PHYSICAL REVIEW B VOLUME 53, NUMBER 21 1 JUNE 1996-I

Crystal structures of Hg-Sr-Ca-Cu-O superconductors with enhanced flux pinning: $Hg_{1-x}Re_xSr_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n=2,3$; $x\approx 0.2-0.25$)

O. Chmaissem and J. D. Jorgensen
Materials Science Division and Science and Technology Center for Superconductivity,
Argonne National Laboratory, Argonne, Illinois 60439

K. Yamaura, Z. Hiroi, and M. Takano
Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan

J. Shimoyama and K. Kishio
Department of Applied Chemistry, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

(Received 9 November 1995)

The crystal structures of $Hg_{1-x}Re_xSr_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n=2,3$; $x\approx 0.2$–0.25) (synthesized at high pressure) were refined using neutron powder diffraction and the Rietveld analysis technique. Superconductivity was not observed in the as-prepared $n=2$ compound while a T_c of 107 K was measured for the $n=3$ sample. Postannealing in evacuated tubes results in creating superconductivity in the $n=2$ sample with a T_c of 90 K and in enhancing it up to 120 K in the $n=3$ sample. The structures of both as-prepared and vacuum-annealed samples were investigated. In both compounds, Re substitutes at the Hg site. Four additional oxygen atoms are incorporated into the (Hg, Re) plane for each Re atom providing an octahedral environment for Re. Thus, for a composition of $x\approx 0.25$, all available oxygen sites in the (Hg, Re) plane are filled. These oxygen atoms shift off the ideal position to form bonds of appropriate length (1.88 Å) with Re. Vacuum-annealed samples show oxygen deficiency in the (Hg, Re) layer suggesting that the actual Re content is below the solubility limit. The enhanced flux pinning for these chemically substituted compounds could result from the observed shortening of the blocking layer by 0.8–0.9 Å and/or from increased interlayer coupling through the blocking layer by possible improvement in electrical conduction. Additionally, Hg-rich regions and/or planar defects (faults) separating domains where the Re-O_6 octahedra are ordered in different ways could act as pinning centers. [S0163-1829(96)04721-2]

INTRODUCTION

The mercury-based copper-oxide compounds $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n=1$, 2, and 3) exhibit the highest T_c's yet observed for any superconductors (135 K for $n=3$).[1,2] However, the flux-pinning properties of these materials are not as good as for some other high-T_c superconductors (e.g., $YBa_2Cu_3O_{6+x}$), limiting their usefulness for applications.[3–5] Shimoyama *et al.* have recently reported significant improvements in the flux pinning of the mercury-based compounds when Hg is partially replaced by Re or Cr and Ba is replaced by Sr.[6–8] These chemically substituted materials also show improved chemical stability.

The flux-pinning behavior is thought to depend on the degree to which pancakelike vortices in the CuO_2 planes couple along the c axis to form vortex lines and the presence of suitable pinning sites that impede the motion of these vortex lines.[9,10] Shimoyama *et al.* have argued that at least two features of the chemically substituted compounds may enhance flux pinning: (1) the substitution of Sr for Ba significantly shortens the ''blocking layer'' distance (the distance between groups of n CuO_2 conduction planes[6,7]); and (2) the chemical substitution at the Hg site may make the blocking layer more metallic.[11] Both of these are thought to increase the coupling along the c axis. In a recent paper, Chmaissem *et al.* also explored the possibility that extended defects in a chemically substituted Hg (Sr)-1201 compound could act as pinning centers.[12]

Chemically substituted $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ compounds for such studies were first synthesized under ambient pressure in sealed quartz tubes.[6–8,12] Using such techniques, substitution of some Re (Cr, etc.) at the Hg site and Sr for Ba could only be achieved if Ca was partially replaced by Y in the case of $n=2$ and 3 compounds. More recently, using high-pressure techniques, it has been possible to synthesize these compounds without the need for substitution of a trivalent cation at the Ca site.[11] These latter materials exhibit better flux-pinning properties than materials where Ca is partially substituted by Y. In both materials T_c is reduced somewhat by the chemical substitution.

In this paper we report the crystal structures of $Hg_{1-x}Re_xSr_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ for $n=2$ and 3 and $x\approx 0.2$ and 0.25, respectively. Throughout this paper, (Hg, Re)-1212 and (Hg, Re)-1223 will refer to samples where Hg is partially substituted by Re and Ba is totally replaced by Sr. The structural refinements are done with neutron powder diffraction data from samples synthesized at high pressure and again after these samples have been postannealed in evacuated quartz tubes. We have determined the local environment around the Re defect, in particular, the incorporation of additional oxygen to complete the Re coordination. We also report how the host structure is distorted to accommodate this defect and speculate on how these structural changes enhance flux pinning.

0163-1829/96/53(21)/14647(9)/$10.00

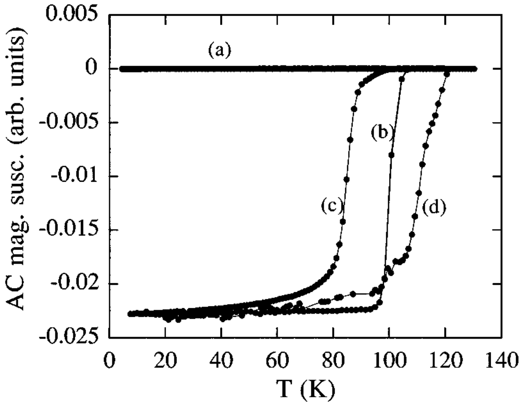

FIG. 1. ac magnetic susceptibiliy measurements for (a) as-prepared $(Hg_{1-x}Re_x)Sr_2CaCu_2O_z$ ($T_c=0$ K), (b) as-prepared $(Hg_{1-x}Re_x)Sr_2Ca_2Cu_3O_z$ ($T_c=107$ K), (c) vacuum-annealed $(Hg_{1-x}Re_x)Sr_2CaCu_2O_z$ ($T_c=90$ K), and (d) vacuum-annealed $(Hg_{1-x}Re_x)Sr_2Ca_2Cu_3O_z$ ($T_c=120$ K).

