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Crystal structure of $(Cu,C)Ba_2Ca_3Cu_4O_{11+\delta}$ ($T_c = 117$ K) by neutron-powder-diffraction analysis

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The crystal structure of the newly discovered 117-K superconductor, $(Cu,C)Ba_2Ca_3Cu_4O_{11+\delta}$, has been refined from time-of-flight neutron-powder-diffraction data. The structure has "average" tetragonal symmetry and is similar to that of Tl(or Hg)$Ba_2Ca_3Cu_4O_y$. C atoms in CO_3 groups substitute at the Cu site in the $(Cu,C)O_{1+\delta}$ layer leading to a chemical composition of $(Cu_{0.68}C_{0.32})Ba_2Ca_3Cu_4O_{11.06}$. This compound has two inequivalent kinds of CuO_2 layers with pyramidal and square coordination of Cu to oxygen. The inner CuO_2 layers with Cu in four coordination are less corrugated than the outer ones with Cu in five coordination, and exhibit a structure very similar to those of infinite-layer compounds.

I. INTRODUCTION

Several authors have recently reported the synthesis at high pressure of superconducting compounds with the general formula $ABa_2Ca_3Cu_4O_y$ and with superconducting transition temperatures (T_c) of 117 K.[1-4] Because of the difficulties of obtaining single-phase materials and of performing detailed structural analysis on the small samples obtained from high-pressure synthesis techniques, it is not yet clear whether these workers have obtained the same compound or whether compounds with the same T_c but with different chemical compositions actually exist.

Ihara *et al.*[1] reported the synthesis of $AgBa_2Ca_{n-1}Cu_nO_y$ in a series of experiments in which they attempted to replace Tl(or Hg) in Tl(or Hg)$Ba_2Ca_{n-1}Cu_nO_y$ with Ag. Although their sample was mixed phase, they observed bulk superconductivity with a T_c of 117 K and a large diamagnetic signal. They concluded that the crystal structure of the 117-K superconducting phase was isostructural with that of Tl(or Hg)$Ba_2Ca_3Cu_4O_y$ [Tl(or Hg)-1234] from x-ray-diffraction data and that the chemical composition was $(Ag_{0.25}Cu_{0.75})Ba_2Ca_3Cu_4O_{11}$ from electron-probe microanalysis. They also observed a $2a \times b \times 2c$ superstructure in an electron-diffraction pattern, and speculated that this resulted from an ordered arrangement of Ag and Cu atoms in the site shared by these atoms.

Kawashima, Matsui, and Takayama-Muromachi[2] isolated a superconducting phase with $T_c = 117$ K during studies of various phases in the Ag-Ba-Ca-Cu-O system. Electron-probe microanalysis of their sample revealed that the 117-K superconducting phase, which was isostructural with Tl(or Hg)-1234, contained no silver, but that it did contain carbon. They also observed a superstructure of $2a \times b \times 2c$ by electron diffraction. They concluded that the chemical composition of their material was $(Cu_{0.5}C_{0.5})Ba_2Ca_3Cu_4O_{11\pm\delta}$ and that the superstructure resulted from ordering of Cu and C atoms. The replacement of Cu atoms by C atoms, in the form of CO_3 units, has been observed in other superconducting materials, such as $(Y_{1-x}Ca_x)_{0.95}Sr_{2.05}Cu_{2.4}(CO_3)_{0.6}O_y$,[5] where C atoms in CO_3 groups partially substitute for Cu atoms on the "chain" site in the $YBa_2Cu_3O_{7-\delta}$ (Y-123) structure. Thus, the structure proposed by Kawashima, Matsui, and Takayama-Muromachi,[2] $(Cu_{0.5}C_{0.5})Ba_2Ca_3Cu_4O_{11\pm\delta}$ with C occurring as CO_3 units substituted on a Cu site, is consistent with what is known about the crystal chemistry of these materials.

