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Incommensurability and transfer mechanism in bismuth high T_c superconductors

G. Pan ⁽¹⁾, S. Megtert ⁽¹⁾ and G. Collin ⁽²⁾

⁽¹⁾ Laboratoire de Physique des Solides, Bt. 510, Université Paris-Sud, 91405 Orsay Cedex, France

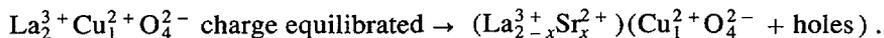
⁽²⁾ Groupe C.P.C.M., L.L.B., CEN Saclay, 91191 Gif sur Yvette Cedex, France

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Abstract. — The structure of bismuth high T_c superconductors is investigated. A correlation is found between incommensurate modulations and transport properties: $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ is not a good metal because the transfer of electrons from the Cu-O₂ layers into the Bi-O bi-layers induces an incommensurate and monoclinic distortion, responsible for the localization of carriers. Substitution of Sr^{2+} by La^{3+} reduces the transfer degree and the distortion; a superconductive transition is therefore observed with the remaining carriers after a monoclinic-orthorhombic phase transition. Further substitution tending to a complete compensation of transfer leads to a compensated insulator. It is suggested that the c^* component of the modulation is linked to the lattice distortion and the b^* component to the charge transfer degree. Similar changes are observed in $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_8$ except that the monoclinic distortion is never present.

1. Introduction.

High critical temperature superconductors, (H.T.S.C.), consist essentially in copper-oxygen layers, responsible for superconductivity with planar formula CuO_2 . These layers are localized in-between M-O layers (M = alkaline-earth or rare earth elements), close to perovskite type packing, which provide the stability of the crystalline framework. Moreover, in some materials additional layers, such as Cu-CuO, Ti-O, Pb-O, Bi-O, ..., are present. The prototype H.T.S.C. compounds are $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, without additional layers and $\text{CuBa}_2\text{YCu}_2\text{O}_7$ ($\text{YBa}_2\text{Cu}_3\text{O}_7$) with one additional CuO layer, « copper chain », distinct from the two CuO_2 layers, « copper planes ». In addition, an essential characteristic of (H.T.S.C.) materials is the presence of a charge transfer. Indeed, copper-oxygen layers are not spontaneously conductor. Thus, La_2CuO_4 is an anti-ferromagnetic insulator and, to make it metallic, it is necessary to « dope » it according to the ionic schema :

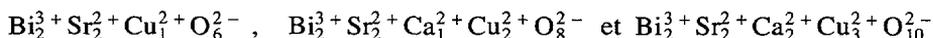


The carriers created by the Sr^{2+} - La^{3+} substitution are transferred into the hybridized copper-oxygen band, thus leading to a metal. This mechanism of *transfer by doping* is quite general in

this type of materials. However, there is another kind of H.T.S.C. materials with *spontaneous transfer*. An example is given by the thallium compounds, with formal equilibrium of charges, but which are spontaneously metallic and even superconducting, through an electron transfer from copper-oxygen layers into additional Tl-O layers. The transfer is stabilized by a valence fluctuation of thallium, $6s^0 6p^0(Tl^{3+}) - 6s^2 6p^0(Tl^{1+})$ according to the schema :



Nevertheless, it is sometimes not so simple to point out the spontaneous transfer mechanism. For example, in bismuth materials like



all of them with formal charge equilibrium, the bismuth 3+ ion is already in a $6s^2 6p^0$ configuration, and, in principle, could not attract additional electrons. However, these materials are superconducting metals ($T_c \approx 20$ K (substituted), 90 K, 110 K respectively). But they are also materials in which strong structural distortions are observed resulting in « incommensurate » superstructures. If these distortions are linked to the transfer mechanism, they could even constitute a direct measurement of the charge transfer degree as we will suggest, by examining single crystals of the simplest of these materials, the « one-layer » compound, $Bi_2Sr_2CuO_6$.

2. Structure of the « one layer » compound $Bi_2Sr_2CuO_6$.

All bismuth materials can be described in a tetragonal cell, $I4/mmm$, $Z = 2$, [1, 2], with the same lattice constant, ($a \approx b \approx 3.8 \text{ \AA}$), and lattice constant c depending on the number of layers. Its value for $Bi_2Sr_2CuO_6$ is $\approx 24.6 \text{ \AA}$ (Fig. 1). In this sub-structure there are three types of cationic sites :

- the strontium site, nine-fold coordinated ;
- the bismuth site, in octahedral coordination (strongly distorted) ;
- the copper site, in a rather regular octahedral coordination.

