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# Oxygen content, thermodynamic stability, and superconductivity of $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$

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The oxygen nonstoichiometry of single phase (Hg, Re)-1201 samples was studied by high-temperature thermodynamic techniques. The relevant structural features and the oxygen occupancy numbers were determined by Rietveld refinements using x-ray and neutron powder diffraction data. Underdoped and overdoped samples for different Re contents obtained by changing oxygen content through suitable post annealing treatments enable us to analyze the effect of both substitutions on $T_c$. The Re doping increases the thermodynamic stability of the Hg-1201 phase due to the incorporation of strongly bonded oxygen atoms. The Re incorporation also makes it possible to easily reach the overdoped regime, without appreciably affecting the maximum $T_c$. The slight decrease of the maximum $T_c$ may be due to the cation disorder introduced by Re. The effect of extra oxygen in the $(Hg,Re)O_\delta$ layer on the $T_c$ of Hg-1201 compound is discussed.

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## I. INTRODUCTION

The $HgBa_2CuO_{4+\delta}$ material discovered by Putilin *et al.*[1] belongs to a series of general formula $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ with $1<n<7$. The $n=1$ member of this series (designated Hg-1201) with a $T_c \cong 97$ K was the first one synthesized at ambient pressure, while the $n=3$ member achieves, to date, the record value for $T_c$ (135 K) at ambient pressure,[2] and at high pressure (164 K at 31 GPa).[3,4]

The advantage of the Hg-1201 material compared to those of higher *n*, for the analysis of the structural defects, is the absence of intergrowth layers. Some intergrowth structures may occur due to the identical atomic configuration of the basal plane of HgO in the higher members of this series and have been observed by high resolution transmission electron microscopy.[5]

Although the average structural model for the simplest Hg-1201 compound is widely accepted, there is poor agreement concerning the possible defects and the amount of oxygen excess $\delta$ and its relation with superconductivity. The variation of extra $\delta$ oxygen modifies the carrier concentration in the $CuO_2$ planes and therefore the $T_c$; nevertheless, the range of oxygen excess and the $\delta$ values corresponding to the maximum $T_c$ show appreciable spread (see as examples Refs. 1,6–13). All workers who carried out structural refinements of this phase report less than ideal occupancy for the Hg site or extremely large Debye-Waller factors for this site and the O(2) site. There are at least four proposals to explain this: (i) a real Hg deficiency, i.e., Hg vacancies,[14] (ii) substitution of Cu on the Hg site,[15–17] (iii) substitution of C, in the form of $CO_3$, at or near the Hg site,[6] (iv) Hg atoms are displaced off the ideal Hg site in a anharmonic way.[18]

In addition, there is one report of two different oxygen defect locations.[7] One of these sites is the usually reported interstitial oxygen site in the Hg plane. The second one is also in the Hg plane, but is at an $(x,x,0)$ site that is displaced towards one of the Hg atoms. However, this second oxygen defect site could be associated with $CO_3$ defects. As differences are seen among samples made in different ways, it is likely that one or more of these defects actually occurs and they depend on synthesis techniques.

Therefore, the lack of consensus about the fine details of the crystal structure may be due to different sample preparation methods, which lead to difficulties in obtaining single phase materials and determining the excess oxygen content. The high vapor pressure of Hg and the high reactivity of the precursors with $CO_2$ and $H_2O$ make the synthesis of single-phase materials much harder than with other high-$T_c$ cuprates.

As for the measurement of the absolute oxygen content, the presence of Hg makes impossible its determination by thermogravimetry. Instead, iodometric titration and neutron powder diffraction data refinements are used for this purpose. However, the oxygen content values obtained with these two techniques show significant differences. The most likely reason is that iodometric titration will not give the real oxygen content unless samples are single phase. X-ray diffraction cannot be used to conclusively check phase purity because impurities can be noncrystalline.[12,15,19,20]

Several authors have reported additional problems in the study of these compounds: a rapid degradation under ambient conditions of apparent single phase samples[20] and a possible decomposition of the phases upon annealing at high temperatures.[8,21] Additionally, using thermogravimetric analysis (TGA) in 1 atm. oxygen pressure Tokiwa-Yamamoto *et al.*[22] have obtained the starting decomposition temperatures of 420, 480, and 520 °C for the Hg-1201, Hg-1212, and Hg-1223, respectively, while Tsuchiya *et al.*[23] calculated 376, 396, and 440 °C for the same values. These temperatures decrease for lower oxygen partial pressures and

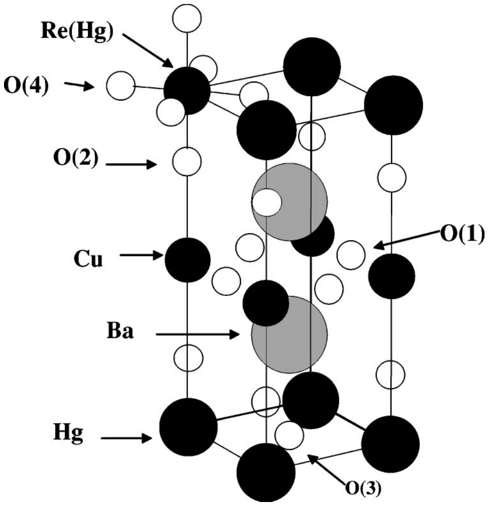

FIG. 1. Unit cell of the Hg(Re)-1201 compound, which corresponds to the tetragonal system *P*4/*mmm* (Ref. 27).