Jin *et al.*[3] and Wu *et al.*[4] also prepared a new superconducting compound in the Ba-Ca-Cu-O system with T_c of 117 K using high-pressure synthesis techniques. They speculated that one of a new homologous series of compounds, $CuBa_2Ca_{n-1}Cu_nO_y$, isostructural to the single-layer Tl- or Hg-based compounds Tl(or Hg)$Ba_2Ca_{n-1}Cu_nO_y$, was responsible for the observed superconductivity. X-ray- and electron-diffraction patterns showed the presence of a tetragonal phase with $a = 3.88$ Å and $c = 18.3$ Å in mixed-phase samples, leading them to conclude that the superconducting material was the $n = 4$ member of the series. Interestingly, they made their samples from oxides rather than carbonates, and did not observe the presence of carbon in their $n = 4$ samples, nor was any superstructure observed.[6] They also tried to synthesize $AgBa_2Ca_3Cu_4O_y$ but observed no silver in the resulting perovskite-related compound.[7]

One explanation that reconciles the observations of these groups is that the superconducting phase is $(Cu_{1-x}C_x)Ba_2Ca_3Cu_4O_y$ where the amount of carbon substituting for the copper site in the "charge-reservoir" layer is variable. Such an explanation would explain why

Kawashima, Matsui, and Takayama-Muromachi[2] observed c-axis lattice constants near 17.9 Å for their compound while Jin *et al.*[3] and Wu *et al.*[4] observed 18.3 Å for their compound that contained no carbon. If this explanation is correct, however, it is puzzling that the T_c does not change with carbon content.

In this paper, we report the results of a structural refinement using neutron-powder-diffraction data for a 117-K superconducting $(Cu,C)Ba_2Ca_3Cu_4O_{11+\delta}$ compound, (Cu,C)-1234, synthesized at high pressure. Other compounds with four CuO_2 layers, such as Tl(or Hg)$Ba_2Ca_3Cu_4O_y$ and $Tl_2Ba_2Ca_3Cu_4O_y$, often contain considerable amounts of intergrowths, which hinder precise structure refinement. The present (Cu,C)-1234 sample, in contrast, shows sharp diffraction peaks suggesting the absence of such intergrowths. Thus, from this refinement, we are able to learn important characteristic structural parameters such as the Cu-Cu distance between the two square (inner) CuO_2 sheets and the O-Cu-O bond angles in these sheets.

II. SAMPLE SYNTHESIS AND NEUTRON DIFFRACTION

A 190-mg sintered powder sample of $(Cu,C)Ba_2Ca_3Cu_4O_{11+\delta}$ was synthesized at high pressure in the same manner as previously reported.[2] A mixture having a composition of $C_{0.5}Ba_2Ca_3Cu_{4.5}O_{11.1}$ was prepared from $BaCuO_2$, Ca_2CuO_3, CuO, and $CaCO_3$. The $BaCuO_2$ compound, which had been prepared from $BaCO_3$ and CuO at 900 °C, contained about 0.95 mass % of carbon. The carbon content of the mixture was adjusted by taking this into account. The oxygen content was controlled by adding an appropriate amount of Ag_2O. No silver was detected in the resulting superconducting phase indicating that Ag_2O worked as only an oxidizing agent. The mixture was sealed in a gold capsule, allowed to react in a flat-belt-type high-pressure apparatus at 5 GPa and 1200 °C for 3 h, and then cooled to room temperature in 30 min. Superconductivity was confirmed by an ac susceptibility measurement in a magnetic field of 1.0 Oe. The T_c of the sample was 117 K and the transition was quite sharp as shown in Fig. 1.

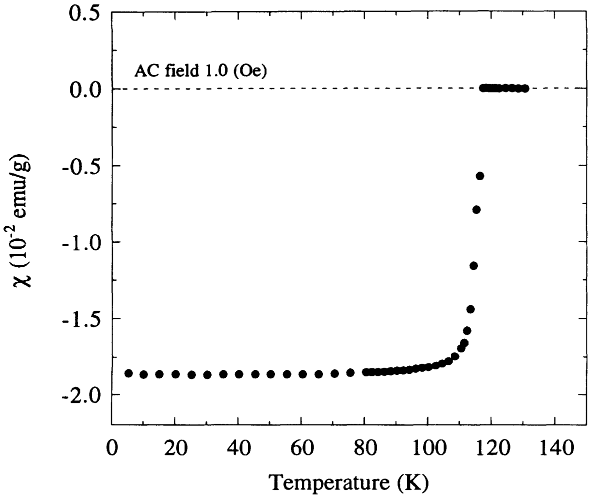

FIG. 1. Temperature dependence of the ac susceptibility for $(Cu,C)Ba_2Ca_3Cu_4O_{11+\delta}$.

Time-of-flight neutron-powder-diffraction data of the sample were collected for 20 h at room temperature on the Special Environment Powder Diffractometer (SEPD) at Argonne's Intense Pulsed Neutron Source (IPNS).[8] The sample was suspended in the neutron beam on an amorphous boron fiber to minimize background. The crystal structure was refined by the Rietveld technique[9] using the high-resolution data from the backscattering ($2\theta = 145°$) detector banks.

