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Unusual hole dependence of T_c in $HgBa_2CuO_{4+\delta}$

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The anion doping effect on the superconducting transition temperature (T_c) of $HgBa_2CuO_{4+\delta}$ has been determined with a wide T_c variation. We found a parabolic variation of T_c with δ over the entire range of superconductivity. Remarkably, the dependence of T_c on p (the number of holes per CuO_2) has richer features: for $\delta \leq 0.28$, T_c is parabolic in p, but with an unusual prefactor and $p = 0.72\delta$, giving significantly less than two holes per oxygen; and for $\delta > 0.28$, a drastic departure from the parabolic $T_c(p)$ occurs. Implications for the occurrence of superconductivity in this material are discussed.

Many cuprates are known to undergo the insulator → superconductor → "normal" metal (I→S→NM) transition as the carrier concentration (n) of these compounds increases continuously with doping. Superconductivity usually occurs only over a limited n range $n_{\min} < n < n_{\max}$ and the superconducting transition temperature (T_c) rises above 1 K at $n = n_{\min}$, peaks with a $T_c = T_c^{\max}$ at an optimal n (n_{op}) and drops back to 1 K at $n = n_{\max}$. In an attempt to understand the occurrence of high-temperature superconductivity (HTS), systematic trends of evolution of HTS with various physical parameters have been sought in these compounds as the I→S→NM transition is induced by doping. Several universal relationships between T_c and n were reported over the last few years, as summarized schematically in Fig. 1. Based on muon-spin-rotation (μSR) measurements, Uemura *et al.*[1] observed a linear T_c-n_s/m^* relation (where n_s is n in the superconducting state and m^* the effective mass of the carrier in the unit of free-electron mass) for wide variety of HTS's with $n \leq n_{\text{op}}$ [Fig. 1(a)]. After examining the pressure effect on T_c, we[2] proposed a universal T_c-X dependence (where X is a yet-to-be determined parameter that depends on n, m^*, and pressure), qualitatively extending the observation of Uemura *et al.*[1] to $n \gg n_{\text{op}}$. On the other hand, Presland *et al.*[3] found that $T_c/T_c^{\max}$ varies parabolically with the number of carriers per CuO_2 (p), i.e., $T_c/T_c^{\max} = 1 - 82.6(p - 0.16)^2$ where p is determined from valence balance[3] or the thermoelectric power (TEP) measurements at room temperature.[4,5] Later, Zhang and Sato[6] proposed a universal $T_c/T_c^{\max}$-p relation where $T_c/T_c^{\max}$ exhibits a plateau for $0.12 \leq p \leq 0.25$, following the analysis of a number of selected data sets [Fig. 1(c)]. Very recently, Niedermayer *et al.*[5] and Uemura *et al.*[7] found that as n (which is $\propto \delta$) increases, although the T_c of the overdoped ($n > n_{\text{op}}$) $Tl_2Ba_2CuO_{6+\delta}$ decreases as expected, n_s/m^* determined by μSR decreases instead, in strong contrast to all the $T_c(p)$ relations mentioned above. By combining results of the underdoped ($n < n_{\text{op}}$) $YBa_2Cu_3O_{6.5+\delta}$ and $La_{2-x}Sr_xO_{4+\delta}$,[1] a double-valued T_c-n_s/m^* relation was proposed[5] [Fig. 1(d)].

Although all universal relations shown in Fig. 1 appear to be an extension of the linear T_c-n_s/m^* relation for $n < n_{\text{op}}$ observed by Uemura *et al.*,[1] the details of the models are different on the overdoped side and may depend on the particular method (e.g., cation substitution, titration, oxygen content, or TEP) used to extract p. This