SYNTHESIS AND CHARACTERIZATION

Samples with nominal Re concentration $x=0.2$–0.25 were prepared at high pressure. The precursor materials prepared from $CaCO_3$, $SrCO_3$, CuO, and ReO_3 were mixed with HgO to achieve nominal compositions of $(Hg_{0.8}Re_{0.2})Sr_2CaCu_2O_y$ and $(Hg_{0.75}Re_{0.25})Sr_2Ca_2Cu_3O_y$. Subsequently, these mixtures were heated at 1270 K for 30 min in gold capsules under an almost isostatic pressure of 6 GPa using a cubic anvil type apparatus. The products were quenched to room temperature. Additional details of the synthesis conditions have been published previously.[11] ac susceptibility measurements showed that the as-prepared $n=2$ compound is not superconducting while the $n=3$ compound is superconducting with a T_c of 107 K. Following the initial measurements the samples were postannealed in evacuated quartz tubes at temperatures around 460–490 °C. As was previously reported,[11] this induced superconductivity in the $n=2$ material and raised T_c in the $n=3$ material. The temperatures required for this annealing are near the decomposition temperatures for these materials. Unfortunately, in the case of the $n=2$ compound, the annealing process resulted in partial decomposition of the sample which created difficulties for precise structural refinement of that sample (to be discussed later).

Figure 1 shows the magnetic susceptibility curves for the samples being investigated in this paper. Irreversibility lines were obtained by measuring the magnetic hysteresis loops of the vacuum-annealed samples (optimal T_c) up to ±7.5 T using a vibrating-sample magnetometer apparatus. The irreversibility line for the (Hg, Re)-1223 sample is shown in Fig. 2. The figure shows that although (Hg, Re)-1223 exhibits a T_c of only 120 K its irreversibility line lies at higher fields than that of $HgBa_2Ca_2Cu_3O_{8+\delta}$.[3] The irreversibility line for our (Hg, Re)-1212 sample could not be measured because of its partial decomposition during the vacuum anneal. However, previous work of Shimoyama *et al.*[6] shows a significant improvement of the Re-doped $n=2$ sample compared to that of undoped Hg(Ba)-1212. More detailed work is currently underway.

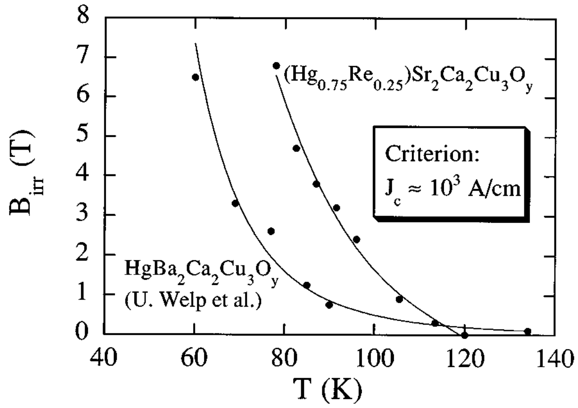

FIG. 2. Irreversibility line for vacuum-annealed $(Hg_{1-x}Re_x)Sr_2Ca_2Cu_3O_z$ compared to that of $HgBa_2Ca_2Cu_3O_z$ [by Welp *et al.* (Ref. 3)].

NEUTRON POWDER DIFFRACTION

Neutron powder diffraction measurements were performed on the Special Environment Powder Diffractometer at Argonne's Intense Pulsed Neutron Source.[13] To obtain enough material for the neutron diffraction experiments, each sample consisted of the product of two high-pressure synthesis runs under identical conditions. Small sintered pellets from the high-pressure synthesis [480 mg for (Hg, Re)-1212 and 300 mg for (Hg, Re)-1223] were suspended on an amorphous boron fiber in the neutron beam to minimize background scattering. Data collection required 20–24 h per sample. Data were analyzed by the Rietveld technique, using the GSAS code[14] over a d-spacing range of 0.5–4 Å, which included 1256 and 1506 Bragg peaks for $n=2$ and 3, respectively. Two phases with the infinite-layer structure[15] but with slightly different lattice parameters (thought to be compounds of the type $Sr_{1-x}Ca_xCuO_2$) appeared as a minor impurity phases in both samples and were included in the refinements. Figure 3 shows the raw diffraction data and best-fit Rietveld profiles for the two samples.

AS-PREPARED SAMPLES

Initial refinements carried out using the tetragonal space group $P4/mmm$ of the Hg(Ba)-$\{12(n-1)n\}$ compounds were found to give satisfactory results with reasonably low R factors. However, selective peak broadening indicated a slight orthorhombic distortion in both data sets. Refinements using the orthorhombic space group $Pmmm$ were attempted and found to give substantially better fits (strongly favored by R-value ratio tests), indicating orthorhombic strains on the order of 0.2%. This result is consistent with the observation by electron diffraction[11] of a face-centered orthorhombic supercell of dimensions $2a\times4b\times2c$ in about 20–50 % of the crystallites in both samples. However, no supercell reflections were visible in the neutron diffraction data. Refinements of the average structure were done in the fundamental orthorhombic cell. Anisotropic temperature factors were assigned to those atoms that showed unusually large isotropic temperature factors. For the $n=3$ compound, it was necessary to apply the constraint $U_{11}=U_{22}$ to the O($1a$) and O($1b$) oxygen atoms because of the small orthorhombic