In fact, an orthorhombic description is most commonly retained, with $a_{\text{ort.}} \approx b_{\text{ort.}} \approx a_{\text{tet.}} \sqrt{2}$. It must also be noticed that, whereas cation-oxygen distances are consistent with lattice dimensions for strontium and copper, this is not the case for the bismuth-oxygen distance, which ideally should be much shorter. Thus, there is a mismatch for this particular distance.

Under these conditions it is not surprising that X-ray diffraction patterns reveal the occurrence of superstructures as shown in figure 2. The actual cell is monoclinic $C2$, with a volume ten times larger than that of the tetragonal sub-structure [3] and with a two component modulation wave vector, along the orthorhombic b^* and c^* directions. In addition, careful determination on a four-circle diffractometer indicates that this superstructure is only approximately commensurate. Indeed, as an example, the strongest satellite reflection, whose ideal indexes in the monoclinic superstructure ($a_{\text{mon.}} = 2 b_{\text{ort.}} + c_{\text{ort.}}$, $b_{\text{mon.}} = a_{\text{ort.}}$, $c_{\text{mon.}} = 5 b_{\text{ort.}}$) should be $-14, 0, 11$, exhibits an incommensurate indexing such as $-14.03(1), 0, -10.94(1)$. The same result is obtained for other satellite reflections, with twice the incommensurability wave vector for second order satellites, ... Moreover, this material exhibits a particular behavior : it is metallic, but with an increase of resistivity at low temperatures, 10-20 K, suggesting a charge localization. Only some of the substituted materials exhibit a superconducting transition between 5 and 25 K [4-7].

In section 1, we have pointed out the difficulties encountered for the interpretation of

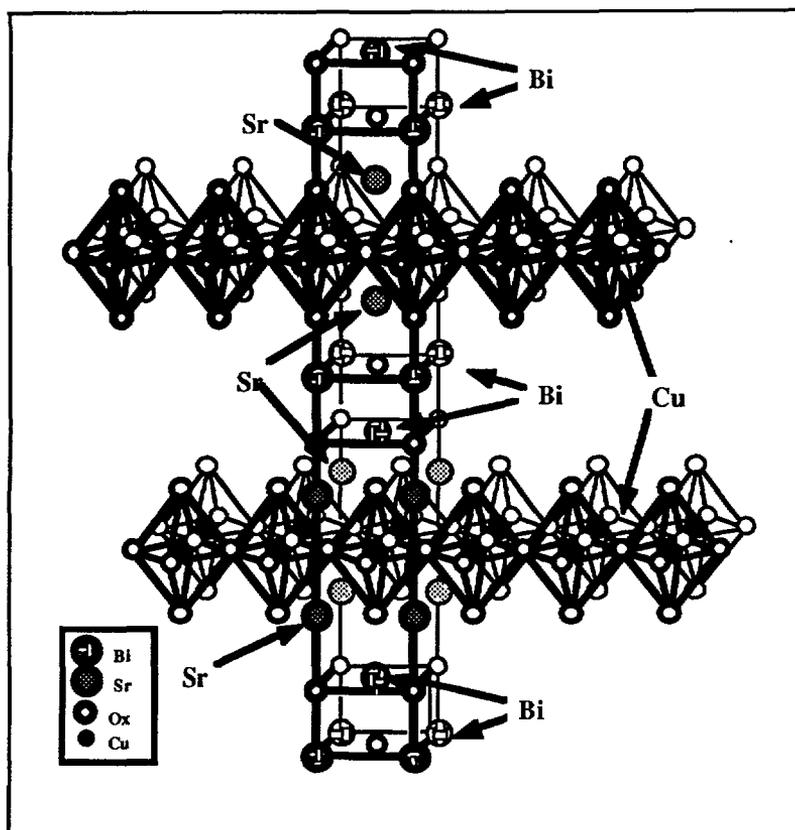


Fig. 1. — Schematic tetragonal structure of $\text{Bi}_2\text{Sr}_2\text{CuO}_6$.

transfer in the bismuth materials. Especially, there is no stable bismuth electronic state to trap the transferred electrons. However, in this kind of layer, it is possible to observe a 6s-6p band coupling with the lattice (the « lone pair »), leading to polaronic states and resulting in alternatively Bi-concentrated and deficient bands as observed by H.R.T.E.M. [8]. The carriers are thus localized and will behave as charged « ions » and modify electrostatic equilibrium within the layers. But, by that very fact, the number of charges has absolutely no reason to be commensurate with the lattice periodicity. Its consequence will be the existence of incommensurate modulations, which are actually observed. The special character of the « one layer » compound is that the magnitude of the distortion induced by charge transfer is large. In addition, we have seen that the super-structure is monoclinic (Fig. 2), with appreciable values of the modulation wave vector components in both pseudo-orthorhombic b^* and c^* directions. We will define incommensurability in this case as (Fig. 3) the reciprocal distance of the position of a first order satellite reflection with respect to the nodes of an average orthorhombic superstructure :

- i.e. along b^* , to the commensurate wave vector in an ideal commensurate superstructure with parameter $a \times 4 b \times c$ as observed in insulating substituted compounds [9, 10] ;
- i.e. along c^* , to the closest commensurate position with odd index.