Tampieri reported a possible Hg loss at a temperature as low as 270 °C in their thermal stability study in air.[24]

The chemical substitutions of Re and other transition elements for Hg has been explored as a means to simplify the synthesis of the Hg compounds.[25] The partial substitution of mercury by a high valence transition metal incorporates extra oxygen atoms into the $HgO_\delta$ plane. In the case of Re substitution, each Re cation introduces four extra oxygen atoms at the O(4) crystallographic site.[26,27] The addition of Re is reported to have beneficial effects on the phase formation and chemical stability of the Hg-1212 and Hg-1223 phases, especially regarding their sensitivity to $H_2O$ and $CO_2$.[28–31]

Figure 1 displays the unit cell of the Hg(Re)-1201 compound proposed by Chmaissem *et al.* from Rietveld refinements of neutron powder diffraction data.[26,27] This figure shows the existence of two types of crystallographic oxygen sites in the $HgO_\delta$ plane. One of them, the O(3) site, corresponds to that of the oxygen doping for the Re-free samples ($HgBa_2CuO_{4+\delta}$). The other one, the O(4) site, is related to the oxygen atoms bonded to each Re cation.

No available studies delineate the thermodynamic and superconducting behavior of Re doped Hg-1201 materials vs oxygen content. In this paper, we present a high-temperature thermodynamic study of the $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ system performed to analyze the thermodynamic stability and the oxygen nonstoichiometry. These data, in addition to neutron powder diffraction (NPD) measurements, allowed the preparation of samples with controlled oxygen content for Re concentrations ranging between 0 and 0.15.

## II. EXPERIMENTAL

Samples of $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ were prepared following a method similar to that proposed by Alyoshin *et al.*[32] High purity HgO, $ReO_2$, CuO, and BaO were the raw materials for these samples. CuO and BaO in the stoichiometric ratio of $Ba_2CuO_{3+\delta}$ were mixed and heated under pure oxygen at 930 °C. The obtained $Ba_2CuO_{3+\delta}$ single phase material was mixed with $ReO_3$ and HgO. The HgO was incorporated with an excess of 10% relative to the stoichiometric composition to compensate for the loss of Hg by volatilization during the synthesis. All sample handling was done in a dry box. The final oxide mixtures were heated in sealed quartz capsules under controlled $p(O_2)$ given by the $CoO/Co_3O_4$ equilibrium. We used a two-zone furnace where the sample was placed in the lower-temperature part of the tube and the $CoO/Co_3O_4$ mixture in the higher-temperature region. Details of the synthesis process will be reported elsewhere.[20]

Powder x-ray diffraction (XRD) data were recorded on a Philips PW-1700 diffractometer using Cu-$K_\alpha$ radiation and a graphite monochromator. The collection time in steps of 0.02 ° was 10 sec per step. X-ray data of the samples were refined by the Rietveld method with the DBWS-9411 program.[33] The quality of the samples was also checked by scanning electron microscopy (SEM) and microanalysis on a Philips 515 SEM microscope fitted with an EDAX 9900 energy dispersive spectrometer (EDS).

Equilibrium $p(O_2)$ data as a function of temperature and oxygen content were obtained using highly sensitive thermogravimetric equipment consisting of a symmetrical thermobalance based on a Cahn 1000 electrobalance coupled to an electrochemical gas blending system.[34] The electrochemical system (zirconia pump and oxygen sensor) provides a controlled Ar-$O_2$ atmosphere for the thermobalance with $p(O_2)$ values ranging between $1\times10^{-6}$ and 1 atm. The error in $p(O_2)$ can be estimated as approximately 2% (including systematic errors). The thermobalance allows the detection of changes in ''$\delta$'' within 0.001 for a sample of about 0.5 g. The time required to approach equilibrium after a change in $p(O_2)$ was typically 24 to 72 h depending on $T$ and $p(O_2)$. The equilibrium criterion used in this work was constant sample mass with time within $\pm 10\ \mu$g verified over 24 h periods and longer. The absolute oxygen contents of the $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ samples were determined by Rietveld refinements of the NPD data.

Time-of-flight neutron powder diffraction data were collected at room temperature on the Special Environment Diffractometer (SEPD) at Argonne's Intense Pulsed Neutron Source (IPNS).[35] Data from the high resolution backscattering detector were analyzed by the Rietveld technique using GSAS code[36] over a *d*-spacing range of 0.5 to 4 Å. Table I summarizes the refined structural parameters for $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ samples prepared at 300 °C in $O_2$.

The presence of superconductivity was detected through dc magnetization (*M*) measurements with a Quantum Design SQUID magnetometer. *M* was measured under a nominal magnetic field of 5 Oe after the samples were cooled from a $T > T_{co}$ to 5 K in (a) zero field (ZFC) and (b) in field (FC).

## III. RESULTS AND DISCUSSION

Figure 2 displays the x-ray diffraction patterns of $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ samples annealed at 300 °C under pure oxygen. The oxygen contents of these samples are practically the same as those of the as-made ones. No reflections of secondary phases are observed, especially in the 27–31° $2\theta$ region where the major reflections of the common impu-

TABLE I. Oxygen content, $T_{co}$ and refined structural parameters (NPD data) of $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ prepared at 300 °C in pure $O_2$; tetragonal symmetry of space group $P4/mmm$ (Ref. 20).