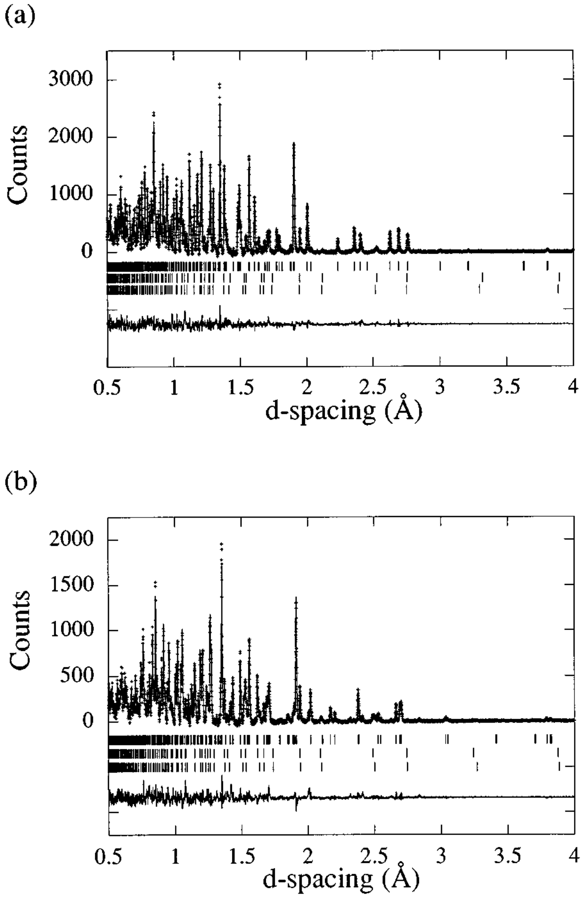

FIG. 3. Best-fit Rietveld refinement profiles for as-prepared $Hg_{1-x}Re_xSr_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($x=0.2$) for $n=2$ (a) and ($x=0.25$) for $n=3$ (b). Plus marks (+) are the raw time-of-flight neutron powder diffraction data. The solid line is the calculated profile. Tick marks below the profiles mark the positions of allowed Bragg reflections. A difference curve (observed minus calculated) is plotted at the bottom.

splitting. Refined structural parameters are given in Table I for (Hg, Re)-1212 and in Table II for (Hg, Re)-1223.

It was found that Re substitutes at the Hg site. Each Re atom is surrounded by four oxygen atoms, O(3), but these are not at the ideal (1/2,1/2,0) site where interstitial oxygen would be incorporated into the normal Hg(Ba)-1212 and Hg(Ba)-1223 structures.[16–19] Rather, these oxygen atoms are displaced to a general site (x,y,z), where $z=0.01$ for $n=2$ and 0 for $n=3$, to achieve appropriate bond lengths (~1.88 Å) with Re. The local structure in the region of this complex Re defect is shown in Fig. 4. For a Re concentration of $x=0.25$, one additional oxygen atom per formula unit (i.e., $\delta=1$) would be incorporated, filling all of the available oxygen sites in the (Hg, Re) plane. Our refinements give Re and O(3) site occupancies one or two standard deviations above these limiting values, suggesting that both samples are near the limit of Re solubility.

If the apical oxygen atoms O(2) remained at $(0,0,z)$ positions, there would be a nearly perfect octahedron of oxygen atoms around each Re atom. However, we observe that a fraction of the O(2) atoms equal to twice the Re content are displaced about 0.3–0.4 Å along the x axis to a new $(x,0,z)$ site, O(2′), resulting in a distorted octahedron. Interestingly, the distortion of the $Re\text{-}O_6$ octahedron is nearly the same for the (Hg, Re)-1212 and (Hg, Re)-1223 structures (Table III) suggesting a common reason for the occurrence of the distortion. We speculate that this distortion lowers the free energy of the $Re\text{-}O_6$ octahedron compared to a perfect octahedron and may be related to the charge state of Re. Because the octahedron is essentially bonded to the rest of the structure only by its apical bonds to the Cu atoms above and below, it is free to distort in a way that would not be allowed if it were bonded in three dimensions. This orthorhombic distortion of the $Re\text{-}O_6$ octahedra is consistent with the orthorhombic distortion of the unit cells of both structures.

Our model for the Re defect is the one most consistent with the diffraction data, but it is, in general, impossible to prove uniqueness. Establishing the exact Re content is difficult. In previous refinements of Hg-1212 and Hg-1223 structures where the Hg site occupancy has been refined, there has been evidence for Hg vacancies or the substitution of some atom with a smaller scattering length (e.g., copper or carbon) on the Hg site.[16,19] For this reason, the refined Re contents in the present refinements cannot be viewed as being reliable. Taken at face value, our refinements would suggest Re contents of 29% to 38% (Tables I–V)—well above the conceptual solubility limit. However, if Hg vacancies or other substitutional defects are present, even in small concentration, our refined values for the Re content would drop below 25%. Because of these difficulties, the best estimate for the Re content is given by the refined occupancies for the associated oxygen atoms O(2′) and O(3). These refined occupancies are consistent with a Re content near the conceptual solubility limit of 25%.

In addition to this difficulty, we cannot rule out the possibility of a different Re configuration for a small fraction of the Re atoms. The rich chemistry of Re could allow for such defects. For example, Re atoms could form local pairs with an associated oxygen-atom environment consistent with the Re clustering. We see no evidence for such configurations in our structure refinements. Our model in which every Re atom is octahedrally coordinated to six oxygen atoms accounts for all of the available Re and for full occupancy of the O(3) oxygen site, but more complex Re defects at a small concentration consistent with the error bars are not precluded.

