Higher superconducting transition temperature by breaking the universal pressure relation

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By investigating the bulk superconducting state via dc magnetization measurements, we have discovered a common resurgence of the superconducting transition temperatures (T_c s) of the monolayer $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$ (Bi2201) and bilayer $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212) to beyond the maximum T_c s ($T_{c-\text{max}}$ s) predicted by the universal relation between T_c and doping (p) or pressure (P) at higher pressures. The T_c of underdoped Bi2201 initially increases from 9.6 K at ambient to a peak at 23 K at 26 GPa and then drops as expected from the universal T_c - P relation. However, at pressures above 40 GPa, T_c rises rapidly without any sign of saturation up to 30 K at 51 GPa. Similarly, the T_c for the slightly overdoped Bi2212 increases after passing a broad valley between 20 and 36 GPa and reaches 90 K without any sign of saturation at 56 GPa. We have, therefore, attributed this T_c resurgence to a possible pressure-induced electronic transition in the cuprate compounds due to a charge transfer between the $\text{Cu } 3d_{x^2-y^2}$ and the $\text{O } 2p$ bands projected from a hybrid bonding state, leading to an increase of the density of states at the Fermi level, in agreement with our density functional theory calculations. Similar T_c - P behavior has also been reported in the trilayer $\text{Br}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (Bi2223). These observations suggest that higher T_c s than those previously reported for the layered cuprate high-temperature superconductors can be achieved by breaking away from the universal T_c - P relation through the application of higher pressures.

BSCCO | cuprate | high- T_c superconductivity | high pressure | T_c - P relation

Raising the transition temperature (T_c) of superconductors has been a primary driving force behind the sustained effort in superconductivity research ever since its discovery due to the scientific challenges and technological promise that superconductivity at higher temperature can offer. This has been particularly true since the discovery of high-temperature superconductivity (HTS) in the late 1980s (1, 2). The most promising stable HTS systems for higher T_c seem to be the layered cuprates (3), Fe-pnictides (4), and Fe-chalcogenides (4). To date, all known stable HTSs with a T_c above 77 K, the liquid nitrogen boiling point, at ambient or high pressure are perovskite-like layered cuprates. For example, $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ exhibits the current record T_c s of 134 K (5) at ambient pressure and 164 K above 30 GPa (6, 7). Superconductivity determined resistively has been reported at up to 109 K in unit cell $\text{FeSe}/\text{SrTiO}_3$ film at ambient pressure (8) (but has not yet been confirmed or reproduced) and at up to 203 K under ~ 155 GPa (9) and ~ 260 K under ~ 190 GPa (10, 11) in H_3S and LaH_{10+x} , respectively, but these compounds are unstable.

Superconductivity can be induced in the stable cuprates from their Mott insulating parents by chemical, pressure, photon (12), or electric-field doping (13). It has been found that, independent of the type of doping, the normalized transition temperature ($T_c/T_{c-\text{max}}$) of cuprates varies parabolically with the hole concentration (p) in a universal manner: that is, $(T_c/T_{c-\text{max}}) = [1 - 82.6(p - p_o)^2]$ (14), where $T_{c-\text{max}}$ is the maximum T_c of a specific compound series when optimally doped with $p = p_o \sim 0.16$ hole per CuO_2 layer. This is in general agreement with the rigid band

model when only small perturbations occur to the electron band structures in their equilibrium state through doping, and doping mainly shifts the Fermi energy as has been demonstrated (e.g., in the $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ compound family for $n = 1, 2$, and 3 ; i.e., for one, two, and three CuO_2 layers per unit cell). The observation of this universal $T_c/T_{c-\text{max}}$ - p (or $-P$) behavior suggests that the usual doping (chemical p or pressure P) of cuprates in their equilibrium state cannot lead to a T_c higher than $T_{c-\text{max}}$. To achieve a T_c higher than $T_{c-\text{max}}$ in cuprates, one may have to modify their electronic structures, such as by inducing a Fermi surface topology change (15, 16) via very high pressures (i.e., $P \gg \sim 20$ GPa, the pressure that most previous experiments on cuprates have reached). In other words, we have to break away from the commonly accepted universal T_c - p (or $T_c/T_{c-\text{max}}$ - p or $T_c/T_{c-\text{max}}$ - P) relation.

