Effect of hydrostatic pressure on $HgBa_2Ca_2Cu_3O_{8+\delta}$ superconductor doped with Re

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Samples of the $Hg_{1-x}Re_xBa_2Ca_2Cu_3O_{8+\delta}$ superconductor (Hg, Re-1223), with varying rhenium (Re) content ($0.00<x<0.30$) were produced with the help of a thermobaric analysis, which can monitor the total pressure inside the quartz tube during the synthesis at high temperatures. The sample quality was verified by means of Rietveld analysis of the x-ray-diffraction data, ac susceptibility, and by ac resistance measurements. The same procedure was used to prepare all the samples with different Re content (reduction of oxygen content in the precursor $Re_xBa_2Ca_2Cu_3O_{7+\delta}$ and the increase of the mercury partial pressure inside the quartz tube). The Re atoms lead to a reduction of the lattice parameter along the *c* axis with a decrease of the lattice volume which is equivalent to an applied hydrostatic pressure of 1 GPa. The aim of this work is a comparative and quantitative study of the chemical and external hydrostatic pressure on the Hg, Re-1223 system. The samples with $0.10<x<0.25$ showed strong magnetic shielding effects and low residual resistance. Resistance measurements as a function of temperature display an increase of the superconducting transition temperature T_C with applied hydrostatic pressure. The $\partial T_C/\partial P$ value depends strongly on the Re doping and the sample with the Re content $x=0.18$ showed the largest measured $\partial T_C/\partial P=6.8(2)$ K/GPa. We argue that the Re concentration does not increase T_C in the same way as external hydrostatic pressure but provides a strong influence on the intrinsic term proposed by Almasan *et al.* [Phys. Rev. Lett. **69**, 680 (1992)].

I. INTRODUCTION

Seven years after the discovery of high-temperature superconductivity (HTSC)[1] the highest T_C of 134 K, at ambient pressure, was recorded in the new family of mercury-based superconductors for $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Ref. 2) compounds. This mercury family, which chemical formula is represented by $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ with $n=1,2,3\ldots$ [Hg-12$(n)(n-1)$], was found in 1993 by Putilin *et al.*[3] Initially, it was possible to stabilize the pure phase of the Hg-12$(n)(n-1)$ series only by sintering at pressures in the order of a few GPa and at temperatures close to 850 °C.[4,5] Later, it was shown that Hg-1223 can be prepared as main phase under normal pressure condition by controlled vapor-solid reaction or by substituting cations with higher valence for Hg.[6–12] This is the case for rhenium (Re) substitution at the Hg site, which allows the preparation of $(Hg, Re)Ba_2Ca_{n-1}Cu_nO_y$ under normal pressures in a quartz tube.

In our previous paper,[13] the synthesis of $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+\delta}$ samples was optimized by the thermobaric analysis (TBA),[14] which is used in the present work to improve the preparation of the $Hg_{1-x}Re_xBa_2Ca_2Cu_3O_{8+\delta}$ samples ($0.00<x<0.25$). In the same way, the oxygen content present in the samples $Hg_{1-x}Re_xBa_2Ca_2Cu_3O_{8+\delta}$, was optimized by controlling the pressure during the synthesis.[15] The knowledge of the best thermal treatment parameters also helped to reduce the amount of $CaHgO_2$ impurity[16] present in the samples.

The physical pressure effects on the Hg-12$(n-1)(n)$ series have been intensively studied since their discovery in 1993,[3] despite the initial difficulty related with their preparation which involves high-pressure sintering. Single crystals grown under normal pressure have been available since 1994.[17,18] One of the remarkable features revealed by high-pressure studies on Hg-1223 is the increase of T_C reaching an increment of the order of 30 K compared to T_C at ambient pressure.[19] Gao *et al.*[20] found that T_C increases in the pressure range of 0.0–2.0 GPa with a rate of 1.7 K/GPa, which in his opinion corresponds to the behavior of an underdoped sample. Other measurements with optimally doped samples up to a higher pressure value (≅ 15 GPa) confirm that T_C increases with a lower rate, reaching 153 K at 15 GPa (Ref. 21) and the maximum T_C as function of pressure [$T_C(P)$]

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rises to 164 K at 30 GPa.[20,22,23] The characteristic $T_C(P)$ curve is an inverted parabola with a linear behavior at low pressures and reaching a maximum in T_C at higher pressure. A linear $\partial T_c/\partial P$ dependence close to 4 K/GPa for the optimally doped samples was found in the low pressure range 0–1.0 GPa.[24,25] This initial $\partial T_c/\partial P$ behavior has a clear dependence on the oxygen content or hole concentration of the sample. Therefore, the control of the oxygen content in the synthesis process is necessary in order to study the $\partial T_c/\partial P$ value associated to the optimally doped samples.