III. STRUCTURAL REFINEMENT

Bragg peaks from small amounts (less than 5% by weight) of metallic Ag and a high-pressure form of Ag_2O (Ref. 10) were observed in the diffraction pattern. Thus, these impurity phases were included in the refinement. The crystal structure of the dominant $(Cu,C)Ba_2Ca_3Cu_4O_{11+\delta}$ phase was first refined in the tetragonal space group $P4/mmm$ based on the expected similarity to the crystal structure of the Tl(or Hg)-1234 compounds. All observed peaks in the neutron-diffraction data were successfully indexed by this model. Although a $2a \times b \times 2c$ superstructure was observed in electron-diffraction patterns for samples prepared in the same way, no Bragg peaks resulting from such a superstructure were seen in the neutron-diffraction data (including the data obtained at lower scattering angles, 90°, 60°, and 30°, but not included in the refinement). Therefore the structural refinement was performed on the basis of the "average" tetragonal symmetry.

In an initial stage of the refinement, occupation of the (Cu1,C) site at a $1a(0,0,0)$ position was assumed to be $(Cu_{0.5}C_{0.5})$ as suggested by previous chemical analyses of samples prepared in the same way,[2] and O1 oxygen site was located at a $2f(0.5,0,0)$ position with a 50% occupancy. The refined thermal parameters of the (Cu1,C) and the O1 sites in the (Cu,C)O plane and the apical O2 site at a $2g(0,0,z)$ position were quite large (about 4 Å^2) suggesting large static displacements as would result from the presence of CO_3 groups in the relevant positions.

We then refined the structure with a model that allowed the partial substitution of C as a unit of CO_3 at the Cu1 site (see Fig. 2). Since the CO_3 unit is inherently inconsistent with tetragonal symmetry, the refinement based on such a model requires some assumptions about the structure to be imposed in the form of constraints. We assumed that the C atom occupies the same site as the Cu1 atom (i.e., no displacements off the ideal Cu1 site were allowed—see Fig. 2) and that Cu1 and C each have their own distinct oxygen coordination. The planar anion $CO_3{}^{2-}$ is a fairly rigid structural unit owing to the covalency of the C-O bonds. We therefore constrained the CO_3 unit to be planar and to be perfectly triangular.

Two of the oxygen atoms bonded to each C atom, O2B shown in Fig. 2, are apical oxygen atoms for CuO_5 pyramids in the neighboring planes. The third oxygen atom, O1B, is on the plane of the Cu1 and C atoms. The Cu1 atoms in the (Cu1,C)O plane were assumed to be coordinated to four oxygen atoms as in the chainlike coordination in the $YBa_2Cu_3O_{7-\delta}$ compound. Two of the four possible oxygen sites O1A around each Cu1 site are occupied to achieve this configuration. The CuO_4 and CO_3 units were assumed to be oriented along the [100] or the equivalent [010] direction. Refinement of the average structure using tetragonal symmetry cannot yield any information about possible ordering involving the orientations or positions of the CuO_4 and CO_3 units. However, one might expect ordering over some length scale from a crystal-chemistry point of view. If the length scale were short, this could explain the observation of a superstructure by electron diffraction, but not neutron diffraction.

This structural model with CO_3 groups and a chainlike oxygen configuration around Cu1 resulted in a significant improvement in the fit. The thermal parameters for the relevant sites decreased considerably. The somewhat large thermal parameter for the (Cu1,C) site (2.6 Å^2) suggests that our assumption that C substitutes exactly on the Cu1 site may not be perfectly correct. However, this constraint is the best choice for modeling the average structure. The refined C-O bond length in the CO_3 cluster is 1.23 Å, which is very close to the observed bond length of C-O in CO_3 groups in other compounds containing carbonate ions.[11-13] This internally consistent result implies that our choice of constraints for the average structure is appropriate.

