Pressure effect on the T_c of HgBa$_2$CuO$_{4+\delta}$ with $0.07 \leq \delta \leq 0.39$

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The superconducting transition temperature (T_c) of HgBa$_2$CuO$_{4+\delta}$ (Hg 1:2:0:1) has been determined under pressures up to 1.7 GPa over a wide δ range. We found that the linear pressure effect on T_c (dT_c/dP) is constant at $+2.0 \pm 0.1$ K/GPa for $\delta < 0.3$, but displays a drastic change around $\delta \sim 0.3$, coinciding with the onset of a quadratic pressure effect on T_c and the "boomerang path" previously reported. Comparison of the present observations for $\delta < 0.3$ with the inverse parabolic carrier density (n) dependence of T_c suggests that the inverse parabolic $T_c(n)$ relation is less universal than originally envisioned, and that the observed large dT_c/dP of optimally doped Hg 1:2:0:1 and other members of the homologous series is a result of the change of electron bands induced by pressure.

I. INTRODUCTION

In an attempt to understand the occurrence of superconductivity in high-temperature superconductors (HTSs), many experiments have been carried out to find possible correlations between the superconducting transition temperature (T_c) and some physical parameters. One of these correlations is the so-called universal inverse parabolic dependence of T_c on the number of carriers per CuO$_2(n)$ in HTS, i.e., $T_c(n) = T_c^{max}[1 - a(n - n_{op})^2]$ with $a = 82.6$ and $n_{op} = 0.16$, observed for a wide variety of HTS compounds.[1] According to this T_c-n correlation, superconductivity occurs mainly in the CuO$_2$ sheets over a limited region of n between $(0.16 - 1/\sqrt{a})$ and $(0.16 + 1/\sqrt{a})$. T_c peaks at T_c^{max} when the compound is optimally doped with $n = n_{op} = 0.16$. The HTS is known as underdoped when $n < n_{op}$, and overdoped when $n > n_{op}$. Several phenomenological models[2-4] have subsequently been advanced to account for the observed pressure effect on $T_c(dT_c/dP)$ based on the above universal T_c-n rather successfully. dT_c/dP has therefore been attributed to two sources: the pressure-induced charge transfer (dn/dP) and the n-independent pressure-induced constant shift in T_c^{max} (dT_c^{max}/dP). However, most of the reported high-pressure experiments have been restricted to the optimally doped samples. This is particularly true for HgBa$_2$Ca$_{m-1}$Cu$_m$O$_{2m+2+\delta}$ with $m = 1$, 2, and 3.[5,6] Unusually high T_c has been achieved under pressure[6,7] and universal $T_c(P)$-behavior was observed for the compounds with different m's.[5,6] Although several studies were made on La$_{2-x}$A$_x$CuO$_4$ (La 2:1:4) with $A = $ Sr and Ba,[6] Tl$_2$Ba$_2$CuO$_{6+\delta}$ (Tl 2:2:0:1),[2,9] and Ca/La doped YBa$_2$Cu$_3$O$_{7-\delta}$ (Y 1:2:3)[3,4] over a relatively wide T_c variation, the T_c range was achieved either through combined anion- and cation doping for La 2:1:4 and Y 1:2:3 or only in the overdoped region for Tl 2:2:0:1. Cation doping is known to induce local strain[10] that may complicate the interpretation of the results. Adding to the complication are the structural instabilities at temperatures above T_c associated with the La 2:1:4 compound system[8] and the effect associated with the linear CuO chain in the Y 1:2:3

compounds.[3] The newly discovered HTS compound HgBa$_2$CuO$_{4+\delta}$ (Hg 1:2:0:1) has been found[11] to display a wide cation-doping range by varying δ, covering almost the whole superconducting region. Its T_c can be varied from below 1 K through a $T_c^{max} = 97$ K and finally $T \sim 20$ K as δ increases continuously, representing the largest T_c variation ever achieved by only a single ion doping. We have therefore systematically investigated the dT_c/dP of Hg 1:2:0:1 with different doping to test the universality of the $T_c(n)$-correlation proposed. In this paper, we report results of the dT_c/dP of the T_c of single-phase samples of Hg 1:2:0:1 with $0.07 \leq \delta \leq 0.39$ under hydrostatic pressures up to 1.7 GPa.