Due to such special properties of the Hg-1223 family and the fact that doping with Re provides an effective chemical pressure, we decided to study the external hydrostatic pressure effect on the Hg, Re-1223 samples by resistance and susceptibility measurements. The influence of the external hydrostatic pressure on the Hg, Re-1223 samples is discussed together with the chemical pressure effects.

II. EXPERIMENTAL PROCEDURES

A. Synthesis procedure

The synthesis of the samples involves as the first step the preparation of the $Re_xBa_2Ca_2Cu_3O_{7+\delta}$ precursor. Initially, $Ba_2Ca_2Cu_3O_{7+\delta}$ (99.9%-PRAXAIR) and ReO_2 (99%-Aldrich) powders were weighted in $1:(x=0.05,0.10,0.15,0.18,0.20,0.25)$ molar ratio. The powder mixture was kept at 930 °C for 10 h. The produced precursor was post-annealed in an Ar (90%)-O_2(10%) gas flux composition[15] with a controlled flow rate using a Quanta Chrome Inc. gas mixer. All precursors were prepared under 1 bar (total pressure) at the same partial oxygen pressure $P_{O(2)}=0.10$ bar.

The $Hg_{1-x}Re_xBa_2Ca_2Cu_3O_{8+\delta}$ samples were synthesized from a stoichiometric mixture of $(1-x)$ HgO (99%, Aldrich) and $Re_xBa_2Ca_2Cu_3O_{7+\delta}$ precursor. Samples with six different Re contents ($x=0.05$, 0.10, 0.15, 0.18, 0.20, and 0.25) were prepared by using the TBA (Ref. 14) with filling factor ff$=0.70$ g/cm^3.[13] The heating was performed with a rate of 300 °C/h up to 700 °C, changed to 120 °C/h until 860 °C was reached[16,26] and kept for 10 h at this temperature. Finally, the samples were cooled to room temperature with 120 °C/h.

B. Sample characterization methods

Powder x-ray-diffraction patterns (Cu-$K\alpha1$) were recorded with a Rigaku D-MAX 2000 diffractometer and the Rietveld analysis[27,28] was performed with the DBWS program.[29]

For the magnetic characterization of the compounds the samples were used in powder form. The pellets were grounded in an agate mortar and dried in an oven in N_2 atmosphere at 105 °C for 1 h. After the latter procedure, the powder was cooled in a dry box during 1 h and mechanically sifted in order to get particles sized below 65 μm.

The ac susceptibility at ambient pressure was measured with a homemade calibrated and automated device using a driving field $H_{ac}=8$ A/m and a frequency $\nu=500$ Hz.[30,31] The induced voltage in the astatic pair of pickup coils was detected by a Lock-In-Amplifier 5210, dual phase, EG&G. Superconducting quantum interference device measurements confirm the ac susceptibility results.

The resistance measurements were made using a Linear Research Inc LR-700 ac bridge at a frequency $\nu=16$ Hz with an ac current $I_{ac}=100$ μA. The resistance at room temperature shows the same value after thermal cycling confirming the good quality of the contacts.

For both measurements (ac susceptibility and ac resistance) a Lake-Shore temperature controller, model 310, was used to set the temperature detected with a calibrated GaAlAs-sensor (GAL 8957).

In order to compare the ac resistance measurement results at ambient pressure, all samples were cut to slabs of $2\times2\times12$ mm^3. The electric contacts on the samples were made with copper wires fixed with DuPont silver conductive paint. The distance between the voltage contacts was 2 mm.

C. Resistance and susceptibility measurements under hydrostatic pressure

The resistance under pressure was performed in a BeCu piston-cylinder cell, similar to the one used in other works,[32,33] with a *n*-pentane-isoamyl alcohol mixture (1:1) as pressure medium providing hydrostatic conditions. Room-temperature pressure was measured by a manganin manometer. The pressure change upon cooling due to thermal contraction effects was calibrated considering the Thompson[34] procedure. The temperature dependence of the resistance at several pressures (0.0–1.0 GPa) was measured by a standard four-probe method on slabs of $0.7\times1.5\times5$ mm^3. The resistance measurements were made using the LR-700 ac bridge at $\nu=16$ Hz and with $I_{ac}=100$ μA. A calibrated GaAlAs sensor (GAL8957) and a Lake Shore temperature controller, model 340, were used to set the temperature. The superconducting transition temperature T_{cd} was determined from the variation of resistance R with temperature for all the pressure values. T_{cd} was defined as the intersection of the tangent through $\partial R/\partial T$, where the $\partial^2R/\partial T^2$ has the highest negative value, with the extrapolation of the normal-state behavior just above $T_{C\text{onset}}$.[35]

