

Structure and superconductivity of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$

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(Received 15 August 1994)

We have investigated the structure, defect concentration, and superconducting properties of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ by neutron powder diffraction, thermogravimetric analysis, and ac susceptibility. Samples with three oxygen contents and T_c 's ranging from 135 to 94 K, obtained through different annealing conditions, were studied. Two defect sites were observed in all samples. The concentration of defect oxygen atoms located at a site in the center of the Hg-O₈ plane, is found to vary from 0.18(2) to 0.10(2) oxygen atoms per formula unit as T_c decreases from 135 to 94 K. An additional defect, which we interpret as oxygen atoms associated with the substitution of Cu on the Hg site, is found to have a fixed concentration of $\sim 0.09(2)$ oxygen atoms per formula unit.

I. INTRODUCTION

The discovery of superconductivity at 94 K in $\text{HgBa}_2\text{CuO}_{4+\delta}$,¹ and subsequently higher T_c 's (up to 135 K) in higher members of the $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ series of compounds,^{2,3} has generated a tremendous amount of interest in these new Hg-based materials. The $n=1, 2$, and 3 Hg compounds possess the highest T_c 's of any known single, double, and triple CuO_2 layer compounds—98, 128, and 135 K, respectively. Under pressure, T_c 's are found to increase by more than 20 K in these compounds, to temperatures exceeding 150 K at 10 GPa for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$.^{4,5}

Structurally, the Hg-based compounds are analogs for the single-thallium-layer series of compounds, differing only in the oxygen content within the Hg(Tl)-oxygen layer. Defects within the Hg-O₈ layers are found to determine the T_c 's of these materials. Here, δ is the total excess oxygen which can be distributed over more than one crystallographic defect site. X-ray and neutron-diffraction studies^{1,6,7} on $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg-1201) have established the variable doping mechanism to be the incorporation of oxygen at the $[1/2, 1/2, 0]$ site. For samples with $T_c \sim 95$ K, 0.06 oxygen atoms per formula unit are found at this interstitial site as determined by neutron-diffraction studies.^{6,7} In the study by Wagner *et al.*,⁶ T_c was found to decrease to 59 K, as the amount of oxygen at this site was reduced to zero. This decrease in oxygen content was also independently determined by thermogravimetric analysis (TGA) measurement on the same single-phase samples used in the diffraction work. Evidence was found that doping is also provided by an additional complex defect involving the partial substitution of copper for mercury coupled with the presence of oxygen on the $[1/2, 0, 0]$ chain site. The occupancy of this second oxygen site was found to be ~ 0.09 atoms per formula unit (resulting in a total defect oxygen concentration of $\delta=0.15$), and remained constant during low-temperature annealing. In light of band-structure calcu-

lations suggesting that self-doping is not present in $\text{HgBa}_2\text{CuO}_{4+\delta}$,⁸ this additional defect is of special importance. The existence of this defect is necessary to account for the relatively high T_c of ~ 59 K in a sample where the $[1/2, 1/2, 0]$ site is found to be unoccupied. It should be noted that Chmaissem *et al.*⁷ found no evidence for this complex defect in their Hg-1201 sample. They found 0.06 excess oxygen atoms solely on the $[1/2, 1/2, 0]$ site. However, additional support for a defect associated with metal-ion substitution comes from the different T_c 's for Hg-1201 samples reported in the literature. While maximum T_c 's are usually achieved for fully oxygenated samples, Itoh *et al.*⁹ have reported maximum T_c 's obtained under reducing conditions. Oxidation actually degraded the superconducting properties of the samples used in that study. More subtle variations in maximum T_c 's (differing by as much as 5 K) were observed for samples annealed in 1 atm of oxygen by Morosin *et al.*¹⁰ These results suggest that oxygen content alone cannot fully account for the different T_c 's for samples annealed in oxygen. The existence of an additional doping defect could explain these differences.