VACUUM-ANNEALED SAMPLES

Both the $n=2$ and 3 samples were vacuum annealed to improve their superconducting properties. The $n=3$ sample was successfully postannealed in an evacuated quartz tube at 460 °C. Unfortunately, the vacuum-annealed $n=2$ sample was partially decomposed resulting in a sample in which 60% of the material was the desired (Hg, Re)-1212 phase. T_c's of 90 and 120 K were measured for the vacuum annealed $n=2$ and 3 samples, respectively.

The vacuum-annealed compounds were found to have tetragonal structures with space group $P4/mmm$. Because of the partial decomposition of the $n=2$ sample, the most reliable structure refinements were those for the $n=3$ sample. O(3) atoms were found to occupy displaced positions around Re atoms as for the previous refinements while apical O(2) atoms were not found to be displaced off the c axis. Thus the

TABLE I. Refined structural parameters for the as-prepared $(Hg_{1-x}Re_x)Sr_2CaCu_2O_{6+\delta}$ sample. Orthorhombic space group Pmmm (No. 47). Lattice parameters are $a=3.8014(1)$ Å, $b=3.8101(1)$ Å, and $c=12.0124(3)$ Å. Final agreement factors are $R_p=4.00\%$, $R_{wp}=6.47\%$, and $\chi^2=1.654$. Constraints are $n(\text{Hg})+n(\text{Re})=1$; $n[\text{O}(2)]+n[\text{O}(2')]=2$; $U(\text{Hg})=U(\text{Re})$ and $U[\text{O}(2)]=U[\text{O}(2)]$.

Atom	Site	x	y	z	U(Å^2)	n
Hg	1a	0	0	0	U_{11}: 0.017(3)	0.66(3)
					U_{22}: 0.014(3)	
					U_{33}: 0.006(1)	
Re	1a	0	0	0	U_{11}: 0.017(3)	0.34(3)
					U_{22}: 0.014(3)	
					U_{33}: 0.006(1)	
Sr	2t	1/2	1/2	0.2115(1)	0.0082(5)	2
Ca	1h	1/2	1/2	1/2	0.0019(7)	1
Cu	2q	0	0	0.36115(15)	0.0043(5)	2
O(1a)	2s	1/2	0	0.3642(8)	U_{11}: 0.000(2)	2
					U_{22}: 0.018(3)	
					U_{33}: 0.017(5)	
O(1b)	2r	0	1/2	0.3682(7)	U_{11}: 0.003(2)	2
					U_{22}: 0.005(2)	
					U_{33}: 0.012(5)	
O(2)	2q	0	0	0.1646(6)	0.004(1)	1.53(9)
O(2′)	4w	0.09(1)	0	0.153(2)	0.004(1)	0.47(9)
O(3)	8a	0.368(3)	0.330(3)	0.011(1)	0.007(3)	1.09(3)

TABLE II. Refined structural parameters for the as-prepared $(Hg_{1-x}Re_x)Sr_2Ca_2Cu_3O_{8+\delta}$ sample. Orthorhombic space group Pmmm (No. 47). Lattice parameters are $a=3.8197(2)$ Å, $b=3.8252(2)$ Å, and $c=15.1709(6)$ Å. Final agreement factors are $R_p=5.84\%$, $R_{wp}=9.60\%$, $R_I=6.56\%$, and $\chi^2=2.049$. Constraints are $n(\text{Hg})+n(\text{Re})=1$; $n[\text{O}(2)]+n[\text{O}(2')]=2$; $U(\text{Hg})=U(\text{Re})$; $U[\text{O}(1a)]=U[\text{O}(1b)]$; $U[\text{O}(2)]=U[\text{O}(2')]$. Note that oxygen atoms have been numbered differently than in previous work (e.g., Ref. 19) to enable an easier comparison with the $n=3$ structure.

Atom	Site	x	y	z	U(Å^2)	n
Hg	1a	0	0	0	U_{11}: 0.013(4)	0.71(5)
					U_{22}: 0.030(5)	
					U_{33}: 0.006(2)	
Re	1a	0	0	0	U_{11}: 0.013(4)	0.29(5)
					U_{22}: 0.030(5)	
					U_{33}: 0.006(2)	
Sr	2t	1/2	1/2	0.1673(2)	0.013(1)	2
Ca	2t	1/2	1/2	0.3914(3)	0.0027(8)	2
Cu(1)	1c	0	0	0.5	0.0041(10)	1
Cu(2)	2q	0	0	0.2845(2)	0.0056(8)	2
O(4a)	1d	1/2	0	1/2	0.001(2)	1
O(4b)	1g	0	1/2	1/2	0.019(4)	1
O(1a)	2s	1/2	0	0.2941(7)	U_{11}: 0.0053(9)	2
					U_{22}: 0.0053(9)	
					U_{33}: 0.018(3)	
O(1b)	2r	0	1/2	0.2848(1)	U_{11}: 0.0053(9)	2
					U_{22}: 0.0053(9)	
					U_{3}: 0.018(3)	
O(2)	2q	0	0	0.1307(12)	0.008(2)	1.50(8)
O(2′)	4w	0.10(1)	0	0.119(2)	0.008(2)	0.50(8)
O(3)	4y	0.371(3)	0.322(3)	0	0.005(3)	1.11(5)