II. EXPERIMENTAL

The Hg 1:2:0:1 samples investigated here were prepared by the controlled solid-vapor reaction techniques.[12] In short, Hg 1:2:0:1 was synthesized by reacting a precursor of Ba$_2$CuO$_x$ and a composite Hg source together. The precursor pellet was obtained by repeatedly heating and pulverizing a mixture of approximate amounts of BaO and CuO in an alumina crucible under 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 $\sim 1:3$ 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's were prepared by heating the as-synthesized samples at different temperatures and O pressures for appropriate periods of time.[13] To reach the underdoped region, the sample was heated in a vacuum of 2×10^{-6} Torr at a temperature between 250 and 500 °C for 20–80 h. For the overdoped samples, the as-synthesized sample was heated in an atmosphere of 1–500 bar between 240 and 400 °C for 10–240 h. The best homogeneous heavily doped samples were usually obtained at low temperatures which facilitate oxygenation and avoid Hg loss. Heat treatment at temperatures

above 500 °C in vacuum resulted in a partial decomposition of the compound. In this work, δ was determined based on the $T_c(\delta)$-curve recently reported[11] after the T_c was measured.

The structure and the phase purity were characterized by powder x-ray diffraction (XRD). The T_c at ambient was measured both resistively by the four-lead method using a Linear Research LR-400 bridge and magnetically using a Quantum Design SQUID magnetometer. Under pressure, the T_c was determined resistively and, for a few samples, by the ac magnetic susceptibility technique. The high-pressure environment was generated inside a Teflon cup in a Be-Cu high-pressure clamp,[14] using 3M fluorinert as the pressure medium. The pressure was measured with a superconducting Pb manometer which was situated next to the sample inside the Teflon cup and the temperature by a chromel-alumel thermocouple above 30 K and a Ge-thermometer below 30 K.

III. RESULTS AND DISCUSSION

The 11 samples studied here are single-phase Hg 1:2:0:1 without any impurities within the resolution of our XRD analysis of ~±4%. The superconducting transition width (ΔT_c) of these samples ranges from ~1 to 6 K (the narrowest for the optimally doped sample), and the resistively and magnetically determined mid-point T_c's of the samples (to be defined below) differ not more than 2 K, suggesting a relatively high quality for these samples. The doping level deduced from T_c is shown in Fig. 1 for the used samples. The value of δ was estimated based on the published $T_c(\delta)$ relation,[11] which shows that T_c varies with δ parabolically and exhibits a T_c^{max} of 97 K at the optimal $\delta_{op}=0.22$. Among the 11 samples examined, three were underdoped with a minimum $T_c=45$ K and seven were overdoped with a minimum $T_c=26$ K, in addition to the optimally doped one.

Two typical sets of resistivity curves $\rho(T)$ are presented in Figs. 2 and 3 representing two samples under different pressures: one optimally doped and the other extremely overdoped, where the onset (T_{C0}), mid-point (T_c), and

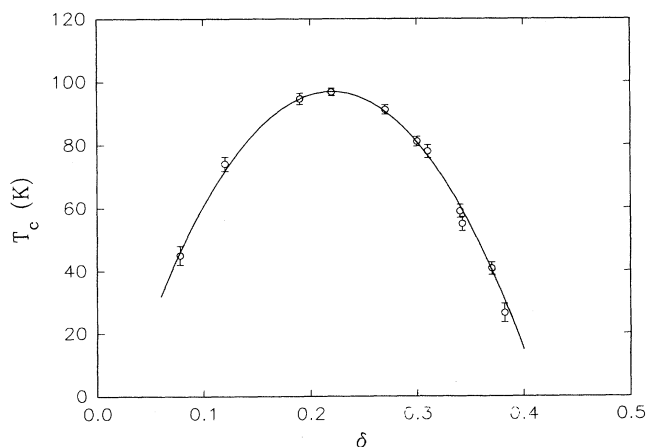offset (T_{cf}) of the T_c's are defined. For the optimally doped (and also the underdoped) sample, the T_c is shifted upward linearly by pressure, and ΔT_c is also increased from ~1 to 3 K as the pressure increases from 0 to 1.5 GPa. However, for the extremely overdoped sample with $\delta \geq 0.3$, the T_c is shifted nonmonotonically by pressure, but the transition width remains the same (Fig. 3). The T_c of three samples under pressure, two of them underdoped and one extremely overdoped, was measured magnetically. The dT_c/dP in one of the samples with $\delta=0.12$ was verified by simultaneously measuring the T_c magnetically and resistively. No difference in the $T_c(P)$-$T_c(0)$ was noted within our experimental resolution. The T_c of the 11 samples under various pressures are summarized in Figs. 4(a) and 4(b), where Fig. 4(a) shows the underdoped (Nos. 1–3) and the optimally doped (No. 4) samples and Fig. 4(b) shows the overdoped ones (Nos. 5–11). The numbers in the figures represent the sequential order of increasing O content (δ) in the samples.