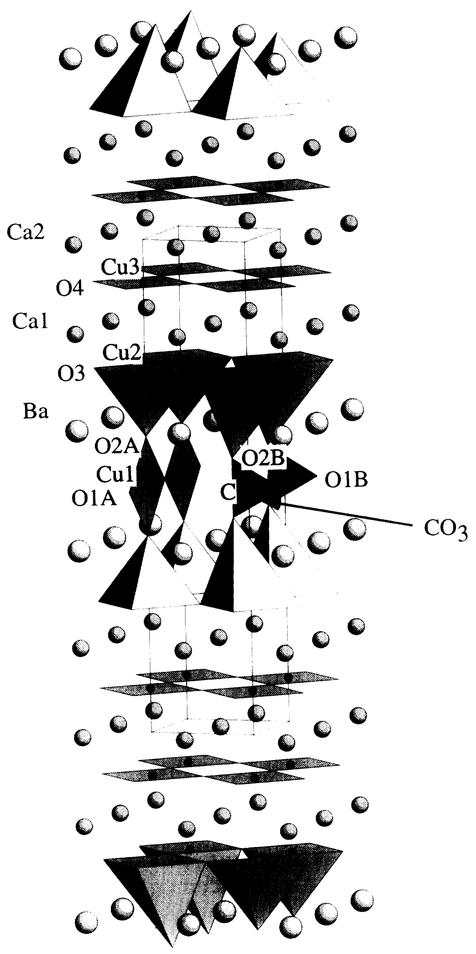

FIG. 2. Structure of $(Cu,C)Ba_2Ca_3Cu_4O_{11+\delta}$. Cu1 and C are located in the shared site. Cu1 has chainlike oxygen coordination (O1A and O2A). C is bonded to three oxygen atoms (O1B and O2B) forming a CO_3 group. Two oxygen atoms in the CO_3 group occupy the apical positions of CuO_5 pyramids, but they are displaced from the ideal $(0,0,z)$ position. Cu2 and O3 are in the outer CuO_2 plane. Cu3 and O4 are in the inner CuO_2 plane. Although the present analysis of the average tetragonal structure cannot yield any information about possible ordering and orientation of the chainlike CuO_4 and CO_3 units, the structure is drawn to be consistent with the $2a \times b \times 2c$ superstructure which is seen in electron diffraction. Cu1 and C are the origin of the average tetragonal unit cell in the refinement (Table I).

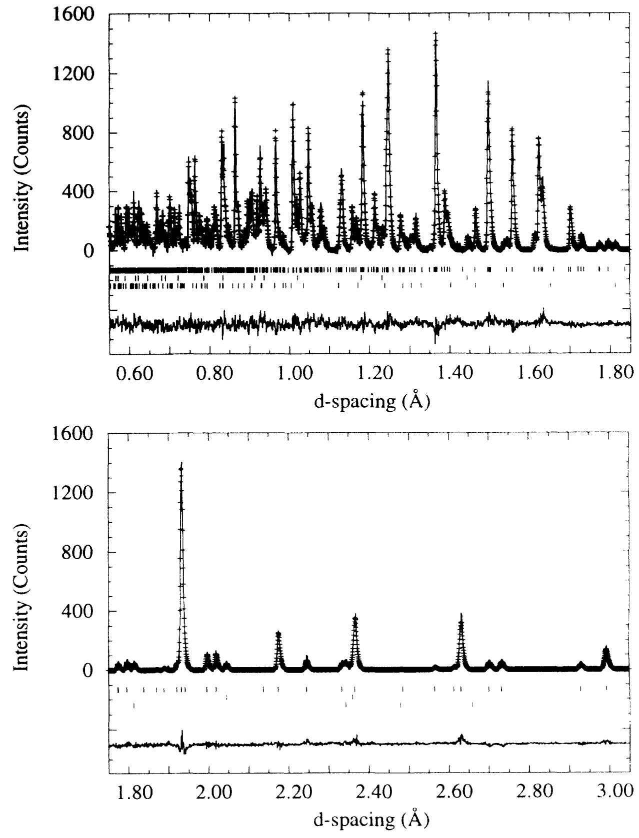

FIG. 3. Neutron-powder-diffraction data and the Rietveld refinement profile for $(Cu,C)Ba_2Ca_3Cu_4O_{11+\delta}$. The raw time-of-flight diffraction data are shown as plus marks; the calculated profile is shown as a solid line. Tick marks below the profile mark the positions of allowed reflections. The differences between the observed and the calculated intensities are shown at the bottom. The sample also contains a small amount of Ag (intermediate marks) and a high-pressure form of Ag_2O (lower marks).