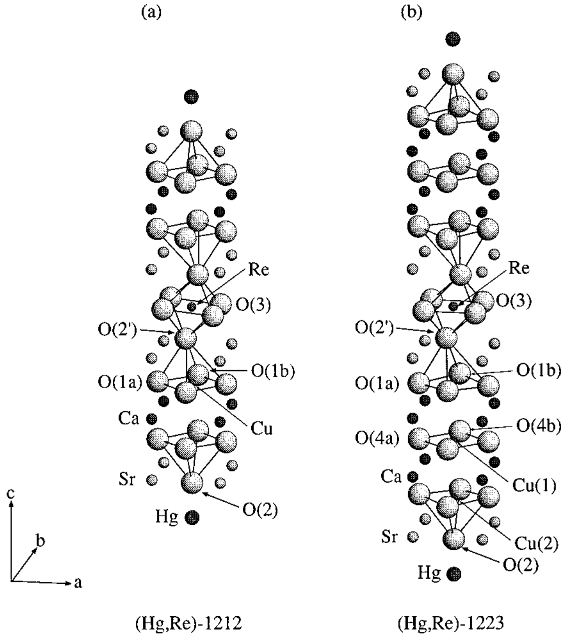

FIG. 4. Portions of the structures of as-prepared $Hg_{1-x}Re_xSr_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ for $n=2$ (a) and $n=3$ (b) showing the configuration of the Re-O_6 octahedra that substitutes for the Hg-O_2 dumbbells in the blocking layer.

Re octahedra are not distorted and have longer apical Re-O(2) distances of 1.931 Å (compared to 1.83–1.87 Å) (Table III). The in-plane Re-O(3) bond lengths remain essentially the same. The refined occupancy factor of the O(3) oxygen atoms is found to show about 90% filled sites. If all Re atoms are assumed to have a full sixfold coordination to oxygen atoms, this suggests a Re substitution of ≈22–23 % (as opposed to the solubility limit of 25%) at the Hg site and that the oxygen removed by postannealing is interstitial oxygen, which is the common doping mechanism in these compounds. This explanation seems most likely to us. However, if another more complex Re defect (e.g., Re clustering) exists at a concentration too small to be seen in our diffraction experiments, changes in oxygen content could also be associated with changes in the concentration of such defects.

Similar features were obtained for the vacuum-annealed $n=2$ sample. Extra impurity lines resulting from the partial decomposition were observed in the neutron diffraction pattern for this sample. Sr_2CuO_3 was identified as an additional impurity phase, however, some lines were not identified. The normalized scale factor of the (Hg, Re)-1212 phase was decreased by about 40–45 %. Multiple-phase Rietveld refinements carried out on this sample gave satisfactory results. Nevertheless, it should be pointed out that parameters which require highly accurate data such as the oxygen occupancy factors should be interpreted with caution. Refined structural parameters for both $n=2$ and 3 vacuum-annealed samples

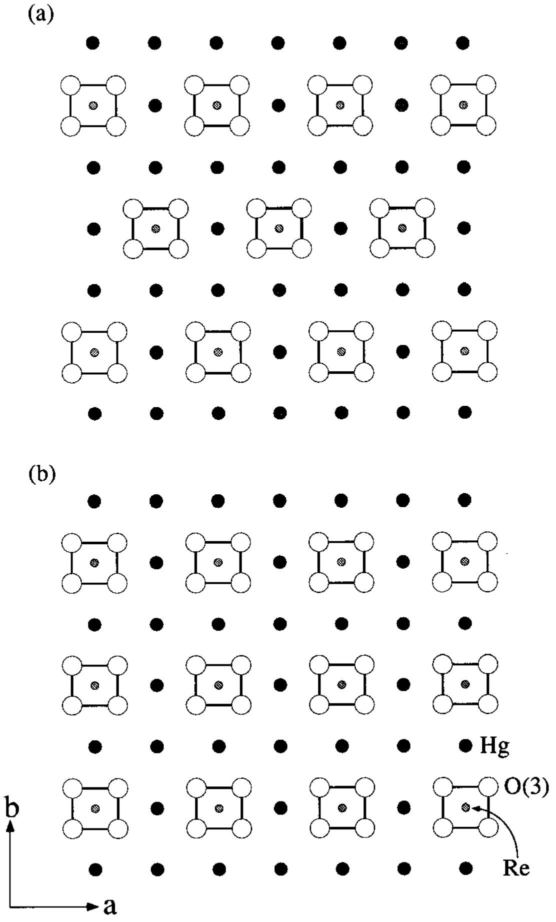

FIG. 5. Idealized view of the a-b plane of $Hg_{1-x}Re_xSr_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ showing two possible ordered arrangements for the Re-O_6 octahedra. The arrangement shown at the top (a) is consistent with the $2a\times4b\times2c$ supercell (Ref. 11) seen by electron diffraction for some crystallites.

TABLE III. Re-O and O-O distances (Å) in the Re-O_6 octahedra.

		$n=2$	$n=2$ (vacuum annealed)	$n=3$	$n=3$ (vacuum annealed)
Re-O(Hg)	×4	1.884 (6)	1.859(12)	1.879(10)	1.883(11)
Re-O(apical)	×2	1.869(25)	1.932(5)	1.83(4)	1.931(5)
O(Hg)-O(Hg)	×2	2.57(2)	2.55(11)	2.46(3)	2.47(3)
O(Hg)-O(Hg)	×2	2.81(2)	2.63(2)	2.84(3)	2.84(4)
O(apical)-O(Hg)	×2	2.56(3)	2.681(9)	2.43(4)	2.697(8)
O(apical)-O(Hg)	×2	2.74(3)	2.681(9)	2.81(4)	2.697(8)

TABLE IV. Refined structural parameters for the vacuum-annealed $(Hg_{1-x}Re_x)Sr_2CaCu_2O_{6+\delta}$ sample (490 °C, 12 h). Tetragonal structure of space group $P4/mmm$ (No. 123). Lattice constants $a=3.8152(1)$ Å and $c=12.0621(5)$ Å. Agreement factors $R_p=5.05\%$, $R_{wp}=7.38\%$, and $\chi^2=2.782$. Constraints are $n(\mathrm{Hg})+n(\mathrm{Re})=1$; $U(\mathrm{Hg})=U(\mathrm{Re})$.

