

# The Effect of Pressure on Superconducting Copper Mixed Oxides

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Received September 29, 1995; accepted October 9, 1995

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This article comprises four sections. The first introduces the subject of pressure-induced syntheses and phase transitions taking place in ionic compounds. Examples are described to illustrate the general trends governing these transformations, namely the increase of the cation and anion coordinations under pressure and the greater compressibility of anions with respect to that of cations. In the second section, pressure-induced phase transitions taking place in superconducting layered cuprates are discussed and the only example known so far, that occurring in  $ACuO_2$  compounds, is illustrated. In the third section, pressure-induced syntheses are discussed. The examples in which pressure has been crucial to obtain new phases are numerous. In some cases, like the Hg-based cuprates, the new compounds are not high pressure phases, but nevertheless the use of pressure has greatly helped to optimize the synthesis of the samples. In other cases, like  $Sr_2CuO_{3+\delta}$ , only the synthesis under pressure yields superconducting samples. In the fourth section, the *in situ* pressure studies carried out at Houston, Grenoble, Birmingham, and Argonne are described. The dramatic increases of  $T_c$  for the first four members of the Hg homologous series are strictly correlated to the shortening of the apical Cu–O distance which in these compounds is anomalously large at ambient pressure. If the structural arrangement responsible for 164 K superconductivity has to be stabilized by substitution, second nearest-neighbor interactions must be taken into account. The synthesis of such compounds should be one of the primary future goals. © 1996 Academic Press, Inc.

## INTRODUCTION

To illustrate the effect of pressure on the structure of multinary copper oxides exhibiting high  $T_c$  superconductivity, it is of interest to describe the general principles governing the effect of pressure on ionic compounds, and more specifically, on oxides. In the late sixties and early seventies we worked in this field and our relative success was due to the continuous use of Professor Wells' book "Structural Inorganic Chemistry" (1). Although Professor Wells did not discuss the effect of pressure on ionic compounds in the 1985 edition all the principles, on which the crystallo-

chemistry under pressure is based, are included, and his book was our "Bible" for envisaging new systems to investigate. In this introduction we cite mainly the work we did in the field of high pressure crystallochemistry, but we do this purposely to show how Professor Wells indirectly influenced our research; we are honored to pay this tribute to him.

When ionic compounds are subjected to high pressure, the volume, as well as some of the interatomic distances, decreases. However, the latter cannot decrease below critical values at which the structure becomes unstable and either the compound decomposes or undergoes a structural transformation. The changes in the interatomic distances are very important parameters for understanding the variation of the physical properties. On the other hand, decompositions and phase transformations may lead to the synthesis of new phases with known or unknown structures.

A close-packed array of anions generates two types of interstices, the tetrahedral and octahedral sites. Specifically, a close-packed array of  $n$  anions contains  $n$  octahedral and  $2n$  tetrahedral sites. If we assume that the anions are spheres of 1.4 Å in radius, which is about that of  $O^{2-}$ , the tetrahedral and octahedral sites can accommodate spherical cations of a diameter around 0.32 and 0.58 Å, respectively.

Let us assume that we have a compound in which the anions form a hexagonal close-packed array and the cations occupy some of the tetrahedral sites. An example of such compounds is ZnO with the wurtzite structure in which the Zn cations occupy half of the tetrahedral sites. By applying pressure to such a compound, one first observes a volume decrease accompanied by a decrease in the cation–anion and anion–anion distances. At a critical value of the pressure, the tetrahedral sites become too small for the Zn cations and a phase transformation occurs, producing a NaCl-type phase in which the O anions form a cubic close-packed array and the Zn cations completely occupy the larger octahedral sites (2). The Zn–O distances increase at the transformation, but the volume decreases because the O–O distances decrease. Such behavior is due

to the fact that in ionic compounds with increasing pressure, anions can decrease in size more readily than cations, or the former are more compressible than the latter.

The increase of the cation coordination and consequently that of the anions is one of the general principles governing the transformations occurring under high pressure in ionic compounds whether or not the anions form a close-packed array. In fact, a NaCl-type structure in which both cations and anions have a sixfold coordination with the Cl anions forming a cubic close-packed array transforms under high pressure to a CsCl-type structure in which the cations and the anions have eightfold coordinations (3). The anion array in the CsCl structure is simple cubic and not a close-packed structure.

With these principles in mind a variety of new phases with known or unknown structures and new compounds have been synthesized in the last thirty years. Sometimes these were retained metastably at ambient pressure by quenching, while in some other cases these new phases, structures, or compounds have been evidenced only *in situ*. The release of pressure would induce the transformation to the structure stable at ambient pressure.

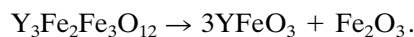
The  $\beta$  phase of  $\text{Ga}_2\text{O}_3$  has a monoclinic structure containing a distorted cubic close-packed array of oxygen atoms in which 1/3 and 1/6 of the octahedral and tetrahedral sites, respectively, are occupied by the Ga cations (4). Besides this monoclinic phase,  $\text{Ga}_2\text{O}_3$  is also known to crystallize with the  $\alpha$  phase of the sesquioxide having the corundum structure. This latter phase is characterized by a distorted hexagonal close-packed array of oxygen atoms in which all the Ga cations occupy 2/3 of the octahedral sites. By taking into account the simple principle described above, it is easy to surmise that  $\alpha$  is a high pressure phase of  $\beta$ . If the synthesis of the corundum phase of  $\text{Ga}_2\text{O}_3$  is carried out at ambient pressure, poorly crystallized powder samples are always prepared and single crystals are impossible to obtain. By subjecting  $\beta$ - $\text{Ga}_2\text{O}_3$  to a pressure of 40 kbar at 1000°C, the  $\alpha$  phase was obtained and by using  $\text{H}_2\text{O}$  as mineralizer, well-formed single crystals are found together with the powder (5).