| Nominal Re content | | $x=0.00$ | $x=0.05$ | $x=0.10$ | $x=0.15$ |
|---|---|---|---|---|---|
| $T_{co}$(K) | | 97.2(4) | 96.0(5) | 95.0(5) | 35(2) |
| $\delta_o$ | $n(O3)+n(O4)$ | 0.15(1) | 0.37(5) | 0.42(4) | 0.58(4) |
| $a$(Å) | | 3.880(1) | 3.872(1) | 3.872(1) | 3.8760(4) |
| $c$(Å) | | 9.527(1) | 9.464(1) | 9.420(1) | 9.390(2) |
| Hg | (0,0,0) | | | | |
| | B(Å$^2$) | $B_{11}=B_{22}=1.1(1)$<br>$B_{33}=0.8(1)$ | $B_{iso}=0.8(1)$ | $B_{iso}=0.8(1)$ | $B_{11}=B_{22}=1.48(7)$<br>$B_{33}=0.57(9)$ |
| | $n$ | 1 [a] | 0.90(4) | 0.86(4) | 0.817(9) |
| Re | $n$ | | 0.10(4) | 0.14(4) | 0.15 [a] |
| Ba | (1/2,1/2, $z$) | | | | |
| | $z$ | 0.299(2) | $z_1=0.305(2)$<br>$z_2=0.276(5)$ | $z_1=0.302(2)$<br>$z_2=0.277(4)$ | 0.2925(2) |
| | $n$ | 1 [a] | $n_1=0.74(8)$<br>$n_2=0.26(8)$ | $n_1=0.65(11)$<br>$n_2=0.35(11)$ | 1 [a] |
| | B(Å$^2$) | $B_{iso}=0.4(1)$ | $B_{1iso}=0.2(1)$<br>$B_{2iso}=0.1(1)$ | $B_{1iso}=0.2(1)$<br>$B_{2iso}=0.3(2)$ | $B_{11}=B_{22}=0.65(7)$<br>$B_{33}=1.26(12)$ |
| Cu | (0,0,1/2) | | | | |
| | B(Å$^2$) | $B_{iso}=0.31(8)$ | $B_{iso}=0.2(1)$ | $B_{iso}=0.3(1)$ | $B_{iso}=0.51(5)$ |
| O(1) | (1/2,0,1/2) | | | | |
| | B(Å$^2$) | $B_{iso}=0.41(9)$ | $B_{iso}=0.4(1)$ | $B_{iso}=0.4(1)$ | $B_{iso}=0.60(5)$ |
| O(2) | (0,0,$z$) | | | | |
| | $z$ | 0.2086(3) | 0.299(2) | 0.2089(2) | 0.2090(2) |
| | B(Å$^2$) | $B_{11}=B_{22}=1.31(8)$<br>$B_{33}=0.7(1)$ | $B_{11}=B_{22}=1.1(1)$<br>$B_{33}=0.8(1)$ | $B_{11}=B_{22}=1.0(1)$<br>$B_{33}=0.9(1)$ | $B_{11}=B_{22}=1.51(7)$<br>$B_{33}=0.93(13)$ |
| O(3) | (1/2,1/2,0) | | | | |
| | B(Å$^2$) | $B_{iso}=0.8$ [a] | $B_{iso}=0.8$ [a] | $B_{iso}=0.8$ [a] | $B_{iso}=1.49(40)$ |
| | $n$ | 0.15(1) | 0.05(1) | 0.02(1) | 0.01(1) |
| O(4) | ($x$,$x$,0) | | | | |
| | $x$ | | 0.316(6) | 0.337(3) | 0.347(2) |
| | $n$ | | 0.32(4) | 0.40(4) | 0.57(3) |
| $R_p$(%) | | 3.2 | 3.2 | 3.2 | 3.59 |
| $R_{wp}$(%) | | 5.0 | 5.0 | 5.0 | 5.62 |
| $\chi^2$ | | 1.23 | 1.25 | 1.23 | 1.279 |

[a] Not refined.

rities appear (see inset in Fig. 2). Although the lack of reflections from second phases does not guarantee single phase material (because second phases are often noncrystalline), SEM and EDS analysis did not show the existence of secondary phases.[20] Well-developed grains of around 5–20 $\mu$m were observed in all samples. Even if there could exist an amorphous coating on grains its contribution will be negligible due to the large grain size of our samples (5–20 $\mu$m).

We found by SEM observations that our Re-free samples remain stable over one year under ambient conditions. The $T_{co}$ and Meissner fraction did not show any significant change with time. The high stability of the samples may be due to the HgO excess in the starting $HgO\text{-}Ba_2CuO_{3+\delta}$ mix which allows us to obtain nearly Hg-stoichiometric and single phase materials. This excess and the thermal cycle used would avoid the formation of secondary phases composed of Ba and Cu oxides which are likely responsible of such degradation in nonproperly made samples.[20]

The lattice parameters obtained by Rietveld refinements in the $P4/mmm$ space group for NPD and XRD data are shown in Fig. 3. These results are in agreement with those of the literature.[26] The linear variation of the $c$ axis as a func-

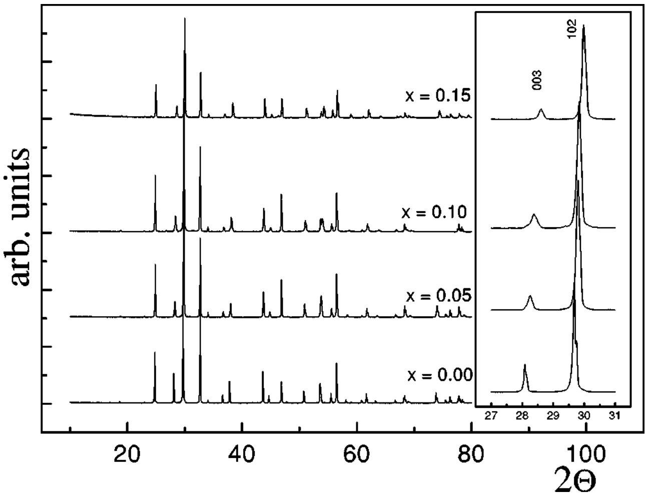

FIG. 2. Powder x-ray diffraction data for $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ samples annealed at 300 °C under pure oxygen. The inset shows in detail the 27°–31° $2\theta$ region where the major reflections of the common impurities appear.

tion of Re content suggests the full incorporation of Re cations in the 1201 structure for $x$ values up to 0.20. In contrast, the $a$ axis does not show appreciable variation as a function of the Re content. However, both parameters decrease as the oxygen content increases, as will be discussed below.

