High pressure effects in fluorinated HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$

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We have measured the pressure sensitivity of $T_c$ in fluorinated HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ (Hg-1223) ceramic samples with different F contents, applying pressures up to 30 GPa. We obtained that $T_c$ increases with increasing pressure, reaching different maximum values, depending on the F doping level, and decreases for a further increase of pressure. A new high $T_c$ record (166 K $\pm$ 1 K) was achieved by applying pressure (23 GPa) in a fluorinated Hg-1223 sample near the optimum doping level. Our results show that all our samples are at the optimal doping, and that fluorine incorporation decreases the crystallographic a-parameter concomitantly increasing the maximum attainable $T_c$. This effect reveals that the compression of the a axes is one of the keys that controls the $T_c$ of high temperature superconductors.

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Since the discovery of high $T_c$ superconductors (HTSC) many efforts have been devoted to understand the sensitivity of $T_c$ to the structural parameters. This knowledge can facilitate the determination of the mechanism beneath superconductivity and can provide a way to increase the $T_c$ of these materials. There is now a consensus, considering the correlation between the appearance of the superconducting state with the structural characteristics of the material, that the highest $T_c$’s can be reached if n=3 flat CuO$_2$ planes and small Cu-O in-plane distances (dCu-O=a/2 for flat planes) can be achieved. To reach the maximum $T_c$, the doping level of the CuO$_2$ planes is also an important factor to consider. It was already established that:

$$T_c(n) = T_c^M \left[ 1 - \beta(n - n_{op})^2 \right], \quad (1)$$

where $\beta \sim 83$, n and n$_{op}$ = 0.16 are the doping level and the optimum doping level of the CuO$_2$ planes, respectively, and $T_c^M$ the maximum attainable $T_c$ for a variation of the doping level. High pressure experiments contributed with significant results in this quest. They have shown, particularly for the Hg-based cuprate superconductors, that $T_c$ increases with increasing pressure, following a quadratic law which depends on the doping level of the sample (n), on the pressure-induced charge transfer ($dn/dP$) and on an intrinsic factor ($dT_c^M/dP$). In this phenomenological model, pressure increases linearly the doping level of the CuO$_2$ planes but also increases $T_c^M$. It can be shown that:

$$T_c(n, P) = T_c(n, 0) + aP + bP^2, \quad (2)$$

where

$$a = \left( \frac{dT_c^M}{dP} \right) + 2(n_{op} - n)\beta T_c^M \left( \frac{dn}{dP} \right),$$

and

$$b = -\beta T_c^M \left( \frac{dn}{dP} \right)^2.$$
different fluorine contents. Our results point out the reduction of the $\alpha$-parameter as the key factor that controls the value of $T^M_c$.

All the fluorinated ceramic Hg-1223 samples (Hg-1223F) studied here were synthesized and characterized previously. Resistivity as a function of temperature ($4 \text{ K} \leq T \leq 300 \text{ K}$) for pressures from 4 GPa to approximately 30 GPa was measured for samples with different fluorine contents labelled #1 ($a=3.8496$ Å, $T^{\infty}_{c}(a) \approx 138$ K) and #2 ($a=3.8536$ Å, $T^{\infty}_{c}(a) \approx 135$ K). The high pressure was applied using a quasi-hydrostatic experimental setup, corresponding to a Bridgman configuration with sintered diamond anvils, where pyrophillite is used as a gasket and steatite as the pressure medium that favors quasi-hydrostatic conditions. The superconducting transition of Lead is used to determine the pressure inside the cell. The pressure gradient was estimated from the width of this transition and corresponds to a 5-10% of the applied pressure, for pressures lower than 10 GPa, with a saturation’s value of 1 GPa for higher pressures and up to 30 GPa. A conventional 4 terminal DC technique was used to measure resistivity under high pressure at different temperatures. Electrical contacts were made using thin Pt wires pressed to the sample’s surface by the pressure setup. A well calibrated Cernox thermometer thermally anchored to the anvils ensures a determination of sample’s temperature with an uncertainty lower than 0.2 K for the whole Tc range studied.

The effect of pressure on the resistance of sample #1 can be observed in Fig. 1. A similar behavior was obtained for samples with other F content. Zero resistance is achieved at low temperatures, in the range of 10-60 K depending on the quality of the intergrain coupling of these ceramic samples. By using the temperature derivative of the resistance we can define the onset critical temperature ($T_{co}$), where the derivative departs from its normal behavior, and a peak transition temperature ($T_{cp}$) determined by the peak of the derivative, as can be observed in Fig. 2. The former criterion is usually dominated by thermal fluctuations and corresponds to the formation of small superconducting droplets. This criterion was also used in Ref. 3. The latter is mostly related to the appearance of a bulk superconductivity and gives a numeric value similar to $T^{\infty}_{c}(a)$. For the whole pressure range studied, the sample #1 shows a $T_{co}$ higher than the one reported for the non-Fluorinated Hg-1223 samples. In particular, at 23 GPa a $T_{co}$ of $(166 \pm 1)$ K is obtained, which to our knowledge, is the highest ever reported.

As it is shown in Fig. 8 $T_{co}$ follows a parabolic dependence with pressure which can be well described with Eq. 2.