In 1967 Shannon and Prewitt (6) found that, under 65 kbar and 1250°C,  $\beta$ - $\text{InGaO}_3$  (in which the In and Ga cations occupy the octahedral and the tetrahedral sites, respectively) transforms to a hexagonal structure  $\text{InGaO}_3$ (II) in which the coordination numbers of the In and Ga cations are six and five, respectively. Furthermore, the oxygen array changes from cubic close-packed, ABC, to a sequence ABACBC. At a higher pressure  $\text{InGaO}_3$ (II) transforms to  $\text{InGaO}_3$ (III) with a corundum or a disordered ilmenite structure (7). It is interesting to point out that the same sequence could exist for  $\text{Ga}_2\text{O}_3$ .

Another interesting example which well describes the behavior of ionic compounds under pressure is that of the polymorphism in  $\text{CaB}_2\text{O}_4$  (8). By varying the pressure at

which the synthesis is carried out, this compound can crystallize with four different structures, three orthorhombic and one cubic. The common trend among these structures is an increase of the cation coordination with increasing pressure. The relevant data for this polymorphism are summarized in Table 1. In the phase stable at ambient pressure all boron atoms are triangularly coordinated while the Ca cations have an eight-fold coordination. In the structure of  $\text{CaB}_2\text{O}_4$ (II), 50% of the B atoms are triangularly coordinated and 50% tetrahedrally coordinated. The Ca cations have the same coordination number 8 as in  $\text{CaB}_2\text{O}_4$ (I). Therefore, in the transition (I)  $\rightarrow$  (II) the only cations that increase their coordination are 1/2 of the boron atoms. The density variation corresponding to this transition is 6.5%. The pressure range of stability of this phase is very narrow, around 12–15 kbar.  $\text{CaB}_2\text{O}_4$ (III) can be synthesized at 900°C under a pressure of about 15–25 kbar. In this phase, 1/3 of the B atoms are triangularly coordinated and 2/3 tetrahedrally coordinated, while 2/3 of the Ca cations are 8-coordinated and 1/3 are 10-coordinated. In the (II)  $\rightarrow$  (III) transition, 1/6 of the B and 1/3 of the Ca cations increase their coordination while the density increases 5.6%. In the (III)  $\rightarrow$  (IV) transition, 1/3 of the B atoms increase their coordination from 3 to 4, whereas 2/3 of the Ca atoms increase their coordination to 9–12 and 1/3 to 12. The density variation corresponding to this transition is 11.5%. By analogy many new phases of borates and polyborates could be synthesized under pressure.

Sometimes the instability of compounds at a given pressure may give rise to their decomposition instead of a phase transition. For example, under pressure the garnet structure decomposes according to the reaction (9)



The garnet structure contains three crystallographically independent cation sites: an eight-fold site where the Y cations are accommodated, and octahedral and tetrahedral sites in the 2:3 ratio where the Fe cations are located. The three Fe cations in the tetrahedral sites are not stable under pressure. In fact, at about 30 kbar and 900°C,  $\text{Y}_3\text{Fe}_2\text{Fe}_3\text{O}_{12}$  undergoes a decomposition resulting in  $\text{YFeO}_3$  with the perovskite-like structure and  $\text{Fe}_2\text{O}_3$  with the corundum structure. This is a relatively important result from the geological point of view because garnets are components of the upper mantle. We used it to show that the decomposition could lead to the synthesis of the  $\text{REGaO}_3$  compounds with small rare-earth elements, which cannot be obtained by direct synthesis as the Fe, Al, Mn, etc. counterparts. In the case of Ga, regardless of the stoichiometric ratio of the starting reactants, the garnet structure is always obtained. This behavior is due to the  $sp^3$  hybridization of the Ga–O bonds and thus to the preference of the Ga cations for the tetrahedral coordination. The orthogallates

TABLE 1  
Polymorphism in  $\text{CaB}_2\text{O}_4$

$\text{CaB}_2\text{O}_4$	Approximate range of stability at 900°C (GPa)	Density ( $\text{g}/\text{cm}^3$ )	Symmetry	% B in $\triangle$	% B in $\triangleleft$	Ca(CN)
I	0–1.2	2.702	Orthorhombic	100	0	8
II	1.2–1.5	2.885	Orthorhombic	50	50	8
III	1.5–2.5	3.052	Orthorhombic	33	67	67% 8 33% 10
IV	2.5–4.0	3.426	Cubic	0	100	67% (9–12) 33% 12

of rare-earth elements smaller than Nd were all synthesized under high pressure and the anomaly of their nonexistence was removed (10).