Figure 4(a) displays the equilibrium $p(O_2)$ measurements as a function of oxygen content $4+\delta$ for the $x=0.00$ sample. The absolute oxygen content values for the undoped sample and for all the Re compositions were computed from data obtained by the NPD refinement for samples annealed under pure oxygen at 300 °C. For the $x=0.00$ sample, the isotherms below 300 °C were reproducible under systematic oxidation or reduction. Exceptions to this were the low $p(O_2)$ data points of the 350 °C isotherm, which presented a continuous drift of the sample mass. The oxidation of this sample from these $T$ and $p(O_2)$ values leads to mass values lower than those previously obtained. This suggests the beginning of a slow decomposition process at 350 °C and $\log_{10}[p(O_2)] < -3.00$, which may be due to Hg loss in the $x=0.00$ sample. This mass loss (0.1 wt. % in two days) is small and therefore, this decomposition can not be detected by x-ray diffraction measurements. This process may occur mainly at the surface of the sample as was observed by SEM.[20] A decomposition involving the bulk of the sample may take place only at higher temperatures.[24]

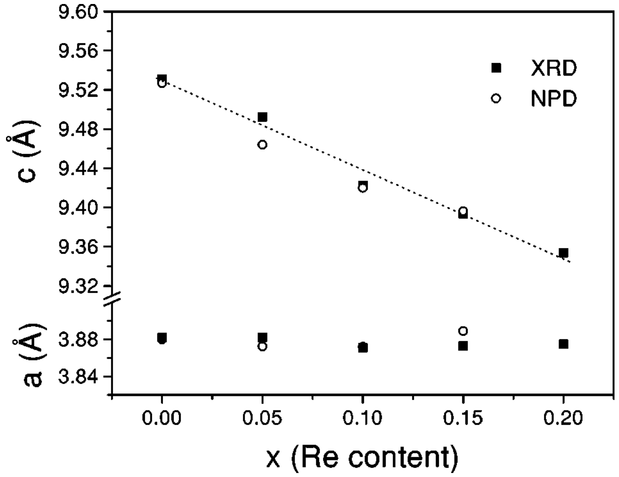

FIG. 3. Lattice parameters a and c as a function of nominal Re content $x$ for $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ samples annealed at 300 °C under pure oxygen.

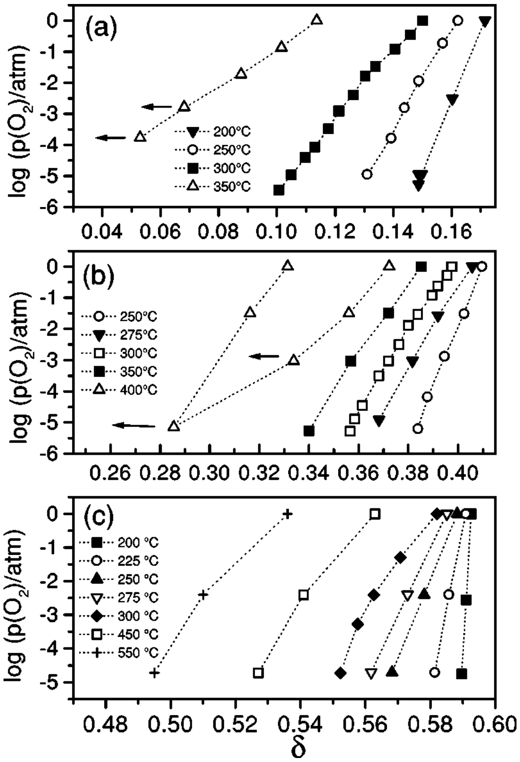

FIG. 4. $\log_{10}[p(O_2)/atm]$ vs oxygen content for $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ samples. (a) x=0; (b) x=0.10; (c) 0.15. The arrows indicate nonequilibrium points.

The decomposition process in our samples is slower and occurs at lower $p(O_2)$ values than has been previously reported.[24,23] Note that the mercury compositions of those studies are 0.9 and 0.92, as determined by electron microprobe analysis and ICP emission spectrometric methods, respectively. These results could indicate that our samples are more stoichiometric in agreement with our EDS analysis.[20]

Equilibrium $p(O_2)$ data for the Hg-1201 compound were previously measured by Marucco *et al.*[8] Their data roughly agree with our $p(O_2)$ measurements. The main differences concern the shape of the isotherms. In Ref. 8 they observe for the 300, 350, and 400 °C isotherms that the slope of $\log_{10}[p(O_2)]$ vs "$\delta$" increases as $p(O_2)$ decreases. This behavior of $p(O_2)$ suggests a stabilization of the oxygen sublattice for a $\delta_r$ value (residual fraction) greater than 4.00. From their $\log(\delta-\delta_r)$ vs $\log p(O_2)$ data, a slope of 1/6 is obtained which indicates the existence of double ionized interstitial oxygen defects. However, we have observed that this slope is extremely sensitive to the absolute value of the oxygen content. Therefore, it is very difficult to assert a defect model based only on these data.