Neutron-diffraction studies¹¹⁻¹⁴ on $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ (Hg-1212) have also established oxygen on the $[1/2, 1/2, 0]$ site as the variable doping mechanism in this compound. The amount of oxygen on the $[1/2, 1/2, 0]$ site has been refined for various Hg-1212 samples with different T_c 's. In these studies, no second defect involving oxygen on the $[1/2, 0, 0]$ site has been found. The maximum T_c for this compounds is ~ 128 K and corresponds to $\delta \sim 0.22$.^{11,12} T_c is found to be reduced to 92 K for $\delta \sim 0.08$ (Ref. 11) and to 104 K for $\delta \sim 0.35$,¹³ indicating that it is possible to both underdope and overdope this compound. Hg-1212 samples with T_c 's intermediate to these extreme values have also been measured,¹⁴ with values of $\delta=0.22$ and 0.35 for T_c 's of 112 and 120 K, respectively. Although these powder neutron-diffraction studies did not detect any appreciable amount of the additional chain oxygen defect, Radaelli

*et al.*¹¹ did report a 4% deficiency in scattering intensity from the Hg site in the Hg-1212 samples studied, which could be interpreted as Cu substitution on the Hg site. Values of defect oxygen concentration determined in these studies are generally in good agreement, yet several questions still remain regarding possible defects present in these materials. A recent x-ray study by Finger *et al.*¹⁵ on single crystals of Hg-1212 reports a significant deficiency in scattering density from the Hg site, which the authors interpret as the substitution of 0.13 Cu atoms on the Hg site, and the presence of 0.10 oxygen atoms on the $[1/2, 0, 0]$ chain site, indicating that the defect found by Wagner *et al.*⁶ in Hg-1201 may also form in other Hg compounds.

Structural studies of the defects in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ (Hg-1223) are somewhat less in number. Neutron powder-diffraction data by Chmaissem *et al.* on a Hg-1223 sample with a T_c of 133 K reports a value of 0.41 oxygen atoms on the interstitial $[1/2, 1/2, 0]$ site.¹⁶ No evidence for additional defects was reported. This is in contrast to recent x-ray-diffraction results of Finger *et al.* on single crystals of Hg-1223, suggesting a substitution of more than 0.10 Cu atoms on the Hg site.¹⁵ Unfortunately, the quality of the single crystal used was insufficient to allow a precise determination of the individual defect oxygen concentrations, but results indicate the total excess oxygen (δ) to be less than 0.35. These studies differ in both the nature and amount of defects present in Hg-1223. Furthermore, there have been no reports of the variation of defect concentrations for samples with differing T_c 's as have been reported for Hg-1201 and Hg-1212.

In this paper we present the results of neutron powder-diffraction studies on three different Hg-1223 samples with T_c 's varying from 135 to 94 K. Two distinct defects, shown as O(4) and O(5) in Fig. 1, are found in all samples studied. The occupancy of the interstitial site, O(4), varies from 0.18(2) to 0.10(2) as T_c is changed from 135 to 94 K. An additional oxygen defect [O(5)] and a deficiency of scattering from the Hg site, as found in Hg-1201, was also observed. The occupancy of O(5) was found to be the same for all samples studied, ~ 0.09 , and did not vary upon reduction or oxygenation of the samples. The copper-apical oxygen distance was found to be unusually long and the copper-oxygen planes are relatively free from buckling, as compared to other known three-layer cuprate superconductors.

II. SAMPLE SYNTHESIS AND CHARACTERIZATION

The Hg-1223 samples examined in this paper were synthesized directly from HgO, BaO, CaO, and CuO. BaO and CaO were obtained from the decomposition of BaCO_3 and CaCO_3 under vacuum at 950°C; HgO and CuO were used as purchased (all starting chemicals were 99.99% purity or higher). Stoichiometric amounts of the starting oxides were intimately ground by hand in a glove bag under a nitrogen atmosphere. The samples were then pelletized, sealed in an evacuated quartz tube, and fired in a tube furnace. Since the unreacted samples readily absorb moisture and CO_2 , great care was used to minimize

the exposure of the pre-fired material to air. The samples were then heated at a rate of 3°C/min to 850°C, held at 850°C for 5 h, and then quenched to room temperature. This technique consistently yielded Hg-1223 samples with phase fractions greater than 90% by weight.

Samples were characterized by x-ray diffraction and ac susceptibility. X-ray-diffraction data were taken on a rotating anode source using the Beno-Knapp technique.¹⁷ ac susceptibility was measured on powdered samples in a 1 G, 100 Hz field using a Lake Shore Cryotronics model 7000 ac susceptometer.

Figure 2 shows the x-ray powder-diffraction pattern for an as-synthesized Hg-1223 sample with peaks indexed with the primitive, tetragonal unit cell. All major peaks in the pattern correspond to Hg-1223. CaO and $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ are the main impurity phases; the peaks corresponding to these phases are marked in Fig. 1. Samples prepared by this method exhibit typical T_c 's of ~ 125 K.