FIG. 2. $\rho(T)$ for the optimally doped Hg 1:2:0:1 at various pressures.

FIG. 1. The T_c vs δ (as deduced from the measured T_c) for all samples used here, compared with the previously measured (Ref. 11) T_c vs δ in Hg-1201 (solid line).

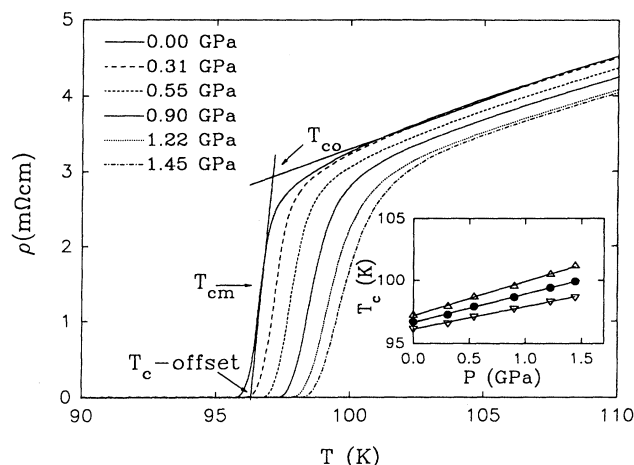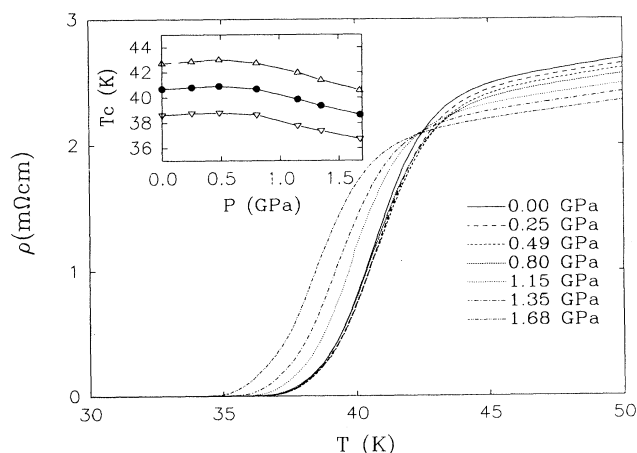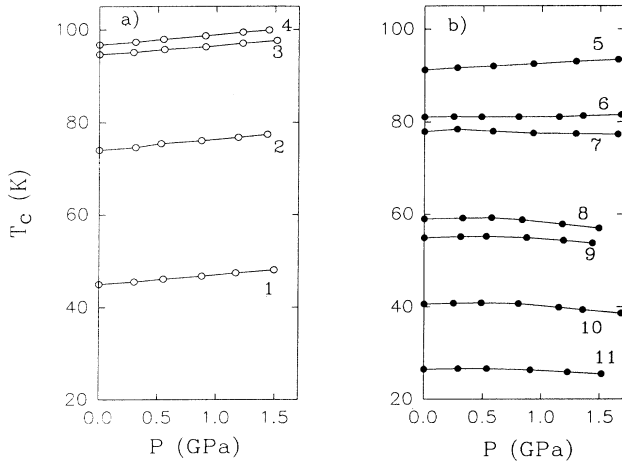FIG. 3. $\rho(T)$ for heavy overdoped Hg 1:2:0:1 with $\delta \sim 0.37$ at various pressures.

FIG. 4. Mid-point $T_c(P)$ of samples with different δ's: (a)—underdoped and optimally doped, with $\delta = 0.22, 0.19, 0.12$, and 0.07 from top to bottom; (b)—overdoped with $\delta = 0.27, 0.30, 0.31, 0.34, 0.36, 0.37$, and 0.39 from top to bottom.

They are, respectively, 0.07, 0.12, 0.19, 0.22, 0.27, 0.30, 0.31, 0.34, 0.36, 0.37, and 0.39.