To explore such a possibility, we have investigated the high-pressure effects on the T_c s of members of the homologous series of $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ (BSCCO) (Fig. 1D) with $n = 1$ and 2 , where n is the number of CuO_2 layers per cell, magnetically up to ~ 56 GPa. Indeed, we have observed the resurgence of their T_c s at higher pressures after reaching the $T_{c-\text{max}}$ predicted by the universal quadratic ($T_c/T_{c-\text{max}}$ - p) relation. Similar T_c resurgence under high pressure has also been reported in the optimally doped $\text{Br}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (Bi2223) with $n = 3$ by Chen et al. (17), although the authors attributed the T_c rise to the possible pressure-induced competition between the pairing and phase

Significance

Achieving higher transition temperature (T_c) is a primary goal in superconductivity research. T_c and doping have been found to have a dome-like universal relation where the peak position is the maximum $T_{c-\text{max}}$, which is consistent with previous experimental results in the lower pressure range. By using the ultrasensitive magnetization measurement technique under high pressure that we developed, we discovered a universal resurgence of T_c passing the peak predicted by the general T_c - p (doping) or $-P$ (pressure) relation for cuprate high-temperature superconductor and attribute the resurgence to a pressure-induced electronic transition, which is supported qualitatively by our density functional theory calculations. This offers a paradigm to raise the T_c of the layered cuprate high-temperature superconductors to a new height.

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Fig. 3. Pressure dependence of T_c in slightly overdoped Bi2212. T_c s were determined by dc magnetization measurements. The two sets of numbers (without and with primes) represent the sequential orders of the experimental runs for two single-crystal samples, with squares representing sample 1 and circles representing sample 2. The triangles are from ref. 23 for slightly underdoped Bi2212. After passing a U-shaped valley under pressure of 20–36 GPa, T_c rises rapidly without any sign of saturation to ~ 90 K at ~ 56 GPa, which is the highest pressure applied. The red dashed line is a guide for the eyes. *Inset* shows the c -lattice parameter of Bi2212 under pressures up to 50 GPa from ref. 24.

predicted by the universal T_c - P relation. It is evident that the pressure effect observed is rather reversible. Fig. 3 shows the T_c behavior under pressures reversibly for two single-crystalline samples of Bi2212. The sample is slightly overdoped as evidenced by its slightly lower T_c . The T_c - P behavior is qualitatively similar to that of Bi2201 at high pressures after reaching its $T_{c\text{-max}}$. Under pressure, T_c decreases rapidly from ~ 90 K at ambient to ~ 71 K at ~ 20 GPa as expected for an overdoped cuprate HTS based on the universal T_c - P relation. It continues to decrease but at a slower rate above ~ 20 GPa, passes a broad minimum of ~ 69 K at ~ 30 GPa, and finally, rises rapidly after ~ 40 GPa to ~ 90 K at ~ 56 GPa, the highest pressure applied, at a rate of $\sim +1.4$ K/GPa. As shown in Fig. 3, the low-pressure effect on the T_c of our samples does not result in the peak previously reported by Chen et al. (23). We attribute the difference to the different doping levels of the samples studied [i.e., our samples are slightly overdoped, while the sample of Chen et al. (23) is slightly underdoped, which may require a higher pressure to induce a resurgence of T_c]. Our observations show that, while the T_c of Bi2201 and Bi2212 under low pressures (e.g., <20 GPa) behaves in accordance with the universal T_c - P relation, a higher T_c emerges at higher pressures, possibly associated with a subtle change of the electron energy structures characteristic of the CuO_2 layers in cuprates. In fact, similar T_c - P behavior has also been reported in Bi2223 (17) with the triple- CuO_2 layers per unit cell [i.e., under pressure, its T_c increases from

