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50 K ENHANCEMENT OF T_c BY PRESSURE IN THE Hg-2212 SUPERCONDUCTOR

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The superconducting properties of mercury cuprates are extremely sensitive to compression. The highest transition temperatures obtained up to date have been measured on Hg-1223 at 25–30 Gpa ($T_c \sim 164$ K at the onset) and imply an increase of about 20 K with respect to the ambient pressure T_{c0}. We report here the largest total pressure effect (>50 K over a span of 20 GPa) ever observed for several samples of bi-mercury layer $Hg_2Ba_2(Y_{1-x}Ca_x)Cu_2O_{8-\delta}$ compositions. Different Ca doping levels give different initial T_cs but retain the same strong pressure dependence. The large T_c increase with pressure for all the Hg-based compounds, independently of their doping level, is revealing the existence of a common structural parameter, which identification will be a guide for future synthesis efforts of record-high T_c materials. © 1997 Elsevier Science Ltd. All rights reserved

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High pressure investigations in high temperature superconductors are a helpful tool in order to understand which are the structural parameters that optimize the superconducting critical temperature (T_c) and to determine strategies to obtain higher T_c materials by adequate chemical replacements.

The Hg-12$(n-1)n$ series had shown large pressure effects in its $T_c[T_c(P)]$ with ~150 K at 30 GPa at mid-transition (164 K at the onset) for the $n = 3$ compound [1–3]. The 20 K increase of T_c is accompanied by the shortening of the long apical Cu–O bonds as observed by structural determinations under pressure [4]. One interpretation is that charge transfer from the reservoir block HgO_δ to the conducting CuO_2 planes is increased for these probably underdoped samples, enhancing T_c. As higher pressures are applied, the T_c decreases [3] probably due to an overdoping of the CuO_2 planes. But still there is not a clear explanation of the $T_c(P)$ behavior.

The Hg-2212 compound, member of two mercury-layer series [5–8] is an interesting material to be studied under pressure. There are similarities and differences between the mono-Hg layer and bi-Hg layer compounds. Both contain long apical oxygen distances and in the former the CuO_2 are flat whereas in the latter these layers are buckled. In this paper, we present the first high pressure resistance measurements on the bi-mercury layer compound as a function of temperature [$R(T)$]. We have applied pressures up to 22 GPa on samples with nominal composition $Hg_2Ba_2Y_{0.6}Ca_{0.4}Cu_2O_{8-\delta}$.

The samples were prepared by mixing a Ba_2(Y, Ca)-Cu_2O_z precursor made of high-purity oxides calcinated at 835°C/24 h under oxygen flow, with the stoichiometric amount of HgO necessary to produce $Hg_2Ba_2(Y_{0.6}Ca_{0.4})Cu_2O_{8-\delta}$ samples. The mixtures were placed in gold capsules and reacted at 1.8 GPa/920°C/2 h. The samples were characterized by X-ray powder diffraction, T.E.M., E.D.S, a.c. susceptibility and resistivity measurements.

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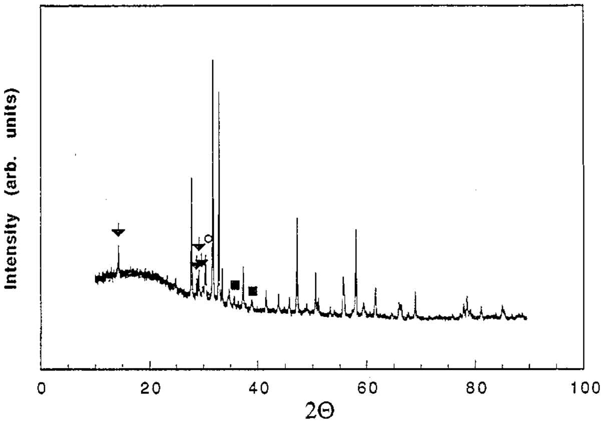

Fig. 1. X-ray powder diffraction pattern for sample Hg-2212 with 40% of nominal Ca content.