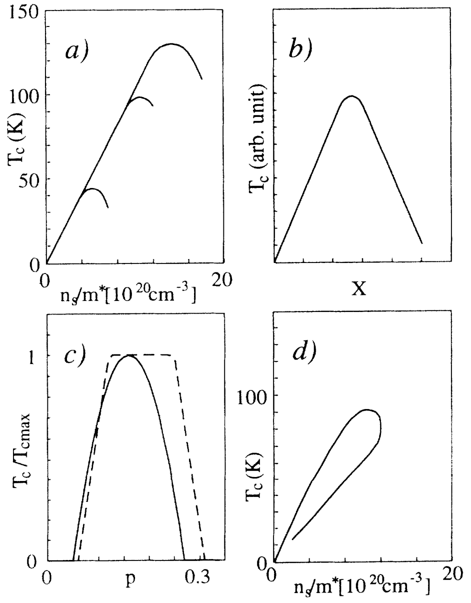

FIG. 1. (a) The measured T_c-n_s/m^* correlation (Ref. 1), (b) the prosed T_c-X correlation (Ref. 2); (c) —— the proposed parabolic correlation in Ref. 3, — — — the proposed correlation in Ref. 6, (d) the T_c-n_s/m^* correlation in Ref. 5.

is not surprising, since many factors, such as self-doping, cation stoichiometry, and defects, may affect these parameters differently. Furthermore, in no case has the obtained T_c covered full range through anion doping only. It is known[8] that cation substitution can introduce disorders that may complicate the $T_c(p)$ dependence.

In this paper, we report on a systematic study of the T_c evolution of $HgBa_2CuO_{4+\delta}$ (Hg 1:2:0:1) over a wide anion-doping range $0.03 \leq \delta \leq 0.4$. We have measured T_c together with δ which was determined by thermogravimetric analysis (TGA), the carrier concentration p from TEP at 290 K, and the lattice parameters a and c. We observed that T_c can be changed parabolically from 1 K to a $T_c^{\max}=97$ K and back to ~ 20 K as δ increases from 0.03 to 0.4. This corresponds to a wide variation of $T_c/T_c^{\max}$ achieved by oxygen doping alone. T_c was found to change also with p parabolically, i.e., $T_c=97$ K $[1-50(p-0.16)^2]$, similarly to the relation previously reported,[3] but only when p is between 0.03 and 0.22. Further oxygenation leads to an increase of TEP at 290 K and therefore a reduction of p while T_c continues to decrease. Such a deviation of T_c from the proposed correlation for $\delta > 0.28$ is also accompanied by an unexpected change in the slope of c-δ. The observations will be compared with the universal relations previously proposed and discussed in terms of the electronic structure of Hg 1:2:0:1.

The Hg 1:2:0:1 samples investigated here were prepared by the controlled solid-vapor reaction technique. Details of the technique have been published elsewhere.[9] In short, Hg 1:2:0:1 is synthesized by reacting a precursor pellet of Ba_2CuO_x and a composite Hg source together. The precursor pellet is obtained by repeatedly heating and pulverizing a mixture of appropriate amounts of BaO and CuO in an alumina crucible in a flowing mixed gas of Ar:O at a ratio of 4:1 at 930 °C for a total of 24 h. The composite Hg source used in this study was a prereacted Hg 1:2:0:1 pellet made by compacting the thoroughly mixed HgO and pulverized precursor powder. A small precursor pellet and a large composite Hg source in a ratio of ~1:3 are sealed inside an evacuated quartz tube, heated to 810 °C and kept at this temperature for 8 h before being cooled to room temperature. Samples with different δ are obtained by heating the as-synthesized samples at different temperatures and O pressures for appropriate periods of time.[10] To reach the underdoped region, the sample was heated in a vacuum of $\sim 2\times 10^{-6}$ torr at a temperature between 250–500 °C for 20–80 h. For the overdoped samples, the as-synthesized compound was heated in a 1–500 bar O atmosphere between 240 and 400 °C for 10–240 h. The best homogeneous heavily overdoped samples were made at low temperatures which facilitate oxygenation. Heat treatment at temperatures above 500 °C in vacuum resulted in a partial decomposition of the compound. δ was measured by TGA and the neutron powder diffraction (NPD), and the cation composition of the samples was determined by NPD, inductance coupled plasma (ICP), and wet-chemistry analysis. The structure was characterized by powder x-ray diffraction and NPD. The dc magnetic susceptibility (χ) was measured as a function of temperature using a Quantum Design superconducting quantum interference device magnetometer, and the electrical resistivity (ρ) was measured using the standard four-lead technique. The TEP was measured with a resolution of $\sim 0.1\ \mu$V/K (Ref. 11) in the temperature region of interest.