All the Hg-1223F samples studied here under high pressure have a $T_c$ near the flat maximum observed in the dependence of $T_c$ vs. the $\alpha$-parameter (see Fig. 3 of reference 15). Thus, in principle, these samples are near or at the optimum doping level. If we assume that sample #1 is optimally doped ($T^{#1}_{c}=T^{M}_{c} = 138 \text{ K}$; $n^{#1}=n_{op}$ = 0.16) then, following Eq. 11, sample #2 ($T^{#2}_{c} < T^{M}_{c}$) should have a different doping level ($| n^{#2} - n^{#1} | \gtrsim 0.02$ holes/CuO$_2$). Contrary to this, the fits of the $T_{cp}(P)$ dependence using Eq. 2 indicate that both fluorinated samples have nearly the same linear coefficient ($\sim 1.7 \pm 0.1 \text{ K/GPa}$). If the pressure-induced charge transfer of these samples is similar to the one reported for the Hg-1223 system, this fact is indicating, according to Eq. 2, that both samples have an optimum doping level ($n = n_{op} \pm 0.005$ holes/CuO$_2$). Indeed, the best fits for the $T_{cp}(P)$ curves of samples #1 and #2 give a pressure-induced charge transfer coefficient very similar for both samples $((dn/dP)^{#1} = (1.7 \pm 0.1) 10^{-3} \text{ holes/GPa}$ and $(dn/dP)^{#2} = (1.6 \pm 0.1) 10^{-3} \text{ holes/GPa})$ that, as we supposed, is near the value obtained for the optimally
oxygenated Hg-1223F. The same $dT^M_c/dP$ ($= 1.7 \pm 0.1$ K/GPa) is also obtained, but a different $T^M_c$ value for both samples. According to these results, F incorporation for these samples is modifying essentially their $T^M_c$ while keeping the doping of the CuO$_2$ planes in the optimum doping. In other words, F is varying one of the structural parameters that controls intrinsically the value of $T_c$. F reduces the structural-disorder as the anion occupancy is higher in the fluorinated than in the oxygenated samples, while the doping level is kept low, probably as a consequence of the charge difference between F and O. As the main structural contribution of fluorine incorporation is the reduction of the $a$-parameter, we may conclude that the decrease of the $a$-parameter is one of the fundamental keys to the increase of $T^M_c$.

The high values of $T_c$ obtained under pressure on the Hg-1223F samples are probably the consequence of having a high intrinsic term ($dT^M_c/dP$) and a small pressure-induced charge transfer which prevents a rapid overdoping of the CuO$_2$ planes, even for samples optimally doped. The intrinsic term can be associated with a positive contribution which comes from the reduction of the $a$-parameter.

The dependence of $T^M_c$ for the Hg-12(n-1)n series to chemical variations of the $a$-parameter can be observed in Fig. 3 where fluorine incorporation has gradually extended this curve to lower values of $a$. It should be noted, indeed, that the $T_c(a)$ dependence for the Hg-1223F samples, near or in the optimum doping, seems to follow the linear dependence of the $T^M_c(a)$ curve for the whole Hg series.

This means that samples #1 and #2 have practically the same doping level, but a different $a$-parameter. We may track their differences to the way in which the samples were prepared, as when synthesized, oxygen from the Hg-O layer was extracted as much as possible and then fluorine was then incorporated. The same doping with a different $a$ may be due to a different F-O relation; the sample with smaller $a$ having a higher F to O ratio. The structural refinements introduced by fluorine incorporation into the Hg-1223 structure can then provide valuable data in order to assess the structural sensitivity of the doping mechanism and the origin of the intrinsic dependence of $T^M_c$.

A simple determination of the pressure sensitivity of $T^M_c$ can be performed using the data from the slope of the curve represented in Fig. 3 from the pressure dependence of the structural parameter $d/dP$. Hence, for pressures up to 10 GPa, we determine that $dT^M_c/dP = dT^M_O/dP \sim 10$ K/GPa, which overestimates the experimental value of $\sim 2$ K/GPa. It is clear that the variations of the $a$-parameter cannot fix solely the value of $T^M_c$. A negative contribution of an additional parameter should be considered, which can be possibly related to the increase of the buckling of the CuO$_2$ layers. The small increase of $dn/dP$ for sample #1, easily noticed by the fact that a lower pressure is needed to reach the maximum $T_c$, may indicate the proximity of a sudden change of this parameter for further doping, as was observed from optimally to highly oxygenated Hg-1201 samples.

Therefore, a large pressure-induced overdoping of the...
CuO$_2$ planes can be predicted for the Hg-1223F samples with a lower $\alpha$-parameter than that of samples #1 and #2 ($\alpha \leq 3.8496$ Å). This is indeed what was observed when a further chemical compression was applied by increasing the fluorine content in the Hg-1223F structure. The overdoping and the chemical difficulties to produce small $\alpha$-parameters without increasing the buckling of the CuO$_2$ planes should be overcome in order to obtain higher $T_c$’s than those obtained for the Hg-1223F compound under pressure.

To summarize, we have studied the pressure dependence of $T_c$ for the Hg-1223F compound. In an optimally fluorine-doped sample we have obtained the highest $T_c$ ever measured up to now. At an approximately constant doping concentration, the optimal one, as neatly determined by our pressure experiments, the $T_{cM}^M$ increases with decreasing the $\alpha$-parameter as a consequence of the variation of the fluorine-oxygen ratio. This implies that $\alpha$ plays a major role on the determination of the superconducting state of the HTSC. Further experimental results would be needed to clarify this issue, determining if effectively uniaxial compressions along the $c$ axis would produce minor effects on $T_{cM}^M$.

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