TABLE II. $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ values for different compounds. These values were computed for the oxygen excess range $\delta$.

| Sample | $\delta$ | $-\Delta\overline{H}_{O_2}$(kJ/mol) | $-\Delta\overline{S}_{O_2}$(J/mol K) | Ref. |
|---|---|---|---|---|
| Gd-123 | 0.1–0.9 | 160–170 | 120–210 | Prado *et al.* (Ref. 37) |
| Y-123 | 0.1–0.9 | 190 | 120–320 | Lindemer *et al.* (Ref. 38) |
| Bi-2212 | 0.26 [a] | 166 | 130 | Xiong *et al.* (Ref. 10) |
|  | 0.41 [b] | 100 | 180 |  |
| Hg-1201 | 0.14 [c] | 136 | 120 | Xiong *et al.* (Ref. 10) |
|  | 0.19–0.24 [a] | 110 | 160 |  |
| Hg-1201 | 0.05–0.16 | 46.3 | 14 | Marucco *et al.* (Ref. 8) |
| Hg-1201 | 0.1–0.13 [c] | 200±30 | 320±30 | this work |
|  | 0.14–0.15 [a] | 170±30 | 280±40 | this work |
| $Hg_{0.9}Re_{0.10}-1201$ | 0.36–0.40 | 107±12 | 170±30 | this work |
| $Hg_{0.85}Re_{0.15}-1201$ | 0.56–0.57 [a] | 130±15 | 225±25 | this work |
|  | 0.58–0.59 [b] | 95±20 | 160±30 | this work |

[a] Optimally doped samples.

[b] Overdoped samples.

[c] Underdoped samples.

In Figs. 4(b) and 4(c) we plot our equilibrium $p(O_2)$ data for the $x=0.10$ and 0.15 samples. The overall oxygen contents for these samples are higher than those of the Re-free ones. This effect is due to the high oxidation state of Re. According to the structural model proposed by Chmaissem *et al.*[27] each Re cation bonds four extra oxygen atoms into the structure. According to the NPD refinements, the total oxygen excess ‘‘$\delta$’’ values can be split into two terms $n(O3)$ and $n(O4)$. The first term corresponds to the oxygen atoms in the O(3) position while the second one is due to the oxygen atoms in the O(4) site bonded the Re atom and should be equal to $4x$. However, the shift of the curves of $T_c$ as a function of $\delta$ is not exactly $4x$.

We have computed the partial molar quantities $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ from the temperature dependence of our $p(O_2)$ data at fixed compositions. The obtained $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ values and data of the literature for Hg-1201 and other high-$T_c$ superconductors are shown in Table II. Due to the small $\delta$ range displayed by this compound in the $p(O_2)$ range used in our experiments ($10^{-6}$–1 atm.), the computed $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ show appreciable scatter and they must be considered only as semiquantitative values. Our values agree roughly with those determined by Xiong *et al.*[10] for the Hg-1201 compound and other superconducting oxides.[37,38] The $\Delta\overline{H}_{O_2}$ values increase as the oxygen content increases, which could indicate a strong defect interaction as was suggested by these authors. The $\Delta\overline{H}_{O_2}$ quantities also increase with Re content which is due to the effect of the additional oxygen atoms bonded to the Re ions.

Furthermore, the equilibrium $p(O_2)$ data provide the following information.

(i) The temperature of the beginning of the decomposition process increases as the Re content increases. For the $x=0.10$ sample, this temperature is 400 °C while for the $x=0.15$ one it is higher than 500 °C, indicating an improvement on the thermodynamic stability of the Hg-1201 phase with the Re doping.

(ii) The oxygen nonstoichiometry range as a function of $p(O_2)$ decreases as the Re content increases. To compare the oxygen nonstoichiometry for samples with different $x$ values we have plotted in Fig. 5 the $p(O_2)$ data at 300 °C vs $\delta-\delta_o(x)$, where $\delta_o(x)$ is the oxygen content value under pure oxygen of each Re-doped sample. These data reveal a stabilization of the oxygen sublattice as a function of the Re content indicating that, in the (Hg,Re)-$O_\delta$ plane, the O(4) oxygen atoms are more strongly bonded than the O(3) ones. This stabilization of the oxygen sublattice is evidenced by the increment of the $\Delta\overline{H}_{O_2}$ quantities as Re content increases.

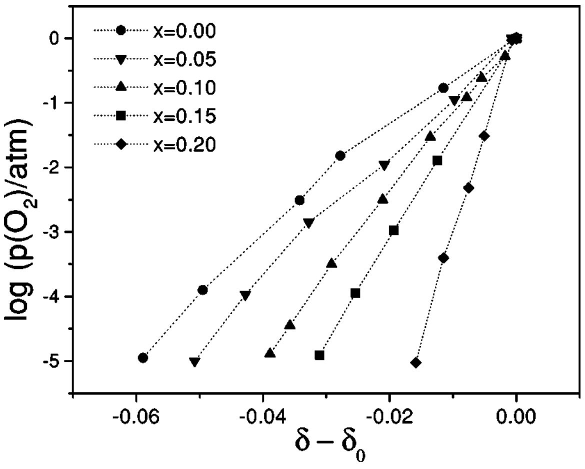

FIG. 5. $\mathrm{Log}_{10}[p(O_2)/\mathrm{atm}]$ at 300 °C vs $\delta-\delta_o(x)$, where $\delta_o(x)$ is the oxygen content value under pure oxygen of each Re-doped sample.

