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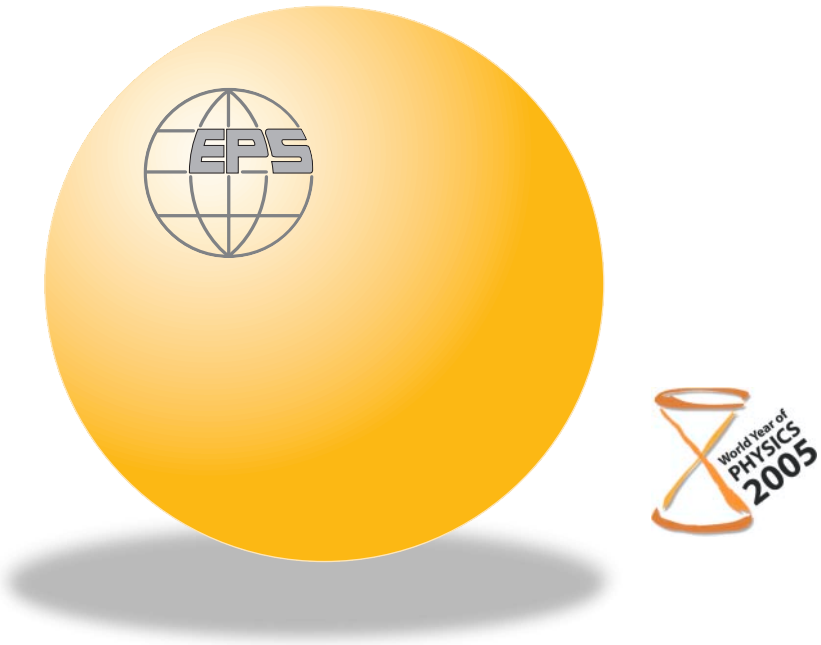

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High-pressure effects in fluorinated $HgBa_2Ca_2Cu_3O_{8+\delta}$

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Abstract. – We have measured the pressure sensitivity of T_c in fluorinated $HgBa_2Ca_2Cu_3O_{8+\delta}$ (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 ($166\,\mathrm{K} \pm 1\,\mathrm{K}$) 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-axis is one of the keys that controls the T_c of high-temperature superconductors.

Introduction. – 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 [1–4]. 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 [3]. 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 [5] that

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

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

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shown, particularly for the Hg-based cuprate superconductors [6–10], 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 ($\mathrm{d}n/\mathrm{d}P$) and on an intrinsic factor ($\mathrm{d}T_c^M/\mathrm{d}P$). In this phenomenological model, pressure increases linearly the doping level of the CuO_2 planes but also increases T_c^M. For doping levels close to the optimum one, it can be shown that [3, 11, 12]

$$T_c(n,P) = T_c(n,0) + AP + BP^2, \tag{2}$$

where

$$A \simeq \left(\frac{\mathrm{d}T_c^M}{\mathrm{d}P}\right) + 2(n_{op} - n)\beta T_c^M \left(\frac{\mathrm{d}n}{\mathrm{d}P}\right),$$

and

$$B \simeq -\beta T_c^M \left(\frac{\mathrm{d}n}{\mathrm{d}P}\right)^2.$$

The question is: what besides doping controls the value of T_c? The origin of this intrinsic factor is still unclear [13, 14]. In some theoretical studies it is argued that T_c^M is regulated by the interlayer [15] or the intralayer [16] coupling, showing in both cases that materials with a larger distance between CuO_2 planes (*i.e.* a larger c-parameter) are generally those with higher values of T_c^M. On the other hand, Marsiglio *et al.* [17] showed that relevant changes on T_c are obtained only when the in-plane Cu-O distances are changed. There are also experimental results [3, 10, 18, 19] that confirm either point of view, indicating that the structural relevant parameter is, on the one hand, the c or, on the other hand, the a-lattice parameter.

