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Superconductivity up to 164 K in $HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}$ ($m=1$, 2, and 3) under quasihydrostatic pressures

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The superconducting transition temperatures (T_c's) of optimally doped $HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}$ (Hg 1:2:$m-1$:m) with $m=1$, 2, and 3 and $Hg_{1-x}Pb_xBa_2Ca_2Cu_3O_{8+\delta}$ [Hg(xPb) 1:2:2:3] have been investigated resistively under quasihydrostatic pressures up to 45 GPa. There seems to be a universal upward shift of T_c under pressure, regardless of m, for all Hg 1:2:$m-1$:m, implying a common origin for all compounds. Record high T_c's of 164, 154, and 118 K were reached for the optimally doped Hg 1:2:$m-1$:m with $m=3$, 2, and 1, respectively. However, the T_c enhancement is suppressed by Pb substitution, suggesting the possibility that Hg plays an important role in these compounds.

Recently, superconductivity up to 94 K was reported[1] in the $m=1$ member of the homologous series $HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}$ [Hg 1:2:$m-1$:m]. Superconductivity above 130 K was subsequently observed[2] in multiphase samples. Later, nearly single-phase samples of Hg 1:2:1:2 and Hg 1:2:2:3 were synthesized.[3] Their superconducting transition temperatures (T_c's) were found to depend on their oxygen content. At ambient pressure, the T_c's of optimally doped Hg 1:2:0:1, Hg 1:2:1:2:, Hg 1:2:2:3 are 97, 128, and 135 K, respectively.[4] Similar to other known high-temperature superconductors (HTS's), Hg 1:2:($m-1$):m has a layered structure with stacks of (HgO_δ), (BaO), (CuO_2) and (Ca) layers, and its T_c increases with the number of CuO_2 layers per unit cell. However, δ is rather small, i.e., <0.4, as a result of the linear oxygen coordination of Hg^{2+} in the compound.[5]

High pressure has been employed extensively in the study of high-temperature superconductivity (HTS).[6] It has provided crucial clues to the possible existence of superconductivity at higher temperatures, useful guidelines in the search for HTS compounds, and important information about the occurrence of HTS. Several experiments on Hg 1:2:0:1 (Ref. 7), Hg. 1:2:1:2 (Ref. 8), and Hg 1:2:2:3 (Ref. 9) under hydrostatic pressures (HP's) up to 1.7 GPa were carried out immediately after the isolation of the phases. A positive dT_c/dP was detected for all these compounds and the oxygen-ordering effect on dT_c/dP was shown to be negligible.[7] The dT_c/dP of Hg 1:2:2:3 was found[9] to be rather unusual. It increases with oxygen doping and grows progressively with pressure, even in optimally doped samples, suggesting[10] that higher T_c's might be obtained at higher pressures. Indeed, the onset T_c (T_{co}) in optimally doped Hg 1:2:2:3 was observed[11] to rise continuously to 153 K as the quasihydrostatic pressure (QHP) was increased to $\sim$15 GPa. The observation was confirmed by resistive[12] and magnetic[13] measurements to 23.5 and 11 GPa, respectively. Similarly, the T_{co} of Hg 1:2:1:2 (Ref. 14) was enhanced to 147 K from 122 K by a QHP of $\sim$18 GPa. Consequently, questions arise concerning the T_c ceiling of this interesting HTS family, and the cause for such a large pressure-induced T_c increase in these optimally doped compounds.