In some cases, compounds with a given stoichiometry do not exist at ambient pressure. They can only be synthesized under high pressure and high temperature conditions and be retained metastably by quenching to ambient conditions. For example, the sesquioxide  $\text{Co}_2\text{O}_3$  has to be synthesized at 8 GPa and 850°C under highly oxidizing conditions (11). This phase exhibits the corundum structure with unit cell parameters  $a = 4.78 \text{ \AA}$  and  $c = 12.96 \text{ \AA}$ . These parameters are very close to those of the  $\text{Al}_2\text{O}_3$  corundum itself ( $a = 4.763 \text{ \AA}$  and  $c = 13.00 \text{ \AA}$ ). Consequently, the two cations,  $\text{Al}^{3+}$  and  $\text{Co}^{3+}$ , should have about the same ionic radii, 0.53 and 0.54  $\text{ \AA}$ , respectively. These values indicate that the  $\text{Co}^{3+}$  cations are in the low  $3d^6$  spin state. By annealing the  $\text{Co}_2\text{O}_3$  phase at 400°C in air for half an hour, the low-spin state  $\text{Co}_2\text{O}_3$  transforms to another corundum structure with larger unit cell parameters ( $a = 4.883 \text{ \AA}$  and  $c = 13.38 \text{ \AA}$ ). In this structure, the  $\text{Co}^{3+}$  cations have a radius of 0.61  $\text{ \AA}$ , which corresponds to the high  $3d^6$  spin state. By comparing the unit cell parameter at room pressure this transformation is accompanied by a 6.7% volume change.

Copper in oxide compounds is a good candidate to give rise to phase transformations under pressure as it has several different coordinations (dumbbell, square, tetrahedral, pyramidal, and octahedral) and three different valence states. However, only a few pressure-induced transformations have been observed in the field of multinary copper oxides, exhibiting high- $T_c$  superconducting properties. This is understandable because with such complex stoichiometries and bonding anisotropy, the probability that a different arrangement with the same stoichiometry could exist at high pressure is almost nil. One could find interesting pressure-induced decompositions, but these possibilities have not been investigated yet. The long apical Cu–O bonds in either octahedra or pyramids make these compounds susceptible to pressure, but on the other hand, this feature makes them quite stable under high

pressures. The only exception so far is the transformation occurring in  $\text{SrCuO}_2$ . It is noteworthy that 1:1:2 is the simplest stoichiometry among the superconducting cuprates. In contrast, the direct synthesis under pressure has been a fertile field, namely the phase does not exist at ambient pressure and can only be obtained under pressure and retained metastably by quenching.

High pressure has also been used to facilitate the formation reaction as in the case of the superconducting Hg-based cuprates,  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+d}$ , which are not high pressure phases.

## PRESSURE-INDUCED PHASE TRANSFORMATIONS

### a. $\text{ACuO}_2$

Takano *et al.* (12) showed that there exist two phases for the  $\text{ACuO}_2$  cuprates with  $A =$  alkali-earth element, one stable at ambient pressure and the other at high pressure. The former structure contains double edge-sharing chains of  $\text{CuO}_4$  squares intercalated by  $A$  cations. (See a schematic representation in Fig. 1). The resulting coordina-

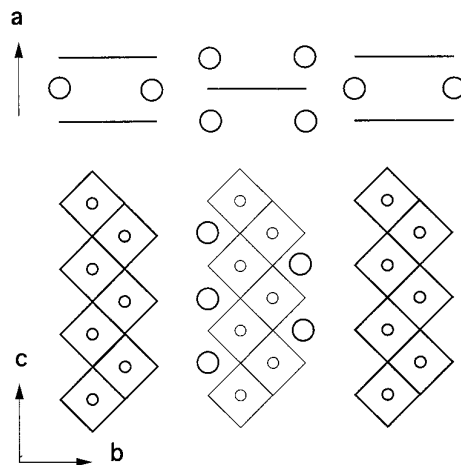


FIG. 1. A schematic representation of the  $\text{SrCuO}_2$  stable at ambient pressure. The black thick segments in the upper part are the infinite edge-sharing square chains shown in the lower part of the figure.

tions are 4 and 7 for the Cu and  $A$  atoms, respectively. Under a pressure of 6 GPa and at 1000°C this phase transforms to a different structure containing corner-sharing sheets of  $\text{CuO}_4$  squares common to all superconducting cuprates, alternating with oxygen-depleted  $A$  layers (Fig. 1). The  $A$  cations are located under or above the empty  $\text{O}_4$  squares. The coordination numbers of the Cu and  $A$  atoms are 4 and 8, respectively. The rule that the coordination number increases under pressure is fulfilled. The high pressure phase can be retained at ambient pressure by quenching. This layer structure may be regarded as the parent structure of all the layered multinary cuprates. Since the Cu valence in such compounds is 2+ for both phases, they were not found to be superconducting. Azuma *et al.* (13) were able to increase the valence of the Cu cations by carrying out the high pressure–high temperature synthesis in the presence of  $\text{KClO}_4$ . This synthesis yielded  $A$ -deficient samples,  $A_{1-x}\text{CuO}_2$ , which exhibited  $T_c$  as high as 110 K. The doping of the conducting  $\text{CuO}_2$  layers is achieved by having  $x > 0$ . Subsequently, Shaked *et al.* (14) argued that the superconductivity with  $T_c \sim 90\text{--}130$  K reported in samples of infinite layer compounds should be attributed to the phases belonging to the homologous series  $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$  ( $n = 1, 2, \dots$ ).