According to the universal inverse quadratic relation $T_c(n) = T_c^{max}[1 - a(n - n_{op})^2]$, one obtains

$$dT_c/dP = [1 - a(n - n_{op})^2](dT_c^{max}/dP)$$
$$- T_c^{max}(n - n_{op})^2(da/dP)$$
$$- 2aT_c^{max}(n - n_{op})(dn/dP)$$
$$+ 2aT_c^{max}(n - n_{op})(dn_{op}/dP) . \quad (1)$$

Therefore, $dT_c/dP = dT_c^{max}/dP$ for $n = n_{op}$, which can be nonzero for reasons unknown. The pressure effects for samples with $n \neq n_{op}$ enable us to examine the relationship between some parameters in Eq. (1). Especially,

$$d(dT_c/dP)/dn = 2(n - n_{op})[-a(dT_c^{max}/dP)$$
$$- T_c^{max}(da/dP)]$$
$$- 2aT_c^{max}[(dn/dP) - (dn_{op}/dP)] . \quad (2)$$

(dT_c^{max}/dP) represents the change in T_c^{max}, (da/dP) the change in the range for HTS to occur, (dn/dP) the charge transfer, and (dn_{op}/dP) the change in the optimal doping, all induced by pressure. The original phenomenological model[2] follows by retaining only the pressure-induced charge-transfer term on the basis of a rigid band model, i.e., $dT_c/dP = -2aT_c^{max}(n - n_{op})(dn/dP)$. This model predicts a linear n-dependent (dT_c/dP), which is positive for samples in the underdoped region (i.e., $n < n_{op}$), negative in the overdoped region (i.e., $n > n_{op}$), and zero for the optimally doped sample (i.e., $n = n_{op}$). A modified model[4] was advanced by retaining the (dn/dP) and part of the (dT_c^{max}/dP) terms, i.e., $dT_c/dP = (dT_c^{max}/dP) - 2aT_c^{max}(n - n_{op})(dn/dP)$.

This model accounts for the nonzero dT_c/dP for the optimally doped Y 1:2:3 in addition to the linear n-dependent dT_c/dP in the original phenomenological model.[2] Unfortunately, neither of the above models can explain the δ or n dependence of dT_c/dP of Hg 1:2:0:1 observed here.

For the Hg 1:2:0:1 compound system, T_c depends on δ inverse parabolically as $T_c = 97[1 - 26(\delta - \delta_{op})^2]$ with $\delta_{op} = 0.22$ over the whole δ range investigated.[11] However, T_c was found[11] to vary with n inverse parabolically as $T_c = 97[1 - 50(n - n_{op})^2]$ only for $n < 0.2$ which corresponds to $\delta < 0.3$, where n was determined by thermopower measurements. For $\delta < 0.3$, n is proportional to δ but each O atom contributes only 0.72 holes to each Cu instead of 2, as predicted by the ionic model, due to strong covalent bonding between O and Hg in the HgO$_\delta$ layer of the compound.[11,15] A "boomerang path" appears in $T_c(n)$ together with a violation of the scaling between δ and n for $n > 0.2$ ($\delta > 0.3$). The drastic change in the scaling and the deviation of the inverse parabolic $T_c(n)$ relation near $\delta \sim 0.3$ have been ascribed to the possible change in the O sites for $\delta > 0.3$, the defect scattering or the contribution of HgO layer to S(290 K).[11] Therefore, the n deduced form of the thermopower should be taken with caution for $\delta > 0.3$, and we will use δ to represent the doping level in the following discussion.

The dT_c/dP of Hg 1:2:0:1 is analyzed in terms of a fit of $T_c(P) = T_c(0) + \alpha P + \beta P^2$. The δ dependences of the linear pressure term α and the quadratic pressure term β are shown in Figs. 5 and 6. A drastic change in both α and β near $\delta \sim 0.3$ is evident, i.e., α is a constant of 2.0 ± 0.2 K/GPa for $\delta \leq 0.25$, decreases rapidly to 0 near $\delta = 0.3$, and returns to 1.0 ± 0.2 K/GPa at $\delta \sim 0.33$ before it falls off again for $\delta > 0.33$ and β is 0 ± 0.02 K/GPa^2 for $\delta \leq 0.30$, starts to drop rapidly near 0.31, and decreases to $\sim -1.7 \pm 0.5$ K/GPa^2 at $\delta = 0.33$ before it rises again for greater δ.

In the discussion that follows, we shall first discuss the dT_c/dP of Hg 1:2:0:1 samples with $\delta < 0.3$ assuming that the inverse parabolic $T_c(n)$ relation is valid at both ambient and high pressure. As shown in Figs. 5 and 6, dT_c/dP is independent of both n and δ for Hg 1:2:0:1
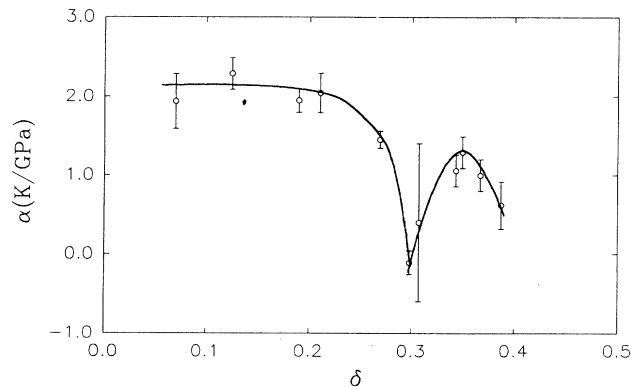