To investigate the effect of oxygen concentration on superconducting and structural properties, samples were subjected to various annealing conditions. Samples A and C were obtained from a single synthesis batch which

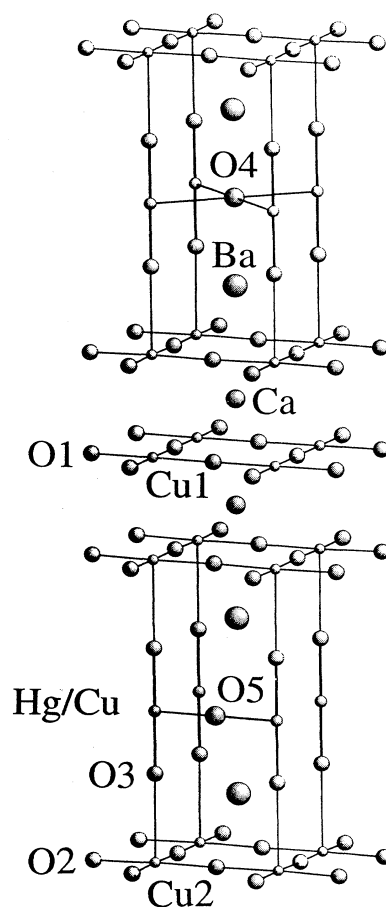


FIG. 1. Crystal structure of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$. The O(4) and O(5) sites are defects that are partially occupied (see text). Incorporation of oxygen at the O(4) site proposed to be coupled with Cu substitution on the Hg site.

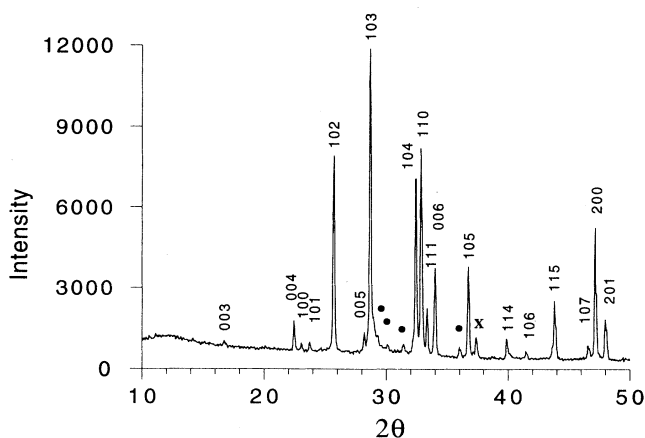


FIG. 2. X-ray-diffraction pattern for an as-synthesized $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ sample with peaks indexed to the tetragonal unit cell. Impurity peaks are marked with (●) for $\text{Ba}_2\text{Cu}_3\text{O}_{5-\delta}$ and (X) for CaO .

was divided into separate 2.5 g samples. Sample *A* was then annealed in flowing oxygen at 400°C and sample *C* was reduced in flowing Ar at 500°C. The ac susceptibility data for these samples are shown in Fig. 3. The oxygenated sample *A* has a sharp superconducting transition with an onset T_c of 135 K and reaches >95% of ideal shielding fraction at 70 K. The reduced sample *C* exhibits a sharp onset T_c of 94 K, and reaches 75% shielding fraction at 70 K.

TGA data in flowing oxygen for sample *C* ($T_c = 94$ K) are shown in Fig. 4. The T_c measured after heating and cooling the sample to 380°C in oxygen was 135 K, identical to that of the oxygenated sample *A*. This establishes the reversible nature of T_c and oxygen content during low-temperature annealing. The weight gain indicates a difference between samples *A* and *C* of 0.13(2) oxygen atoms per formula unit and provides an independent measure of the difference in δ between the samples used in the neutron study. The stability of Hg-1223 under reduction in flowing argon gas was also investigated. The inset in Fig. 4 shows the percent weight loss due to Hg volatility at temperatures above 500°C, resulting from the decomposition of Hg-1223. The weight loss was mea-

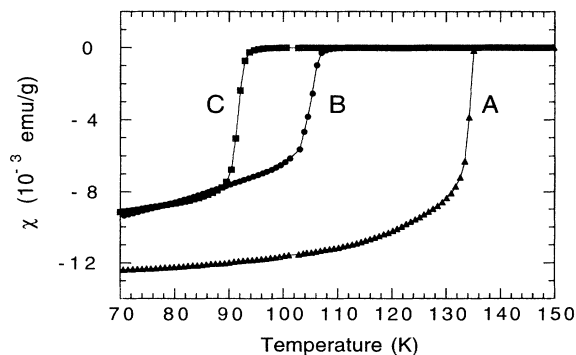


FIG. 3. ac susceptibility for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ samples *A*, *B*, and *C*.