High pressure resistance measurements (HPR) were performed with the Bridgman sintered diamond anvil configuration used in [2] in quasi-hydrostatic conditions, on three chips extracted from larger ceramic samples labelled A, B and C. Steatite was used as the pressure transition medium and pyrophillite as a gasket. Pressure was estimated by means of the superconducting transition of lead and the resistance was measured using a standard four contact d.c. technique. Sample's current densities ranged from 0.1 A cm^{-2} to 10 A cm^{-2}.

The X-ray powder pattern of a typical sample is shown in Fig. 1. The sample contained a Hg-2212 phase with lattice parameters $a = 3.855(1)$ Å, $c = 28.94(1)$ Å, together with impurities such as $CaHgO_2$, HgO and CuO, marked in the powder pattern with arrows, circles and squares, respectively. Reflections of the Hg-12$(n-1)n$ phases were not detected. TEM showed that the Hg-2212 phase was well crystallized. No grains of phases of the Hg-12$(n-1)n$ or "123" families were observed. Although the nominal calcium concentration was of 0.4, E.D.S. analysis gave a calcium concentration of 0.15. A.c. susceptibility measurements made on powders show a single superconducting phase with T_c onset at ~40 K and more than a 50% of superconducting volume fraction (Fig. 2).

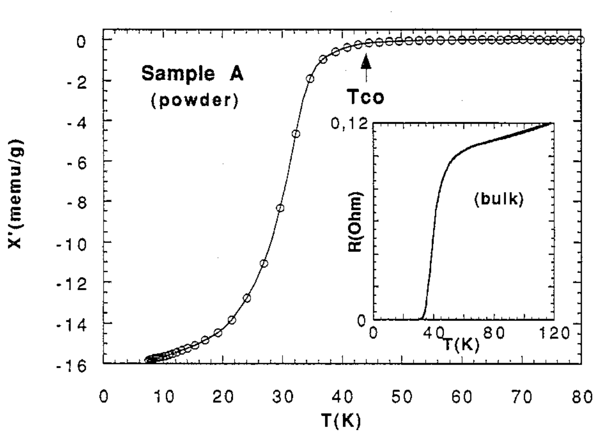

Fig. 2. Powder a.c. susceptibility measurement for Hg-2212 (15% of Ca, sample A) before compression, showing a single-phase with $T_{co} \sim 44$ K. The inset shows the resistivity transition measured on the bulk sample.

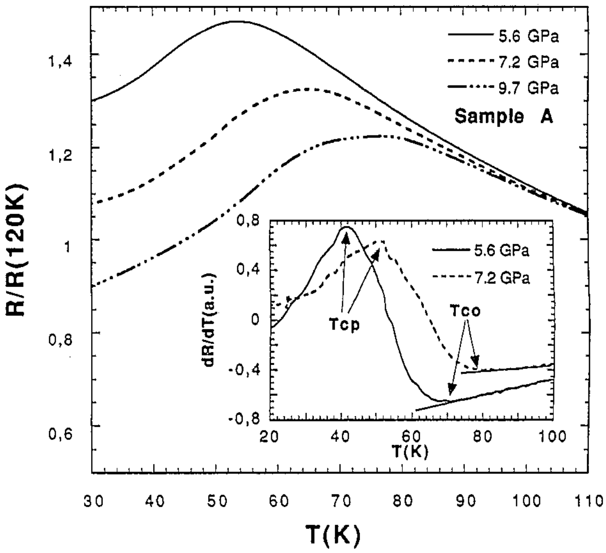

Fig. 3. Superconducting transition of Hg-2212 (15% of Ca, sample A) for some of the applied pressures, monitored by its resistance (normalize to its value at 120 K). The inset shows the slope of these curves and the criteria to define the critical temperatures T_{cp} and T_{co}.