The incorporation of fluorine into the structure of the Hg-1223 superconductor [20] and the study of the pressure sensitivity of its T_c gave us an opportunity to contribute experimentally to this search. Fluorine partially replaces the oxygen located in the (HgO_δ layer), producing a reduction of the in-plane Cu-O distance, while the small CuO_2 plane buckling is maintained. As a consequence, the onset of the superconducting transition determined by ac susceptibility ($T_c^{\chi ac}$) increases from 134 K to 138 K for optimally oxygenated and optimally fluorinated compounds, respectively.

In this paper we have studied the pressure dependence of the T_c of the fluorinated Hg-1223 compounds, with different fluorine contents. Our results point out the reduction of the crystallographic a-parameter as the key factor that controls the value of T_c^M.

Experimental. – All the fluorinated ceramic Hg-1223 samples (Hg-1223F) studied here were synthesized and characterized previously [20]. Resistivity as a function of temperature ($4\,\mathrm{K} \leq T \leq 300\,\mathrm{K}$) for pressures from 4 GPa to approximately 30 GPa was measured for samples with different fluorine contents labelled #1 ($a = 3.8496$ Å, $T_c^{(\chi_{ac})} \simeq 138\,\mathrm{K}$) and #2 ($a = 3.8536$ Å, $T_c^{(\chi_{ac})} \simeq 135\,\mathrm{K}$). 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 Pb or Bi 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

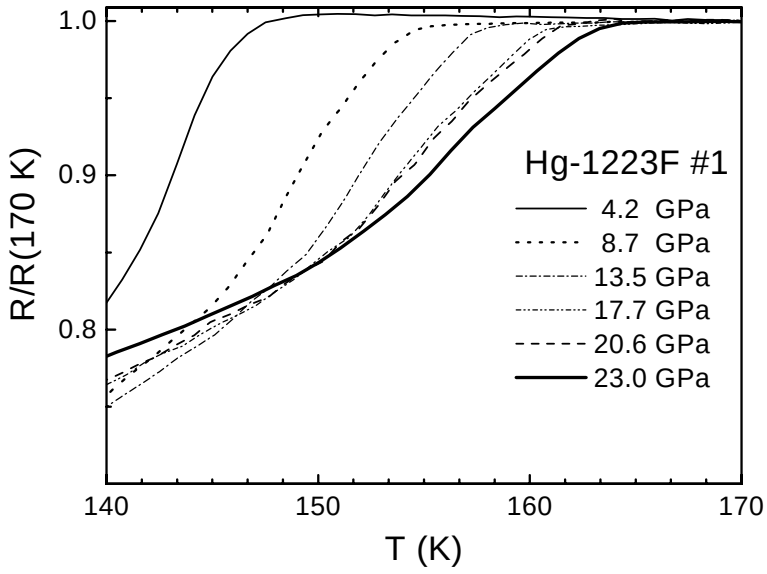

Fig. 1 – Normalized resistance of sample #1 as a function of temperature for different applied pressures.

the anvils ensures a determination of the sample's temperature with an uncertainty lower than 0.2 K for the whole T_c range studied.

Results. – 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 by Gao *et al.* [7] to report, up to now, the highest T_{co} of 164 K at 31 GPa for optimally doped Hg-1223. The latter is mostly related to the appearance of a bulk superconductivity and gives a numeric value similar to $T_c^{(\chi_{ac})}$.

The pressure dependence of both T_{co} and a T_{cp} for the #1 and # 2 Hg-1223F samples can be observed in fig. 3. For comparison, we have also included the data of the non-fluorinated Hg-1223 samples of Gao *et al.* [7]. For the whole pressure range studied, the sample #1 shows a T_{co} and a T_{cp} higher than those reported for the non-fluorinated Hg-1223 samples. In particular, at 23 GPa the highest T_{co} (166 ± 1 K) is obtained. It can also be noticed that T_{co} follows a parabolic dependence with pressure, which can be well described by eq. (2).