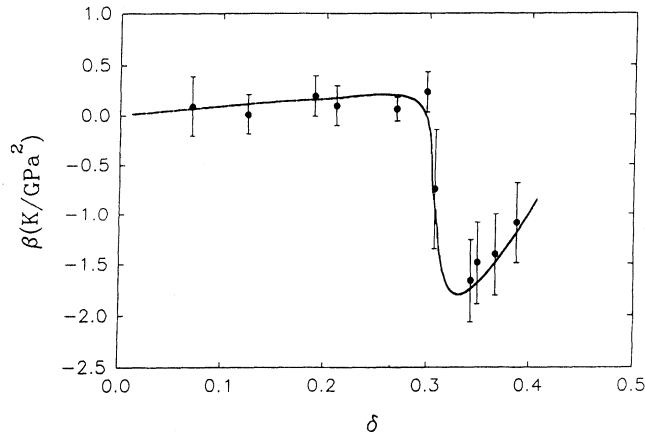FIG. 5. δ dependence of linear pressure effect $\alpha = dT_c/dP|_{P=0}$ on T_c.

FIG. 6. δ dependence of quadratic pressure effect $\beta = (d^2 T_c / dP^2)|_{P=0}$ on T_c.

with $\delta \leq 0.25$ which spans the underdoped and slightly overdoped regions. For $n = n_{op}$ and $d(dT_c/dP)/dn = 0$, Eq. (2) gives $(dn/dP) = (dn_{op}/dP)$. This shows that the optimal concentration n_{op} should shift with pressure if the pressure induces a non-negligible charge transfer. Similar result has been suggested before.[16] In such a case, the observed large T_c enhancement for the optimally doped Hg 1:2:0:1[4] is a very natural result. The pressure-induced shift in n_{op} implies that the electronic bands of Hg 1:2:0:1 and other members of the Hg-12$(m-1)m$ (and possibly other cuprate HTS's) are not rigid, so the inverse parabolic T_c-n or -δ relation would vary accordingly. Even the inverse parabolic relation itself may only be valid under a set of more restrictive conditions than were originally envisioned.

The sudden appearance of nonzero β values for Hg 1:2:0:1 with $\delta \geq 0.3$ (or $n > 0.22$) under pressure below 1.5 GPa as shown in Fig. 6 coincides with the onset of the "boomerang path" in $T_c(n)$ previously observed[11] Tl$_2$Ba$_2$CuO$_{6+\delta}$ is a similarly overdoped compound. However, its T_c varies parabolically with n determined from

the thermopower measurements without the boomerang behavior and displays only the linear pressure effect. We therefore propose that the drastic change of dT_c/dP near $\delta \sim 0.3$ as shown in Figs. 5 and 6 may be associated with the scattering effect due to the presence of extra O sites in heavily overdoped Hg 1:2:0:1 as previously suggested.[11] Details of the process are currently under study.

IV. CONCLUSION

We have determined systematically the dT_c/dP for Hg 1:2:0:1 with $0.07 \leq \delta \leq 0.39$. Both the linear and quadratic effects on T_c, i.e., α and β in $T_c(P) = T_c(0) + \alpha P + \beta P^2$, were observed. α was found to be positive and almost constant at $+2.0 \pm 0.2$ K/GPa for δ up to 0.24 and drops drastically to ~ 0 K/GPa at $\delta = 0.3$ and returns to 1.0 ± 0.2 K/GPa before it falls off slowly, while β is 0 for $\delta < 0.3$, and drops to -1.5 K/GPa^2 at ~ 0.34 before it increases again. The results for $\delta < 0.3$ were compared with predictions of the inverse parabolic $T_c(n)$ relation and previous phenomenological models on $T_c(P)$. We conclude that the inverse parabolic $T_c(n)$ relation and its universal parameters are valid only under conditions more restrictive than originally envisioned and that the unusually large dT_c/dP observed in optimally doped Hg 1:2:0:1 and other homologous members of the series Hg-12$(m-1)m$ can be understood in terms of a pressure-induced shift in n_{op}, the doping level for maximum T_c. The drastic change in dT_c/dP with $\delta > 0.3$ is attributed to the possible scattering effect associated with the oxygen in the heavily overdoped samples, where the boomerang path occurs in $T_c(n)$. Detailed process responsible for the observation remains unknown.

ACKNOWLEDGMENTS

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