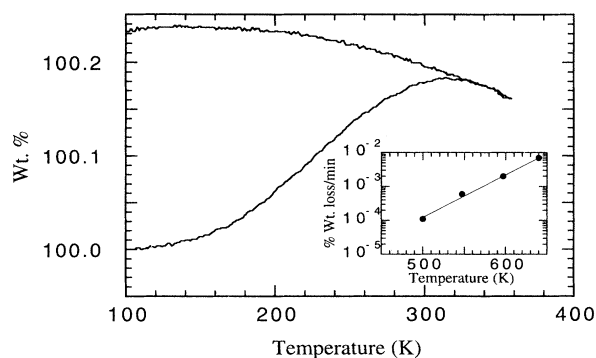


FIG. 4. TGA plot of weight % vs temperature in flowing oxygen for sample *C*. The inset shows the weight % loss vs temperature for samples held at fixed temperatures between 500 and 650°C (see text).

sured over a 12 h period at each temperature and varied from less than 0.07% at 500°C to more than 4% at 650°C. This indicates that the reducing process used for sample *C* does not result in any significant decomposition.

The main impurity phase in our as-made samples, $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$, has an unknown structure with an incommensurate modulation.¹⁸ Its structure is also found to change with varying oxygen content δ . Therefore, it is difficult to exactly account for all peaks in the diffraction data for samples containing even trace quantities of $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$. Samples *A* and *C* contain small amounts (~5%) of $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$. Sample *B* was processed in a way that decomposed this impurity phase, in an attempt to achieve a more straightforward refinement. $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ is readily decomposed into BaCuO_2 and CuO at high temperatures (>750°C) and at low oxygen partial pressures.¹⁹ However, Hg-1223 quickly decomposes in an open system at these temperatures, due to the high Hg vapor pressure. Hg loss can be avoided by enclosing the sample in a sealed quartz tube. To produce sample *B*, a pellet of Hg-1223 was sealed in a quartz tube with an excess of liquid Hg and Cu_2O , at a position separated from the sample, and held at 750°C for 5 h. Hg and Cu_2O were added to set the Hg and oxygen vapor pressure (60 and 10^{-4} bars, respectively),^{20,21} to values where Hg-1223 is stable but $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ is unstable. X-ray diffraction after this process confirmed the decomposition of $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ and the introduction of BaCuO_2 in this sample. Some Hg-1201, and Hg-1212 as additional impurity phases were also observed. Although the phase fraction of Hg-1223 was reduced somewhat by this procedure, the resulting impurity phases possess well characterized structures that can be modeled during Rietveld refinement. This sealed reduction step resulted in a T_c of 107 K, intermediate to that of the oxygenated and reduced samples *A* and *C*.

The results of these annealing experiments suggest that sample *A*, which was annealed in 1 atm of oxygen, is optimally doped. Samples *B* and *C*, obtained through reduction, appear to be underdoped. This is consistent with previous reports on Hg-1223.¹⁰

III. NEUTRON POWDER DIFFRACTION

Neutron powder-diffraction data on samples *A* and *C* were collected on the General Purpose Powder Diffractometer (GPPD). Sample *B* was run on the Special Environment Powder Diffractometer. Both instruments are at Argonne's Intense Pulsed Neutron Source (PNS).²² The samples (~ 2.5 g) were measured in the form of loose powders inside 0.25 in. diam thin-walled vanadium sample holders. Samples containing $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ (*A* and *C*) were run on the higher resolution GPPD instrument to allow for easier separation of impurity peaks from the main phase, so that the impurity peaks could be excluded from the refinement.

The powder-diffraction data were analyzed utilizing the IPNS time-of-flight Rietveld code.²³ Only data from the high-resolution backscattering detector banks were used in the refinements. Figure 5 shows a portion of the Rietveld refinement profile for sample *A* ($T_c = 135$ K). Bragg peak widths from all three samples are instrument resolution limited.

The crystal structure of Hg-1223 has $P4/mmm$ (No. 132) space-group symmetry. The structure with the atomic sites labeled is shown in Fig. 1. In the initial refinements, the O(1), O(2), O(3), Ca, Cu(1), and Cu(2) sites were found to be fully occupied. The occupancies of these sites were fixed to their nominal values in all subsequent refinements to achieve optimal sensitivity for other refined parameters.