The ac susceptibility under pressure was measured in a diamond-anvil cell.[36–38] Hydrostatic conditions were obtained with a methanol-ethanol mixture (4:1) in a pressure cavity of 0.4 mm diameter of a CuBe gasket prepressed to 0.3 mm. The pressure was detected by a superconducting manometer (Pb, 99.9999%, Koch-Light-Lab.) placed in the gasket hole next to the sample. The primary coil (200 turns) and the astatic pair of pickup coils ($2\times$ 470 turns) were produced with copper wire of 45 μm diameter. An additional compensation coil was used to trim the offset. The ac susceptibility was measured with a driving field $H_{ac}\approx200$ A/m and a frequency $\nu=483$ Hz. The induced voltage in the pickup coil was measured using a Stanford SR 810 Lock-In amplifier. In order to hold the amplitude of the ac field constant over the whole temperature range and to minimize the noise, a special current source (Rahf Co) was used, leading to a signal-to-noise ratio better than 10:1. A platinum resistance (Pt-100) and a Conductus LTC-20 temperature controller were used for the high-temperature range (Hg, Re-1223). For the low-temperature range (Pb), a ruthenium oxide resistance, an AVS-45 Automatic Resistance Bridge and a modified Thor 2020 ramp heater were used. We observed the changes on $T_{C\text{onset}}$ of the Pb sample to verify the pressure.

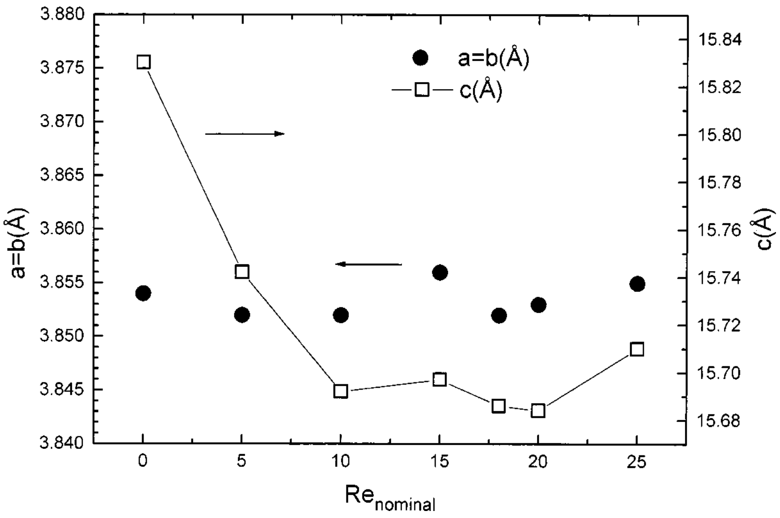

FIG. 1. The variation of the lattice parameters for the $Hg_{1-x}Re_xBa_2Ca_2Cu_3O_{8+\delta}$ samples as a function of the different nominal Re content. The left axis refers to the *a, b* unit-cell parameters (tetragonal $P4/mmm$ space group symmetry) and the right one to the *c* parameter. The parameters were determined by Rietveld analysis of the x-ray powder-diffraction patterns.

$T_{C\mathrm{onset}}$ was also used as the criterion of critical temperature for the probed $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+\delta}$ sample.

III. RESULTS AND DISCUSSION

A. Sample characterization

Figure 1 displays the lattice parameter variation with the Re content. The left and the right axis are related with the *a*, *b* and *c* parameters, respectively. The parameters of the Hg-1223 compound without Re are an average taken from Ref. 19. The other parameters were obtained from our samples by Rietveld analysis taken into account the results of Chmaissen *et al.*[39] and considering the $P4/mmm$ space-group symmetry. The details of the fit quality are listed in Table I.

The Re ion in fact does substitute the Hg ion in the $Hg_{1-x}Re_xBa_2Ca_2Cu_3O_{8+\delta}$ compound. It is surrounded by the usual four oxygen ions located in the HgO plane and two extra oxygen neighbors, above and below, completing the octahedral coordination. This kind of structural analysis was already done by Kishio *et al.*[40] for the $Hg_{0.75}Re_{0.25}Ba_2Ca_2Cu_3O_{8+\delta}$ sample, in agreement with Chmaissen *et al.*,[39] concerning the number of oxygen coordination for the Re ion. The increase of the Re concentration from $x=0.05$ up to $x=0.10$ decreases the *c* parameter, while the *a* and *b* parameters remain almost constant. Therefore, there is a reduction of the cell volume when the Re content increases up to 10%, while for $x=0.10$ up to 0.25 the content yields no significant variation of the lattice parameters.