In $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, the incommensurability components, as previously defined, are respectively 0.24 and 0.66 along b^* and c^* direction.

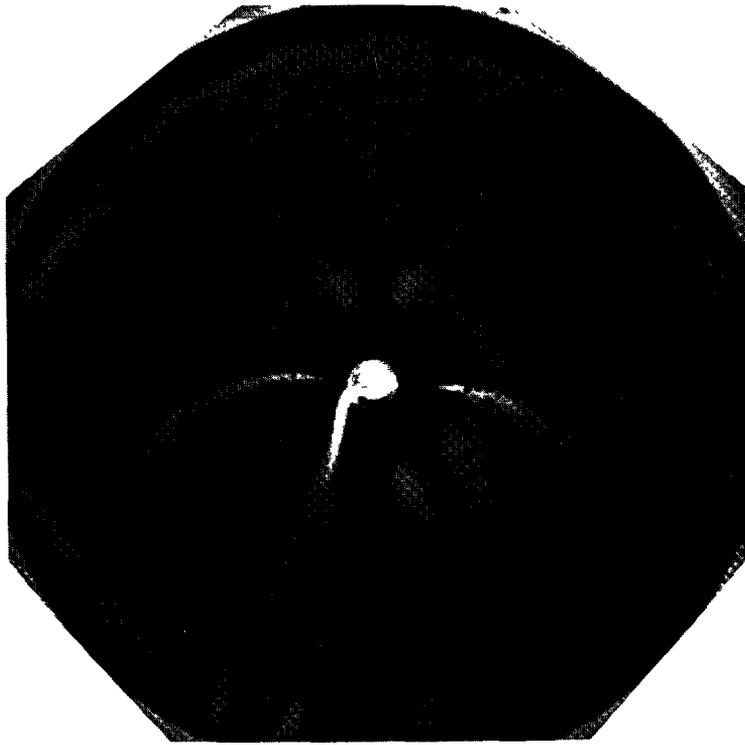


Fig. 2. — Diffraction pattern (MoK_α) of the $0kl$ layer of pure $\text{Bi}_2\text{Sr}_2\text{CuO}_6$. The modulation wave vector direction is indicated by the Q arrow.

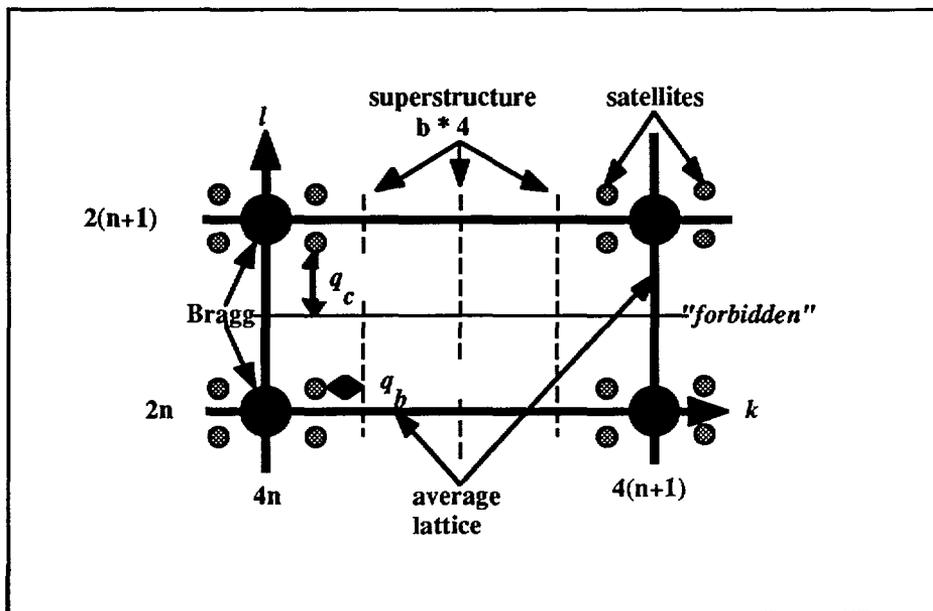


Fig. 3. — Definition of the b^* and c^* wave vector components.