Of particular interest are the defect occupancies of the interstitial oxygen sites O(4) at $[1/2, 1/2, 0]$ and O(5) at $[1/2, 0, 0]$, and their relationship to superconductivity. For these sites, occupancies and thermal parameters could not be refined simultaneously, as is often the case for defects. Therefore, the isotropic thermal parameters were fixed at values of 1.0 \AA^2 for all three samples and the occupancies refined. Attempts to displace O(4) off the

$[1/2, 1/2, 0]$ position within the plane resulted in position parameters converging back to the high-symmetry position, indicating that O(4) is located in the center of the Hg-O₈ plane. Similarly, the O(5) site was refined to the $[1/2, 0, 0]$ position. Refinement models in which the O(5) site was displaced along the *z* direction [as was reported for Hg-1201 (Ref. 6)] were not statistically favored over the model with this atom in the $[1/2, 0, 0]$ position.

For sample *B*, the impurity phases of CaO (6%), BaCuO_2 (8%), Hg-1201 (9%), Hg-1212 (5%) were included along with the predominant Hg-1223 structure in the refinement. Structural parameters are listed in Table I. Values for the oxygen defect occupancies were found to be 0.13(2) and 0.09(2) for the O(4) and O(5) site, respectively, giving a total δ of 0.22(4) for this sample.

Values for the defect oxygen concentration refined in samples *A* and *C* were found to be dependent on the way than $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ was handled in the refinements. This dependence shows that the presence of this structurally unknown phase introduces systematic errors that are strongly correlated with the defect oxygen concentration in the analysis, and special care is necessary in these refinements to insure accuracy. Refining the data without accounting for the contributions from $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ resulted in nearly identical values for total δ of 0.14(4) and 0.12(4) for samples *A* and *C*, respectively. The difference in these total δ 's is not consistent with TGA results. An "averaged" structural model¹⁸ was found to poorly account for the intensities of $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ in a multiphase refinement, although it did increase the difference in total δ between the two samples. However, the best fits to the data were achieved by excluding regions of the data where $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ peaks were present. Nine regions that correspond to major peaks of the powder neutron-diffraction pattern of $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ (measured in a separate experiment) were selected for exclusion in the refinement. These regions appear in Fig. 5 as small segments where the observed and calculated data have been set to zero. Since $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ has a variable oxygen stoichiometry that can lead to subtle shifts in peak positions, the excluded regions were adjusted individually for the oxygenated and reduced samples. This was done by examination of the difference curve for the refinements and excluding only those regions where peaks due to $\text{Ba}_2\text{Cu}_3\text{O}_{5+\delta}$ were evident. Care was taken to minimize the amount of data excluded. The refined values of total δ in samples *A* and *C* using this refinement strategy were 0.27(4) and 0.18(4), respectively. These values are consistent with the TGA data. Structural results reported for samples *A* and *C* are for refinements using these excluded regions.

It is important to check whether the value chosen for the fixed temperature factors of O(4) and O(5) introduce a bias into the refined site occupancy values resulting from correlation between the temperature factor and occupancy of a given atom. Because time-of-flight data extend to small *d* spacings (0.5 \AA for these refinements), these correlations are generally smaller than for refinements of data from fixed-wavelength diffractometers. To test the sensitivity of our result to this potential systematic error, additional refinements were done with *B*[O(4)] and

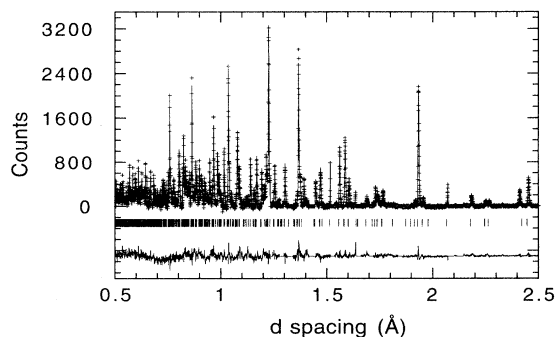


FIG. 5. Rietveld refinement profile of neutron powder-diffraction data for sample *A* ($T_c = 135$ K). The plus signs (+) are the time-of-flight diffraction data with the background subtracted. The solid line is the calculated profile. Tick marks below the profile indicate the position of Bragg peaks for the $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ phase. A difference curve (observed minus calculated) is plotted at the bottom. Nine excluded regions, where the observed, calculated, and difference curves are set to zero, are used in the refinement. These regions are most easily seen in the difference curve at the bottom of the figure.