We have therefore examined resistively the T_c of optimally doped Hg 1:2:0:1, Hg 1:2:1:2, and Hg 1:2:2:3 under QHP's up to 45 GPa as well as the Pb-doped Hg 1:2:2:3, i.e., $Hg_{1-x}Pb_xBa_2Ca_2Cu_3O_{8+\delta}$ [Hg(xPb) 1:2:2:3] up to 15 GPa. We found that the T_{co}'s of Hg 1:2:($m-1$):m shift almost universally under pressure, and reach $\sim$164, 154, and 118 K for Hg 1:2:2:3 at $\sim$31 GPa, Hg 1:2:1:2 at $\sim$29 GPa, and Hg 1:2:0:1 at $\sim$24 GPa, respectively. The universal T_c shift under pressure suggests a common origin for HTS in these compounds. The large T_c enhancement corresponds to a $\sim$24 to 30 K increase of T_c over their ambient values, almost independent of m, which is much larger than that in other optimally doped HTS's. However, the T_{co} of the optimally doped Hg(xPb) 1:2:2:3 with the same ambient $T_{co}\sim 134$ K peaks at 151 K near 10 GPa for $x=0.1$, but at only $\sim$145 K near 9 GPa for $x=0.2$. The dramatic effect of Pb doping on $T_c(P)$ leads us to attribute the parallel T_c shift and the unusually large T_c enhancement by pressure observed in all Hg 1:2:($m-1$):m compounds to the presence of Hg, which displays a linear oxygen coordination in the compounds. The electronic band effect,[15] in addition to these effects already discussed in the recent phenomenological models,[16] may be needed to describe the obtained dT_c/dP effect in Hg 1:2:($m-1$):m. Nonhydrostatic pressure may also have a positive influence on the T_c of layered HTS's, which is contrary to conventional wisdom on isotropic low-temperature superconductors.

All samples of Hg 1:2:($m-1$):m examined here were synthesized and studied previously.[4,8,11,14] Details of the synthesis steps are published elsewhere.[3,4] A detailed studies of the effect of doping on the T_c of Hg 1:2:($m-1$):m with $m=1$, 2, and 3 have been made.[4] The effect of doping on T_c for the nearly optimally doped samples is presented in Fig. 1, inset, where n is the number of carriers per CuO_2 layer obtained from thermoelectric power measurements, fol-

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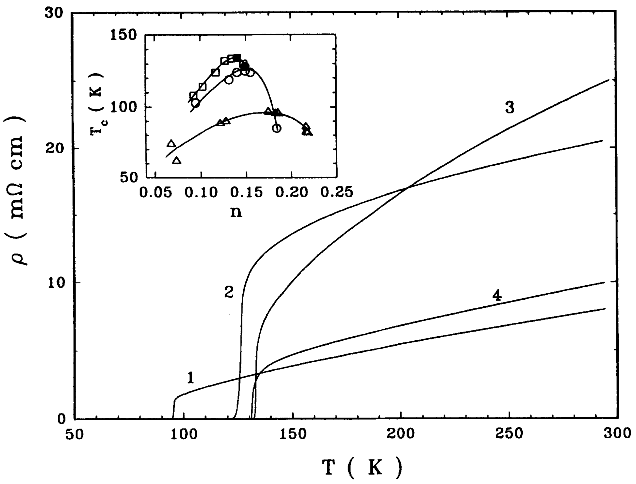

FIG. 1. $\rho(T)$ of several Hg based samples: (1) Hg 1:2:0:1, (2) Hg 1:2:1:2, (3) Hg 1:2:2:3, (4) Hg (0.1Pb) 1:2:2:3. Inset: T_c vs n, where n is the number of carriers per CuO_2 layer: □ Hg 1:2:2:3, ○ Hg 1:2:1:2, △ Hg 1:2:0:1; solid symbols: samples used in this study.

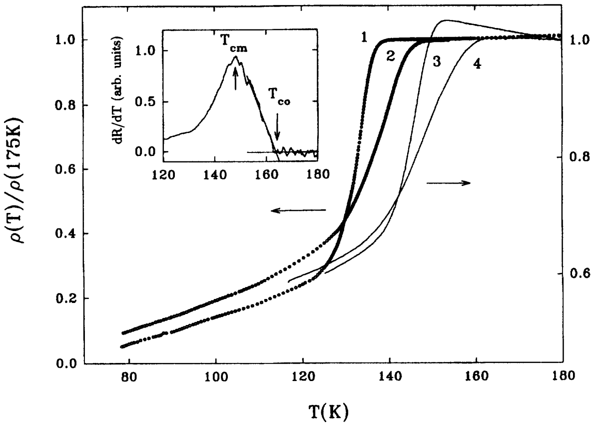

FIG. 2. $\rho(T)$ of Hg 1:2:2:3 under pressures of (1) 0.5 GPa, (2) 5 GPa in WC (circles) and (3) 11 GPa, and (4) 31 GPa in DAC (lines). Note the WC data use the scale on the left and the DAC data use the scale on the right. Inset: dR/dT vs T at 31 GPa where T_{co} and T_{cm} are defined.