Atom	Site	x	y	z	U(Å^2)	n
Hg	1a	0	0	0	U_{11}:0.021(2) U_{22}:0.021(2) U_{33}:0.022(4)	0.62(6)
Re	1a	0	0	0	U_{11}:0.021(2) U_{22}:0.021(2) U_{33}:0.022(4)	0.38(6)
Sr	2h	1/2	1/2	0.2168(3)	0.017(1)	2
Ca	1d	1/2	1/2	1/2	0.010(2)	1
Cu	2g	0	0	0.3647(3)	0.0005(8)	2
O(1)	4i	1/2	0	0.3660(3)	U_{11}:0.0000(1) U_{22}:0.013(2) U_{33}:0.014(2)	4
O(2)	2g	0	0	0.1601(4)	U_{11}:0.016(2) U_{22}:0.016(2) U_{33}:0.004(3)	2
O(3)	8p	0.354(2)	0.335(2)	0	0.018(4)	1.15(6)

are given in Tables IV and V. Selected bond lengths are given in Tables VI and VII.

DISCUSSION

Based on the refinements, if we consider the as-prepared compounds to have fully occupied oxygen sites in the (Hg, Re) plane, the stoichiometry would be $(Hg_{0.78}Re_{0.23})Sr_2Ca_2Cu_3O_9$ for the $n=3$ sample. Assuming that Re atoms have a valence of +7, the Cu valence is approximately +2.28, suggesting that the sample is slightly overdoped. This is consistent with the increase of T_c by vacuum annealing. The same argument, applied to the $n=2$ sample, suggests that the sample is even further overdoped (Cu valence ≈2.5) explaining the absence of superconductivity in that sample prior to annealing. This hypothesis is

TABLE V. Refined structural parameters for the vacuum-annealed $(Hg_{1-x}Re_x)Sr_2Ca_2Cu_3O_{8+\delta}$ sample (460 °C, 12 h). Tetragonal structure of space group $P4/mmm$ (No. 123). Lattice constants $a=3.8265(1)$ Å and $c=15.2126(5)$ Å. Agreement factors $R_p=4.57\%$, $R_{wp}=7.55\%$, and $\chi^2=2.148$. Constraints are $n(\mathrm{Hg})+n(\mathrm{Re})=1$; $U(\mathrm{Hg})=U(\mathrm{Re})$.

Atom	Site	x	y	z	U(Å^2)	n
Hg	1a	0	0	0	U_{11}:0.027(2) U_{22}:0.027(2) U_{33}:0.003(2)	0.68(4)
Re	1a	0	0	0	U_{11}:0.027(2) U_{22}:0.027(2) U_{33}:0.003(2)	0.32(4)
Sr	2h	1/2	1/2	0.1699(2)	0.013(1)	2
Ca	2h	1/2	1/2	0.3924(3)	0.0033(8)	2
Cu(1)	1b	0	0	0.5	0.0040(9)	1
Cu(2)	2g	0	0	0.2850(2)	0.0053(7)	2
O(4)	2e	1/2	0	1/2	U_{11}:0.014(2) U_{22}:0.008(2) U_{33}:0.007(2)	2
O(1)	4i	1/2	0	0.2896(2)	U_{11}:0.0036(8) U_{22}:0.0036(8) U_{33}:0.026(2)	4
O(2)	2g	0	0	0.1269(3)	U_{11}:0.032(2) U_{22}:0.032(2) U_{33}:0.000(2)	2
O(3)	8p	0.371(5)	0.323(4)	0	0.006(4)	0.90(4)

TABLE VI. Selected bond lengths (Å) for $(Hg_{0.8}Re_{0.2})Sr_2CaCu_2O_{6+\delta}$ compared with those of $HgBa_2CaCu_2O_{6+\delta}$ (from Ref. 16).

	$HgBa_2CaCu_2O_{6+\delta}$	$(Hg_{1-x}Re_x)Sr_2CaCu_2O_{6+\delta}$ (as prepared)	$(Hg_{1-x}Re_x)Sr_2CaCu_2O_{6+\delta}$ (vacuum annealed)
Hg-O(2)	1.986(2)	1.978(7)	1.932(5)
Hg-O(3)	2.726(1)		
Re-O(2)			1.932(5)
Re-O(2′)		1.869(25)	
Re-O(3)		1.884(6)	1.859(12)
Sr-O(1*a*)	2.767(2)	2.644(7)	2.623(4)
Sr-O(1*b*)		2.675(6)	
Sr-O(2)	2.841(1)	2.749(2)	2.7828(16)
Sr-O(2′)		2.56(2)/3.03(3)	
Sr-O(3)	2.786(2)	2.55(2)/2.79(2)	2.747(5)
CaO(1*a*)	2.481(1)	2.508(6)	2.500(2)
CaO(1*b*)		2.473(6)	
Cu-O(1*a*)	1.928(1)	1.9011(2)	1.90766(7)
Cu-O(1*b*)		1.9070(4)	
Cu-O(2)	2.775(3)	2.361(8)	2.468(6)
Cu-O(2′)		2.52(3)	

supported by the observed lengthening of the apical Cu-O bonds from 2.32–2.36 to 2.41–2.47 Å upon vacuum annealing.