The $T_{co}$ values as a function of the oxygen content (4

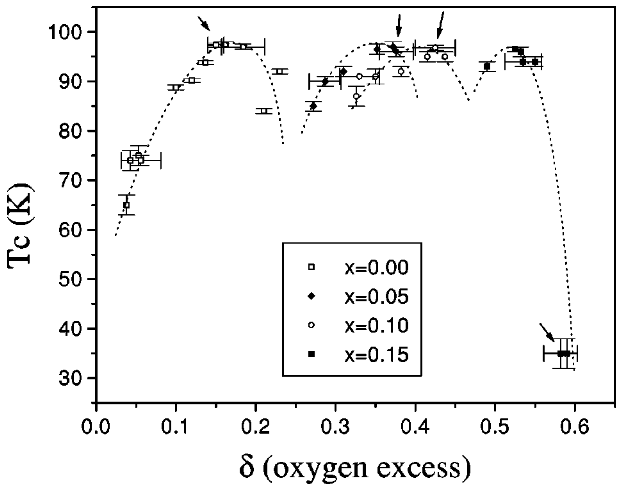

FIG. 6. $T_{co}$ as a function of oxygen excess "$\delta$" for $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ samples prepared with controlled oxygen contents determined by NPD and TGA. The *x* error bars are only present for NPD data. The arrows indicate samples annealed at 300 °C under pure oxygen, which were used as references for the oxygen content.

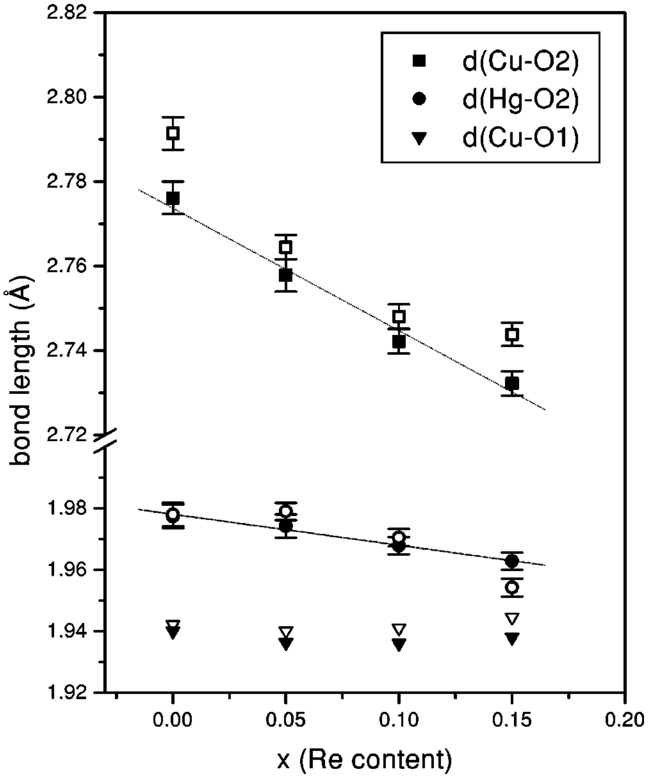

FIG. 7. Bond distances Cu-O2, Cu-O1, and Hg-O2 as a function of Re content for samples annealed under 1 atm (closed symbols) and vacuum (open symbols) at 300 °C.

$+\delta$) for samples of $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ ($0.00<x<0.15$) are plotted in Fig. 6. The oxygen contents were obtained by thermogravimetry taking as a reference those oxygen content values determined by NPD; the later are indicated by arrows. The samples were prepared by annealing at $200<T$ (°C) $<300$ under $10^{-9}<\log_{10}[p(O_2)/\mathrm{atm}]<2$. In order to cover the underdoped and overdoped regions it was necessary to perform annealing treatments under $p(O_2)$ values higher and lower than those given by our electrochemical system [$10^{-6}<p(O_2)<1$ atm.].

The $x=0.00$ samples show a maximum of $T_c$ at $\delta_{\max}\sim0.16$. Nevertheless, a small plateau is observed between 0.15 and 0.18 which is in agreement with data reported by Jorgensen *et al.*[7] The literature data for $\delta_{\max}$ cover the range between 0.08 to 0.18.[6–13] The sources of such large discrepancies may be due to different sample preparation methods and annealing treatments.

The bond distances Hg-O(2), Cu-O(1), and Cu-O(2) of the oxygen annealed and vacuum annealed samples as a function of Re content (*x*) are plotted in Fig. 7. The decrease in the *a* and *c* parameters with the oxygen content, for a given Re concentration, is mainly the result of the shortening of the Cu-O(1) and Cu-O(2) bond distances. The Hg-O(2) bond distance at fixed Re content shows a more erratic behavior with the oxygen content. The analysis of these structural data indicates the following.

(i) The Hg-O(2) and Cu-O(2) bond distances decrease with Re content giving rise to a shortened *c* axis. The change of these distances with the oxygen content is a second order effect as compare with their dependence with Re concentration.

(ii) The Cu-O(1) bond distances remain practically constant with Re content.

In Fig. 8 is plotted the $T_c$ of the as-made samples and the $T_c$ maximum ($T_{c\,\max}$) as a function of the Re content *x*. The as-made samples become progressively overdoped as the Re content increases. However, it is possible to get optimally doped samples by oxygen removal. The obtained $T_{c\,\max}$ values are nearly the same as for the unsubstituted sample and decrease slightly as a function of Re content.