TABLE I. Refined structural parameters for $(Cu,C)Ba_2Ca_3Cu_4O_{11+\delta}$. B is the isotropic thermal parameter and n is the occupation number per unit cell. Numbers in parentheses are standard deviations of the last significant digit. Parameters with no standard deviations were not refined. Structural parameters of the impurity phases were also refined [Ag: cubic, $Fm3m, a=4.0859(3)$ Å; Ag_2O: trigonal, $P\bar{3}m1, a=3.070(1)$, $c=4.957(2)$ Å]. Space group, $P4/mmm$; $a=3.86192(4)$ Å, $c=17.9512(4)$ Å; $R_{wp}=10.68\%$, $R_{exp}=8.30\%$. Chemical composition determined by the refinement is $(Cu_{0.68}C_{0.32})Ba_2Ca_3Cu_4O_{11.06}$.

Atom	Position	x	y	z	B (Å^2)	n
Cu1,C	1*a*	0.0	0.0	0.0	2.6(1)	0.68(1),0.32
Ba	2*h*	0.5	0.5	0.1219(3)	0.92(7)	2.0
Cu2	2*g*	0.0	0.0	0.2332(2)	0.31(5)	2.0
Ca1	2*h*	0.5	0.5	0.3187(3)	1.3(1)	2.0
Cu3	2*g*	0.0	0.0	0.4117(2)	0.24(4)	2.0
Ca2	1*d*	0.5	0.5	0.5	0.4(1)	1.0
O1A	2*f*	0.5	0.0	0.0	2.4(3)	0.74(3)
O1B	4*l*	0.318(5)	0.0	0.0	2.4 [$=B$ (O1A)]	0.32 [$=n$(C)]
O2A	2*g*	0.0	0.0	0.1000(4)	1.7(2)	1.36 [$=2\times n$(Cu1)]
O2B	8*s*	0.159(3)	0.0	0.0593(10)	1.7 [$=B$ (O2A)]	0.64 [$=2\times n$(C)]
O3	4*i*	0.5	0.0	0.2376(2)	0.95(6)	4.0
O4	4*i*	0.5	0.0	0.4130(2)	0.76(5)	4.0

In the final stage of the refinements, site occupancies of Cu1 and C in the shared site were refined, with the total occupancy of the site being constrained to be 1. Site occupancies of the oxygen sites, O1B, O2A, and O2B, were constrained to be consistent with the Cu1:C ratio, and that of the O1A site was refined without any constraint. Although the Cu1:C ratio in the (Cu1,C) site was expected to be 1:1 according to the previous chemical analysis for the samples synthesized in the same way,[2] our refinement gave a significant decrease in the R factor (from 11.43 to 10.68) when this ratio converged to 0.68:0.32. The refined occupation number of O1A is 0.74, which is very close to the refined occupation number of Cu1, 0.68. This result is consistent with our assumption of a chainlike oxygen configuration around the Cu1 atom. However, it is impossible to conclude whether the possible chain oxygen sites are fully occupied or whether oxygen sites between chains are partially occupied without knowing the orientation of the CO_3 units (which cannot be learned from the present refinements). It is most logical from the point of view of oxygen-oxygen repulsion that the CO_3 units are oriented perpendicular to the chains. If this assumption is correct, the occupation of 0.74 for the O1A site implies that $0.26(=1.0-0.74)$ possible chain sites remain vacant. If the CO_3 groups are oriented parallel to the chains, $0.06(=0.74-0.68)$ oxygen atoms per formula unit are required to be located between chains.

TABLE II. Selected interatomic distances (Å) and bond angles (deg) of $(Cu,C)Ba_2Ca_3Cu_4O_{11+\delta}$. Numbers in parentheses are standard deviations of the last significant digit.

Bond	l or ϕ		
Cu1-O1A	1.93096(1)	(×2)	chainlike coordination
Cu1-O2A	1.795(7)	(×2)	
C-O1B,O2B	1.23(2)	(×3)	CO_3 group
O1B(O2B)-C-O2B	120.0		
Cu2-O3	1.9325(2)	(×4)	pyramidal coordination
Cu2-O2A	2.392(8)	(×1)	
Cu2-O2B	3.18(2)	(×1)	
O3-Cu2-O3	175.4(3)		
Ca1-O3	2.418(4)	(×4)	
Ca1-O4	2.569(4)	(×4)	
Cu3-O4	1.9311(1)	(×4)	square coordination
O4-Cu3-O4	178.6(4)		
Ca2-O4	2.483(2)	(×8)	

Since we have imposed a number of constraints on the atomic configuration in the $(Cu1,C)O_{1+\delta}$ layer, our refined values for the carbon and oxygen contents may not be accurate. However, in light of the results of Jin *et al.*[3] and Wu *et al.*,[4] who reported the synthesis of a sample with $T_c=117$ K containing no carbon, it seems reasonable that the Cu:C ratio in this layer is variable and depends on synthesis conditions. Further experiments are required to confirm this issue and to determine whether the oxygen content (related to the occupancy of the O1A site) is also variable, allowing a means for changing the superconducting properties.