Important features of the (Hg, Re)-1212 and (Hg, Re)-1223 structures are compared to those of the ideal structures in Table VIII. The substitution of Sr for Ba and the incorporation of Re at 22–23 % of the Hg sites shortens the blocking layer distances by 0.78–0.90 Å for $n=2$ and 0.75–0.80 Å for $n=3$. The c axes are shortened by a slightly smaller amount because the spacing between adjacent CuO_2 planes actually increases by about 0.1 Å. The apical Cu-O bonds are shortened significantly to 2.32–2.36 Å for those associated with Hg in the blocking layer [Cu-O(2)] and to 2.52–2.54 Å for those associated with Re in the blocking layer [Cu-O(2′)]. This is probably what gives rise to the increased buckling of the CuO_2 planes. It has been previously argued that flat CuO_2 planes and long Cu-O apical bonds are required to achieve the highest T_c's in these compounds.[16,19] Thus the reduction

TABLE VII. Selected bond lengths (Å) for $(Hg_{0.75}Re_{0.25})Sr_2Ca_2Cu_3O_{8+\delta}$ compared with those of $HgBa_2Ca_2Cu_3O_{8+\delta}$ (from Ref. 19).

	$HgBa_2Ca_2Cu_3O_{8+\delta}$	$(Hg_{1-x}Re_x)Sr_2Ca_2Cu_3O_{8+\delta}$ (as prepared)	$(Hg_{1-x}Re_x)Sr_2Ca_2Cu_3O_{8+\delta}$ (vacuum annealed)
Hg-O(2)	1.972(3)	1.995(13)	1.931(5)
Hg-O(3)	2.7208(3)		
Re-O(2)			1.931(5)
Re-O(2′)		1.83(4)	
Re-O(3)		1.879(10)	1.883(11)
Sr-O(1*a*)	2.772(6)	2.713(8)	2.641(4)
Sr-O(1*b*)		2.612(8)	
Sr-O(2)	2.828(6)	2.757(3)	2.7837(15)
Sr-O(2′)		2.58(3)/3.05(5)	
Sr-O(3)	2.744(4)	2.674(4)	2.718(5)
Ca-O(1*a*)		2.415(8)	2.471(4)
Ca-O(1*b*)		2.502(7)	
Ca-O(4*a*)		2.525(3)	2.518(3)
Ca-O(4*b*)		2.523(3)	
Cu(2)-O(1*a*)	1.9239(2)	1.9155(9)	1.9145(2)
Cu(2)-O(1*b*)		1.91263(12)	
Cu(2)-O(2)	2.741(6)	2.320(13)	2.406(6)
Cu(2)-O(2′)		2.54(4)	
Cu(1)-O(4*a*)		1.90986(11)	1.91323(5)
Cu(1)-O(4*b*)		1.91262(12)	

TABLE VIII. Some features of the (Hg, Re)-1212 and (Hg, Re)-1223 structures compared to those of the ideal structures (Refs. 16 and 19).

	Hg-1212 (Ref. 16)	As-prepared (Hg, Re)-1212 (this work)	Vacuum-annealed (Hg, Re)-1212 (this work)	Hg-1223 (Ref. 19)	As-prepared (Hg, Re)-1223 (this work)	Vacuum-annealed (Hg, Re)-1223 (this work)
a (Å)	3.8552(1)	3.8014(1)	3.8152(1)	3.84786(4)	3.8197(2)	3.8265(1)
b (Å)		3.8101(1)			3.8252(2)	
c (Å)	12.6651(2)	12.0124(3)	12.0621(5)	15.7782(3)	15.1709(6)	15.2126(5)
Cu-O$_{\text{apical}}$	2.775(3)	2.4405 (av.)	2.468(6)	2.741(6)	2.43 (av.)	2.406(6)
Cu-O$_{\text{in plane}}$	1.928(1)	1.90405 (av.)	1.90766(7)	1.9239(2)	1.91407 (av.)	1.9145(2)
Buckling angle:						
O-Cu-O (deg) (x direction)	179.4(2)	177.8(6)	178.9(34)	178.4(4)	179.649(4)	175.8(3)
(y direction)		174.9(5)			171.2(7)	
Cu-Cu (Å)	3.147(1)	3.336(4)	3.267(7)	3.176(3)	3.270(3)	3.270(3)
Blocking distance:						
Cu→Hg→Cu (Å)	9.5792	8.677(4)	8.800(5)	9.4259	8.630(6)	8.674(5)

in T_c is consistent with these structural changes.

Under the assumption that each Re atom has four oxygen atom neighbors in the (Hg, Re) plane, two Re defects cannot be adjacent to one another. Clustering of Re defects is not allowed and 25% Re substitution is the solubility limit. For 25% Re substitution, there are two possible arrangements of Re-O$_6$ octahedra in the a-b plane, as shown in Fig. 5. One of these [Fig. 5(a)] is consistent with the $2a \times 4b \times 2c$ supercell observed by electron diffraction.[11] The existence of the three-dimensional supercell depends on this stacking arrangement and also on its ordering along the c axis i.e., alternating Re and Hg. The fact that such a supercell was observed only for part of the crystallites of the (Hg, Re)-1212 and (Hg, Re)-1223 samples suggests that the local ordering of Re-O$_6$ defects may not persist over long distances in these materials.

The structures of these compounds are consistent with the ideas previously proposed by Shimoyama *et al.* to explain the enhanced flux-pinning—shortening of the blocking layer and changes in its electronic structure that could increase coupling.[6] This shortening of the blocking layer distance arises from the substitution of Sr for Ba. The coupling of pancake vortices to form vortex lines could also be enhanced by a change in the electronic structure due to the difference between Re-O$_6$ octahedra and Hg-O$_2$ dumbbells in the blocking layer. For compositions with 25% Re (the solubility limit) there should be no Hg or Re-rich defects that would act as pinning centers for vortex lines, unless there is a small concentration of Re-cluster defects below our limit of detectability in the diffraction measurements. However, our results suggest 22–23% Re substitution which means that in localized regions Hg atoms could cluster to form Hg-rich regions. These Hg-rich regions would be about 15–16 Å in diameter if only one Re atom were removed from the plane. Furthermore, two-dimensional faults separating regions in which the Re-O$_6$ octahedra are ordered in the two different ways shown in Fig. 5 are likely to occur and could also act as pinning centers.