Discussion. – 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 a-parameter (see fig. 3 of Lokshin *et al.* [20]). Thus, in principle, these samples are near or at the optimum doping level. If we assume that sample #1 is optimally doped ($T_c^{\#1} = T_c^M = 138$ K; $n^{\#1} = n_{op} =$

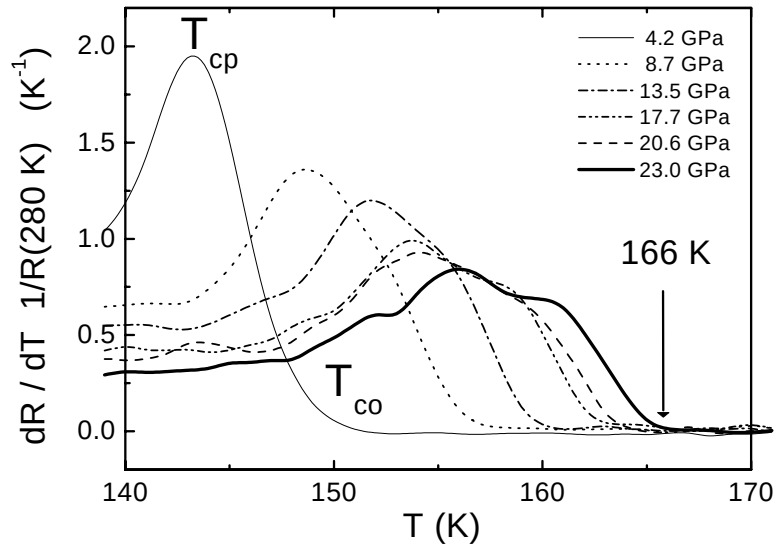

Fig. 2 – Temperature derivative of the resistance of sample #1 at different pressures. T_{cp} and T_{co} illustrate how the peak and the onset transition temperature are defined for $P = 4.2$ GPa, respectively.

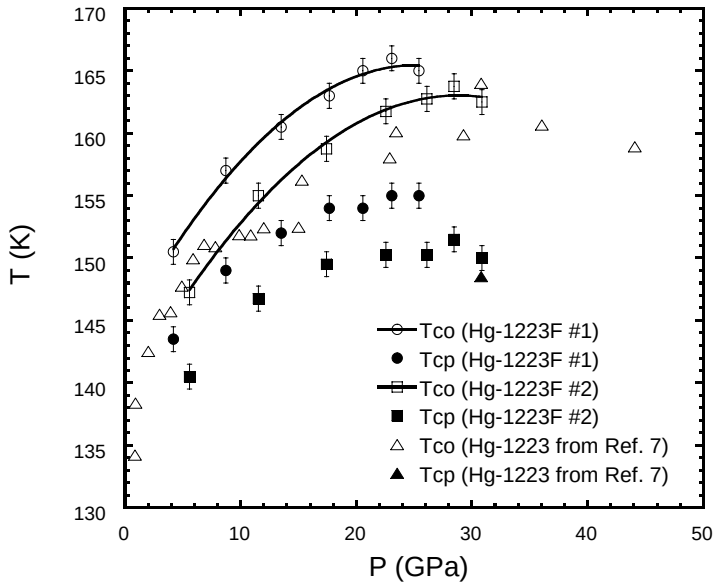

Fig. 3 – Pressure dependence of T_{co} and T_{cp} for samples #1 and #2. For comparison, the data of Gao *et al.* [7] is also included. Lines are fits using eq. (2).

0.16) then, following eq. (1), sample #2 ($T_c^{\#2} < T_c^M$) should have a different doping level ($\mid n^{\#2} - n^{\#1} \mid \sim 0.02$ holes/CuO_2). Contrary to this, the fits of the $T_{co}(P)$-dependence using eq. (2) indicate that both fluorinated samples have nearly the same linear coefficient ($\sim 1.7 \pm 0.2$ K/GPa). The same conclusion can be extracted from the $T_{cp}(P)$ data. If the pressure-induced charge transfer of these samples is similar to the one reported for the Hg-1223 system, this fact indicates, 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 $T_{co}(P)$ curves of samples #1 and #2 give a pressure-induced charge transfer coefficient very similar for both samples [$(dn/dP)^{\#1} = (1.7 \pm 0.1)\ 10^{-3}$ holes/GPa and $(dn/dP)^{\#2} = (1.6 \pm 0.1)\ 10^{-3}$ holes/GPa] that, as we supposed, is near the value obtained for the optimally oxygenated Hg-1223. [21] The same dT_c^M/dP ($= 1.7 \pm 0.2$ K/GPa) is also obtained, but a different T_c^M value for both samples. According to these results, F incorporation for these samples is modifying essentially their T_c^M 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_c^M.

