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Valence state for bismuth in the superconducting bismuth cuprates

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X-ray-absorption near-edge spectra (XANES) of high-T_c bismuth superconductors (2:2:0:1, 2:2:1:2, and 2:2:2:3) have been recorded at the Bi L_{III}, L_{I}, and Cu K edges. With respect to the reference Bi_2O_3 [Bi(III) valence state], edge shifts towards low energies have been found in the spectra of all the superconducting cuprates at the Bi L_{III} edge. This has been interpreted in terms of a reduced bismuth valency smaller than Bi(III). This result is a characteristic of the superconducting intergrowths, since other layer compounds with Bi cations in similar environments, $Bi_2SrNb_2O_9$ and $Bi_2Sr_2CaFe_2O_9$, do not present any shift with respect to Bi_2O_3. The copper formal valency has been deduced either from charge-balance considerations assuming a well-known oxygen stoichiometry or edge shifts at the copper K edge. High copper valencies have been found, especially in the 2:2:0:1 compound, but again, as was observed before in thallium and lead-substituted thallium cuprates, critical temperatures increase when the copper valency decreases, i.e., when the number of holes per copper in an oxygen-like p band decreases, provided this number stands above a critical value estimated previously to be 0.17.

I. INTRODUCTION

High-T_c superconductivity has been found in the Bi-Sr-Cu-O system[1] and then improved in the Bi-Sr-Ca-Cu-O (Refs. 2–7) and (Bi,Pb)-Sr-Ca-Cu-O systems.[8,9,10,11] The substitution of bismuth by thallium led to the same intergrowth structures with the highest critical temperatures known up to now ($T_c = 125$ K in the 2:2:2:3 compound). The compound $Bi_2Sr_2CuO_6$ (2:2:0:1 in the standard notation) was the first member of this series of intergrowths to be discovered[1] where double Bi-O rock salt-like layers alternate with CuO_3 axially distorted octahedral sheets.

The other compounds of the bismuth family $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2) and $Bi_{1.6}Pb_{0.4}(Sr,Ca)_4Cu_3O_{10}$ (2:2:2:3) are also built from double Bi-O layers. X-ray and neutron diffraction have shown no trace of oxygen in the calcium planes between the copper planes, and the oxygen stoichiometry is very close to the expected one with Bi(III) and Cu(II). Such a question about formal valencies has been already raised in the thallium bilayer cuprates and it was suggested by Raveau *et al.*[12] that the Tl-O layers could play the role of an electron reservoir in order to create holes in the CuO_2 sheets.

X-ray-absorption spectra (XAS) recorded at the Tl L_{III} and L_{I}-edges did not allow the observation of any reduced or mixed valence states of thallium ions, based on the filling of 6*s* levels, in the superconducting oxides.[13] On the other hand, XAS at the Pb L_{III} edge has shown that lead is unambiguously in the Pb(II) state in the Cava's phase $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_8$ and in the Pb(IV) state in some lead substituted thallium cuprates.[14] From the determination of the valence states of the elements (Pb, Tl, and Cu) in these compounds, a formal copper valence, i.e., the number of holes per copper in an oxygen-like p band, has been deduced provided the oxygen stoichiometry is properly determined.

In this paper, we present x-ray-absorption spectra at the Bi L_{III} and L_{I} edges and at the copper K edge in three bismuth superconductors 2:2:0:1, 2:2:1:2, and 2:2:2:3 in order to look for possible mixed or reduced valence states of bismuth and to deduce the mean copper valence state. At the same time x-ray-absorption near-edge (XANES) spectra of reference compounds in which bismuth is known to exist in the Bi(V) ($NaBiO_3$) or in the Bi(III) (Bi_2O_3 and $Bi_2SrNb_2O_9$) states and metallic bismuth have been recorded at the Bi L_{III}, L_{I} edges to calibrate the energy shifts as thoroughly as possible.

Another bismuth intergrowth phase, based on the complete substitution of copper by iron $Bi_2Sr_2CaFe_2O_9$ has been added to the set of compounds in order to look at possible bismuth valence changes between superconducting and normal cuprates having similar structures.

II. EXPERIMENT

Bismuth compounds were prepared by reacting in appropriate amounts Bi_2O_3 and $SrCO_3$ with $CaCO_3$, PbO, and CuO for the superconducting cuprates $Bi_2Sr_2CuO_6$ (2:2:0:1), $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2), and $Bi_{1.6}Pb_{0.4}(Sr,Ca)_4Cu_3O_{10}$ (2:2:2:3), with $CaCO_3$ and Fe_2O_3 for the bismuth iron oxide $Bi_2Sr_2CaFe_2O_9$ isostructural with the 2:2:1:2 superconductor, and with Nb_2O_5 to obtain $Bi_2SrNb_2O_9$, an Aurivillius type phase taken as a reference.