In our hypothesis of an incommensurate super-structure linked to charge transfer, it is clear that any modification of the transfer degree will lead to structural modifications, which will manifest by a change of the incommensurate modulation. This is why we will examine substituted materials in the next section.

3. Substitution.

Several kinds of substitution are possible in this compound. We will only examine here substitution on the strontium site, the only cationic site exhibiting complete charge transfer. Two types of simple substitution can be performed.

3.1 « ISO-ELECTRONIC » SUBSTITUTION. — $\text{Bi}_2(\text{Sr}_{2-x}\text{M}_x)\text{CuO}_6$, in which $\text{M} = \text{Ca}^{2+}$ or Ba^{2+} is substituted to Sr^{2+} , then without modification of charge equilibrium. In this case, only slight structural modifications are observed, as indicated in the first two columns of table I.

Table I. — *Lattice constants and shifts with respect to commensurability of satellite reflection indexes, in a $(a \times 4b \times c)$ (Pseudo-) orthorhombic cell and in a $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ monoclinic cell.*

	$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	$\text{Bi}_2(\text{Sr}_{1.4}\text{Ca}_{0.6})\text{CuO}_6$	$\text{Bi}_2(\text{Sr}_{1.4}\text{La}_{0.6})\text{CuO}_{\text{«6»}}$
a (Å)	5.378(1)	5.372(1)	5.419(1)
b (Å)	5.380(1)	5.368(1)	5.449(1)
c (Å)	24.621(4)	24.537(3)	24.166(5)
α (°)	90.11 (2)	90.15 (1)	90.00 (1)
β (°)	90.00 (1)	90.00 (1)	90.00 (2)
γ (°)	90.00 (1)	90.00 (1)	90.00 (2)
$q_a^{\text{orth.}}$	0.00 (1)	0.00 (1)	0.00 (1)
$q_b^{\text{orth.}}$	0.24 (1)	0.23 (1)	0.04 (1)
$q_c^{\text{orth.}}$	0.66 (1)	0.58 (1)	0.00 (1)
$q_a^{\text{mon.}}$	+ 0.03 (1)	- 0.03 (1)	- 0.47 (1)
$q_b^{\text{mon.}}$	0.00 (1)	0.00 (1)	0.00 (1)
$q_c^{\text{mon.}}$	- 0.06 (1)	- 0.03 (1)	+ 0.18 (1)

This result is in agreement with our previous interpretation; as an « iso-electronic » substitution does not change the charge equilibrium, transfer is only modified at a second order, essentially by the geometrical change in distances due to the difference in ionic radius.

3.2 « NON-ISO-ELECTRONIC » SUBSTITUTION. — $\text{Bi}_2(\text{Sr}_{2-y}\text{M}_y)\text{CuO}_6$, in which $\text{M} = \text{La}^{3+}$ or Bi^{3+} is substituted to Sr^{2+} , then with a modification of charge equilibrium. The substituted 3+ ions will counterbalance the transfer, playing the role of « anti-dopant ». Under these conditions, appreciable structural modifications are observed (column 3, Tab. I), with, for lanthanum, for example (Fig. 4):

— a first region, for $0.00 < y_{\text{La}} < 0.07$, where the lattice remains monoclinic with two components for the modulation wave vector. However, a rapid decrease of the incommensurability along c^* is observed;

— a second region, for $0.07 < y_{\text{La}} < 0.20$, characterized by an orthorhombic lattice, due to a zero component along c^* , where the incommensurability along b^* keeps a finite value, which decreases with increasing y_{La} ;

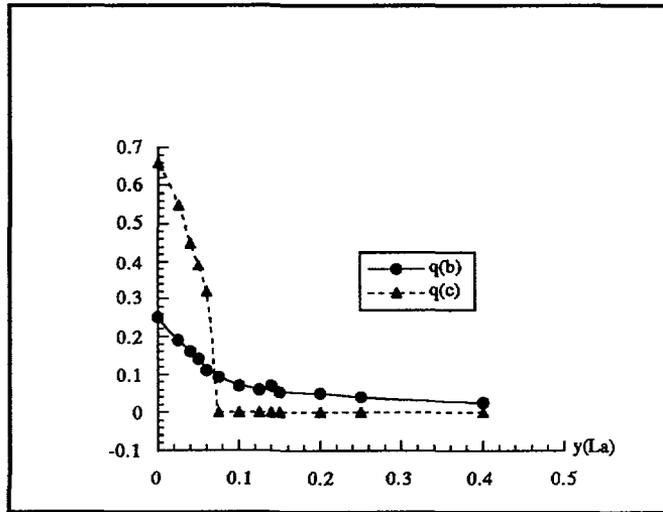


Fig. 4. — Change of b^* and c^* wave vector components in $\text{Bi}_2(\text{Sr}_{2-y}\text{La}_y)\text{CuO}_6$ versus y_{La} .