Partial substitution of Ca for Ba was also suggested by chemical analysis of the previous samples.[2] However, refinements in which the occupancy of the Ba site was allowed to vary gave no evidence for such a substitution in the present sample.

The neutron-powder-diffraction data and Rietveld refinement profile based on the final model are shown in Fig. 3. The refined values of the structural parameters are listed in Table I. Selected bond lengths and bond angles are listed in Table II.

IV. DISCUSSION

It is instructive to compare structural features of $(Cu_{0.68}C_{0.32})Ba_2Ca_3Cu_4O_{11.06}$ with those of other layered copper oxide superconductors. (Cu,C)-1234 has two inequivalent kinds of CuO_2 layers. In the outer layers, Cu2 atoms have pyramidal coordination to oxygen, while in the inner layers, Cu3 atoms have square coordination to oxygen. As one might expect, based on Coulomb repulsion of the adjacent charged layers, the inner layers are less corrugated than the outer ones; the O4-Cu3-O4 angle is 178.6°, while the O3-Cu2-O3 angle is 175.4°. The spacings between adjacent CuO_2 layers are also slightly different; 3.17 Å between the two inner layers (Cu3-Cu3 distance) and 3.20 Å between the inner and outer layers (Cu2-Cu3 distance).

The inner CuO_2 layers, separated by Ca atoms, exhibit a structure very similar to those of infinite-layer compounds. Table III gives a comparison of bond lengths along the *a* and *c* axes and bond angles in the CuO_2 plane between the present (Cu,C)-1234 compound and the infinite-layer materials.[14,15] The values for the hypothetical compound $CaCuO_2$ were obtained by Takano *et al.*[15] from the data for $(Sr_{1-x}Ca_x)CuO_2$ materials by extrapolating to $x=1$. Cu-O bond lengths along both the *a* and *c* axes for (Cu,C)-1234 are very close to those of infinite-layer compounds. This structural similarity to the infinite-layer compounds is consistent with the need to use high pressure to stabilize the four-layer structure of (Cu,C)-1234. Both the present (Cu,C)-1234 material and superconducting infinite-layer compounds are stabilized by synthesis under high pressure. Although the infinite-layer materials crystallize at ambient pressure in a very narrow composition range near Sr:Ca=0.1:0.9, e.g., $Sr_{0.14}Ca_{0.86}CuO_2$,[14] high pressure is required to stabilize the infinite-layer structure over a wider composition range.[15] High-pressure synthesis appears to provide a way to stabilize copper oxides with four or more CuO_2 layers. For example, such an approach is being used to attempt the synthesis of $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ compounds with $n \geq 3$.[16]

The surroundings of the chainlike coordinated Cu1 atom are quite similar to those of the Cu1 atom in $YBa_2Cu_3O_{7-\delta}$. The bond length between the Cu1 and the apical oxygen O2A along the *c* axis is 1.80 Å, which is comparable with 1.86–1.80 Å in $YBa_2Cu_3O_{6.9-6.1}$.[17] The introduction of CO_3 units, with their smaller dimensions along the *c* axis, may tend to compress these bonds.

The $(Cu_{0.68}C_{0.32})O_{1.06}$ layer acts as a charge reservoir. The incorporation of $CO_3{}^{2-}$ anions produces holes in the system which are presumably transferred to the CuO_2 conduction planes. Cu1 could have a variable oxidation state, which could also modify the charge transfer. However, if we assume that Cu1 atoms are divalent, the refined composition of $(Cu_{0.68}C_{0.32})Ba_2Ca_3Cu_4O_{11.06}$ implies 1.48 holes per unit cell from simple ionic considerations, and gives a nominal Cu valence of 2.37 for the copper atoms in the inner and outer CuO_2 planes. This value is in reasonable agreement with those calculated for other superconducting copper oxides. From the present experiment we have not learned whether the carrier concentration, and thus the T_c, can be varied by changing the CO_3 or oxygen contents.

TABLE III. Comparison of the interatomic distances and bond angles in the structural unit of CuO_2-Ca-CuO_2 for the (Cu,C)-1234 and infinite-layer compounds. The values for the hypothetical compound $CaCuO_2$ were obtained by Takano *et al.* (see Ref. 15).