Other cation substitutions (Me = V, Mo, Cr, W, Ti, S, Se) in the Hg site of the Hg-1201 compound decrease $T_c$ appreciably.[25,39,40] These samples would be overdoped due to an increment of the oxygen content caused by the higher valence of the incorporated cations. Nevertheless, no studies

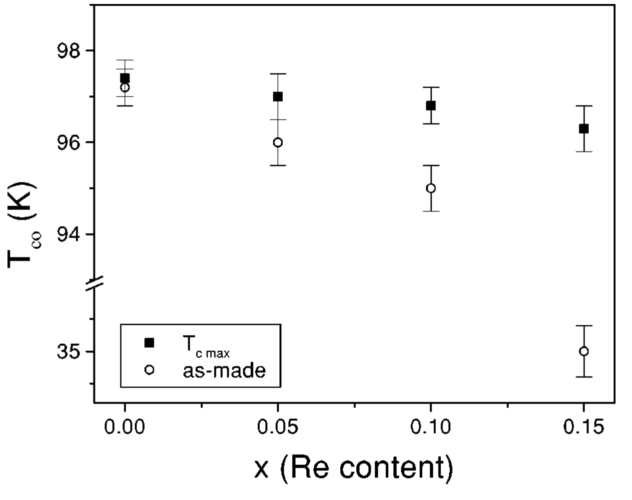

FIG. 8. $T_c$ of the as-made and optimally doped samples ($T_{c\,\max}$) as a function of Re content.

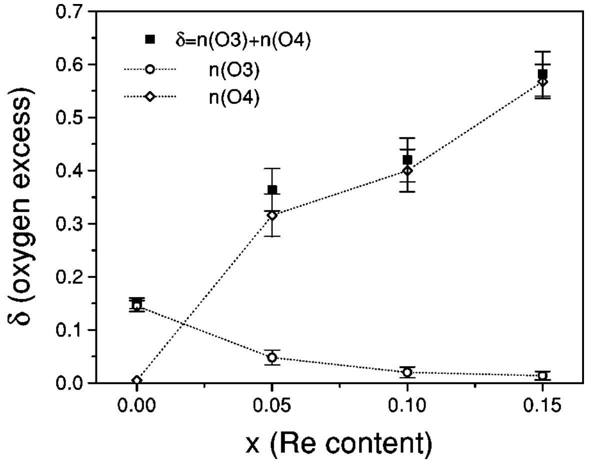

FIG. 9. O(3) and O(4) occupancy numbers $[n(\mathrm{O}3)$ and $n(\mathrm{O}4)]$ determined by NPD for samples annealed at 300 °C under 1 atm. of pure oxygen.

detail the effect of different annealing treatments in these (Hg, Me)-1201 compounds and it is possible that their oxygen content has not been optimized.

Although the Re substitution for Hg causes important structural changes such as shortening of the *c* axis, the effect on $T_{c\,\max}$ is small. The contraction of the structure due to Re substitution compresses the Cu-O(2) distance more than the Hg-O(2) distance as shown in Fig. 7. Similar variation of the Cu-O(2) distance as a function of Re content and a small buckling were observed for (Hg,Re)-1212 and (Hg,Re)-1223 compounds.[27] However, no evidence of buckling (e.g., an increase in the temperature factors for the oxygen atoms in plane) was observed in our samples. Therefore, the variation of these distances has minimal effect on $T_{c\,\max}$. The small observed decrease in $T_{c\,\max}$ (from 97.4 to 96 K) may be caused by cation disorder affecting the electronic structure.

It had been previously suggested that the *c*-axis shortening and metallic character of $\mathrm{ReO_3}$ should result in an interlayer metallization, and thus a change in the dimensionality of these superconductors, which would be manifested as a significant enhancement of $\sigma$, the muon relaxation rate.[41] However, new $\mu$SR experiments carried out recently on our samples do not reveal any evidence for interlayer metallization induced by Re,[42] in accordance with some recent results obtained for the compounds with two and three Cu-O layers.[43]

In order to discuss the effect of the oxygen atoms bonded to Re on $T_c$, the O(3) and O(4) occupancy numbers $[n(\mathrm{O}3)$ and $n(\mathrm{O}4)]$ determined by NPD for samples annealed at 300 °C under 1 atm. of oxygen are plotted in Fig. 9. These data show that for the Re-free sample the oxygen excess ($\delta$) is only at the O(3) crystallographic site, determining the carrier concentration. $n(\mathrm{O}3)$ decreases as the Re content increases, with values near zero for the $x>0.05$ samples. Therefore, for the (Hg,Re)-1201 samples, the O(4) oxygen atoms dope holes into the $\mathrm{CuO_2}$ plane.

Preliminary measurements of thermoelectric power (TEP, i.e., Seebeck coefficients) indicate a hole concentration $p=0.16$ for our oxygen optimally doped $x=0.10$ sample, with occupancy numbers of 0.40 and 0.02 for the O(4) and O(3) sites, respectively. In addition, for the Hg-1201 compound it has also been reported that the $T_c$ maximum occurs at $p=0.16$ as for all other high-$T_c$ cuprates.[10]

TABLE III. $\delta_{\max}$, $T_{c\,\max}$, and the numbers of holes per oxygen atom assuming $p=0.16$ for $\mathrm{Hg_{1-x}Re_xBa_2CuO_{4+\delta}}$ samples.

| $x$ | $T_{c\,\max}(K)$ | $\delta$ | holes/oxygen atom |
|---|---|---|---|
| 0.00 | 97.4 | 0.162 | 0.99 |
| 0.05 | 97.0 | 0.372 | 0.43 |
| 0.10 | 96.8 | 0.425 | 0.38 |
| 0.15 | 96.3 | 0.525 | 0.30 |