## PRESSURE-INDUCED SYNTHESSES

### a. $\text{LaCuO}_3$

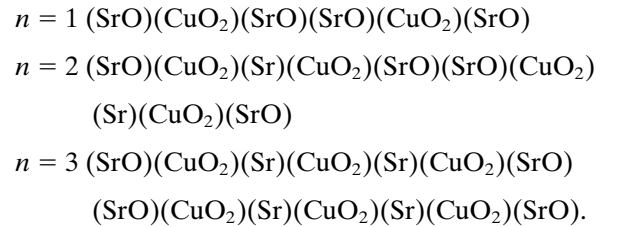
This compound was obtained under pressure because of the 3+ state of the Cu cations. It was synthesized for the first time by Demazeau *et al.* (15) in 1973 by using a pressure of 6 GPa. It has a distorted perovskite arrangement with trigonal symmetry ( $a = 5.431 \text{ \AA}$  and  $\alpha = 60.51^\circ$ ) and exhibits metallic conductivity. This important result generated great interest, especially after Raveau and co-workers around 1980 demonstrated that the 3+ state of Cu can be stabilized at ambient pressure by introducing an alkali-earth element into the structure (16). These authors showed that mixed copper oxides containing Cu cations in intermediate valence state between 2+ and 3+ may exhibit metallic conductivity. The discovery in 1986 by Bednorz and Müller (17) of a superconducting transition at a relatively high temperature (28 K) in Ba-doped  $\text{La}_2\text{CuO}_4$  showed the importance of the pioneering work of the Bordeaux and Caen groups.

### b. $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$

This homologous series has been prepared under pressure, but the different phases with  $n = 1, 2$  and 3 can be retained at ambient pressure by quenching. They have an oxygen-deficient structure which is strictly related to that of the homologous series  $\text{La}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ . This becomes clearer when their formula is written as  $\text{Sr}_2\text{Sr}_{n-1}\text{Cu}_n\text{O}_{2n+1+\delta}$

in which the Sr cations occupy both the LaO layers of the  $\text{K}_2\text{NiF}_4$  structure and those intercalating the  $\text{CuO}_2$  layers. Hiroi *et al.* (18) and almost simultaneously Adachi *et al.* (19) showed that the member with  $n = 1$  becomes superconducting at  $T_c = 70$  K while those with  $n = 2$  or 3 have a  $T_c$  of about 100 K. Mitchell *et al.* (20) showed that the first member of the series can be prepared at ambient pressure in 1 atm oxygen. However, this sample was not found to become superconducting. Han *et al.* (21) were able to increase  $T_c$  of  $\text{Sr}_2\text{Cu}_3\text{O}_{5+\delta}$  samples synthesized at high oxygen pressure (5.7 GPa) from 70 to 94 K with heat treatments.

The structures of  $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$  are stabilized by oxygen vacancies. The structural arrangements of these compounds have been determined by high resolution electron microscopy and we do not have any direct evidence as to where the oxygen vacancies are located in the structures. If we do not take them into account the structures of these compounds contain the following sequences:



### c. $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$

This general formula should actually be written as  $\text{Sr}_n\text{Cu}_{n+1}\text{O}_{2n+1}$  with  $n \geq 1$  in which case there is a member for every value of  $n$ . This is a very important homologous series because every member of the series is an infinite-layer compound and in principle could be the parent structure of a series of layered cuprates. The difference between the high-pressure structure of  $\text{SrCuO}_2$  and those of these compounds is in the stoichiometry of the copper–oxygen layers. In the former the copper–oxygen layers are the conventional  $\text{CuO}_2$  layers comprising corner-sharing  $\text{CuO}_4$  squares, while in the latter the copper–oxygen layers still comprise  $\text{CuO}_4$  squares, but these share corners as well as edges in an ordered fashion. Figure 2 shows the copper–oxygen layers in  $\text{SrCu}_2\text{O}_3$ , the member with  $n = 1$ , and in  $\text{Sr}_2\text{Cu}_3\text{O}_5$ , the member with  $n = 2$ . The Sr cations intercalate these layers and they occupy the sites corresponding to the empty squares. These compounds, which were synthesized by Hiroi *et al.* (22) under a pressure of 6 GPa and 1000°C, are both insulators, but have different magnetic ground states. Note that the stoichiometry of these new layers is  $[\text{Cu}_2\text{O}_3]$  and  $[\text{Cu}_3\text{O}_5]$ , respectively. It is possible that with the proper doping they might become superconductors. The structural arrangements have been determined by high resolution electron microscopy and struc-

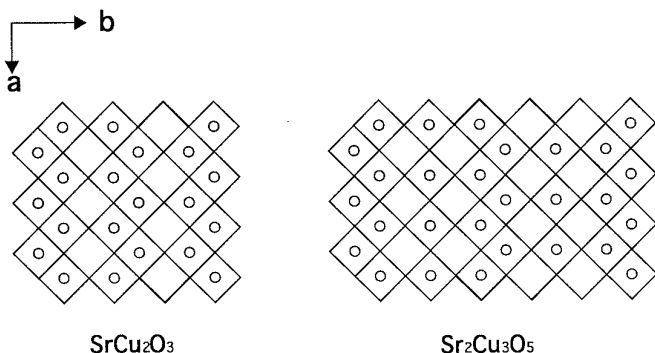


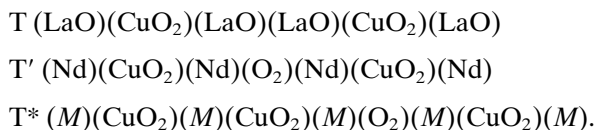
FIG. 2. The  $\text{CuO}_4$  square layers in the first two members of the  $\text{Sr}_n\text{Cu}_{n+1}\text{O}_{2n+1}$  series. The Sr cations are above and below the empty squares.

tural details are needed in order to tailor an effective cation or anion doping. Kazakov *et al.* (23) have been able to produce almost pure samples of these phases with the high pressure–high temperature technique. A structural refinement based on neutron powder diffraction data is in progress.