$B[\text{O}(5)]$ fixed at 0.5 \AA^2 and 2.0 \AA^2 . For sample *A*, the total variation in the resulting values for δ was ± 0.007 . Similar results were obtained for the other samples. We conclude that our assumption about the fixed values of the temperature factors for the oxygen defect sites does not introduce a significant systematic error in the determination of δ .

IV. DISCUSSION

The refined occupancies of the O(4) interstitial sites are 0.18(2), 0.13(2), and 0.10(2) oxygen atoms per formula unit, for samples having T_c 's of 135, 107, and 94 K, respectively. We conclude that it is these changes in oxygen content that are responsible for the variations in T_c . In all three samples there is evidence for a second defect site at $[1/2, 0, 0]$ [O(5)] with a nominally constant concentration of ~ 0.9 atoms per formula unit if the defect is assumed to be an oxygen atom. A similar second defect site, whose concentration did not change upon oxidation or reduction of the sample, was observed previously in

Hg-1201.⁶ The constant concentration of oxygen at this second defect site suggests that O(5) is more tightly bonded than O(4). The total change in oxygen content between sample *A* and *C* is found to be 0.08(4) from the refinements, which agrees reasonably well with the value of 0.13(2) determined independently by TGA measurements.

The site occupancies obtained in our refinements for the interstitial O(4) site are much smaller than that found by Chmaissem *et al.*¹⁶ in a neutron-diffraction study of a Hg-1223 sample synthesized at high pressure. Chmaissem reported $n[\text{O}(4)] = 0.41(2)$ and no evidence for a second oxygen defect. However, Finger *et al.* reported at least 0.10 Cu substitution for Hg, ~ 0.10 oxygen atoms on the O(5) site, and less than 0.25 oxygen atoms on the O(4) site based on a single-crystal x-ray study. It should be noted that x-ray diffraction is a more sensitive probe of Cu/Hg substitution than neutron diffraction due to the large difference in x-ray scattering power for these atoms, but a less sensitive probe of oxygen. A conclusion consistent with all of these results is that the formation of the

TABLE I. Refined structural parameters from neutron powder-diffraction data at room temperature for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ samples with T_c 's from 94 to 135 K.

T_c (onset) (K)	Parameter			
		<i>A</i>	<i>B</i>	<i>C</i>
		135	107	94
	a (\AA)	3.847 86(4)	3.854 53(6)	3.854 65(3)
	c (\AA)	15.778 2(3)	15.825 2(4)	15.825 1(2)
	V (\AA^3)	233.613(5)	235.123(7)	235.135(4)
	Hg ($x=y=z=0$)			
	n	0.95(2)	0.90(2)	0.95(1)
	B (\AA^2)	1.52(8)	1.23(8)	1.47(7)
	Ba ($x=y=1/2$)			
	z	0.1739(9)	0.1776(3)	0.1773(2)
	B (\AA^2)	1.16(8)	0.97(8)	0.76(6)
	Ca ($x=y=1/2$)			
	z	0.396 7(3)	0.397 4(4)	0.397 6(3)
	B (\AA^2)	0.53(6)	0.76(7)	0.54(5)
	Cu(1) ($x=y=0, z=1/2$)			
	B (\AA^2)	0.57(7)	0.48(7)	0.44(6)
	Cu(2) ($x=y=0$)			
	z	0.298 7(2)	0.300 4(2)	0.300 3(2)
	B (\AA^2)	0.67(5)	0.42(5)	0.56(4)
	O(1) ($x=0, y=z=1/2$)			
	B (\AA^2)	0.71(6)	0.97(8)	0.65(5)
	O(2) ($x=1/2, y=0$)			
	z	0.300 4(2)	0.301 2(2)	0.300 9(2)
	B (\AA^2)	0.76(5)	0.48(5)	0.53(2)
	O3 ($x=0=y=0$)			
	z	0.125 0(2)	0.124 4(3)	0.124 3(2)
	B (\AA^2)	1.17(7)	1.18(9)	1.13(6)
	O(4) ($x=y=1/2, z=0$)			
	n	0.18(2)	0.13(2)	0.10(2)
	B (\AA^2)	1	1	1
	O(5) ($x=1/2, y=z=0$)			
	n	0.09(2)	0.09(2)	0.08(2)
	B (\AA^2)	1	1	1
	δ	0.27(4)	0.22(4)	0.18(4)
	R_{wp} (%)	7.698	5.198	7.807
	R_{exp} (%)	4.735	3.012	4.764
	χ	1.626	1.726	1.638

second defect depends on synthesis conditions, and that, once formed, this defect is stable with respect to oxidation and reduction.