The $\delta_{\max}$, $T_{c\,\max}$ and the numbers of holes per oxygen atom assuming $p=0.16$ for all samples are displayed in Table III. Thus, the doping level on the Cu layer corresponds to one hole per oxygen atom for $x=0$ samples, which is in good agreement with previous measurements.[10] This doping level decreases as the Re content increases. This fact would indicate that the *average* covalent bonding in the $\mathrm{(Hg,Re)O_\delta}$ layer is stronger as the oxygen content increases. This explanation agrees with local density approximation calculations which indicates a doping level of one additional hole per occupied O(4) site for Hg-1223.[45]

An alternative explanation could be supported by the quantitative analysis made by Jansen *et al.*[46] for the oxygen-doping effects on $T_c$ based on indirect-exchange pairing. These authors obtained numerical results for the indirect-exchange coupling upon approximating the wave functions of two electrons by simple Gaussian functions of parameters $\alpha$ and $\beta$.[47] The latter is thus a ‘‘localization’’ parameter of conduction electrons. Their results indicate that a change in the $\beta$ parameter, which reflects the density of ‘‘active’’ oxygens, is related to the change in the *c*-axis length. These authors concluded that the relation between $p$ (the carrier concentration) and $\delta$ denotes a fictitious carrier concentration which contains the effect of changing the $\beta$ parameter.[46]

Another way to estimate the effective valence of the excess oxygen atoms may be done by simple making a charge balance. From the bond lengths, the Re valences were estimated using the Brown-Altermatt[44] bond-valence sum method. The calculations give an average Re valence (over all samples measured by NPD) of 6.37, 6.52, and 5.89 for $x=0.05$, 0.10, and 0.15, respectively. Although these numbers should be interpreted carefully, it is possible, from the difference between Re and Hg valence, to estimate the charge transfer of the O(4) atoms to the superconducting $\mathrm{CuO_2}$ planes (the number of ‘‘active’’ extra oxygen atoms which modifies the carrier concentration in the $\mathrm{CuO_2}$ planes). The O(4) valence obtained for $x=0.10$ and 0.15 samples [assuming $\delta\sim n(\mathrm{O}4)$] is roughly 1.3. Therefore, each O(4) atom borrows one electron from the Re cation and about 0.3 from the $\mathrm{CuO_2}$ planes. Thus, although the valence of the O(4) atoms may be higher than that of the O(3) atoms, they transfer less holes to the superconducting planes, because they are tightly bound to the high valence Re cations, as was discussed above.

The data of Fig. 9 show a $n(\mathrm{O}4)$ of approximately $4x$ for the as-made samples according to the Chmaissen model. One exception is the $x = 0.05$ sample, where the refinements of the NPD data also indicate a Re content of 0.10(4) in disagreement with the nominal value.

Even though the oxygenated samples for $x = 0.10$ and 0.15 show a $n(\mathrm{O}4)$ of approximately $4x$, they are overdoped as is shown in Fig. 8. Therefore, it is necessary to remove oxygen atoms from the O(4) site to reach the optimal and underdoped regime, which is confirmed by the $n(\mathrm{O}4)$ refinement for samples with lower oxygen content than those of the oxygenated ones (see Fig. 6).

It has been reported that a high-pressure high-temperature technique is necessary to obtain highly overdoped Hg-1201 phases. However, these samples seem to favor the replacement of Hg by C and easily decompose into $BaCO_3$, CuO, and $BaHgO_2$.[6] Another possibility to obtain overdoped Hg-1201 samples is through a very long time thermal annealing (240 h) at moderates temperatures (around 200 °C).[10] The present work indicates that the overdoped regime can be reached more easily as the Re content of the samples increases. Thus, it is possible to study the behavior of overdoped samples with chemically stable samples.

## IV. CONCLUDING REMARKS

Our study of single phase $Hg_{1-x}Re_xBa_2CuO_{4+\delta}$ samples allows us to distinguish the effects of Re substitution and oxygen contents on the behavior of $T_c$ for the Hg-1201 compound. The equilibrium $p(O_2)$ measurements indicate that Re doping increases the thermodynamic stability of the 1201 phase, increasing the low-temperature limit for decomposition due to the incorporation of highly bonded oxygen atoms in the (Hg,Re)-$O_\delta$ planes. The improvement of the 1201 stability is reflected by the increment of $\Delta\overline{H}_{O_2}$ values as a function of oxygen and Re.

The high valence of Re introduces extra oxygen in the (Hg,Re)-$O_\delta$ layers, which overdopes the superconducting $CuO_2$ layers, as reported in this and other similar substitutions.[25,39,40,48] Therefore, the as-made samples for $x > 0.05$ are overdoped and their oxygen contents are approximately $4x$. However, it is possible to get optimally doped and underdoped samples by oxygen removal with suitable treatments under vacuum at high temperatures. Some oxygen must be removed from the O(4) crystal site to get optimally doped samples.

The contraction of the 1201 structure due to Re substitution compresses the Cu-O(2) distance more than the Hg-O(2) distance without inducing buckling in the $CuO_2$ planes. The O(3) oxygen atoms dope holes to the $CuO_2$ layer for the Hg-1201 compound while the hole doping mainly depends on the O(4) oxygen atoms for the (Hg,Re)-1201 ones. The carriers provided by these extra oxygen atoms in the $CuO_2$ planes decrease in number as the Re content increases. This reduced charge transfer to the $CuO_2$ planes may be related to a strong covalency between Re and O (Ref. 45) or to a change in the $\beta$ parameter due to $c$-axis length shortness.[46]

Finally, Re doping allows us to easily reach the overdoped regime by increasing the oxygen solubility, without affecting appreciably the maximum $T_c$. This small decrease in $T_c$ may be due to the cation disorder introduced by Re which affect the electronic structure.

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