Results of the HPR measurement in samples A, B and C are given in Fig. 3. They show a broad superconducting transition with no percolation path and a non-metallic dependence ($dR/dT < 0$) in the normal state, even though the original bulk sample showed a metallic conduction (shown in the inset of Fig. 2) and more than 50% of superconducting volume fraction when measuring its powder by a.c. susceptibility. Sample degradation during the HPR manipulation and a small amount of non-conducting impurities in grain boundaries would account for this behaviour [7]. The superconducting critical temperature was resolved using both the onset (T_{co}) and the peak (T_{cp}) of the derivative dR/dT (inset of Fig. 3). T_{cp} is ~40% lower than T_{co} and gives the same pressure dependence. We have checked that both T_{co} and T_{cp} are current-independent in order to confirm that they are associated directly to the superconducting phase and not just to the intergrain coupling, which depends on the impurity contents of each sample. Figure 4 shows the variation of T_{co} with pressure [$T_{co}(P)$]. $T_{co}(0)$ values were obtained extrapolating these curves to $P = 0$. Samples A, B and C display different $T_{co}(0)$ values, 45 K, 42 K and 27 K, respectively. These T_c differences could be related either to small differences in the Ca content or to another doping factor, like oxygen

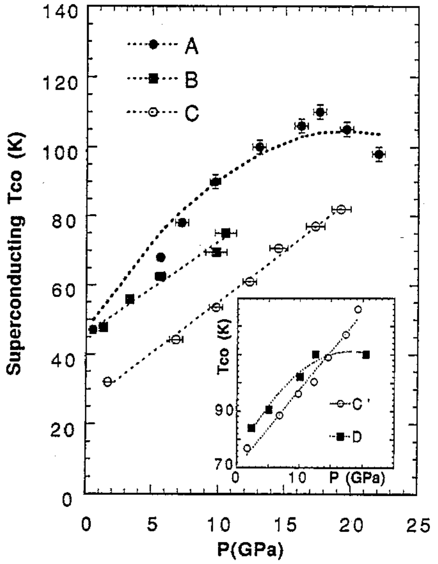

Fig. 4. Superconductivity onset (T_{co}) as a function of pressure for samples A, B and C (~15% of Ca). The inset shows $T_{co}(P)$ for samples C′ and D (~40% of Ca).

stoichiometry. However, heat treatments performed on the samples did not produce any appreciable variation of T_c or lattice parameters. In some of our samples a phase with higher T_c (70 K) but with a small volume fraction, also appeared. The EDS analysis shows a Ca concentration of 0.40 for this phase. The $T_{co}(P)$ dependence for two samples of this phase (labelled C′ and D) is shown in the inset of Fig. 4 and exhibits the same features as that of the 40 K phase. As the increase of the real Ca content rises the T_c, it is clear that the optimum doping is not reached in these samples as a consequence of its low Ca solubility range. When doped with Tl the Ca solubility is increased to $x = 1$ and a maximum $T_c(x) \sim 84$ K is reached [7].

Thus, for all the samples, independently of the real calcium concentration of the phase (in the underdoped region), i.e. of the sample's degree of doping, the pressure dependence of T_c shows the same strong enhancement. The overall increase in T_c can be as high as 65 K (sample A) and in some cases no saturation is observed up the highest accessible pressure of our apparatus [2]. This can be compared with the largest increases observed for other compounds, where an enhancement of 30 K for pressures up to 12 GPa was noticed for the $YBa_2Cu_3O_{7-\delta}$ (underdoped) [9] and the $YBa_2Cu_4O_8$ compounds [10]. We also obtained a positive dT_c/dP with initial values ranging from 2.7–3 K GPa^{-1} (samples B, C, C′, D) to 4.5 K GPa^{-1} (sample A) below 10 GPa.

Large increases of T_c with pressure are a common feature both for the mono-Hg layer series of superconductors [1–3] and the bi-Hg layer compound, as our results state, but this property is present in a much stronger way for the latter compound. The clue for the stabilization of the 150 K phase certainly resides in the understanding as to why the Hg-bearing superconductors are so susceptible to pressure.