#### d. $\text{RE}_2\text{CuO}_4$ Compounds ( $\text{RE} = \text{Pr}–\text{Nd}$ )

Three phases exist for the  $\text{RE}_2\text{CuO}_4$  double oxides.  $\text{La}_2\text{CuO}_4$  has the  $\text{K}_2\text{NiF}_4$ -type T structure and becomes a  $p$ -type superconductor when properly doped. The Pr, Nd, Sm, and Eu 2:1:4 compounds, instead, become  $n$ -type superconductors when the rare-earth cations are partially substituted by tetravalent cations. These compounds have the  $\text{Nd}_2\text{CuO}_4$ -type T' structure containing square coordinated Cu cations and eight-coordinated RE cations. Although  $\text{Gd}_2\text{CuO}_4$  has the same structure it does not become superconducting by doping.

$\text{La}_{0.9}\text{Sm}_{0.9}\text{Sr}_{0.2}\text{CuO}_4$  has the T\* structure, which is intermediate between the T and T' structures. In T\* half of the cell is T and the other half T' (24). This is illustrated by the following sequences contained in these structures:



In the T\* structure  $M$  represents  $(\text{La}_{0.9}\text{Sm}_{0.9}\text{Sr})$ .

Okada *et al.* (25) and subsequently Bordet *et al.* (26) have shown that in order to prepare the  $\text{RE}_2\text{CuO}_4$  compounds with heavier lanthanides (Tb–Tm) and yttrium, the synthesis must be carried out under pressure. They have the T' structure, but so far, as in the case of  $\text{Gd}_2\text{CuO}_4$ , no sign of superconducting transition has been detected by doping them.

By comparing the T and T' structures one can see that

the difference lies in the positions of the oxygen atoms of the La layers. In the former structure these oxygen atoms are approximately co-planar with the La cations and together they form two LaO layers. In the latter structure, there are two oxygen deficient RE layers which sandwich an  $\text{O}_2$  layer. In the T structure the La and Cu cations are nine- and six-coordinated, respectively, while in the T' structure they are eight- and four-coordinated, respectively. By the high-pressure cation-coordination rule it can be surmised that the T structure is the high-pressure phase of T' and the transformation  $\text{Nd}_2\text{CuO}_4$ -type to  $\text{La}_2\text{CuO}_4$ -type should occur under pressure. Actually, the sequence with increasing pressure should be  $\text{T}' \rightarrow \text{T}^* \rightarrow \text{T}$ . We have tried this experiment and we are aware that other groups having access to a high pressure facility have done so too. However, the  $\text{RE}_2\text{CuO}_4$  ( $\text{RE} = \text{Pr}–\text{Tm}$ ) phases with the T structure have not been reported yet. Either the transition pressure is too high for our apparatus or the T phase of these compounds is not quenchable.

The  $\text{T}' \rightarrow \text{T}$  transformation implies the movement to the two RE layers of the oxygen atoms sandwiched between the two RE layers, one above and one below. Such a movement is highly reversible and this would be why one fails to quench the high pressure phase. *In situ* experiments are needed to demonstrate that the  $\text{T}' \rightarrow \text{T}$  transition occurs.

#### e. $(\text{Cu}_{1-x}\text{C}_x)\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+y}$

The copper, barium, calcium carbocuprate series was simultaneously reported early in 1994 by Alario-Franco *et al.* (27) and Wu and co-workers (28). While trying to totally replace Hg by Ag in the Hg-based cuprates,  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ , these two groups obtained multiphase samples exhibiting relatively high superconducting transitions (between 85–120 K). The syntheses were carried out by the high pressure–high temperature technique. As in the case of the Hg-based cuprates, it was thought that the high pressure would favor the reaction between the precursor and  $\text{Ag}_2\text{O}$ . X-ray and electron diffraction revealed that the samples included layered cuprates similar to those of the Hg series. The electron diffraction patterns were indexed on an orthorhombic cell  $2a_p \times a_p \times 2c$ , where  $a_p$  is the parameter of the simple cubic perovskite cell and  $c$  is equal to about  $8.5 + 3.2(n - 1)$ ,  $n$  being the number of  $\text{CuO}_2$  planes per unit cell. EDS analysis, the unit cell parameters, and high resolution electron microscopy indicated that the general formula of the series was  $\text{Cu}_{0.5}\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+y}$ . This meant that  $\text{Ag}_2\text{O}$  did not react with the precursor and only half of the Hg sites are occupied by Cu. The superstructure doubling the  $a$  and  $c$  axes would be due to the ordering of the Cu cations over the Hg sites. Subsequently, Kawashima *et al.* (29) pointed out that empty Hg sites are actually occupied by C atoms possibly