Table II shows the fraction of the other phases, as $Ba_4CaCu_3O_y(CO_3)$, $BaCuO_{2+y}$, $HgCaO_2$, $Ca_{0.85}CuO_2$,[41] for each sample with different Re content. The results are in agreement with Reder *et al.*[42] and no signature of the Hg-1212 phase was observed. Taking into account the phase distribution and the stoichiometric conservation, it is clear that there was a Re content increment on the Hg, Re-1223 phase when it is compared with the initial nominal composition. Therefore, as we have shown,[43] the Hg, Re-1223 phase is optimized when the sample is produced by quartz tube method with a filling factor ff$=0.70$ g/cm^3 (Ref. 13) and the precursor is treated with low oxygen partial pressure.[15]

X-ray-diffraction pattern also revealed the reduction of $CaHgO_2$ in the samples suggesting that the reduction of oxygen content of the precursor ($Re_xBa_2Ca_2Cu_3O_{7+\delta}$) and the concomitant increase of the partial mercury pressure reduce the amount of $CaHgO_2$ in the Hg system, i.e., it led to an improvement of the superconductor formation phase.[16]

B. ac susceptibility

Figure 2 shows the temperature dependence of the ac magnetic susceptibility data at ambient pressure with different Re contents. The measurements were done on powder samples with controlled size smaller than 65 μm, chosen in order to reduce the influence of intergrain magnetic shield-

TABLE I. The lattice parameters carried out by Rietveld analysis (Refs. 27–29). For the Hg-1223 without Re case it was written using the average of Ref. 19. The Re$_{\mathrm{nom}}$ (nominal) values take into account only the initial stoichiometric of the samples. The *S* parameter is equal to a ratio R_{wp}/R_{exp} and shows the goodness-of-fit.

Re$_{\mathrm{nominal}}$	*a,b* (Å)	*c* (Å)	R_{wp}	R_{exp}	$S=R_{wp}/R_{\mathrm{exp}}$
0%	3.854(2)	15.835(9)			
5%	3.8536(6)	15.742(4)	18.6%	9.42%	1.97
10%	3.8513(2)	15.692(2)	20.3%	7.29%	2.79
15%	3.8563(5)	15.697(3)	21.5%	6.05%	3.56
18%	3.8519(6)	15.686(3)	19.1%	4.51%	4.23
20%	3.8534(3)	15.684(3)	22.0%	5.40%	4.07
25%	3.8548(8)	15.710(4)	23.0%	5.34%	4.30

TABLE II. The ratio among different phase distribution, as obtained from the Rietveld analysis, presents in the each different Re content. It was used in Refs. 39–41 to choose the Rietveld initial parameters of the $Ba_4CaCu_3O_y(CO_3)$, (412 C) and the Hg/Re-1223 phases.

Re$_{\mathrm{nom}}$	Hg,Re-1123	$CaHgO_2$	412C	$Ca_{0.85}CuO_x$	$BaCuO_{2+x}$
5%	86.0(5)	4.6(5)	1.0(4)	2.3(6)	3.9(5)
10%	82.7(6)	5.7(5)	0.8(5)	3.0(5)	5,6(5)
15%	95.8(3)	1.1(2)	0.9(3)	0.9(3)	1.2(3)
18%	94.8(3)	1.2(2)	0.8(2)	0.8(2)	1.4(2)
20%	88.9(4)	5.4(3)	1.5(3)	1.7(2)	2.5(3)
25%	85.3(6)	6.4(5)	1.6(5)	2.2(5)	3.2(5)

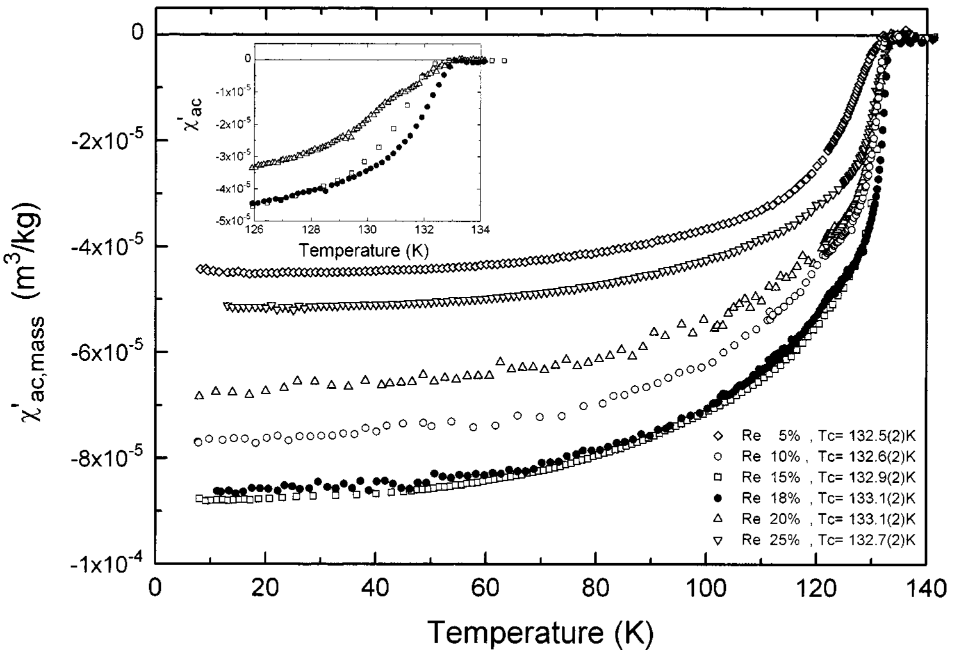

FIG. 2. The magnetic ac susceptibility of the different samples in powder form. The insert reveals the sharper onset of the superconducting transition of the Re 18% as compared with Re 15% and Re 20% samples.