In a simplified approach, there are two main reasons that account for the behaviour of T_c under pressure. The first is that there is an increase of charge transfer between the reservoir blocks and the CuO_2 layers, that, if linear with pressure, should transcribe the known inverse parabolic dependence of T_c with carrier concentration onto the $T_c(P)$ dependence. The second reason is an intrinsic structural pressure-dependent factor, non-related with charge transfer, which is held responsible for any observed linear term with pressure.

In this respect it is useful to examine the band structure calculations done for the mono-Hg layer cuprates [10, 11]. In the limit of mercury planes with zero oxygen content, the calculations suggest a doping of the CuO_2 planes by the crossing of the Fermi level of a largely empty band mainly formed from Hg p and apical oxygen p orbitals [7, 12]. In an ionic approach for the extra oxygens, they should just increase the hole concentration of the CuO_2 planes. This is in accordance with the charge transfer assumption.

However, when the oxygen concentration reaches 0.5, band calculations [13, 14] predict that strong covalency appears between the dopant O atoms and Hg atoms. Some antibonding O-p Hg-d states occur in this case above the Fermi energy and the hole doping of the CuO_2 layers is reduced by nearly half of that expected from ionic considerations. Pressure has the effect to shift these states below the Fermi level, increasing the charge transfer to the CuO_2, but at a small rate ($dn/dP < 10^{-3}$ holes GPa^{-1}) [10], that wouldn't account for the overall pressure induced T_c increase. For this case, it will be necessary to consider other mechanism than the charge transfer to explain the $T_c(P)$ relation. As there are still no band calculations for Hg-2212, it would be difficult to tell if the electronic structure will allow the charge doping as an explanation for the increase of T_c with pressure.

We can also analyze our results using a straightforward formulation of the variation of T_c with pressure [15–17], supposing that we have essentially two effects: the variation of carrier transfer dn/dP and an intrinsic T_c change independent of charge transfer, dT_c^i/dP. Let us assume a linear dependence on pressure for $n(P)$ and considering the general expression $T_c(n) = T_c^{\max}(P)[1 - \eta(n_{op} - n)^2]$ we arrive to the following equations for $T_c(n, P)$

$$T_c(n, P) = T_c(n, 0) + \alpha(n)P + \beta(n)P^2, \quad (1)$$

with

$$\alpha(n) = dT_c^i/dP + 2\eta T_c^{\max} dn/dP(n_{op} - n), \quad (2)$$

and

$$\beta(n) = -\eta T_c^{\max}(\mathrm{d}n/\mathrm{d}P)^2, \tag{3}$$

where $T_c^{\max}$ is the maximum T_c obtained with doping for $P = 0$, n_{op} the optimal doping and η a constant related to n_{op} and to the minimum doping for obtaining a superconducting state.

As for our samples the $T_c(P)$ relation is almost linear up to 10 GPa, independently of the doping level, it is obvious, considering expressions (1)–(3) that there is a negligible carrier doping with pressure ($\mathrm{d}n/\mathrm{d}P$). We estimate that $\mathrm{d}n/\mathrm{d}P$ could be as low as 10^{-4} holes GPa^{-1} (for samples C and C′ with $\eta = 83$ and considering the $T_c n)$ dependence of the Tl doped [7] Hg-2212). Then, the large enhancement of T_c observed can be due exclusively to the intrinsic term $\mathrm{d}T_c^i/\mathrm{d}P \sim 3\ \mathrm{K\,GPa}^{-1}$. The $HgBa_2CuO_{4+\delta}$ (Hg-1201) compound showed [18] the same features, even for samples beyond the optimum doping ($\delta \leq 0.27$), with a sudden increase of ($\mathrm{d}n/\mathrm{d}P$) regulated by the oxygen content ($\delta > 0.3$). Band calculations [8] agree with this picture for $\delta = 0$, showing that no charge transfer is obtained for pressures below 5 GPa. Thus, for these materials, depending on its oxygen content, there is a small, if any, pressure-induced charge transfer to the CuO_2 planes from the HgOδ.

