The superconducting oxycarbonates

(Tl, M)_1(Sr, Ba)_4Cu_2(CO_3)_7 and (Hg, M)_1(Sr, Ba)_4Cu_2(CO_3)_7:
three classes of closely related structures

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Starting from the «1201» structure and the Sr_2CuO_2CO_3 (S_2CC) structures more than sixteen oxycarbonates with an original structure can be generated. They can be classified according to their structure in three series. The single intergrowth of the «1201» and S_2CC structures formulated [1201], [S_2CC], represents the first class. The two other classes, called collapsed oxycarbonates, derive from the first series by shearing mechanisms. The second class corresponds to the appearance of a shearing phenomenon in the (100) plane, i.e. a shifting of c/2 in the [1201], [S_2CC] intergrowth may appear every m octahedra (m = 3, 4 or m = 3 and 4 alternately). The third class is characterized by a shearing phenomenon in the (110) plane of c/2 every m octahedra (m = 5, 6 or m = 5 and 6 alternately, or m = 4 and 5 alternately). Incommensurate distributions of the (100) and (110) shear planes are also observed. One remarkable feature deals with the fact that all these oxycarbonates are superconductors with T_c ranging from 17 K to 80 K.

Keywords: Superconductivity, Oxycarbonates, Intergrowths, Shearing mechanism

Los oxicitarentos superconductores (Tl,M)_1(Sr,Ba)_4Cu_2(CO_3)_7 y (Hg,M)_1(Sr,Ba)_4Cu_2(CO_3)_7; tres clases de estructuras estrechamente relacionadas

Partiendo de la estructura «1201» y las estructuras Sr_2CuO_2CO_3 (S_2CC), más de 16 oxicitarentos, con una original estructura, pueden ser formados. Estos pueden ser clasificados de acuerdo a su estructura, en tres series. La formada a partir de la interpenetración de las estructuras «1201» y S_2CC y formulada como [1201], [S_2CC], representa la primera clase. Las otras dos clases, denominadas oxicitarentos colapados, derivan de la primera serie a través de mecanismos de distorsión. La segunda clase corresponde a la aparición de un fenómeno de distorsión en el plano (100), producido, por ejemplo, por un desplazamiento de c/2 en la Estructura [1201], [S_2CC], en cada m octaedros (m = 3, 4 o m = 3 y 4 alternativamente). La tercera clase está caracterizada por un fenómeno de distorsión en el plano (110) de c/2 cada m octaedros (m = 5 ó m = 5 y 6 alternativamente, ó m = 4 y 5 alternativamente). Inadecuadas distribuciones de las distorsiones en los planos (100) y (110) son también observadas. Otra característica notable es que todos estos oxicitarentos son superconductores en un rango de temperaturas críticas de 17K a 80K.

Palabras clave: Superconductividad, Interpenetración, mecanismos de distorsión.

1. INTRODUCTION

A great deal of work has been devoted to superconducting oxycarbonates these last four years. Most of these compounds derive from the cuprates by introducing triangular carbonate groups between the layers of CuO_2 pyramids or of CuO_2 octahedra. Among them, the oxycarbonates with the generic formulation (Tl,M)_1(Sr,Ba)_4Cu_2(CO_3)_7 and (Hg,M)_1(Sr,Ba)_4Cu_2(CO_3)_7, that have been recently discovered, are of great interest, owing to their close structural relationships with the «1201» cuprates such as Tl_35Pb_65Sr_4Cu_2O_7 (1) or HgBa_2CuO_4+delta (2). The great flexibility of these structures makes that intergrowth and shearing phenomena can be combined in the same matrix, allowing the generation of new materials without destroying superconductivity.

We report herein on the structure and superconductivity of these materials that can be classified in three series: one class of single intergrowths of the «1201» and «S_2CC» (Sr_2CuO_2CO_3) structures formulated (1201), (S_2CC), and two classes of collapsed oxycarbonates derived from the (1201), (S_2CC) structure by shearing phenomena along the (100) and (110) planes respectively.