lowing the method proposed by Obertelli *et al.*[17] Samples examined in this study (solid symbols, Fig. 1 inset) are optimally doped. Structure characterization was carried out with a Rigaku D-MAX/BIII powder diffractometer. The dc magnetization at ambient pressure was measured by a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The QHP environment up to 45 GPa was provided by a helium membrane, diamond anvil cell (DAC) with a stainless steel gasket. Samples of sizes $\sim 300\times 300\times 25\ \mu m^3$ were loaded into the hole in the gasket with MgO as the pressure medium. The pressure was generated by a diaphragm press[18] at the desired temperatures and kept constant during the measurements. Pressure was determined with an uncertainty of $\pm 5\%$ at several temperatures by the temperature-corrected ruby fluorescence method[19] on several $\sim 3\ \mu m$ sized ruby crystals spread across the sample. The pressures reported correspond to the pressure at T_{co}. QHP up to ~18 GPa was generated by a modified WC anvil clamp[20] using a pyrophyllite gasket with two steatite disks as a pressure medium. Samples of size $\sim 800\ \mu m$ diameter $\times 50\ \mu m$ were used. The pressure was changed only at room temperature and determined with an overall uncertainty of $\pm 15\%$ by converting the applied load at room temperature which was calibrated against a Pb manometer. The temperature was measured by a chromel-alumel thermocouple or a diode thermometer, which was situated closely to the sample with an uncertainty of ±0.1 K. The superconducting transition was determined resistively by the standard four-lead technique in the WC anvil or by a pseudo four-lead technique in the DAC. A pseudo four-lead resistance measurement[21] was made by pressing two tungsten leads onto the sample. Insulation from the gasket was achieved by a thin layer of $0.3\ \mu m$ Al_2O_3 and epoxy mixture.

All samples examined here are of the highest quality available at the present time. The x-ray data revealed that these samples have a phase purity of ~80% for Hg 1:2:2:3, 90% for Hg 1:2:1:2, and ≥95% for Hg 1:2:0:1. The dc magnetic susceptibility (χ) results showed large superconducting volume fractions consistent with the above phase purities. The resistivity (ρ) at ambient pressure is shown as a function of temperature in Fig. 1. The superconducting transitions are rather sharp and occur between 94 and 134 K for various compounds, which is in agreement with previous reports.[8,11,14]

Three optimally doped Hg 1:2:2:3 samples and one sample each of the optimally doped Hg 1:2:1:2 and Hg 1:2:0:1 phases (Fig. 1, inset, solid symbols) were measured using both the WC and the DAC methods. $\rho(T)$ of one of these samples at several QHP's is displayed in Fig. 2. A well-defined superconducting transition is clearly evident, although there is a long tail and often a nonzero ρ background which is ascribed to possible defects and microcracks introduced during thinning and pressurizing, as well as to the contact resistance between the sample and the leads due to the nature of the pseudo four-lead technique used in the DAC measurements. The transition is shifted toward higher temperatures and broadened by pressure. To better define T_c, we have chosen to examine the $d\rho/dT$ displayed in Fig. 2, inset. The T_{co} and the midpoint T_c (T_{cm}) are also defined there. We previously found[11] that T_{co} so defined indeed represents the onset temperature of a genuine superconducting transition and T_{cm} is consistent with that determined magnetically. The pressure dependences of the T_{co}'s are shown in Fig. 3 together with previous results using the WC anvil-clamp method. Initially, T_{co}'s increased with pressure and reached ~164 K at ~31 GPa for Hg 1:2:2:3, ~154 K at ~29 GPa for Hg 1:2:1:2, and ~118 K at ~24 GPa for Hg 1:2:0:1, before they either dropped slightly or saturated beyond the respective pressures cited. The present results at low pressures appear to be in good agreement with previous results obtained in a WC anvil clamp[11,14] (Fig 3). T_{cm} is lower than T_{co} but follows the general T_{co} behavior under pressure. The pressure effects were not reversible and showed a degradation in T_c upon pressure reduction as shown in Fig. 3 for Hg 1:2:2:3.