— a last region, for $y_{\text{La}} > 0.20$, in which the b^* incommensurability is around 0.03-0.04 and does not change further.

Moreover, and for any substitution $\text{Sr}^{2+}-\text{M}^{3+}$ ($\text{M} = \text{La}, \text{Pr}, \text{Bi}$), the same type of change in lattice constants, as reported in figure 5 for the La case, is systematically observed at the monoclinic-orthorhombic transition, with a non-linear behavior for the b and $c = f(y_{\text{M}})$ curves, the two axes which define the modulation plane.

Thus, and contrary to the « iso-electronic » substitution, a modification of charge transfer by the introduction of excess electrons from the La^{3+} substitution induces strong structural changes : monoclinic-orthorhombic transition, large change in lattice constants, increasing for a and b on one hand, and decreasing for c on the other hand, incommensurability lowered along b^* and cancelled along c^*

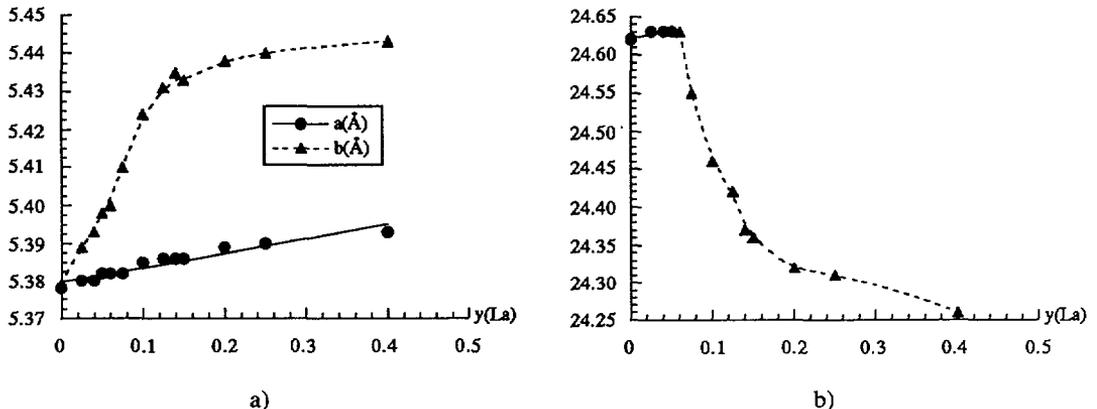


Fig. 5. — Change of lattice constants versus (La^{3+}) substitution level, 1) a and b , 2) c .

3.3 THE SUPERCONDUCTING TRANSITION. — Results concerning these substituted materials, and the reference $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ compound itself, are rather controversial. Different authors [4-7, 11, 12], have published contradictory results, most often obtained with ceramics ; they are described sometimes as superconductors and sometimes without any superconducting transition, for the same materials with the same nominal composition. We will come back later on an additional source of problem due to the preparation conditions and specially those concerning the role of oxygen present during the synthesis. However, with our results, obtained exclusively on single crystals, it is possible to propose the following interpretation :

— a comparison between « one-layer » materials on the one hand and « two- and three-layer » materials on the other hand is rather enlightening. Indeed, the « two- and three-layers » compounds are spontaneously superconductors, which suggests that a spontaneous charge transfer between copper-oxygen and bismuth-oxygen layers occurs. There is absolutely no reason that such a transfer does not exist in the « one-layer » material, only the transfer degree could change from one material to the other ;

— however, $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, is not superconducting (we have verified this point on single crystals), but exhibits a quite specific structural distortion. Indeed, only this particular material exhibits a monoclinic distortion, whereas « two- and three-layer » compounds remain orthorhombic ;

— only « one-layer » materials substituted by $3+$ ions, exhibit a superconducting transition [4, 5], but for a substitution level larger than $y_M \approx 0.10$, that is to say with the orthorhombic structure, identical for the « one-layer » compound to that spontaneously formed in the other members of the family.

