mechanism of superconductivity in cuprates remains one of the big challenges of condensed matter physics. High-Tc cuprates crystallize into a layered perovskite structure featuring copper oxide octahedral coordination. Due to the Jahn Teller effect in combination with the strong static Coulomb interaction, the octahedra in high-Tc cuprates are elongated along the c axis, leading to a 3dx2-ry2 orbital at the top of the band structure wherein the doped holes reside. This scenario gives rise to 2D characteristics in high-Tc cuprates that favor d-wave pairing symmetry. Here, we report superconductivity in a cuprate Ba2CuO4yro, wherein the local octahedron is in a very exceptional compressed version. The Ba2CuO4yro compound was synthesized at high pressure at high temperatures and shows bulk superconductivity with critical temperature (Tc) above 70 K at ambient conditions. This superconducting transition temperature is more than 30 K higher than the Tc for the isostructural counterparts based on classical La2CuO4. X-ray absorption measurements indicate the heavily doped nature of the Ba2CuO4yro superconductor. In compressed octahedron, the 3dx2-ry2 orbital will be lifted above the 3dx2-ry2 orbital, leading to significant 3D nature in addition to the conventional 3dx2-ry2 orbital. This work sheds important light on advancing our comprehensive understanding of the superconducting mechanism of high Tc 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-Tc superconductivity in Ba2CuO4yro with two unique features: an exceptionally compressed local octahedron and heavily overdoped hole carriers. These two features are in sharp contrast to the favorable criteria for all previously known cuprate superconductors. Thus, the discovery of high-Tc superconductivity in Ba2CuO4yro calls into question the widely accepted scenario of superconductivity in the cuprates. This discovery provides a direction to search for additional high-Tc superconductors.


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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 Ba214 samples are synthesized at high pressure (~18 GPa), much higher than usually used (~6 GPa) for the high-pressure synthesis of oxide materials \((15, 18, 19)\), and at high temperature (~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 Ba214 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 \( M \) vs magnetic susceptibility measurements as high as 30% indicated the bulk superconductivity behavior. The conclusion is further supported by magnetic susceptibility measurements (\( \mu \)SR) and the specific heat measurements. All three measurements guarantee the bulk superconducting phenomenon of the samples. This is fairly large for samples synthesized under high pressure. A high-pressure-synthesized Ba214 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 ~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 Ba214 samples to examine the phase purity (a representative XRD pattern is shown in Fig. 2) and is consistent with the La2CuO4-type structure with space group \( I\bar{4}m\text{mm} \). 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 \( d_A = 1.86 \) Å. The Cu–O bond lengths for Ba214 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 \( d_A \)). These values should be taken as average values of the bond lengths. The 2.00 Å in-plane Cu–O bond length of Ba214 is the longest among hole-doped cuprates, normally ranging from 1.88 to 1.96 Å \((21–23)\). By contrast, the apical oxygen distance \( d_A = 1.86 \) Å is the shortest known among the cuprates: about 25% shorter than the typical value of 2.42 Å in La2CuO4. The large ionic radius of Ba\(^{2+}\) without any other nearby spacer layers in Ba214 expands the in-plane Cu–O bond dramatically. Also, it is inferred that the short apical oxygen distance might arise from the electroneutral [Ba2O2] spacer layer. This neutral [Ba2O2] 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 Cu3d and O2p states can be...
obtained from the study of soft X-ray absorption spectra (XAS) at the Cu–L₃ edge and the O–K edge (24–26). In particular, the O–K XAS spectrum provides the number of doped holes quantitatively, since the doped holes in cuprates mainly locate at the 3dₓ²−ᵧ² orbital level. Hence, the doped holes reside 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-Tc cuprates pushes the 3dₓ²−ᵧ² orbital level above the 3dᶻ² orbital level. This makes the 3dᶻ² 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 Cu₀.₇₅M₀сход₅Sr₂YCu₂O₇.₅₄, which is 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 LaCuO₃, the intensity of B is strongly reduced due to the strong hybridization between neighboring Cu3dₓ²−ᵧ² and O2pₓ,ᵧ 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” LaCuO₃ (p = 1) (27). In the Cu–L₃ XAS spectrum of Ba₂₁₄, the B peak is also subdominant as in the case of LaCuO₃ (where the copper is in the extreme high valence of Cu⁴⁺), 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 Ba₂₁₄ 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 Ba₂₁₄, consistent with the estimated y values. The combined results of the O–K and Cu–L₃ 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 high background in the low-angle range is from a covering organic layer on the sample. The longer apical oxygen distance (i.e., an elongated octahedron) generically seen in high-Tc cuprates pushes the 3dₓ²−ᵧ² orbital level above the 3dᶻ² orbital level. Hence, the doped holes reside predominantly on the strongly hybridized Cu–O orbitals, like the Z–R singlet also in this cuprate.
in the heavily overdoped regime ($\rho \sim 0.46$) with $d_{1}=2.165$ 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$_3$ cuprate reported here). The other is a monolayer Cu$_2$O$_2$ deposited on a single crystal of Bi$_2$Sr$_2$CuO$_8$ (30). The monolayer Cu$_2$O$_2$ is thought to be heavily overdoped due to charge transfer at the interface (31). Density functional theory gives a simulated hole density of $\rho \sim 0.9$ and an apical oxygen distance $d_{1}=2.11$ Å with elongated octahedron (32). Both are supposed to be multiband systems with multiple Fermi surface pockets with 3$d^5$$\gamma$- and 3$d^4$- 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$_2$Cu$_4$ 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 Ba$_2$O and CuO in a molar ratio Ba$_2$CuO$_3$:1:3. The powders were mixed 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 Ba$_2$O$_3$ and CuO with a molar ratio of 9:2:1 in a dry glove box to protect hygroscopic reagents. The role of Ba$_2$O$_3$ is to create an oxygen atmosphere during the high-pressure synthesis of Cu$_{12-\gamma}$-In 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 implemented from alien oxidizers (such as KClO$_3$). The samples are further subjected to high-pressure synthesis at 18-GPa pressure and at 1,000 °C temperature for 1 h with a Walker-type multianvil high-pressure apparatus and then, quenched to room temperature before releasing the pressure. The 18-GPa pressure was necessary to stabilize the 214 tetragonal phase. The Ba$_2$Cu$_{4}$ tetragonal 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. 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 μs$^{-1}$ below $T = 10$ K. This confirms the absence of strong magnetism background in the observed TF spectra, which exhibit the effect of the superfluid density (34). The two signals in the time spectra in TF were interpreted as a part 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 the 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, and the mass of the cured varnish was 0.54 mg. Note that the $\gamma$ 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$_{6-\delta}$ (YBCO) at $T = 4.2$ 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$_2$Cu$_4$ sample, which provides additional evidence for bulk superconductivity (Fig. 1C). A crude estimate of the jump $\Delta C$ divided by $T_c$ gives $\Delta C/T_c \sim 33$ 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 diffraction meter 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.


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