ing. The maximum shielding for all powder samples occurs close to 40 K and the stronger magnetic shielding is obtained with samples having $0.10<x<0.25$ Re content. As can be seen in the inset, the $x=0.18$ (Re 18%) content shows the sharpest onset of the superconducting transition.

The ac susceptibility signal can be divided into a real and an imaginary part, $\chi_{\mathrm{ac}}=\chi'_{\mathrm{ac}}+i\chi''_{\mathrm{ac}}$. The χ'_{ac} corresponds to the magnetic shielding, and the χ''_{ac} is related to a dissipation process. Considering the dissipation component χ''_{ac}, the intragrain region is associated with the low-angle discordance defects between crystal planes, while the intergrain one is associated with junctions between the grain regions. In the samples with pellet shape, the χ''_{ac} signal value reveals the influence of intergrain and intragrain component on the magnetic shielding. Considering the previous measurements of the χ''_{ac} signal value for all powder samples and the Kramers-Kronig relations,[44] it can be estimated that only 20% of the maximal magnetic shielding, shown in χ'_{ac} at 10 K, is due to the intergrain effect. Therefore, basing on the models of Bean[45] and Kim,[46] it can be concluded that samples with $0.10<x<0.20$ Re content show the higher critical current I_C, and this result is in agreement with the magnetic measurements of Reder *et al.*[42]

C. The ac resistance

Figure 3 shows the variation of the resistance with temperature at ambient pressure for all samples. Above the transition temperature, low resistance values were found for samples in the $0.10<x<0.25$ Re doping range, in agreement with the stronger magnetic shielding found in the ac susceptibility measurement. The $x=0.18$ (Re 18%) sample shows the lowest normal-state resistance as well as the lowest residual resistance (metallic behavior). The temperature at which the resistance reaches its lowest value varies with the Re content. The derivation $\partial R/\partial T$ for samples with $x=0.15$ and 0.18 shows a maximum at 133 K and the normal resistance displays metalliclike behavior (linear temperature dependence of the resistance). Out of the $0.15\leqslant x\leqslant 0.20$ range, the value of the resistance in the normal state is 100 times higher and there is no signature of the metalliclike temperature dependence.

D. The ac resistance and susceptibility under pressure up to 1 GPa

The typical temperature variation of the resistance under different pressures up to 0.92 GPa for $\mathrm{Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+\delta}}$ (Re 18%) is shown in Fig. 4, indicating the expected increase of T_C with hydrostatic pressure. In order to define the transition temperature, we adopted the criterion which is based on the different pressure dependencies of the intergrain and intragrain part of the $\partial R/\partial T$ curve.[47] Following the arguments in the Ref. 47, we decided to use only the maximum of the intragrain part of the $\partial R/\partial T$ curve, which has a small transition width Δ, as a definition of T_C. A value of $\Delta\approx 3$ K was obtained for the sample with the optimum Re content (Re 18%) from the fits of $\partial R/\partial T$ with two Lorentzian curves.

The results of the ac susceptibility measurements of the Re 18% sample under pressure are shown in Fig. 5. The pressure dependence of $T_{C\mathrm{onset}}$ was plotted in Fig. 6 (open square) together with the ac resistance data. At low pressures, the data of both methods agree. Unfortunately, no ac susceptibility data at higher pressure were available until now, since our diamonds were damaged during this experiment.

Under similar conditions, the resistance for five different Re samples and the variation of the critical transition temperature with hydrostatic pressure were measured, and the results are shown in Fig. 6.