2. THE SINGLE INTERGROWTHS (1201), (S_2CC)

The comparison of the «1201» structure (Fig. 1a) observed for Tl_35Pb_65Sr_4Cu_2O_7 (1) with the structures of the oxycarbonate Sr_2CuO_2CO_3 (3) (Fig. 1b) suggests the possibility to realise an intergrowth, due to their bidimensional accord. This is the case of the oxycarbonate Tl_35Pb_65Sr_4Cu_2(CO_3)_7 (4) whose structure (Fig. 1c) consists of a regular stacking of these two kinds of layers. The important point deals with the fact that the oxycarbonate Tl_35Pb_65Sr_4Cu_2(CO_3)_7 exhibits a sharp superconducting transition with a high diamagnetic volume fraction, with T_c up to 70 K after optimisation (Fig. 2), whereas the two components of the structure...
have never been formed superconductors whatever this annealing treatment they were submitted. The replacement of lead by bismuth allows an isotypic phase to be synthesized, with the formulation Tl$_{1-x}$Bi$_x$Sr$_2$Cu$_2$(CO$_3$)$_3$O$_y$ (5); the critical temperature of the latter is however lower than for the lead phase, ranging from 48 K for $x = 0.3$ to 54 K for $x = 0.5$. It is remarkable that no thallium oxycarbonate that would correspond to the composition Tl$_4$Sr$_4$Cu$_2$(CO$_3$)$_7$ (5) could be synthesized up to date. Curiously the partial substitution of molybdenum for thallium, allowed a similar intergrowth to be isolated for the composition Tl$_{1-x}$Mo$_x$Sr$_2$Cu$_2$(CO$_3$)$_3$O$_y$ (6); the critical temperature of this phase can be increased up to 80 K by annealing in a hydrogen argon flow (10% H$_2$) at low temperature (280 °C).

Hg (II), owing to its electronic d$^{10}$ configuration similar to Tl(III) and to its similar size, exhibits also isotypic oxides, in spite of the fact that mercury adopts the twofold linear coordination. The oxides Hg$_{1-x}$Pb$_x$Sr$_2$Cu$_2$(CO$_3$)$_3$O$_y$ (7) and Hg$_{1-x}$Bi$_x$Sr$_2$Cu$_2$(CO$_3$)$_3$O$_y$ (8), are characterized by the «1201» structure like the thallium cuprates, and differ only from the latter by an oxygen deficiency. Like the thallium phases, these mercury cuprates do not superconduct. In a very similar way, the assemblage of the «1201» mercury cuprate structure with the S$_2$CC structure allows new superconductors to be generated. This is the case of the oxycarbonates Pb$_{1-x}$Hg$_x$Sr$_2$Cu$_2$(CO$_3$)$_3$O$_y$ (9) and Hg$_{1-x}$Bi$_x$Sr$_2$Cu$_2$(CO$_3$)$_3$O$_y$ (10) that both exhibit the same structure as Tl$_{1-x}$Pb$_x$Sr$_2$Cu$_2$(CO$_3$)$_3$O$_y$ (Fig. 1c), mercury replacing thallium, and anionic sites at the mercury level being partly vacant. Contrary to the «1201» parent oxides and to Sr$_2$Cu$_2$(CO$_3$)$_3$O$_y$, these two oxycarbonates are superconductors; the lead phase Pb$_{1-x}$Hg$_x$Sr$_2$Cu$_2$(CO$_3$)$_3$O$_y$ has a $T_c$ of 70 K (Fig. 3 curve a), after optimisation in a reducing atmosphere, i.e. very similar to Pb$_{1-x}$Tl$_x$Sr$_2$Cu$_2$(CO$_3$)$_3$O$_y$. Curiously, a much lower $T_c$ of 17 K (Fig. 3 curve a)
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3. THE COLLAPSED (100)-(1201)(S2CC)1 INTERGROWTH

Starting from the single intergrowth, (1201),(S2CC)1 (Fig. 1c), a shearing mechanism can be applied along the (100) plane of the structure by introducing barium on the strontium sites, leading to a new structure, that consists of slices of the (1201),(S2CC)1 intergrowths, shifted of c/2 with respect to each other.