108 K at ambient, peaks at 123 K ($T_{c\text{-max}}$) at 12 GPa, decreases to 118 K at 23 GPa, and finally, increases to 136 K at 36 GPa at a rate of $\sim +1.4$ K/GPa]. The final T_c increase at high pressures was ascribed by Chen et al. (17) to a pressure-driven transition of the inner CuO_2 layer from the competing order to a superconducting state, thus specific to the triple- CuO_2 layer cuprates. However, we attribute the T_c rise at higher pressure after reaching its peak to an electronic transition generic to the CuO_2 layers in cuprates under very high pressures, independent of the number of CuO_2 layers per unit cell as summarized in Table 1. It is interesting to note that, after the T_c resurgence for Bi2201, Bi2212, and Bi2223, their dT_c/dP values are large and rather similar, but the sign of the dT_c/dP at low pressures depends on the compound's initial doping state. The observations, therefore, suggest that higher T_c s than those previously reported in layered cuprate HTSs can be achieved by breaking away from the universal T_c - P relation via inducing a transition in the electronic spectrum of the CuO_2 layer by the application of higher pressures.

Numerous structural studies on BSCCO have been made under pressures up to 50 GPa at room temperature (17, 24–26). None have displayed any pressure-induced structure transition, although charge redistribution within the cell under pressure has been suggested from the Raman studies (17). The absence of any pressure-induced structure transition is consistent with our proposed electronic transition, such as the Lifshitz transition (15, 16), which may not be accompanied by a structural change. However, despite the absence of a structural transition, anomalies appear in the c -lattice parameter of Bi2212 at ~ 30 GPa (24), coinciding with the broad U-shaped T_c valley that we have observed as shown in Fig. 3, *Inset*.

Discussion

In searching for the microscopic origin of the unusual pressure enhancement effect on T_c , we have performed quantum mechanical computations based on the DFT + U method, where the Hubbard U term is used to treat the strong onsite Coulomb interaction of localized Cu 3d electrons on Bi2201 and Bi2212. The excess oxygen δ s are estimated, according to the T_c - δ relation, to be 0.17 (27) and 0.25 (28) for Bi2201 ($T_c \sim 10$ K) and Bi2212 ($T_c \sim 90$ K), respectively. Our calculations show that the excess oxygen δ resides energetically favorably between the BiO layers. Both hydrostatic and nonhydrostatic pressures were applied to shrink the supercell volume while allowing the shape of the supercell to relax. The experimental compressibility values of the a and c axes were used as the input for the nonhydrostatic case (24, 25). We have calculated the total DOS, the partial DOS, and the band structures near the Fermi level at selected pressures. Fermi surface topology changes are induced by pressures above ~ 37 GPa for Bi2201 and above ~ 42 GPa for Bi2212 as shown in *SI Appendix, Fig. S3*. The projected electronic band Cu 3d _{x^2-y^2} variations with pressure are displayed in Fig. 4*A* and *B*. The accompanying evolutions of the band-state occupancy with pressures are shown in Fig. 4*C*. The DOSs vary with pressure in a fashion qualitatively similar to that with the T_c s. For these compounds, the calculations also clearly show that pressure inhomogeneity has a rather large effect on the electronic transition as

Table 1. dT_c/dP for BSCCO with $n = 1, 2$, and 3 under different pressure ranges

Bi2201	Bi2212	Bi2223
0–26 GPa: +0.5 K/GPa	0–22 GPa: –0.9 K/GPa	0–12 GPa: +1.3 K/GPa
26–41 GPa: –0.4 K/GPa	22–42 GPa: ± 0.2 K/GPa	12–23 GPa: –0.5 K/GPa
41–51 GPa: +1.5 K/GPa	42–56 GPa: +1.4 K/GPa	23–36 GPa: +1.4 K/GPa

The dT_c/dP values for Bi2223 were estimated from the results reported in ref. 17. For Bi2201, Bi2212, and Bi2223, the signs and magnitudes of dT_c/dP at low pressures depend on the compound's initial doping state, and the dT_c/dP values at higher pressures, after the T_c resurgences, are large and rather similar. Boldface text is used to emphasize the dT_c/dP at the pressure range where the T_c -resurgence took place.

calculations. The observations, therefore, provide a path to higher T_c s than previously achieved in layered cuprates by breaking away from the universal T_c -P relation. They will certainly stimulate future experimental and theoretical investigations on the T_c resurgence in other cuprates as well as in Fe-based superconductors.