As can be seen in Fig. 6, despite the fact that the samples with $x=0.15$ and $x=0.18$ are not too much different with respect to variation of resistance and susceptibility with temperature, they show a different response to hydrostatic pressure. Samples with $x=0.05$ and 0.15 show an increase of T_C with pressure similar to the one reported by Chu *et al.*[21] for

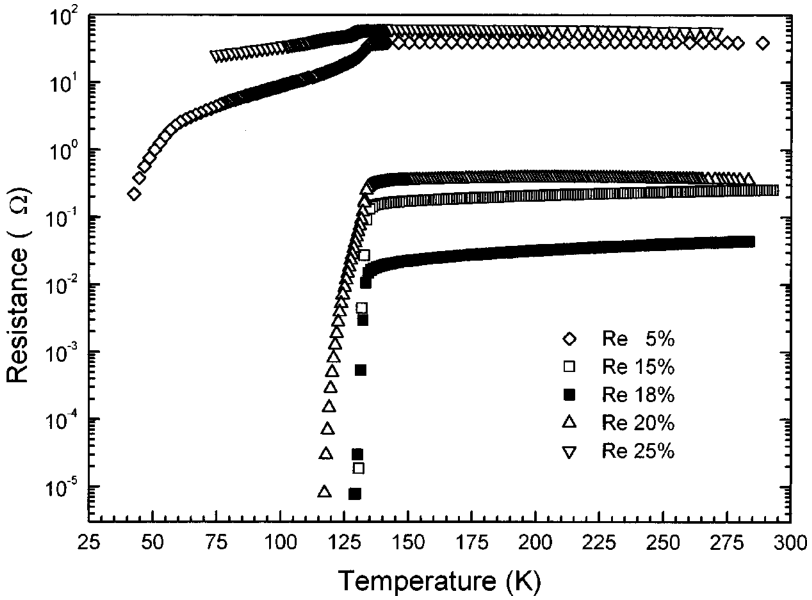

FIG. 3. The resistance of the sample pellets as a function of temperature measured by four-probe ac method. The Re 18% sample shows the lowest resistance value and a metalliclike behavior.

Hg-1223 without doping. A linear fit to the data of the Re 18% sample yields $\partial T_C/\partial P = 6.8(2)$ K/GPa, which is probably one of the largest values reported. We will discuss more about this important feature further below.

E. Discussion

The chemical and external hydrostatic pressure

As shown in our previous work[43] for a $Hg_{0.95}Re_{0.05}Ba_2Ca_2Cu_3O_{8+\delta}$ sample, there is no agreement between external hydrostatic pressure and chemical pressure when only the relative volume reduction is taken into consideration. In this case, the volume compressibility for Hg-1223 compound ($\kappa_v \approx 9 \times 10^{-3}$ GPa) (Ref. 48) was assumed to be the same for the $Hg_{0.95}Re_{0.05}Ba_2Ca_2Cu_3O_{8+\delta}$ (Re 5%). Therefore, an external hydrostatic pressure of about 0.9 GPa leads to a volume reduction $\Delta V/V_0 \approx -0.8\%$ in the Re 5% sample, and such a volume change corresponds to $\Delta T_C \approx 3$ K for external hydrostatic pressure at optimal oxygen doping. On the other hand, in Fig. 1 the x-ray Rietveld analysis already indicates a volume reduction of about 0.4% in the structure of the Hg, Re-1223,[40,42] when the Re content varies from $x = 0.05$ up to 0.10. However, no change in T_C is observed (ac susceptibility, Fig. 2). Thus, it seems that an isotropic decrease of the unit cell (external hydrostatic pressure) leads to an increase of T_C, while the anisotropic decrease of the *c* axis alone does not change T_C. Such nonequivalent behavior between external hydrostatic pressure and chemical pressure has already been found in other systems.[32,41] Therefore, the change in volume is not the only important factor to influence T_C, and this information may need to be taken into account in theoretical models.

It is now generally accepted that an applied external pressure *P* induces a charge transfer (PICT) to the CuO_2 planes, which produces a change in T_C.[49–54] However, since T_C can increase above the optimal doping $T_C^{\max}$, it is clear that another pressure effect, probably due to structural changes, is present and this is known as ‘‘*intrinsic effect*.’’ Thus one assumes, for a given compound with a charge density or hole concentration *n*, an expansion of $T_C(n,p)$ in powers of *P*

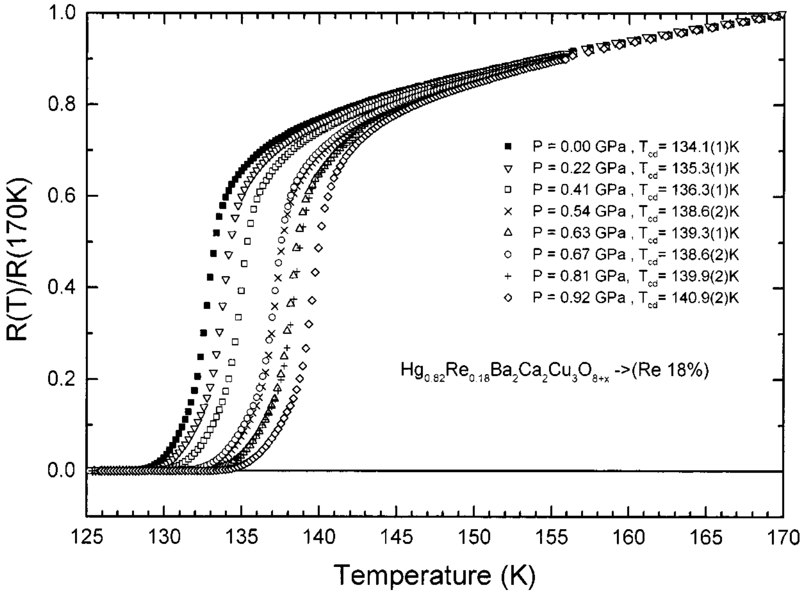

FIG. 4. The pressure dependence of the normalized resistance vs temperature, using the four-probe ac resistance method (Re 18%).