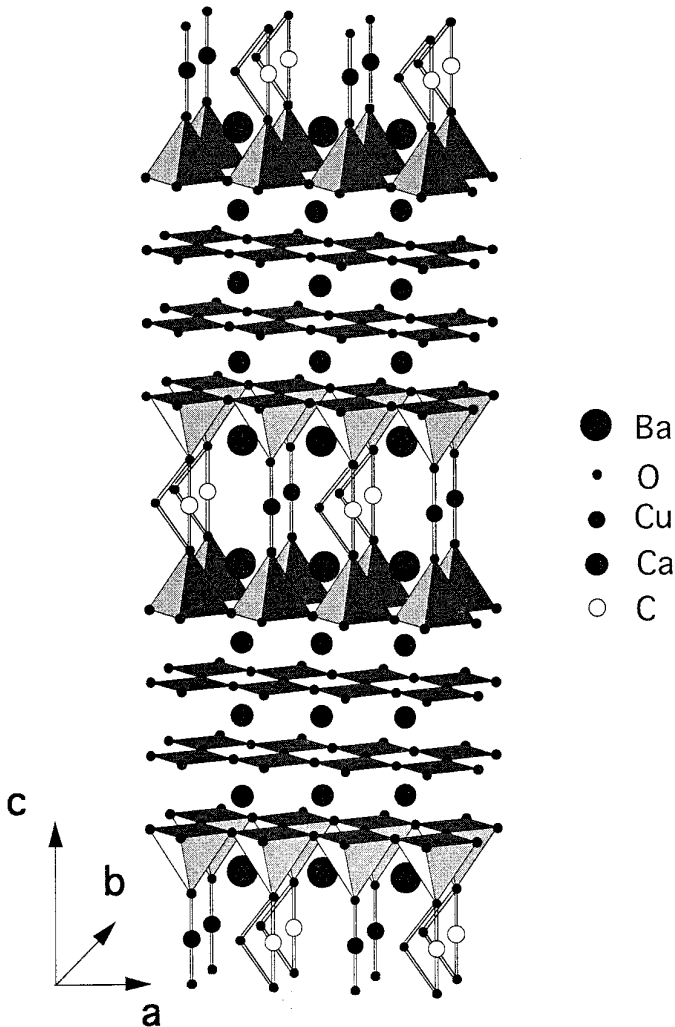


FIG. 3. Structural model of  $\text{Cu}_{0.5}\text{C}_{0.5}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ .

forming carbonate groups with the two apical oxygen atoms above and below and an extra oxygen atom in the same layer (see the structural model in Fig. 3).

The samples prepared by Alario *et al.* (30) were obtained by using precursors prepared from nitrates and all manipulations were carried out in a dry box. However, it is conceivable that some “contamination” may occur from  $\text{CO}_2$  from the air, which gets in the reaction via  $\text{BaO}$  acting as a  $\text{CO}_2$ -getter. The carbocuprate structure must be very stable if it forms under such conditions and its stability is enhanced by the high pressure because the O–C–O bonding shortens the  $c$  axis and induces a decrease of the volume.

Members of the series with  $n = 3$  and 4 have been prepared as almost pure phases and it has been determined that the former has a  $T_c \approx 86$  K while the latter has a  $T_c \approx 117$  K. Note that the highest  $T_c$  corresponds to the member with  $n = 4$ . This feature is unique as in all the other homologous superconducting series the highest  $T_c$

corresponds to  $n = 3$ . The high-resolution electron micrographs of some of the samples showed that some crystallites contained sequences corresponding to  $n = 5, 6$ , or 7. This possibility, shared with the Hg-based cuprates, would indicate that the  $\text{CuO}_2$  layers in the carbocuprates are flat as in the Hg ones. The  $n = 1$  and  $n = 2$  for the carbocuprate series have not been obtained yet, whereas they are well known for the Hg series.

We will be able to verify all these conjectures when the structure of the carbocuprates are determined in detail. Shimakawa *et al.* (31) tried to carry out a structural determination based on neutron powder diffraction data. They were able to confirm the arrangement deduced from electron microscopy and diffraction, but their results on the structural arrangement of the (Cu, C) layer were not conclusive. This is the charge reservoir and the knowledge of its structure should on one side reveal the doping mechanism and on the other allow one to change and eventually optimize the superconducting properties.

This carbocuprate series seems very attractive and may prove to be very important because, besides exhibiting relatively high  $T_c$  values, it does not contain any toxic element like Hg, Tl, or Bi.

#### f. $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$

These compounds are synthesized by reacting to a precursor containing barium, calcium, and copper in the appropriate proportion with  $\text{HgO}$ . The latter compound decomposes at a relatively low temperature at ambient pressure and this decomposition prevents the formation reaction to take place. Thus, the reaction is carried out in sealed tubes, inside which a relatively low pressure is generated. This pressure increases the decomposition temperature of  $\text{HgO}$  to values high enough for the reaction to produce the Hg cuprate (32). At the very beginning when syntheses in sealed tubes yielded only multi-phase samples because it was difficult to control the decomposition of  $\text{HgO}$  (33), we decided to utilize the high pressure techniques. Besides yielding samples with which one could determine and refine the structure by using powder neutron diffraction data, the syntheses carried out under pressure produced samples which present specific structural and superconducting properties (34).

Recently, sealed-tube syntheses have been able to produce very pure and monophasic samples, especially for Hg-1201 where intergrowths are not possible (35). There is a claim now (36) that good samples of Hg-1223 can even be obtained by a solid state reaction in air.