CONCLUSIONS

Using the neutron diffraction technique, we were able to determine the structure resulting from substitution of Re atoms on the Hg sites in (Hg, Re)Sr$_2$Ca$_{n-1}$Cu$_n$O$_z$. Substituting 25% of Hg with Re (the solubility limit) will result in forming an ordered network of Re and Hg atoms and in filling all available oxygen sites in the (Hg, Re) plane to complete the coordination shells of the Re octahedra. There would be no sites where oxygen interstitials or vacancies could be formed to control the doping level and optimize T_c. Our work and that of Yamaura *et al.*[11] shows that as-prepared samples of the $n=2$ compound exhibit zero or near-zero superconducting fractions which were increased dramatically by postannealing in evacuated quartz ampoules. For the $n=3$ sample, the T_c is raised by postannealing. Thus our work suggests that the as-prepared samples are slightly Re deficient ($x < 0.25$) and oxygen overdoped and that oxygen is removed by the post annealing to achieve the proper doping level. Neutron diffraction results are consistent with this oxygen being removed from the interstitial sites in the Hg/Re layer. Based on these results, one could speculate that T_c could be raised by varying the Re content below the solubility limit of 25%. Samples with lower Re contents ($x < 0.25$) would allow a greater range of variable oxygen concentration (providing a means for adjusting T_c) and may also support the formation of various defects that could act as pinning centers. It may then be possible to optimize flux pinning while minimizing the reduction of T_c.

ACKNOWLEDGMENTS

We wish to acknowledge John Mitchell for useful discussions concerning Re crystal chemistry and D. N. Argyriou and S. Short for help with data collection. The work at Argonne was supported by the U.S. Department of Energy, Division of Basic Energy Science–Materials Sciences, under Contract No. W-31-109-ENG-38 (J.D.J.) and by the National Science Foundation, Office of Science and Technology Centers under Grant No. DMR 91-20000 (O.C.). The work at Kyoto University and University of Tokyo was supported by a Grant-in-Aid for Scientific Research by the Ministry of Education, Science and Culture of Japan.

[1] S. N. Putilin, E. V. Antipov, O. Chmaissem, and M. Marezio, Nature (London) **362**, 226 (1993).

[2] A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott, Nature (London) **363**, 56 (1993).

[3] U. Welp, G. W. Crabtree, J. L. Wagner, D. G. Hinks, P. G. Radaelli, J. D. Jorgensen, and J. F. Mitchell, Appl. Phys. Lett. **63**, 693 (1993).

[4] A. Umezawa, W. Zhang, A. Gurevich, Y. Feng, E. E. Hellstron, and D. C. Larbalestier, Nature (London) **364**, 129 (1993).

[5] P. Estrela, C. Abilio, M. Godinho, J. L. Tholence, and J. J. Capponi, Physica C **235–240**, 2731 (1994).

[6] J. Shimoyama, S. Hahakura, R. Kobayashi, K. Kitazawa, K. Yamafuji, and K. Kishio, Physica C **235–240**, 2795 (1994).

[7] J. Shimoyama, K. Kishio, S. Hahakura, K. Kitazawa, K. Yamaura, Z. Hiroi, and M. Takano, in *Advances in Superconductivity VII*, edited by K. Yamafuji and T. Morishita (Springer-Verlag, Tokyo, 1995), pp. 287–290.

[8] J. Shimoyama, S. Hahakura, K. Kitazawa, Y. Yamafuji, and K. Kishio, Physica C **224**, 1 (1994).

[9] K. E. Gray and D. H. Kim, Physica C **180**, 139 (1991).

[10] K. E. Gray, Appl. Superconductivity **2**, 295 (1994).

[11] K. Yamaura, J. Shimoyama, S. Hahakura, Z. Hiroi, M. Takano, and K. Kishio, Physica C **246**, 351 (1995).

[12] O. Chmaissem, D. N. Argyriou, D. G. Hinks, J. D. Jorgensen, B. G. Storey, H. Zhang, L. D. Marks, Y. Y. Wang, V. P. Dravid, and B. Dabrowski, Phys. Rev. B **52**, 15 636 (1995).

[13] J. D. Jorgensen, J. Faber, Jr., J. M. Carpenter, R. K. Crawford, J. R. Haumann, R. L. Hitterman, R. Kleb, G. E. Ostrowski, F. J. Rotella, and T. G. Worlton, J. Appl. Crystallogr. **22**, 321 (1989).

[14] A. C. Larson and R. B. VonDreele, General Structure Analysis System, University of California (1985–1990).

[15] T. Siegrist, S. M. Zahurak, D. W. Murphy, and R. S. Roth, Nature (London) **334**, 231 (1988).

[16] P. G. Radaelli, J. L. Wagner, B. A. Hunter, M. A. Beno, G. S. Knapp, J. D. Jorgensen, and D. G. Hinks, Physica C **216**, 29 (1993).

[17] S. M. Loureiro, E. V. Antipov, J. L. Tholence, J. J. Capponi, O. Chmaissem, Q. Huang, and M. Marezio, Physica C **217**, 253 (1993).

[18] O. Chmaissem, Q. Huang, E. V. Antipov, S. N. Putilin, M. Marezio, S. M. Loureiro, J. J. Capponi, J. L. Tholence, and A. Santoro, Physica C **217**, 265 (1993).

[19] J. L. Wagner, B. A. Hunter, D. G. Hinks, and J. D. Jorgensen, Phys. Rev. B **51**, 15 407 (1995).