	(Cu,C)-1234	$(Ca_{0.86}Sr_{0.14})CuO_2$	$CaCuO_2$
Cu3-O4 (Å)	1.93	1.93 $(=a/2)$	1.92 $(=a/2)$
O4-Cu3-O4 (deg)	178.6	180.0	180.0
Cu3-Cu3 (Å)	3.17	3.20 $(=c)$	3.16 $(=c)$

The size of the so-called block-layer unit has been proposed to be an important parameter for determining the irreversibility-line behavior for high-T_c copper oxides. Table IV shows the interatomic distances of Cu2-Cu2 along the *c* axis, which corresponds to the sizes of the block-layer units, for the (Cu,C)-1234, Y-123,[17] Tl-1223,[18] and Hg-1223 (Ref. 19) compounds. This distance for (Cu,C)-1234 is smaller than for Tl-1223 and Hg-1223, but slightly larger than for Y-123. Kumakura *et al.*[20] have recently reported that (Cu,C)-1234 shows a higher irreversibility field than does Hg-1223 but smaller than Y-123, which is consistent with the expected behavior based on the size of the block layer.

An interesting structural feature of the $(Cu_{0.68}C_{0.32})Ba_2Ca_3Cu_4O_{11.06}$ is the wide variation in apical Cu-O distances for the pyramidal CuO_5 units. This results from the presence of the CO_3 groups. The corresponding apical oxygen atoms, O2B, are displaced from the ideal $(0,0,z)$ position resulting in distorted pyramids. Thus, two kinds of apical Cu-O bond lengths exist; one (Cu2-O2A) is 2.39 Å long and the other (Cu2-O2B), associated with the CO_3 group, is 3.18 Å long. It should be noted that the latter value is dependent on the constraints used in the structural model. For example, if we had used a model that allowed C atoms to be displaced from the ideal Cu1 sites, the CuO_5 pyramids capped by O2B would perhaps be less distorted, resulting in a somewhat shorter Cu2-O2B bond. However, in any model, this apical bond would be required to be unusually long in order to allow the required CO_3 configuration.

It is somewhat surprising that the existence of the outer CuO_2 layers with distorted apical oxygen atom positions does not appear to substantially lower T_c in the present compound; the T_c of 117 K is very close to those reported for other four-layer compounds such as Tl-1234 (122 K),[21] Tl-2234 (108 K),[22] and Hg-1234 (126 K).[16] In the case of the 90-K superconductor, $YBa_2Cu_3O_{7-\delta}$, Shaw *et al.*[23] reported that CO_3 substitution on the chain Cu site lowered T_c to 50 K. However, it was not clear

TABLE IV. The interatomic distances of Cu2-Cu2 that correspond to the size of the block-layer units for the (Cu,C)-1234, Y-123, Tl-1223, and Hg-1223 materials.

	(Cu,C)-1234	Y-123(92 K)	Tl-1223	Hg-1223
Cu2-Cu2 (Å)	8.37	8.31	9.26	9.43

whether this resulted from the structural distortions associated with the displaced apical oxygen sites or from a change in the number of charge carriers. One explanation for the present result is that, even though the presence of distorted apical oxygen sites degrades superconductivity for the two outer CuO_2 layers, the two inner layers support superconductivity with a high T_c. The recently discovered $HgBa_2CaCu_2O_{6+\delta}$ compound exhibits a T_c of 128 K, the highest value observed for a two-layer compound,[24] supporting the idea that a T_c of 117 K should be possible for the present compound even if only the two inner CuO_2 layers were contributing.

If such a hypothesis were true, one would expect that insertion of CO_3 units would lower T_c more for compounds with a smaller number of CuO_2 layers. The available data cannot provide a definitive test of this idea because T_c may not have been optimized after the incorporation of CO_3 units in individual studies. In addition, the chemistry is not identical (e.g., no Ba is present in some compounds). However, it is instructive to consider the properties of several CO_3-containing cuprates that have been found so far. The single-layer compound $Sr_2CuO_2CO_3$, which has a structure with CuO_6 octahedra, is not superconducting.[11] This material can be made superconducting by appropriate hole doping, such as $(Ba_xSr_{1-x})_2Cu_yO_{2y+\delta}(CO_3)_{1-y}$ (Ref. 25) and $Sr_2CuO_2(CO_3)_{1-x}(BO_3)x$,[26] with T_c's of 46 and 32 K, respectively. Thus, it is immediately clear that the partial incorporation of CO_3 units into the charge reservoir, giving rise to distortions in the apical oxygen positions, does not preclude superconductivity. Two-layer compounds where C atoms in CO_3 groups substitute for Cu atoms on the chain site in the $YBa_2Cu_3O_{7-\delta}$ structure include the nonsuperconductor $(C_{0.4}Cu_{0.6})Sr_2(Y_{0.86}Sr_{0.14})Cu_2O_7$,[12] and the superconductor