Figure 4 shows the structure of the Hg-1223 compound. In the Hg-based cuprate the doping mechanism involves the incorporation of oxygen on the Hg layers. Under pressure, overdoped samples can be obtained because the incorporation of oxygen increases the copper valence of the

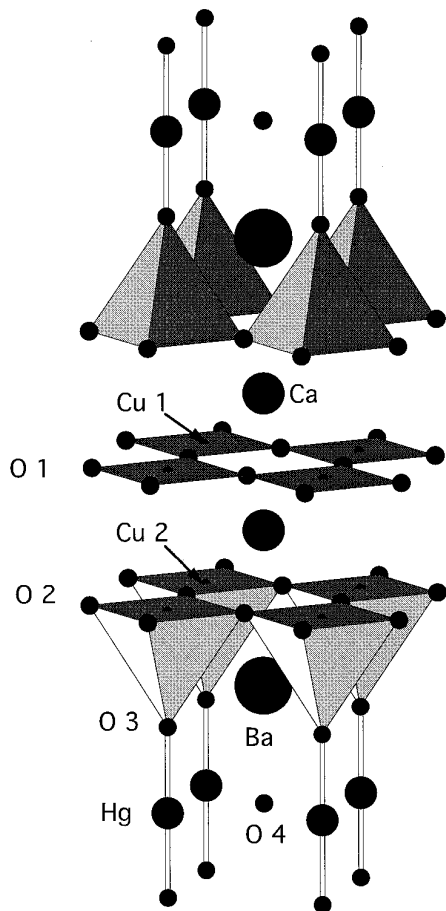


FIG. 4. Structural model of  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ .

$\text{CuO}_2$  layers, leading to a decrease of the Cu–O distances. Because the layers are almost flat the  $a$  parameter is about twice the in-plane Cu–O distance and if this distance decreases the  $a$  parameter decreases, as well as the volume.

A disadvantage of the high pressure synthesis of Hg-based cuprates is the possible incorporation of carbonate groups in the place of Hg. There is now strong evidence that this incorporation does take place under pressure. For example, every structure of Hg-based cuprates, prepared under high pressure, exhibits a large Debye–Waller factor for the Hg cations in high correlation with the occupancy factor of the same cations. The high pressure synthesis always yields samples with a large  $a$  parameter and a shorter  $c$  axis. Moreover, the highest  $T_c$  for any given member is always smaller for the high pressure samples than for that of the corresponding sample obtained by the sealed-tube technique. All these specific features could be explained by assuming that the high pressure technique favors the incorporation of carbonate groups replacing the Hg cations.

Kopnin *et al.* (37) have purposely prepared samples of

Hg-1223 by using high pressure and precursors obtained from carbonates. The unit cell parameters of these samples were  $a = 3.8653(5)$  Å and  $c = 15.671(4)$  Å, which differ largely from those corresponding to a Hg-1223 sample prepared under pressure but from nitrate precursors ( $a = 3.8532(6)$  Å and  $c = 15.818(2)$  Å) (38). This variation of the unit cell parameters cannot be attributed to different oxygen contents, because a variation of  $\delta$  would change both parameters along the same direction. The Hg-1223 sample prepared from a carbonate precursor undergoes a superconducting transition with a  $T_c$  onset = 69 K, which is much lower than the record-high  $T_c$  onset quoted for Hg-1223 (133 K) (39). Ultra-high resolution electron microscopy shows that the samples having the lower  $T_c$  clearly contain C in the place of Hg.

The replacement of Hg by C in the Hg based cuprates seems to induce a decrease or even a suppression of the superconducting transition. This is so because this replacement provides an appreciable reduction of the Cu valence in the  $(\text{CuO}_2)$  layers. Instead, in the copper carbocuprates the substitution of Cu by C seems to lead to Cu valences optimal for superconductivity. In the hypothetical C-free Cu cuprates the  $(\text{CuO}_2)$  layers would be highly overdoped and the incorporation of C reduces the Cu valence.

#### THE IN SITU EFFECT OF PRESSURE ON CUPRATES

It has been shown since the beginning of the high  $T_c$  superconductors that for increasing pressure  $T_c$  may increase or decrease. The largest increase of  $T_c$  with pressure has been observed by Chu and his collaborators for Ba-doped  $\text{La}_2\text{CuO}_4$  (40). The  $dT_c/dP$  was found to be 6.1 K/GPa. Another large increase of  $T_c$  for increasing pressure has been observed for  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $dT_c/dP = 5.5$  K/GPa) (41). The first attempt to study the effect of pressure on  $T_c$  for the Hg compounds was made by Klehe *et al.* (42) who found that the variation of  $T_c$  with  $P$  for Hg-1201 was positive with a  $dT_c/dP = 1.75$  K/GPa up to 1 GPa. More spectacular results were obtained for Hg-1223 by Chu and co-workers (43, 44) and almost simultaneously by Nunez-Regueiro *et al.* (45).

These authors showed that the transition temperature of Hg-1223 increases dramatically with the application of hydrostatic pressure (43, 45) reaching a maximum value of 164 K at 31 GPa (44); this represents a record value for  $T_c$  in any kind of environment and at a temperature only  $\sim 20$  K below the lowest recorded ground temperature on this planet. Gao *et al.* (44) measured the pressure effect on  $T_c$  for Hg-1201 and Hg-1212 up to 35.5 GPa while Nunez-Regueiro *et al.* measured that of Hg-1234 (46). The behavior of the members of the Hg series is very similar to that of the record Hg-1223 compound. For example,  $T_c$  of Hg-1201 increases from 94 K at ambient pressure to 118 K at about 16 GPa where saturation is attained. The

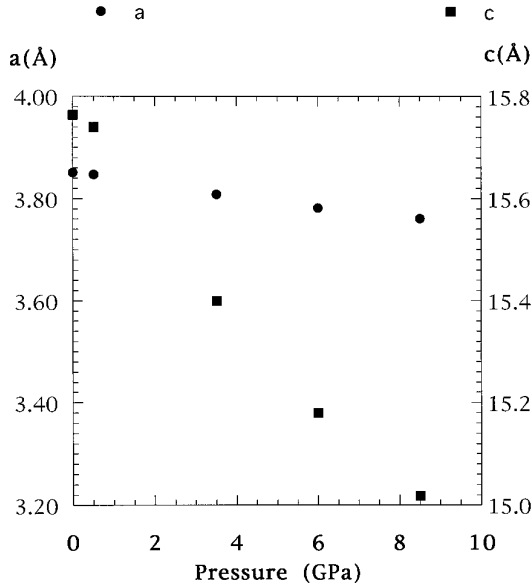


FIG. 5. The  $a$  and  $c$  parameters vs  $P$  for  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ .

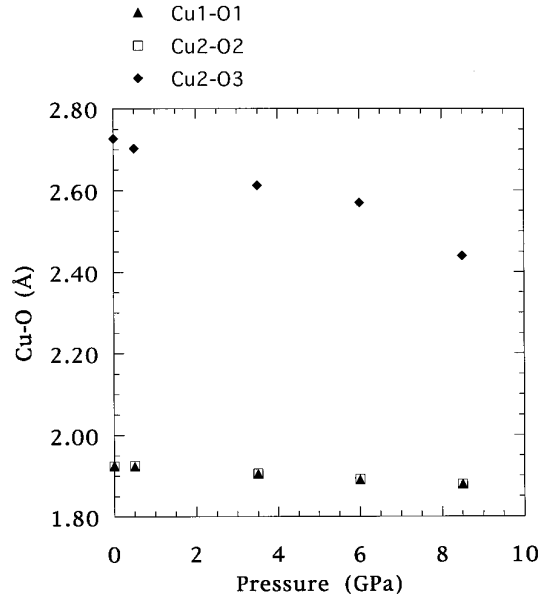


FIG. 6. Cu–O distances vs  $P$  for  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ .

corresponding parameters for Hg-1212 are 126 K, 150 K, and 30 GPa while those of Hg-1234 are 118 K, 132 K, and 20 GPa.

In order to relate the structural changes to the variation of  $T_c$  with pressure, an *in situ* structural determination as a function of pressure for Hg-1223 was made by using powder neutron diffraction data (47). These experiments were carried out at the Rutherford Appleton Laboratory. The pressure up to 8.5 GPa was generated in a tungsten carbide opposed anvils cell. Measurements were made at ambient pressure, 0.5, 3.5, 6.0, and 8.5 GPa. As can be seen from Fig. 4 the values of the unit cell parameters as a function of pressure indicate that their decrease is somewhat linear with  $da/dP - 0.011 \text{ \AA/GPa}$  and  $dc/dP - 0.090 \text{ \AA/GPa}$ , the decrease of the  $c$  parameter being more than eight times that of the  $a$  parameter. The structural refinements based on the neutron data show that the apical Cu–O distance decreases about 11% on going from ambient pressure to 8.5 GPa (see Fig. 5). In the ambient pressure structure this distance is abnormally large (2.78 Å); it decreases to 2.42 Å at 8.5 GPa. The decrease of the  $c$  axis is due in large part to the decrease of the Cu–O apical distance. For comparison, in superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  the same distance at ambient pressure is 2.28 Å. The apical Hg–O distance which also lies entirely along the  $c$  axis remains practically unchanged within the same pressure interval. The three in-plane distances, two Cu–O and one Hg–O, decrease accordingly to the decrease in the  $a$  axis (see Figs. 5 and 6). The two Cu–O distances decrease from 1.91 Å at ambient pressure to 1.89 Å at 8.5 GPa while the Hg–O distance decreases in the same pressure interval from 2.71 to 2.68 Å (see Fig. 7). Similar behavior as a

function of pressure of the corresponding distances was observed for Hg-1201 and Hg-1212 by Hunter *et al.* (48).

A major experimental goal now would be to stabilize at ambient pressure the structural arrangement responsible for the 164 K transition. This can be realized by appropriate synthesis and substitutions. Just looking at the structure one can surmise that the effect of pressure is simulated by putting Sr in place of Ba. This would shorten the  $c$  axis and move the apical oxygen toward the  $(\text{CuO}_2)$  layer.

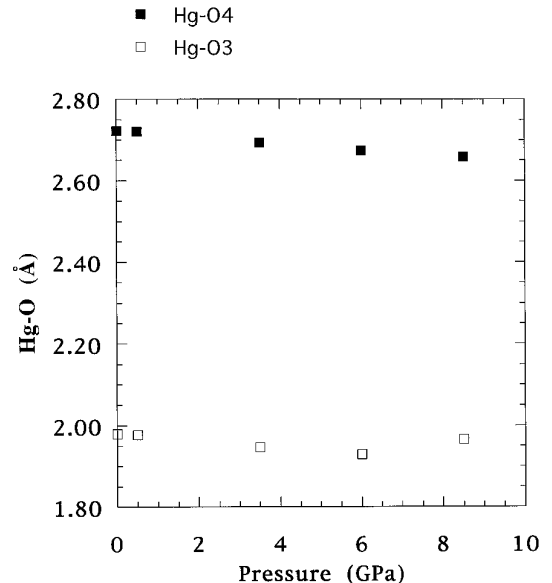


FIG. 7. Hg–O distances vs  $P$  for  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ .



However, Sr-substituted Hg-1223 samples exhibit transition temperatures which are lower than those of unsubstituted samples. This indicates that the second-nearest-neighbor interactions and electronic factors must be taken into account to stabilize the structure of the 164 K superconductor.

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