It is therefore possible to assign the following specific kinds of behavior to each one of the homogeneity range regions :

Region 1) the transfer degree is maximum for the reference material, but the charges trapped in the Bi-O bi-layers induce a strong distortion, which is coupled from Bi-O bi-layer to bi-layer, leading to the monoclinic structure. This distortion, because of the c^* component of the modulation wave vector, is not limited to the bismuth-oxygen layers but also concerns the whole structure, and specially the copper-oxygen layers [13, 15]. The carriers (holes) created within this plane are thus trapped by localization due to the incommensurate modulation. Therefore, the material is an « *insulator by distortion or by localization* ». In this first region we are dealing with a two-component (q_b, q_c) modulation wave vector. The incommensurability along b^* could be associated with the transfer degree, producing an in-plane distortion due to the excess charges, and the incommensurability along c^* could reflect the degree of interplanar coupling of the lattice distortions. A substitution by M^{3+} ions counter-balances the spontaneous charge transfer leading to a decrease of incommensurability along b^* , and a reduction of the lattice distortion with a rapid decrease of c^* component of incommensurability (Fig. 4).

Region 2) for larger M^{3+} concentration, we are now within the « *metallic region* », the transfer and consequently the distortion, being reduced, the monoclinic coupling between successive Bi-O bi-layers vanishes, and the orthorhombic structure appears, with only a strong in-place incommensurability, but without interplanar component as in the 2-2-1-2 compound with the same orthorhombic structure, thus with a reduced distortion of the Cu-O₂ planes [15]. As charge transfer is not completely compensated by M^{3+} counter-transfer ions, superconductivity can occur. However, the increase of the substitution amount progressively reduces this charge transfer and results in a decrease of T_c , up to the critical concentration $y_M \approx 0.3$.

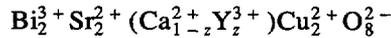
Region 3) for higher concentrations, the electrons injected by the substituant compensate the charge transfer, and the incommensurability along b^* is stabilized at a low value and does

not change further. We are in the presence of a « *compensated insulator* ». In fact, in this context, a residual transfer remains (non-zero incommensurability along b^*), but it is not large enough to produce a metallic behavior. Zero transfer leads to a perfect commensurability as observed in the case of substitution on the copper site [10].

4. The « two-layers » material.

The « two-layer » material, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, exhibits a very similar behavior [14, 15], except that the monoclinic distortion is never observed. The transfer degree is very high with copper-oxygen coupled bi-layers instead of single layers, but the Bi-O bi-layers are much more shifted (and screened) from one another and the « transverse » coupling, responsible for the monoclinic distortion observed in the « one-layer » compound, does not occur. The material adopts an orthorhombic structure, with only one component of the modulation wave vector, along b^* , similar to that observed for the « one-layer » material within the so-called *metallic region*.

A completely parallel study can be carried out by performing an yttrium 3+ substitution on the calcium 2+ site (lanthanum substitutes on both strontium and calcium sites and leads to similar results but more difficult to interpretate). This corresponds to the solid solution



between metallic ($\text{Bi}_2^{3+} + \text{electrons}$) $\text{Sr}_2^{2+} + \text{Ca}_1^{2+} + (\text{Cu}_2^{2+} + \text{O}_8^{2-} + \text{holes})$ and insulating $\text{Bi}_2^{3+} + \text{Sr}_2^{2+} + \text{Y}_1^{3+} + \text{Cu}_2^{2+} + \text{O}_8^{2-}$. Its phase diagram coincides with that of the previously mentioned 2) and 3) regions of the « one layer » compound: the regions with a strictly orthorhombic structure and with only one incommensurate component, along b^* .

Region 2') for $0 < z < 0.4$, the « *metallic region* », the b^* incommensurability decreases between 0.16 and 0.10, which corresponds in our interpretation to a decrease of the transfer degree which can be associated with a lowering of the superconducting transition temperature.

Region 3') for $z > 0.4$, the material is a « *compensated insulator* » and the residual b^* incommensurability does not change further.

5. Structural distortion and charge transfer.

From these results we can extract some trends, associating structural properties and superconductivity, as schematically presented in figure 6.

— Superconductivity is linked to orthorhombic structure in which copper-oxygen plane(s) are only slightly distorted. In this framework, the pure « one-layer » material is not superconducting because these planes are strongly distorted [15]. In this case, the incommensurability along c^* and the monoclinic distortion result from a strong coupling between substantially charged Bi-O bi-layers. As a consequence the in-between Cu-O layers are sizeably distorted. When the substitution level is increased, this distortion cancels and the material becomes a superconductor. However, this cancellation of distortion is caused by a reduction of the charge transfer and, therefore, the critical temperature observed is rather low (≈ 20 K). Figure 6a suggests that, if pure $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, with a high transfer degree, could be obtained without a monoclinic distortion, its critical temperature could be compared to that of the thallium equivalent (undistorted), $\text{Tl}_2\text{Ba}_2\text{CuO}_6 \approx 90$ K. On the contrary, for the « two-layer » compound, and in spite of a high transfer degree, the structure does not exhibit any monoclinic distortion, and consequently a high T_c is obtained.