Materials and Methods

Crystal Growth. The polycrystalline Bi2201 was prepared by the standard solid-state method followed by a prolonged oxygen annealing. The stoichiometric mixture of high-purity Bi_2O_3 (99.9995%), SrCO_3 (99.99%), and CuO (99.995%) was pressed into a pellet and then sintered in a temperature range from 700 °C to 850 °C in oxygen atmosphere. This procedure was repeated at least four times with intermediate grinding. It displayed a superconducting transition around 10 K similar to that previously reported (27). The single-crystalline Bi2212 was grown by the floating zone technique (32).

dc Magnetization Measurements Under High Pressure. We developed a mini-DAC fabricated from BeCu alloy with length of ~ 3 cm and outer diameter of ~ 8.8 mm, which was adapted into a Quantum Design Magnetic Property Measurement System (MPMS) for ultrasensitive magnetization measurements at temperatures down to 1.8 K and in fields up to 7 T under high pressure. A pair of 300- μm -diameter culet-sized diamond anvils was used for all of the measurements under high pressure. The gaskets are made from nonmagnetic Ni–Cr–Al alloy. Each gasket was preindented to ~ 20 –40 μm in thickness, and a 100- to 120- μm -diameter hole was drilled to serve as the sample chamber. Thermal grease was used as the pressure-transmitting medium. The applied pressure was measured by the fluorescence line of ruby powders and the Raman spectrum from the culet of the top diamond anvil. Samples with diagonal ~ 80 –100 μm and thickness of a few micrometers were prepared to provide a sufficient magnetic signal. The reproducibility of the background signal under different magnetic fields and thermal cycles was confirmed. The variance of different runs of background measurements is below 2×10^{-8} emu/Oe, which offers a good platform to analyze the superconducting signal under high pressure. A piece of calibration Pb sample with diagonal ~ 100 μm was tested with the mini-DAC at ambient pressure. A sharp superconducting transition at 7.2 K was detected.

Density Functional Calculations. The Vienna ab initio simulation package (33, 34) with the projector-augmented wave method (35) was used for all of the calculations in this study. The plane wave cutoff energy was set to 450 eV, and the generalized gradient approximation (GGA) with the semilocal Perdew–Burke–Ernzerhof (36) function was adopted to describe the exchange correlation interactions. The Brillouin zone was sampled with Γ -centered k meshes with a spacing of $0.027 \text{ \AA}^{-1}$ for the crystal structure optimization and $0.013 \text{ \AA}^{-1}$ for the electronic structure calculations. The tetrahedron method with Blöchl corrections was carried out to obtain the accurate DOS. The criteria of convergence for energy and force were set to 10^{-5} eV and $0.005 \text{ eV/\AA}$, respectively. Onsite Coulomb repulsion of Cu 3d electrons was corrected by the GGA + U method (37), with $U_{\text{eff}} = 4$ eV according to previous theoretical reports (38).

In the hydrostatic model, lattice parameters under different pressures are obtained by shrinking the supercell under free relaxation of the lattice parameters with fixed volumes. Under these conditions, the pressures along each direction are the same (i.e., homogeneous pressure). However, the difference between our theoretical lattice parameters under hydrostatic conditions and the reported lattice parameters measured by synchrotron X-ray diffraction (24, 25) indicates that the actual pressure along the *ab* plane is smaller than that along the *c* axis above a certain pressure, which is affected by the hydrostatic limit of the pressure-transmitting medium as well as the strength anisotropy of the testing material. To better simulate the inhomogeneous pressure condition, we used the experimental data as a reference to adjust the pressure along different directions accordingly.

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