The mixtures were ground, pressed into pellets, heated in air at temperatures ranging from 840 to 900 °C and then cooled to room temperature. Times of heating varied from a few hours for 2:2:0:1, 2:2:1:2 superconductors and $Bi_2SrNb_2O_9$ to 100 h for 2:2:2:3 and the bismuth iron oxide.

Several authors[8,11] report a nonstoichiometric composition with extra calcium, less strontium, and an addition of lead is needed to obtain the pure 2223 phase. In our case the pure phase was obtained from the starting composition $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_{2.4}Cu_3O_{10}$.[10]

The neodymium compound was prepared from a mixture of Nd_2O_3 and CuO oxides, pressed into pellets, and heated in air for 12 h up to a maximum temperature of 1100 °C.

All samples were characterized by x-ray powder diffraction analysis which showed that the samples were single phase. Resistance measurements were made using a dc four-probe method with excitation current of a few mA. Zero resistance is assumed when the voltage drops down to 10^{-6} V. Thermal treatments and T_c of the three superconductors are given in Table I.

XANES spectra have been recorded in transmission mode at the Bi L_{III} and L_{I} edges (13 424 and 16 392 eV) and at the Cu K edges (8979 eV) at room temperature. The experiments were performed at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE) Orsay using the synchrotron radiation from the DCI storage ring. The electron energy was 1.85 GeV and the current 250 mA. X rays were monochromatized by a Si 331 channel cut and the absolute precision on the energy scale has been estimated to be ±0.25 eV.

A. Structure

The low-temperature monoclinic form of the bismuth oxide Bi_2O_3 has a complex and unique structure [Fig. 1(a)] in which Bi atoms occupy two types of irregular coordination polyhedra; the first type of Bi atom has five oxygen nearest neighbors at five of the vertices of a distorted octahedron at distances ranging from 2.08 to 2.63 Å (and a sixth at 3.25 Å) while the second type has an octahedral arrangement of six oxygen nearest neighbors at distances ranging from 2.14 to 2.80 Å; three of these are closer to the Bi cations (2.14–2.29 Å) than the other three (2.48–2.80 Å).

Another compound, $Bi_2SrNb_2O_9$, has been chosen as a reference for the Bi (III) state: its structure [Fig. 1(b)] is an intergrowth of $[Bi_2O_2]$ layers, in which Bi atoms occupy the top of a square pyramid of oxygen, and double perovskite layers $[SrNb_2O_6]$. This arrangement of bismuth has been proposed by several authors[2-9] for the double Bi-O layers in the superconducting compounds.

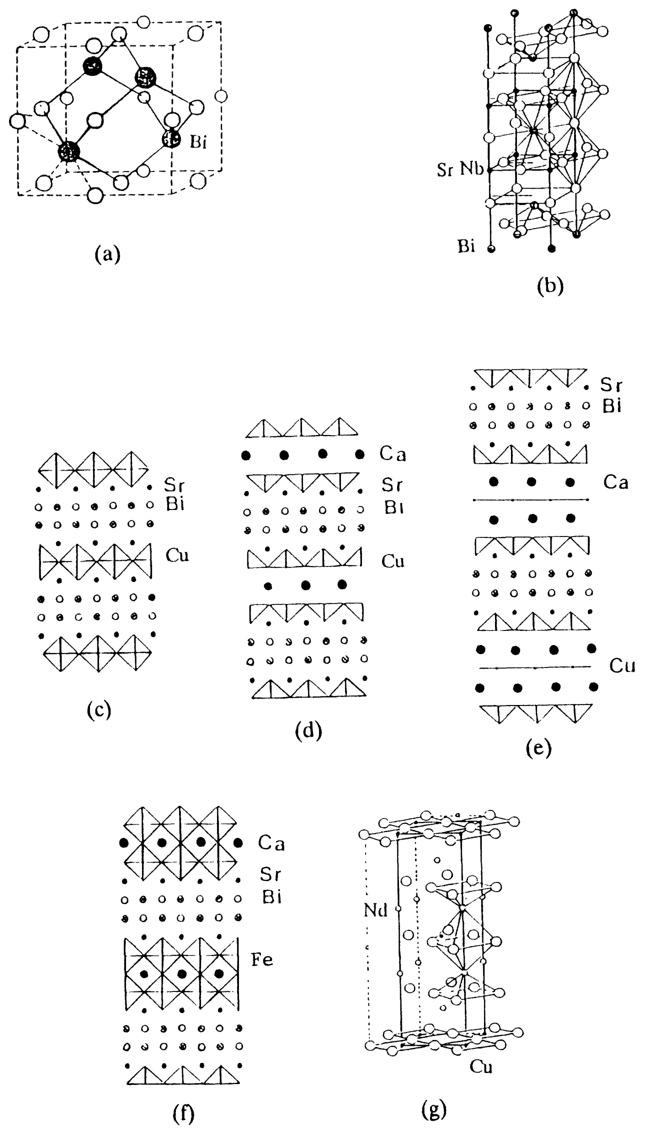

FIG. 1. Schematic structures of bismuth cuprates and a copper reference: (a) Bi_2O_3; (b) $Bi_2SrNb_2O_9$; (c) $Bi_2Sr_2CuO_6$ (2:2:0:1). (d) $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2). (e) $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_{2.4}Cu_3O_{10}$ (2:2:2:3); (f) $Bi_2Sr_2CaFe_2O_9$; (g) Nd_2CuO_4.