— the incommensurability along b^* measures the in-plane distortion in the Bi-O planes and is linked to the transfer degree, responsible for the charge injection coming from the Cu-

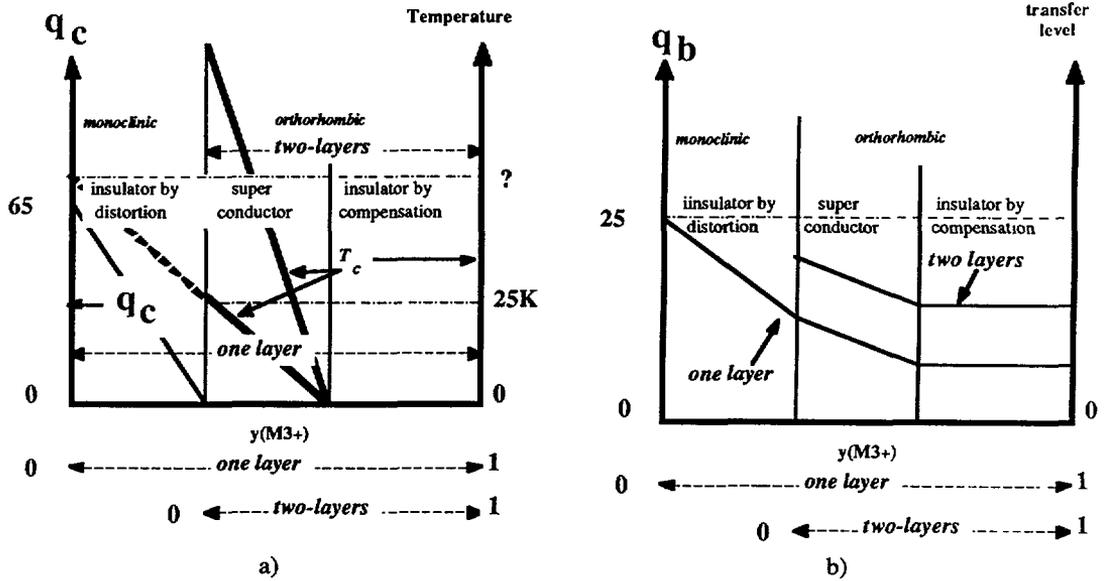


Fig. 6. — Superconducting versus structural properties in bismuth compounds.

O_2 planes producing this distortion. A decrease of the charge transfer results in a lowering of this particular incommensurate component. This is illustrated in figure 6b, which points out the strict parallel between « one-layer » and « two-layer » materials.

Moreover, some generalization could be attempted (Fig. 7). Indeed, when, in $(Bi_{2-x}Pb_x)Sr_2CuO_6$, bismuth (3+) is replaced by lead (2+), the charge transfer should be enhanced by this substitution. This experimentally results in the fact that, in the concentration range $0 < x_{Pb} < 0.07$, the incommensurate distortion is also increased, in both b^* and c^* components of the modulation wave vector, in agreement with our interpretation. However, this regime rapidly becomes unstable and, for $x_{Pb} > 0.07$ the modulation wave vector splits into two distinct vectors, as shown on the diffraction pattern of figure 8, which stresses the fact the composition of pure $Bi_2Sr_2CuO_6$ is not a particular (locking) point in the phase diagram.

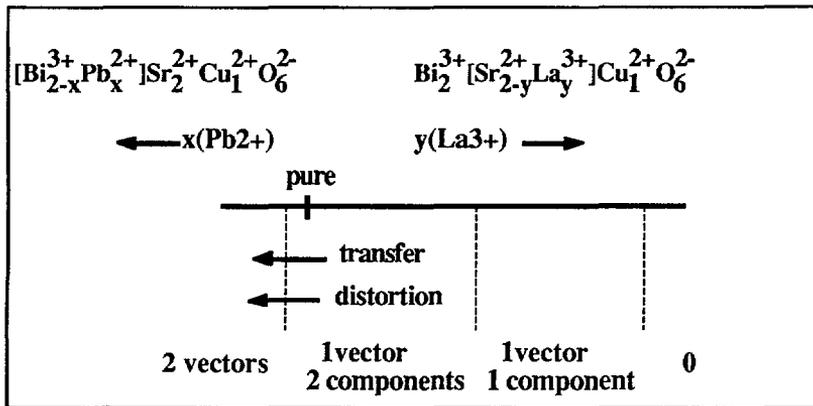


Fig. 7. — Proposed generalized phase diagram for substitution in $Bi_2Sr_2CuO_6$.