All samples investigated display a single phase of Hg 1:2:0:1 within the resolution of our x-ray diffraction (±5%) and neutron diffraction (±5%). The cation stoichiometry in the as-synthesized Hg 1:2:0:1 is Hg:Ba:Cu=0.98:2:1, as shown by NPD,[12] in contrast to the value ~0.7:2:1 as determined by the ICP technique and the wet-chemical method.[10] The microprobe method, which is commonly used to determine the cation ratios, failed because of sample surface degradation induced by polishing. The Hg content was the same after annealing at lower temperatures (≤ 300 °C) over short periods of time (≤ 10 h), but apparently decreased up to ~5% after prolonged heat treatment (> 100 h) at high temperatures (400 °C) based on our TGA and NPD data. This small Hg loss did not result in any significant irreversible change in T_c (< 1 K) or superconducting volume fraction ($\leq 5\%$) according to the zero-field-cooled (ZFC) magnetization results on powder samples and thus, is not expected to affect the discussion that follows. However, it does lead to an irreversible increase in ρ (up to ~15% for the most heavily overdoped sample with a $T_c \sim 20$ K) due to the degradation of the grain boundaries. Therefore, exact ρ evolution with oxygenation is yet to be determined.

The $\rho(T)$ and $\chi(T)$ of the Hg 1:2:0:1 samples were carefully measured after various heat treatments. In general, the removal of oxygen results in a rapid ρ increase for the underdoped samples with $\delta < \delta_{\rm op}$ but only a slow ρ increase for the overdoped ones with $\delta > \delta_{\rm op}$, where $\delta_{\rm op}=0.22$ is the δ at the optimal doping level. The superconducting signal ($\Delta\chi$) of all samples was found to be $>5\%$ and $>20\%$ of a perfect superconductor as determined in the field-cooled (FC) and zero-field-cooled (ZFC) modes, respectively, demonstrating bulk superconductivity in all samples examined. However, it should be pointed out that $\Delta\chi$ decreases with the decrease in T_c in both the $\delta < \delta_{\rm op}$ and $\delta > \delta_{\rm op}$ regions. This could be attributed to the increase of the penetration depth. The superconducting transition of these samples was relatively narrow with a width <5 K. The T_c so obtained was found to depend on δ parabolically as 97 K$[1-26(\delta-\delta_{\rm op})^2]$ where $\delta_{\rm op}=0.22$ over the entire doping range of $0.03 \leq \delta \leq 0.4$ as displayed in Fig. 2.

The TEP(T)'s of samples with different δ's were determined. A few examples are shown in Fig. 3, inset. In general, a δ increase shifts the TEP(T) curve downward in parallel, rapidly for samples with $\delta < \delta_{\rm op}$ but only slowly for those with $\delta > \delta_{\rm op}$, similar to that observed previously.[4] However, the TEP(T) reaches a minimum at $\delta=0.28$, and further oxygenation shifts the whole TEP(T) curve upward instead. Following the universal correspondence of room-temperature TEP with p, proposed by Obertelli *et al.*,[4] the p's of the samples with

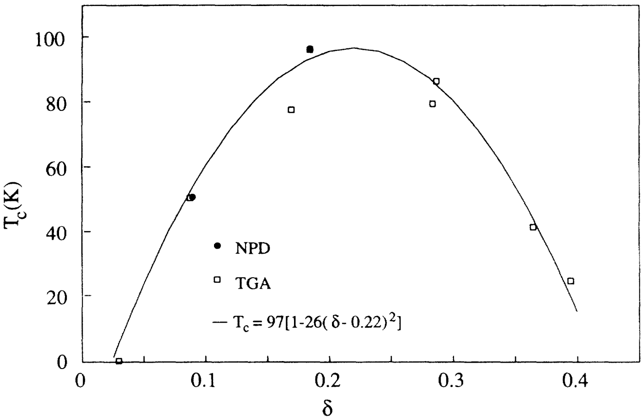

FIG. 2. T_c vs δ in Hg 1:2:0:1: ● NPD data, □ extracted from TGA and normalized to NPD data at $\delta = 0.18$. —— fit of $T_c = T_c^{\max}[1 - 0.26(\delta - 0.22)^2]$.