In $YBa_2Cu_3O_{7-\delta}$ ($\delta < 0.1$), where there is now a more clear picture of the T_c pressure dependence [19], the observed intrinsic variation is $\sim$0.5–1 K GPa^{-1} [9]. For this material, the decrease of the buckling of the CuO_2 planes under pressure [20] could be correlated with this positive intrinsic effect. Less buckled copper oxide planes empirically give higher T_cs [21]. As in other superconducting compounds [22], as well as in the Hg-2212 samples [6], when Y is replaced by Ca, the buckling of the CuO_2 planes decreases, we would expect in Hg-2212 less buckled layers and more sensitivity to pressure than in $YBa_2Cu_3O_{7-\delta}$.

Experiments done in the LSCO system also showed that the buckling degree was reduced with pressure and it can be correlated with T_c [23]. The most unexpected results for this system are the pressure independent Hall coefficient (up to 1.3 GPa at 60 K) and the nearly constant $\mathrm{d}T_c/\mathrm{d}P$ (2–3 K GPa^{-1}) for the different doping concentrations [24]. So that also in this case, the pressure induced charge transfer is negligible and the linear $T_c(P)$ relation can be related to an intrinsic term associated with the buckling degree.

For the mono-Hg layer series it is not possible to associate the intrinsic term only with the buckling of the CuO_6 octahedras, as pressure increases the buckling [25], producing therefore a negative pressure effect in T_c. Novel reasons would be needed to explain the observed intrinsic positive contribution. Also, reports [1–3, 26, 27], from different groups on the behaviour of Hg-1223 under pressure do not totally agree. Although they coincide in a strong non-linear increase at lower pressures, indicative of some charge transfer, the behaviour above $\sim$10 GPa differs. Some samples show a decrease of the rate of change of T_c without attaining 150 K. This can be attributed to the formation of the $Hg{-}O_{0.5}$ band at high oxygen concentrations and suggests that oxygen doping may not be enough to reach the highest T_c for this material and that it also controls the charge transfer under pressure. Other type of dopants, besides chemical pressure, should be tested to try the stabilization of higher T_cs in Hg-1223.

Thus, the large enhancement of T_c for all the Hg-based superconductors could then be due exclusively to the intrinsic term $\mathrm{d}T_c^i/\mathrm{d}P \sim 1.8\text{–}3\ \mathrm{K\,GPa}^{-1}$, depending on samples particular structural characteristics and assisted with a low charge transfer ($10^{-4} < \mathrm{d}n/\mathrm{d}P < 2 \times 10^{-3}$ hole GPa^{-1}), which is probably regulated by the oxygen content of the sample.

Coming back to the Hg-2212 system, T_cs above 125 K (onset) should be reached by applying higher pressures, before saturation effects appear. The fact that $T_c(P)$ saturates for some of the samples (A, D) is probably related to a considerable increase of the $\mathrm{d}n/\mathrm{d}P$ contribution, which may be controlled by the oxygen content, as for the Hg-1201 compound.

In summary, we have shown a large T_c increase with pressure for the Hg-2212 compound, independently of the doping level of the samples. This rapid enhancement of T_c below 10 GPa, also observed in all Hg compounds, can be viewed within two perspectives. Either we consider that in all these materials we are in the highly underdoped regime, i.e. at the beginning of the parabolic increase in the relation between T_c and carrier density; or we accept that this enhancement corresponds to a linear $T_c(P)$ behaviour indicating a negligible charge transfer and a large intrinsic term.

If the first assumption is correct, it would mean that doping with oxygen is unefficient, as suggested by calculations that predict the formation of a partially unfilled Hg–O covalent band at high oxygen concentration [9]. In this case, other type of doping such as replacement of Ca or Ba by alkaline metals, may perhaps lead to higher-T_cs materials. If we accept the second interpretation, only chemical pressure would possibly produce the same effects.

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