The most current member of this series is represented by the oxycarbonates TlBa2Sr2Cu2(CO3)O7 (13), TlHgBaSrCu2(CO3)O7 with x = 0.2 and 0.5 (14). In this structure two successive (1201),(S2CC)1 slices that are m = 4 CuO6 octahedra thick are shifted of c/2 in the (100) plane as schematised on figure 5. From this shearing mechanism, it appears that the (CuO6) layers and the (SrO)2 layers of each block remain unchanged and form infinite layers parallel to (001). This is not the case for the (TIO)8 ribbons which are limited to four Tl atoms along b and are connected to ribbons of four CO3 groups. Thus the (TIO)8 and (CO)4 layers of the structure TlHgBaSrCu2(CO3)O7 are replaced by mixed layers (TIO)8(CO)4 characterized by a sequence of four thallium atoms and four carbonate groups along b.

This shearing phenomenon with respect to TlHgBaSrCu2(CO3)O7 is evidenced by the (100) HREM images. The contrast can be described from rectangular areas (Fig. 6) which correspond to half a cell «b/2 x c».

4. RESULTS

This shearin phenomenon, which implies the coexistence of thallium and carbon within a same layer rises the issue of the adaptation of these elements owing to their large size differences which imply Tl-O apical distances of about 2.00 Å, much larger than the C-O distan-
ces along c (about 1.30 Å). The answer to this question is given by changing the focus of the (100) HREM image. For some focus values (Fig. 7), the atoms of the (CuO₂)₆ layers are highlighted: it can be seen that these layers undulate with a rather large amplitude. Thus the structure of TiBa₂Sr₄Cu₆(CO₃)₀₇ (Fig. 5) consists of single perovskite undulating layers involving the (CuO₂)₆ and the (SrO)₆ sheets connected through (TiO₆)(CO₃)₆ layers. As a result the cell is orthorhombic, and characterized by a superstructure along 1/2 with respect to the single intergrowth: a = aₚ - 3.8Å, b = 8 x aₚ, c = 17 Å.

In a more general way, the (100) plane is a crystallographic shear plane, along which a shifting may appear every m octahedra, so that the (100) - collapsed oxycarbonates will be characterized by a super lattice a = aₚ, b = 2m x aₚ, c = 17Å; the above phases correspond to m = 4.

Different shearrings may appear that lead to various superstructures: (100) - shearing phenomena were indeed observed in the system TiSr₄Ba₄Cu₆(CO₃)₀₇ (15) leading to the superlattice a = aₚ x 6aₚ, b = 17Å that corresponds to m = 3, and to the super lattice a = aₚ x 7aₚ, c = 17Å that corresponds to a (100) shearing phenomenon every three (m = 3) and four (m = 4) octahedra alternately. This shearing mechanism is sometimes more complex as shown for instance in the oxycarbonate Ti₃⁺⁺H₆0₃Sr₄Ba₄Cu₆(CO₃)₀₇ (14) that exhibits an incommensurate structure a = aₚ x 7.5aₚ, c = 17Å, which implies that the distribution of the (100) shear planes is modulated along the b direction of the actual cell.

It is remarkable that all these (100)-collapsed (1201),(S₂CC) oxycarbonates are superconductors with critical temperatures ranging between 60 K and 70 K. This is in agreement with the fact that the (CuO₂)₆ planes are not interrupted by the shearing phenomenon. Moreover this shows that the waving of the copper oxygen layers does not destroy the superconducting properties of these materials. At the present time, the role of barium in the (100)-shearing phenomenon is not explained. In particular, it is not known whether barium is absolutely necessary for the appearance of (100) shear planes.