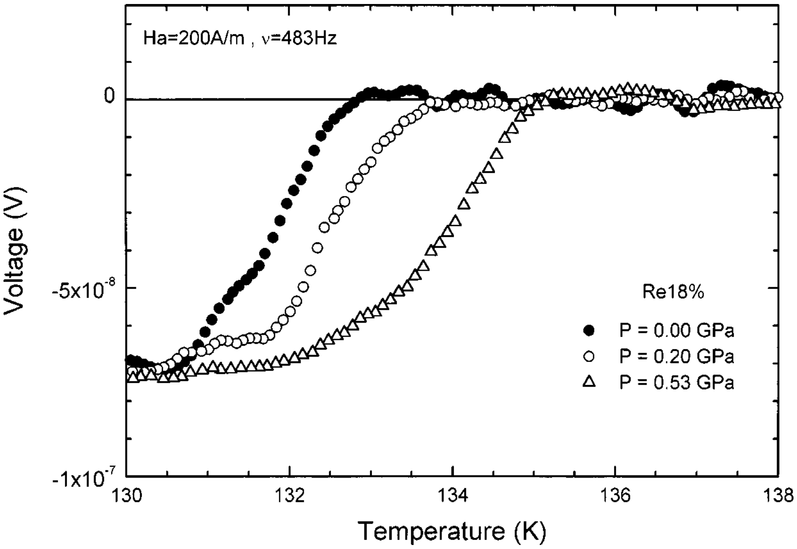

FIG. 5. The ac susceptibility of the Re 18% sample at different pressures.

where the linear coefficient (on the pressure) is given by[51–54]

$$dT_C/dP=\partial T_C^i/\partial P+[\partial T_C/\partial n][\partial n/\partial P], \qquad (1)$$

where $\partial T_C^i/\partial P$ is the intrinsic term and $[\partial T_C/\partial n][\partial n/\partial P]$ is attributed to PICT. Both $\partial T_C^i/\partial P$ and $\partial n/\partial P$ depend on the given compound. The derivative $\partial T_C/\partial n$ may be estimated phenomenologically through the T_C-x-n diagram for $P=0$ which satisfies an inverse *''universal''* parabolic behavior given by the following equation:

$$T_C(n)=T_C^{\max}[1-\eta(n-n_{\mathrm{op}})^2], \qquad (2)$$

where $T_C^{\max}$ is the maximum $T_C(n)$ at the optimal doping n_{op}. Concerning the intrinsic term, there is no theory about its origin, despite some attempts that have been made to relate it with changes in the phenomenological attractive potential of an extended Hubbard model.[53,54]

As can be seen from Fig. 4, our sample $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+\delta}$, Re 18%, has nearly the same $T_C\approx 133$ K as the pure optimal doped Hg-1223. This result seems to indicate that the addition of Re does not produce a detectable charge transfer. If this is true for every doping regime (or hole content), it can be assumed that the Re-doped compounds have the same $P=0$ parabolic $T_C(n)$ of the pure Hg-1223 and consequently the same $\partial T_c/\partial n$.

Figure 6 shows an unusual high $dT_C/dP=6.8$ K/GPa, at low pressures for our Re 18% sample (starting at 133 K), which is about three times higher than the value measured for optimal doped Hg-1223 (Gao *et al.*[22]) or the recently measured $Hg_{1-x}Au_x$-1223 (Acha *et al.*[55]), and about twice of that measured for $Bi_2Sr_2CaCu_2O_{8+y}$ (Huang *et al.*[56]). Now, if our $Hg_{1-x}Re_x$-1223 compound is optimally doped, which is assured by its high $T_C\approx 133$ K,[15] the second term in the right-hand side of Eq. (1) is zero or be very small, which implies that this high $dT_C/dP\approx 6.8(2)$ K/GPa is due almost entirely to the intrinsic term.