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_c^M/dP) and a small pressure-induced charge transfer which prevents a rapid overdoping of the CuO_2 planes, even for samples optimally

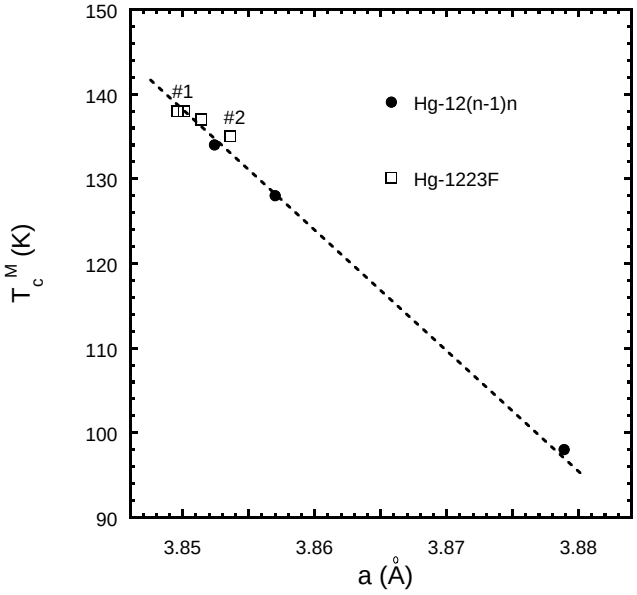

Fig. 4 – Structural sensitivity of the maximum critical temperature T_c^M on the chemical variation of the a crystallographic parameter for the optimally doped $n = 1, 2$, and 3 members of the Hg-12$(n-1)n$ series, determined by X-Ray diffraction refinements. Intermediate points for other Hg-1223F samples than sample #1 and sample #2 are also included. The dashed line is a guide to the eye.

doped. The intrinsic term can be associated with a positive contribution which comes from the reduction of the a-parameter.

The dependence of T_c^M for the $n = 1, 2$, and 3 members of the Hg-12$(n-1)n$ series on chemical variations of the a-parameter can be observed in fig. 4, where the increasing fluorine incorporation to the $n = 3$ member has gradually added more points to this curve [20], extending its range to lower a values. It should be then noted, indeed, that the $T_c(a)$-dependence for the Hg-1223F samples with fluorine contents between sample #1 and sample #2 seems to follow the same linear dependence of the $T_c^M(a)$ curve for the $n = 1$, 2 and 3 members of the Hg series. This fact reinforces the conclusion extracted from their $T_{co}(P)$-dependence, which indicated that these samples were optimally doped in spite of their different fluorine contents or their 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 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_c^M.

A simple determination of the pressure sensitivity of T_c^M can be performed using the data from the slope of the curve represented in fig. 4 and from the pressure dependence of the structural parameters [22]. Hence, for pressures up to 10 GPa, we determine that $\frac{\mathrm{d}T_c^M}{\mathrm{d}P} = \frac{\mathrm{d}T_c^M}{\mathrm{d}a}\frac{\mathrm{d}(a)}{\mathrm{d}P} \sim 10\,\mathrm{K/GPa}$, which overestimates the experimental value [10, 23, 24] of $\sim 2\,\mathrm{K/GPa}$. It is clear that the variations of the a-parameter cannot fix solely the value of T_c^M. 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 [20, 25]. The small increase of $\mathrm{d}n/\mathrm{d}P$ 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 [8].

Therefore, a large pressure-induced overdoping of the CuO_2 planes can be predicted for the Hg-1223F samples with a lower a-parameter than that of samples #1 and #2 ($a \leq 3.8496$ Å). This is indeed what was observed when a further chemical compression was applied by increasing the fluorine content in the Hg-1223F structure [20]. The overdoping and the chemical difficulties to produce small a-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, T_c^M increases with decreasing a-parameter as a consequence of the variation of the fluorine-oxygen ratio. This implies that a 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_c^M.

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