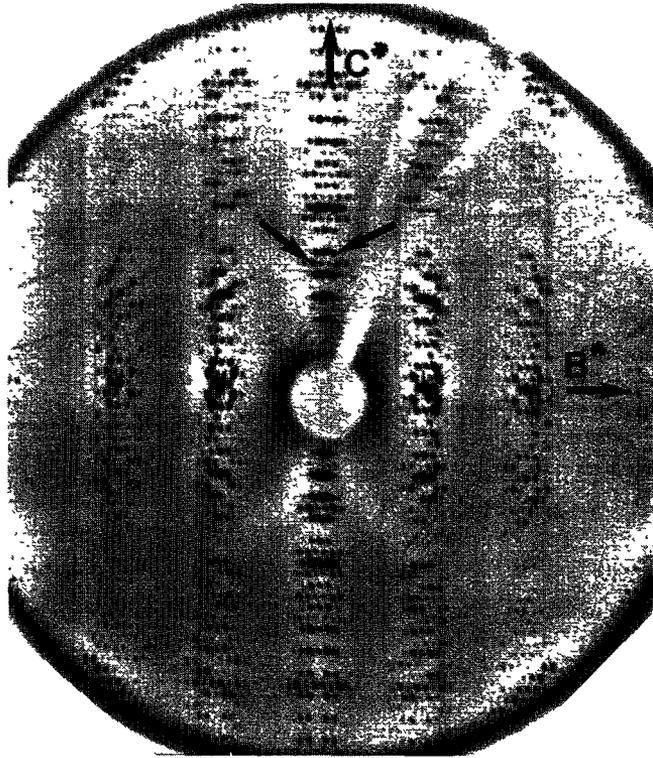
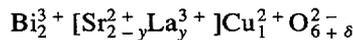


Fig. 8. — Diffraction pattern (MoK_α) of the 0 *kl* layer of (Bi₁₋₉-Pb_{0.1})Sr₂CuO₆. The two different satellite types associated with each wave vector are indicated by arrows.

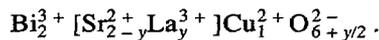
6. The role of oxygen.

All the previous results are obtained when the crystal growth process is carried out in nitrogen (10⁻³ O₂). When crystals are prepared in air or in pure oxygen, another phase diagram is obtained characterized by a much more dramatic change in lattice constants and incommensurability. Everything occurs as if additional oxygen atoms could be trapped within the structure and if they played the role of very efficient counter-transfer elements. Even if the exact nature of this phenomenon is not completely solved, we suggest that the final formulas of substituted materials are not equivalent. In case i) below, substituted materials retaining a formula close to O₆ are out of equilibrium from the point of view of formal charges. On the contrary, in case ii) below, if additional oxygen atoms, corresponding to the Sr²⁺-La³⁺ substitution, are absorbed by the lattice as suggested by Zandbergen *et al.* [16], a spontaneous equilibrium can be reached :

i) in nitrogen, out of equilibrium



ii) in oxygen, equilibrated



This is manifest in case ii) by an increased range of homogeneity for La substitution, at least

up to $y_{La} = 1$, and strong changes in lattice constants and incommensurability. In particular, the orthorhombic modification is never stable and the lattice remains monoclinic as shown by the comparison of the lattice parameters for single crystals of pure $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ and $\text{Bi}_2[\text{SrLa}]\text{CuO}_{6+\delta}$.

	a (Å)	b (Å)	c (Å)	α	q_b	q_c
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	5.38	5.38	24.62	90.10°	0.24	0.65
$\text{Bi}_2[\text{SrLa}]\text{CuO}_{6+\delta}$	5.45	5.51	23.82	90.78°	-0.14	-0.36

7. Conclusion.

In this paper we propose a correlation between physical and structural properties of high T_c superconductors. Bismuth materials appear to be especially interesting because they exhibit a charge transfer process different from that of $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$, where the transferred electrons are trapped in a *chemical bond*, on the Sr(2+) ions, and also different from that of $\text{Tl}_2\text{Ba}_2\text{CuO}_6$, where « *nearly free electrons* », weakly coupled to the lattice, are created in the empty Tl 6s band. In our interpretation, bismuth compounds could represent the case of charge stabilized by a coupling to the lattice, which makes them very sensitive to any change introduced which modifies the charge equilibrium, such as substitution by trivalent ions.

A general and complete analysis of displacive mode symmetry associated with the various observed phases is under progress and will be soon published elsewhere.

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