Thus, based on the analysis above, it can be concluded that the chemical pressure made by the Re doping produces a change in the *c*-axis lattice parameter, as shown in Fig. 1, which under hydrostatic pressure gives a very large intrinsic term. Furthermore, it is expected that our Re 18% samples behave similarly to the other 3-CuO_2-layer compounds analyzed by Wijngaarden.[57] For pressures greater than 12 GPa, the T_C vs P curves for some three-layer compounds may be fitted by two parabolas, which may be interpreted as due to a nonequivalence of the charge distribution as estimated from the model of Hailes and Tallon.[58] This model supports the idea that the charge of the ''outer'' layers increases with faster rate than that of the ''inner'' layers.[57] Due to the low-pressure limitation of our equipment, no detectable double parabolic behavior was found, but it may be possible that the measured very large dT_C/dP value is only due to the outer CuO_2 layers.

In contrast with our results for the chemical pressure on the lattice parameter (Fig. 1) and the large intrinsic effect (Fig. 6) under external hydrostatic pressure reported above, Wijngaarden[57] points out that several experiments suggest a strong influence of the in-plane (*a* or *b* axis) lattice parameter on the intrinsic term. A number of interesting experiments mentioned in Ref. 58 provide some evidence that structural changes along the *c*-axis influence the charge content of the CuO_2 planes, and those along the *a* or *b* axis mainly influ-

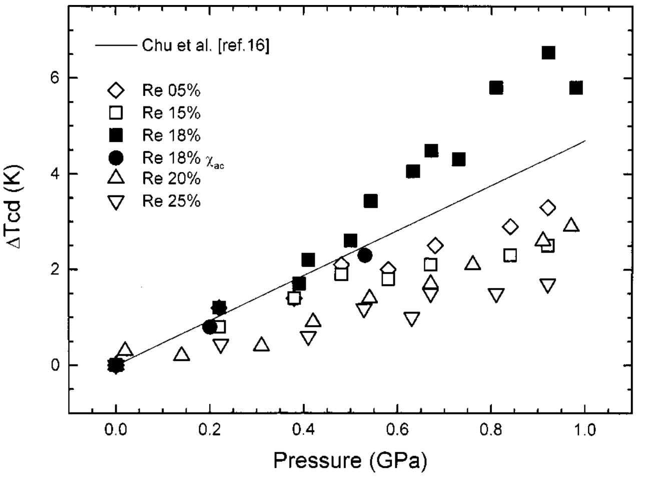

FIG. 6. Pressure dependence of the transition temperature T_{cd} obtained by the temperature variation of the resistance under hydrostatic pressure up to 0.92 GPa. The closed circles are related to T_{Conset} determined by the ac susceptibility.

ence the intrinsic term. Therefore, we arrive at the following two tentative explanations for our novel data:

Case 1: Following the discussion above, our Re-doped compound may be in the optimally doped regime and is, as far as we know, the first HTSC to exhibit such an enormous increase of the intrinsic term in comparison with the pure Hg compound, concomitantly with a larger structural change on the c axis than that on the a or b axis.

Case 2: An optimal oxygen-doped Re 18% sample[15] has a higher T_C than pure Hg-1223, i.e., our Re 18% doped compound may be underdoped. Under hydrostatic pressure there is some non-negligible charge transfer, probably strongly enhanced by the derivative $\partial n/\partial P$ which, due to the presence of the Re, becomes much larger than that of the pure Hg compound. The larger dT_C/dP is in this case, mainly due to the large PICT term and the intrinsic term may be of the order of Hg-1223, which agrees with the general trends described in Ref. 57 for structural rearrangements mainly along the c axis.

Independent of whether case 1 or 2 is relevant, the reported dT_C/dP values are one of the largest measured on HTSC compounds. The nature of the mechanism and the appropriate interpretation of this large effect will be clarified in future by *in situ* thermopower studies and the analysis of other samples with different oxygen content, having different charge densities.

IV. CONCLUSIONS

This work suggests that the maximum variation of T_C with external hydrostatic pressure, determined from ac resistance and ac susceptibility measurements, can be related to the optimal oxygen doping present in the Re 18% samples. From the Rietveld analysis the nominal Re 18% contents correspond to 20% of rhenium content present in the HgRe-1223 phase. For this sample with Re 18% content it was observed that all physical properties showed the best values, and in special the linear T_C-pressure dependence [6.8(2) K/GPa] reveals a higher rate compared with the one already determined for the Hg family of superconductors without Re doping. The estimated maximum of T_C that one may reach under applied pressure could not be achieved because it is above the limit of our present experimental conditions. The pressure experiments, however, have shown that there is a clear nonequivalence between chemical and external hydrostatic pressure for all Re-doped samples $Hg_{1-x}ReBa_2Ca_2Cu_3O_{8+\delta}$. This nonequivalence behavior can be interpreted, in the low (applied) pressure limit, as due to different effects related to the ‘‘*intrinsic*’’ term and the PICT term of Eq. (1).[52–54,58] Thermopower experiments are under way in our group to get more information for the development of a better model to explain the external and chemical pressure influence on the samples, especially their effect on the PICT and intrinsic term.

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