different δ's were determined. The bond-valence summation method was also used to determine p. The value of the as-synthesized samples obtained is ~ 0.17, which compares well with the value of 0.15 as determined by the thermoelectric power method. As shown in Fig. 3, T_c was found to vary with p parabolically as 97 K$[1 - 50(p - 0.16)^2]$ as T_c rises from 1 K to the $T_c^{\max} = 97$ K in the underdoped region and then decreases to ~ 75 K in the overdoped region. This T_c region where the parabolic T_c-p relationship holds corresponds to a δ range, varying from 0.03 to 0.28. A deviation from the parabolic $T_c(p)$ dependence occurs for $T_c < 75$ K in the overdoped region, corresponding to $\delta > 0.28$.

The lattice parameters a and c were also determined for samples with different δ's. c was found to decrease continuously with δ increase for $\delta < 0.28$ but to change only very slightly with further increase of δ, as shown in Fig. 4. The break in the $c(\delta)$ curve coincides with the departure from the parabolic $T_c(p)$ behavior at $\delta \sim 0.28$.

The T_c changes with δ parabolically (Fig. 2) as observed previously in other cuprates HTS's.[1–5] The $T_c(p) = 97$ K$[1 - 50(p - 0.16)^2]$ observed for Hg 1:2:0:1 shown in Fig. 3 is in qualitative agreement with the parabolic universal relation $T_c(p) = T_c^{\max}[1 - 82.6(p - 0.16)^2]$ where p is determined from the same TEP measurements at room temperatures.[3–5] It is particularly true that $T_c^{\max}$ of Hg 1:2:0:1 occurs at the same $p = 0.16$ as for all other cuprates HTS's. However, the prefactor of 50 observed here is smaller than the 82.6 for other HTS's. The extrapolated superconducting range of $\Delta p = 0.28$ for Hg 1:2:0:1 is therefore significantly greater than that of 0.22 for other HTS's.[3,4] The difference observed here appears to exceed that arising from the uncertainty ±0.015 of p for the cuprates examined in Ref. 4. Our results may therefore suggest that the charge reservoir can affect T_c through roles other than the well-accepted one as a carrier supplier.[13] The observed $T_c(\delta)$ and $T_c(p)$ gave $p = 0.72\delta \pm p_0$ with $p_0 = 0 \pm 0.01$, implying that Hg 1:2:0:1 is not self-doped, as suggested by the band-structure calculation of Novikov and Freeman.[14] This p-δ relation disagrees with the ionic model, which predicts $p = 2\delta$, giving two carriers per oxygen. This can be attributed to the strong covalent bonding between Hg and O(4) in the HgO_δ layer recently proposed by Singh and Pickett.[15] Details will be published elsewhere.[16]

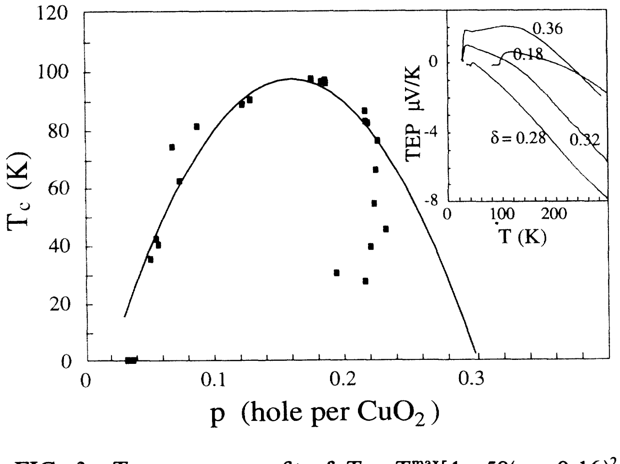

FIG. 3. T_c vs p. —— fit of $T_c = T_c^{\max}[1 - 50(p - 0.16)^2]$. Inset: Typical TEP vs T for several δ's.