$$(Y_{1-x}Ca_x)_{0.95}Sr_{2.05}Cu_{2.4}(CO_3)_{0.6}O_y$$

with T_c of 63 K.[5] For the (Cu,C)-12($n-1$)n series, Kawashima, Matsui, and Takayama-Muromachi[2] reported $T_c=67$ K for the $n=3$ member and $T_c=117$ K for the $n=4$ member (present compound). Therefore a series of compounds from $n=1$ to 4 in (Cu,C)-12($n-1$)n exists and shows superconductivity. The $n=4$ compound shows the highest T_c among the series of the compounds. Empirically, in Tl- and Hg-based superconductors, $n=3$ compounds show the highest T_c's and T_c's go down as n increases further.[16,22] Although the data are admittedly not complete, the (Cu,C)-12($n-1$)n series seems to violate this empirical rule.

This unusual superconducting behavior suggests at least two additional experiments. If one accepts the argument that the inner CuO_2 layers are mostly responsible for the T_c as high as 117 K, the present (Cu,C)-1234 compound is effectively a two-layer compound. It then becomes important to attempt the synthesis of the $n=5$ member of the series (which may be possible at high pressure) in hopes of obtaining a T_c higher than 117 K. On the other hand, optimization of the T_c for the $n=3$ compound is interesting in connection with the empirical rule that the $n=3$ compounds show the highest T_c's in one series of compounds. It may exhibit a T_c higher than 117 K.

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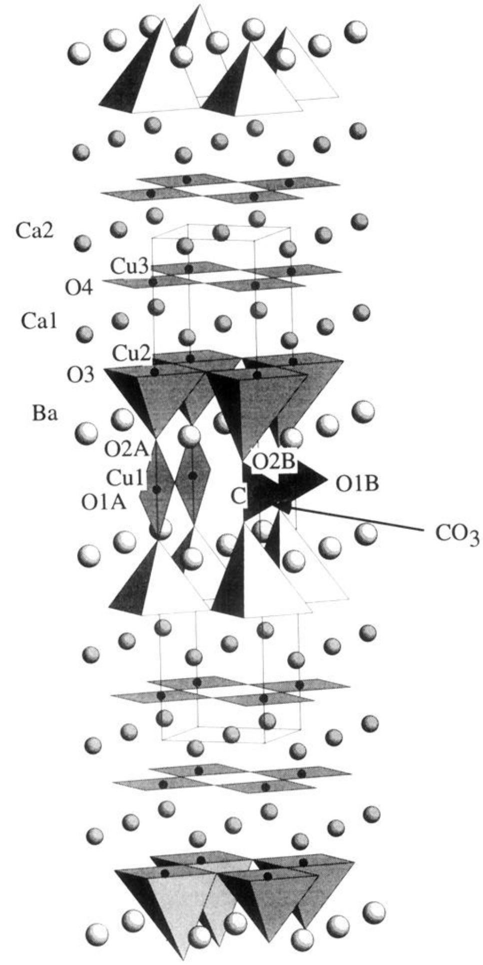

FIG. 2. Structure of (Cu,C)$Ba_2Ca_3Cu_4O_{11+\delta}$. Cu1 and C are located in the shared site. Cu1 has chainlike oxygen coordination (O1A and O2A). C is bonded to three oxygen atoms (O1B and O2B) forming a CO_3 group. Two oxygen atoms in the CO_3 group occupy the apical positions of CuO_5 pyramids, but they are displaced from the ideal $(0,0,z)$ position. Cu2 and O3 are in the outer CuO_2 plane. Cu3 and O4 are in the inner CuO_2 plane. Although the present analysis of the average tetragonal structure cannot yield any information about possible ordering and orientation of the chainlike CuO_4 and CO_3 units, the structure is drawn to be consistent with the $2a \times b \times 2c$ superstructure which is seen in electron diffraction. Cu1 and C are the origin of the average tetragonal unit cell in the refinement (Table I).