4. THE COLLAPSED (110)-(1201),(S₂CC) INTERGROWTH

The introduction of transition elements on the thallium sites of the S₂CC-1201 oxycarbonate allows also a shearing phenomenon to be induced. This is the case of the oxycarbonates Ti₂₃/₅Cr₁₃/₅Sr₄Cu₂(CO₃)₀₇ and Ti₃/₅Ba₂Sr₄Cu₂(CO₃)₀₇ (11).

Nevertheless, in these oxycarbonates the shearing plane is no more the (100) plane but the (110) plane. In order to evidence the atomic arrangements of these oxides, the crystals were viewed along (100). This direction corresponds to (110) or (110) plane but the (110) plane. Two images of the Ti₃/₅Sr₄Cu₂(CO₃)₀₇ compound are given in figures 8 and 9 illustrating the typical contrasts which have been registered; their interpretation, especially the identification of the layers, was made with the help of the (110) simulated images, calculated for an ideal unmodulated structure. In figure 8 the heavy Tl(Cr or V) and Sr atoms appear as dark spots, for a focus value close to -50Å. The contrast of this image consists mainly of three rows of bright and grey spots: in the intermediate row, five bright spots correlated to the carbonate positions alternate with five dark spots correlated to the heavy Tl(Cr or V) and Sr atoms. In figure 9 the three rows of bright spots correspond to the (SrO) layers. The copper layers, which appear as rows of grey spots, are intercalated between the (SrO) layers; they undulate with a rather large amplitude: they, indeed, sandwich the bright spots at a significantly smaller distance than the dark spots. In figure 9, the contrast is different so that the thallium and strontium atoms, which appear as bright spots, are clearly evidenced; the three rows of highlighted spots are correlated to the SrO-TI(CrO)oxycarbonate layers and the row of grey spots to the copper layers. For a focus value close to 200Å, the existence of mixed thallium (Cr)-carbon layers is easily imaged, as

Fig. 7: (100) HREM image of TiBa₂Sr₄Cu₆(CO₃)₀₇: the (CuO₂)₆ layers are highlighted.

Fig. 8: (100) HREM image of the (110)-collapsed Ti₂₃/₅Cr₁₃/₅Sr₄Cu₂(CO₃)₀₇ oxycarbonate. The simulated image is 35Å and focus value -50Å is insert has been calculated for the unmodulated subcell. The carbon segments appear as fine successive dots.
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Fig. 9: [010] HREM image for a focus value close to -580Å where the cation positions are correlated to the bright spots. The calculated image is in insert.

Fig. 10: Idealized drawing of the (110)-collapsed structures: a) (Tl, M)Sr₂Cu₂(CO₃)₇ and b) HgBa₂Sr₂Cu₂(CO₃)₇.

well. These images indicate, without any ambiguity, that the atomic arrangements of Tl₂/3Cr¹/₃Sr₄Cu₂(CO₃)₇ and Tl₂/₃V¹/₃Sr₄Cu₂(CO₃)₇ are that of a (110) collapsed- S₂CC-1201 structure, characterized by mixed intermediate layers where m = 5 (Tl + Cr) atoms alternate with m' = 5 carbon atoms along b (Fig. 10 a).

The oxycarbonates HgBa₂Sr₂Cu₂(CO₃)₇ and HgBa₂Sr₂Ba₂Sr₃Cu₂(CO₃)₇exhibits also the (110) shearing plane. But in that case the 1201-S₂CC structure is shifted by 6 every six and five CuO₆ octahedra alternately along (110) (Fig. 10b) leading to a periodicity along (110) of 11a V₂. In the same way, the HREM image obtained for HgBa₂Sr₂Cu₂(CO₃)₇ (17), that implies a periodicity = 9a V₂ along (110), can be interpreted by a (110) shearing of the (1201)S₂CC intergrowth every five and four octahedra alternately. The possibility to obtain an incommensurate distribution of the (110) shear planes in this structure has also been observed. This is for instance the case of Tl₂/3Hg¹/₃Ba₂Sr₂Cu₂(CO₃)₇ that exhibits 4.7 times incommensurate structure along the (110) direction.