Two optimally doped Hg(xPb) 1:2:2:3 samples with

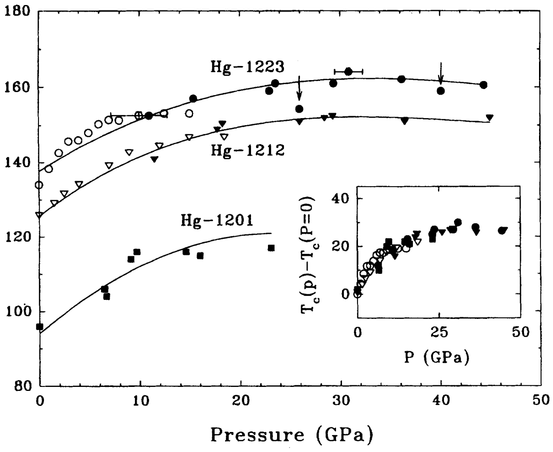

FIG. 3. T_{co} vs P for Hg 1:2:2:3, Hg 1:2:1:2, and Hg 1:2:0:1. Inset: $T_{co}(P)$-$T_{co}(P=0)$ for these three compounds. Open symbols taken from Refs. 11, and 14, solid symbols, this work. Arrows indicate data obtained for Hg 1:2:2:3 upon pressure reduction.

$x=0.1$ and 0.2 were examined by the WC anvil clamp method. T_{co} and T_{cm} were defined in a similar fashion to that described above. The pressure dependence of T_{co} is included in Fig. 4 together with the undoped Hg 1:2:2:3 obtained by the same WC method. Although the two Hg(xPb) 1:2:2:3 samples are also optimally doped and with ambient T_c's about the same as that for Hg 1:2:2:3, the T_{co} increases and peaks at only ~151 K near 10 GPa for the $x=0.1$ sample, and peaks at ~145 K at ~8 GPa and falls off at higher pressures for the $x=0.2$ sample. Again T_{cm} follows the same behavior of T_{co} under pressure.

For all previously known HTS's[6] that display a positive dT_c/dP, T_c initially increases with pressure, passes through a peak and finally decreases at higher pressures. The maximum T_c enhancement ($\Delta T_c^{\max}$) usually decreases for a compound with doping close to the optimal level and is rather small for optimally doped samples. A $\Delta T_c^{\max}$~24 to 30 K in Hg 1:2:$(m-1)$:m is unusually large and nearly independent of the number of the CuO_2 layers per unit cell in the compounds. In fact, $[T_{co}(P)-T_{co}(P=0)]$ seems to be a universal function of P within our experimental uncertainties for all optimally doped Hg 1:2:$m-1$:m samples (inset of Fig. 3). Compared with the otherwise very similar Tl and Bi families, which have a $\Delta T_c^{\max}<10$ K,[6] this large $\Delta T_c^{\max}$ is, indeed, unusual. Since $\Delta T_c^{\max}$ decreases from ~30 K in Hg 1:2:2:3 to ~12 K with moderate Pb doping of $x=0.2$ in Hg(xPb) 1:2:2:3 (Fig. 4), the large $\Delta T_c^{\max}$ may be related more closely to the characteristic of the Hg layer than the CuO_2 blocks which are common to Hg 1:2:$m-1$:m and other HTS's. For example, it may be related to the linear oxygen coordination of Hg, which results in a large number of voids in the Hg planes. These voids may allow a proper modulation doping[22] in Hg 1:2:$(m-1)$:m, which is known to take place in semiconductor heterostructures by introducing carriers to one layer through the donors residing in another layer. Consequently, one may be able to vary the number of carriers in the CuO_2 layers without generating undesired defects and thus to enhance T_c more effectively. Another possibility is due to the proposed[17] van Hove singularities and the associated fine structure near the Fermi surface of Hg 1:2:$m-1$:m. The universal $[T_{co}(P)-T_{co}(0)]$ observed for all members of Hg 1:2:$m-1$:m is intriguing and suggests that layers between the CuO_2 blocks may play an important role in dT_c/dP. No similar data exist for other HTS families for comparison at the present time.