Scattering from the Hg site was found to be 5–10 % deficient in the present samples, similar to what was observed in previous work on Hg-1201 (Ref. 6) and Hg-1212.¹¹ This scattering deficiency can be interpreted in terms of the substitution of an atom with a smaller scattering cross section. The neutron-scattering lengths for Cu and Hg are 0.77 and 1.27×10^{-12} cm, respectively. Thus, the observed deficiencies correspond to 12–24 % substitution of Cu for Hg. This amount of Cu substitution is larger than expected for the amount of oxygen seen in the O(5) site. However, our estimate of the amount of substitution on the Hg site could be subject to significant systematic errors, as will be discussed below.

The isotropic thermal parameters of Hg are found to be somewhat large in these samples: ranging from 1.21 to 1.52 (\AA^2). Chmaissem *et al.*¹⁶ in previous neutron powder-diffraction work reported $B(\text{Hg}) = 3.9 \text{\AA}^2$. Finger *et al.* reported $B(\text{Hg}) = 1.3 \text{\AA}^2$ based on single-crystal x-ray diffraction.¹⁵ All of these values are unusually large, suggesting a contribution from static displacements of the Hg atoms. Such displacements would be expected in response to the incorporation of the O(4) defects in random positions. If the average spatial distribution of Hg atoms (averaged over time and space) is not well modeled by the harmonic temperature factors assumed in the structure refinements, correlations between refined values of temperature factors and site occupancies are likely. The differences in refined $B(\text{Hg})$ values obtained by different authors may result from this problem. With time-of-flight data extending to small d spacings, correlations between temperature factors and site occupancies should be minimized. For example, if we assume full occupancy of the Hg site for sample *A*, our refined value for $B(\text{Hg})$ increases from 1.52 \AA^2 to 1.70 \AA^2 . Thus, we conclude that errors in our refined values for $B(\text{Hg})$ and $n(\text{Hg})$ due to this correlation are small. Nevertheless, it is impossible to rule out systematic errors in the determination of the amount of Cu on the Hg site from these effects. Thus, our estimate of the amount of Cu substitution may have error bars much larger than those indicated by the refinement.

Trends in the position and thermal parameters for the

Ba atom as δ is varied show the effect of varying the oxygen content at the O(4) site. The nominal Ba-O(4) bond length is $\sim 2.8 \text{\AA}$ (see Table II and Fig. 1). As the occupancy of the O(4) site increases from 0.10 to 0.18, the average Ba-O(4) bond distance decreases by $\sim 2.3\%$. This is by far the largest change of any bond length, and corresponds to an average movement of the Ba atom towards the Hg-O₈ plane of 0.06 \AA . Since this represents the average for displaced Ba atoms that have O(4) neighbors and Ba atoms that have no O(4) neighbors, the actual displacement of a Ba atom adjacent to an O(4) defect must be much larger than this. The increasing spatial delocalization of the Ba position with increasing oxygen content on the O(4) site is also reflected by an increase of the temperature factor for Ba from 0.76 to 1.16 \AA^2 as $n[\text{O}(4)]$ changes from 0.10 to 0.18. Unlike $B(\text{Ba})$, $B(\text{Hg})$ shows little variation with respect to $n[\text{O}(4)]$. This is expected since $B(\text{Hg})$ should be affected primarily by the O(5) occupancy, which is found to be constant in these samples.

V. CONCLUSIONS

The $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ structure has two different CuO_2 layers, containing the Cu(1) and Cu(2) atoms as shown in Fig. 1. The Cu(1) atoms have fourfold, square-planar coordination, while the Cu(2) atoms have fivefold pyramidal coordination. The Cu(1)-O(1) layer is located in the center of the unit cell and is required to be flat by symmetry. The Cu(2)-O(2) layer, on the other hand, has no such constraint and may be buckled. The refined Cu(2)-O(2)-Cu(2) angles listed in Table II are a measure of the buckling of these layers (a flat layer would correspond to an angle of 180°). The Cu(2)-O(2) layers are found to be nearly flat with Cu(2)-O(2)-Cu(2) angles varying from 178.4° to 179.4° as T_c changes from 135 to 94 K, respectively. The buckling of the CuO_2 layer is also found to be closely related to the copper-apical oxygen distance in the two and three-layer mercury compounds. The buckling of the Cu-O plane is observed to increase as the apical oxygen moves toward the plane. For similar copper-apical oxygen distances, the buckling of the Cu-O layers is found to be the same in these compounds.¹¹ This behavior can be understood by a simple Coulomb repulsion model involving the in-plane and out-of-plane oxy-

TABLE II. Selected bond lengths and angles from structural parameters listed in Table I for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ samples.