As the (100) «collapsed» oxycarbonates, the (110) collapsed oxycarbonates are all superconductors in agreement with the fact that the (CuO₆)₉ layers are not interrupted by the shearing mechanism. HgBa₂Sr₂Cu₂(CO₃)₇ is superconductor up to 65 K, whereas critical temperatures ranging from 55 K to 68 K were observed for HgBa₂Sr₂Ba₂Sr₃Cu₂(CO₃)₇ (x = 0, 1.2). The critical temperature of the as-synthesized Tl₂/3Sr₃3/3Sr₄Cu₂(CO₃)₇ (Fig. 11 curve a) is significantly higher than that observed for other thallium oxycarbonates (Tc(onset) = 72 K, Tc(midpoint) = 68 K). Moreover successive annealings in an Ar/H₂ flow show that Tc is significantly increased (Tc(onset) = 77 K, Tc(midpoint) = 74 K) (Fig. 11 curves b-c-d-e).

5- CONCLUSION

These results show the extraordinarily flexibility of the oxycarbonate structures that should allow other phases to be generated. A systematic study of these complex systems will be necessary to understand the relationships between structure, non stoichiometry and superconductivity.
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6. REFERENCES


6. F. Letroux, C. Martin, A. Maignan, C. Michel, M. Hervieu, B. Raveau. «New superconducting cuprates with mixed TI-Mo layers: TIQ5M03SrCu02Og, TIQ5M03SrCu0g+3 and TIQ5M03SrCu0g+5». Physica C, submitted for publication.

7. F. Gautenaire, P. Daniel, M. Hervieu, G. Van Tendeloo, C. Michel, A. Maignan, B. Raveau. «New mercury based Superconductors with the «1201» structure: Hg05Pb6Sr4Cu0g+3 and Hg05Pb6Sr4LaCu0g+3». Physica C 216 (3) 293-299 (1993).


9. C. Martin, M. Hervieu, M. Huvé C. Michel, A. Maignan, G. Van Tendeloo, B. Raveau. «Lead mercury based superconductors: the 1212 cuprate Pb2Hg05Sr4Cu0g+3 and the new oxide carbonate Pb2Hg05SrCu0g+3». Physica C 222 (1) 19-25 (1994).


11. A. Maignan, D. Pelloquin, S. Malo, C. Michel, M. Hervieu, B. Raveau. «Stabilisation of three new oxide carbonates by V and CR substitutions: the superconductors (TI, M)V2SrCu0g(CO3)02 (M = Cr, V) and (Hg, V)2SrCu0g(CO3)02.». Physica C, in press.

12. D. Pelloquin; M. Hervieu, S. Malo, C. Michel, A. Maignan, B. Raveau. «Two transition metal substituted superconducting mercury based oxide carbonates, Hg2M2SrCu0g(CO3)02 (M = Cr and Mo)». Physica C. 246 (1) 1-10 (1995).


15. Y. Matsumi, M. Ogawa, M. Yehara, H. Nakata, J. Akimitsu. «Incommensurate and commensurate superstructures in the oxide superconductor TIQ5Hg05Sr4Cu0g+3». Physica C. 217 (2) 287-293 (1993).


17. M. Uehara, S. Sahoda, H. Nakata, J. Akimitsu and Y. Matsui. «New Hg Based oxide carbonate superconductor Hg6Ba2Sr4Cu0g+3(CO3)2». Physica C. 222, (1) 27-32 (1994).