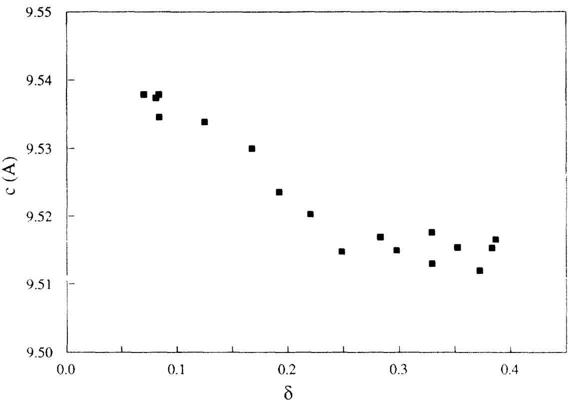

FIG. 4. Lattice constant c vs δ.

For $\delta > 0.28$, $T_c(p)$ is no longer parabolic as shown in Fig. 3. The dramatic departure from the parabolic $T_c(p)$ of Hg 1:2:0:1 appears for $T_c < 75$ K or $\delta > 0.28$ in the overdoped region. In spite of the continuous increase of δ and the continuous decrease of T_c and $\rho(T)$, p shows a small but distinct decrease in a contrast to expectation. This p decrease coincides with the reverse trend of TEP and c various in $\delta \geq 0.28$ (Figs. 3 and 4). The observed $T_c(p)$ in Hg 1:2:0:1 for $p > 0.22$ is qualitatively similar to the $T_c(n_s/m^*)$ in $\mathrm{Tl_2Ba_2CuO_{6+\delta}}$ reported by Niedermayer *et al.*[5] and Uemura *et al.*[7] in the overdoping region, which has been attributed to the strong depairing effect of the extra carriers,[5] to the failure of scaling between normal state n and n_s, or to an increase in m^*.[7] However, it should be noted that a parabolic $T_c(p)$ was detected for $\mathrm{Tl_2Ba_2CuO_{6+\delta}}$ throughout the overdoped region. The departure of $T_c(p)$ of Hg 1:2:0:1 with $\delta > 0.28$ from the parabolic $T_c(p)$ behavior may therefore arise from a different cause. It has been observed that the lattice parameter c contracts in all double Tl(Bi)-layer HTS's but expands in the single Tl-layer compounds, because of the different sites in the compound that oxygen enters.[3] The nearly constant c with oxygenation $\delta > 0.28$ observed in Hg 1:2:0:1 (Fig. 4) is very different from the continuous decrease with δ for $\delta < 0.28$. This may imply that there are two different types of sites for oxygen to enter Hg 1:2:0:1, one presumably in the HgO_δ layers and the other off the HgO_δ layers. The latter will be occupied when δ is large. It follows that although excess O atoms in both sites suppress T_c and possibly the superconducting condensate n_s in the overdoped region, they contribute to the transport properties in the normal state differently, i.e., one enhances TEP(T) and the other suppresses TEP(T). It will not be surprising if oxygen in the different sites will also be discovered to have different effects on other superconducting properties, such as pinning. To test the above conjecture, several experiments on the sites of excess oxygen, the superconducting concentrates, and field effects on χ of samples with different δ's are underway.

In conclusion, we have carried out a systematic study on the O-doping effect on Hg 1:2:0:1 over a wide anion-doping range. The T_c was found to vary parabolically with δ throughout the doping range where T_c rises from 1 to 97 K and loops back to 20 K with a continuous δ increase, which is in agreement with the previous reports. For $\delta < 0.28$, T_c was observed to vary also parabolically with p, but with a prefactor different from other cuprate HTS's, with $p = 0.72\delta$, significantly less than the expected two carries per oxygen. This implies a possibly important role, other than that of carrier supplier to the CuO_2 layers, of the charge reservoir in inducing superconductivity in layered cuprates. However, T_c departs from the parabolic $T_c(p)$ relation known for other HTS's for $\delta > 0.28$, coinciding with the anomalous $c(\delta)$ behavior detected. While the departure observed here in Hg 1:2:0:1 appears to be similar for $T_c(n_s/m^*)$ reported recently in $Tl_2Ba_2CuO_{6+\delta}$, our observation suggests that excess oxygen may have entered different sites when $\delta > 0.28$ and that oxygen in different sites may influence the properties of the compounds in their normal and superconducting states differently. The results also suggest that $T_c(p)$ may depend on the specifics of the material system, particularly in the heavily overdoped region, and that no universal relation of the type previously suggested exists.

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