Bond length/angle	<i>A</i> ($T_c = 135$ K)	<i>B</i> ($T_c = 107$ K)	<i>C</i> ($T_c = 94$ K)
Cu(2)-O(2)	1.9239(2)	1.9273(2)	1.9274(2)
Cu(2)-O(3)	2.741(6)	2.786(7)	2.785(6)
Cu(1)-Cu(2)	3.176(3)	3.159(3)	3.160(3)
Hg-O(3)	1.972(3)	1.968(5)	1.967(3)
Hg-O(4)	2.7208(3)	2.7256(4)	2.7256(3)
Hg-O(5)	1.9239(1)	1.9273(1)	1.9273(1)
Ba-O(2)	2.772(6)	2.746(6)	2.746(5)
Ba-O(3)	2.828(6)	2.853(7)	2.852(6)
Ba-O(4)	2.744(4)	2.810(5)	2.806(3)
Cu(2)-O(2)-Cu(2) (°)	178.4(4)	179.3(4)	179.4(4)

TABLE III. Structural features of Cu-O planes for selected three-layer cuprate superconductors. The values listed for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ are from the present study.

Compound	T_c (K)	Cu-O (apical) (Å)	Cu-O-Cu (°)
$\text{PbBaYSrCu}_3\text{O}_8$ (Ref. 24)	50	2.157	173.4
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Ref. 25)	108	2.215	169.3
$\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9+\delta}$ (Ref. 26)	110	2.698	178.1
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Ref. 27)	125	2.725	178.3
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.27}$	135	2.741	178.4
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.18}$	94	2.785	179.4

gen atoms.

Structural features of other known triple-layer cuprate superconductors are listed in Table III. As can be seen, $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ has the longest copper-apical oxygen bond length and flattest CuO_2 planes of any known three-layer material. Unusually long copper-apical oxygen bond lengths and flat CuO_2 planes are also characteristic of the single and double-layer Hg compounds,^{11–14} and we speculate that these are essential features for the record high T_c 's found in the Hg-based materials.

In the present study the occupancy of any oxygen defect site at $[1/2, 1/2, 0]$ is found to vary systematically from 0.18 to 0.10 as T_c is changed from 135 to 94 K, and is the variable doping defect for this compound. These conclusions from the structural refinements are unambiguous. Additionally, there is evidence for a second defect site at $[1/2, 0, 0]$ that contains ~ 0.09 atoms per formula unit if the scattering is assumed to come from oxygen atoms. The occupancy of this site is found to be essentially constant for all samples. We have interpreted this

defect as being additional oxygen atoms associated with the substitution of Cu at the Hg site. Our assumption of Hg site substitution is supported by the observation of a scattering deficiency at the Hg site (since Cu has a smaller neutron-scattering cross section than Hg). However, the refined amount of Cu substitution is larger than would be expected for the amount of O(5) oxygen observed. It is important to remember that from neutron diffraction it is impossible to actually identify the elements giving rise to the scattering or to differentiate between vacancies and substitutional defects. Moreover, if the Hg atoms (or some of them) are statically displaced from their ideal positions in a way that is not adequately modeled by the harmonic thermal motion model assumed in the refinement, our refined values for the Hg site occupancies could be subject to significant systematic error. Thus, although we have good evidence for the incorporation of a second defect involving these sites, our identification of the defect is speculative. Alternate interpretations of the defect could be proposed. For example, the defects could involve the incorporation of CO_3 ions substituting for Hg atoms rather than Cu atoms and their associated oxygen atoms. Further studies, such as anomalous x-ray scattering in which sensitivity for a particular atom type can be enhanced, will be required to resolve this issue.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation Office of Science and Technology Grant No. DMR 91-20000 (J.L.W., B.A.H.), and by the U.S. Department of Energy, Division of Basic Energy Sciences—Materials Sciences, under Contract No. W-31-109-ENG-38 (J.D.J., D.G.H.).

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