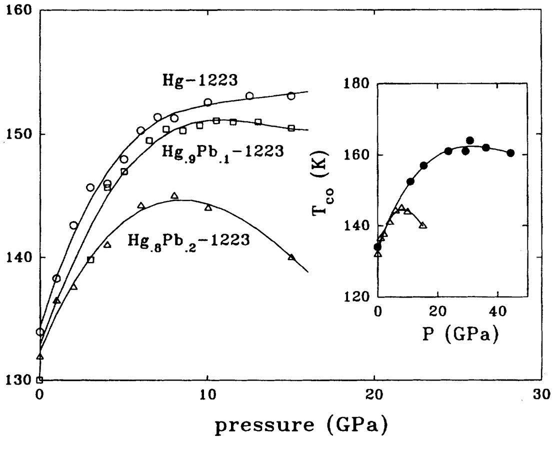

FIG. 4. T_{co} vs P obtained in WC cells for Hg 1:2:2:3 Hg(0.1Pb) 1:2:2:3, and Hg(0.2Pb) 1:2:2:3. Inset: T_{co} vs P for Hg(0.2Pb) 1:2:2:3, WC data; T_{co} vs P for Hg 1:2:2:3, DAC data.

All HTS's are derivable[23] from their corresponding insulating parent compounds through doping. Their T_c initially increases with the carrier concentration (n), passes a peak at the optimal n_o, and finally drops as n continues to increase. While a pressure-induced change in n plays an important role in dT_c/dP,[6] recent studies show[16,24] that it alone is not sufficient to account for the $T_c(P)$ observed. This is particularly true since dT_c/dP often remains positive even for $n>n_o$.

Finally, we would like to comment on the effect of shear stress, which inevitably exists in a QHP environment, on the superconducting transition of a HTS. Shear stress is known[25] to be detrimental to the conventional low-temperature superconductors, most of which have an isotropic structure. For the cuprate HTS's, which have a highly anisotropic layered structure, we propose that shear stress can have a positive effect on T_c. It has been shown[24] from uniaxial stress experiments that stress perpendicular to the CuO_2 plane induces a charge transfer. Its effect on T_c along the c axis (dT_c/dP_c) is n dependent and would be small at an optimally doped level. However, the stress effects along the a and b axes (dT_c/dP_a and dT_c/dP_b) can be of opposite (for $YBa_2Cu_3O_{7-\delta}$) (Ref. 26) or same [for $YBa_2Cu_4O_{8+\delta}$ (Ref. 24)] sign. In a QHP environment, grains of the layered HTS's tend to orient themselves so that the c axis is more likely to be perpendicular to the anvil surface.[27] Thus, shear stress can more effectively vary the interatomic spacing along the CuO_2 layers. A reexamination of previous QHP and HP studies on T_c of HTS's reveals the effects stated above.[28] For an optimally doped sample, although dT_c/dP_c may be small in a rigid band approximation, a large $\Delta T_c^{\max}$ may be detected due to the dT_c/dP_a effect in Hg 1:2:2:3. This implies that, by changing the scattering or coupling between carriers in the CuO_2 layers, T_c may be enhanced more effectively than by just varying n. Therefore, it is conjectured that the high T_c of Hg $1:2:(m1):m$ observed under QHP may be retained most effectively by the combined effects of chemical doping and shear stress. The latter may be achieved, for example, by the epitaxial thin-film technique[29] which has been shown to create a stress of ~5 GPa in the $YBa_2Cu_3O_7$ thin overlayer. It should be noted that the observed irreversible degradation of T_{co} under QHP suggests that undesirable defects were also generated under QHP conditions. The leveling off in the T_c of Hg $1:2:(m-1):m$ at high QHP may be associated with the presence of these defects and, hence, an even higher T_c may be obtainable by optimizing the pressure effect while minimizing the defects.

In summary, a universal large T_c enhancement was observed in Hg $1:2:m-1:m$ for $m=1$, 2, and 3, implying a common origin of HTS in these compounds. A record high temperature of 164 K was reached in Hg 1:2:2:3 at 31 GPa. However, moderate Pb doping drastically depresses the enhancement for all members of the HTS family, suggesting a unique character for the HgO_δ layer. A complete understanding of these observations requires further investigation.

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