The reference for the Bi (V) state, $NaBiO_3$, presents an ilmenite structure with bismuth atoms in a regular oxygen octahedron ($d_{\text{Bi-O}} = 1.91$ Å).

Nd_2CuO_4 presents a layer structure characteristic of Cu (II) in a square planar oxygen environment [Fig. 1(g)]: layers of square planar copper alternate with Nd-O layers. Square planes lead to a typical feature of double

TABLE I. Thermal treatments and resistivity transition temperatures for the three bismuth superconducting cuprates.

Nominal composition	Thermal treatment	$T_c^{(R=0)}$ (K)
$Bi_2Sr_2CuO_6$	20 h 850 °C	22
$Bi_2Sr_2CaCu_2O_8$	20 h 850 °C	85
$Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_{2.4}Cu_3O_{10}$	12 h 800 °C + 100 h 865 °C	110

peaks at the copper K edge due to the splitting of the $4p\sigma$ levels as has been shown.[14]

The compounds $Bi_2Sr_2CuO_6$, $Bi_2Sr_2CaCu_2O_8$, $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$, [Figs. 1(c)–1(e)] are three members of a large family of high-T_c superconductors which can be described as intergrowths of multiple distorted rock salt-type layers with multiple oxygen deficient perovskite layers according to the formulation $[AO]_n[A'CuO_{3-y}]_m$ where A=Bi, SrPb and A'=Sr, Ca.[15] They correspond to the intergrowth of a triple rock salt-type layer [$(BiO)_2(SrO)$] with respectively single-[$SrCuO_3$], double-[$SrCaCu_2O_5$], and triple-[$SrCa_2Cu_3O_7$] oxygen deficient perovskite layers, formed of sheets of corner sharing CuO_6 octahedra, CuO_5 pyramids, or CuO_4 square planes interleaved with calcium ions. $Bi_2Sr_{3-x}Ca_xFe_2O_9$ $(0 \leq x \leq 1)$ has been also observed by x-ray absorption spectroscopy because it presents a structure [Fig. 1(f)] very close to the 2:2:1:2 superconductor differing in the double perovskite layer which is built of FeO_6 octahedra.[16,17]

All these oxides exhibit an incommensurate structure. Their electron diffraction patterns are indeed characterized by satellites in incommensurate positions both for the superconducting bismuth cuprates and the iron compound.[2–9,16,17] This particular behavior can be explained by the stereoactivity of the $6s^2$ lone pair of Bi(III), which tends to take the place of an anion and induces a distortion of the rock salt type layers. This results in a nonperiodic displacement of the Bi(III) cations in the layers and consequently of the oxygen atoms. Moreover, an excess of oxygen may be introduced into such layers.[16] Thus, the issue of the valence states of bismuth in these oxides is still to be understood and can be considered as an important element for the understanding of superconductivity in these materials.

III. RESULTS AND DISCUSSION

A. XANES spectra

1. *Bi L_{III} edge*

The selection rules for the photoelectric excitation in the dipolar approximation allow only the final states with a symmetry L_f differing from the initial state L_i by ± 1 unit. Thus, at the L_{III} edge, not only the $6d$ states are accessible but also the $6s$ states when they are empty.

XANES spectra have been recorded at the Bi L_{III} edge for the reference compounds $NaBiO_3$, Bi_2O_3, metallic bismuth, and $Bi_2SrNb_2O_9$ (Fig. 2); for bismuth metal, Bi_2O_3 and three superconductors 2:2:0:1, 2:2:1:2, 2:2:2:3 (Fig. 3), and for Bi_2O_3, $NaBiO_3$, 2:2:0:1, and the bismuth iron oxide $Bi_2Sr_2CaFe_2O_9$ (Fig. 4). The last figure has been enlarged in order to show the shift between the edges of the various compounds.

As can be seen in Fig. 2, an energy shift appears between $NaBiO_3$ [Bi(V)] and Bi_2O_3[Bi(III)], Bi_2O_3 and metallic bismuth, and, as expected, the edges energies, taken at the midpoint of the main step of the curves increase with increasing valence state of bismuth (Table II).

One can observe a prepeak B in the $NaBiO_3$ spectrum

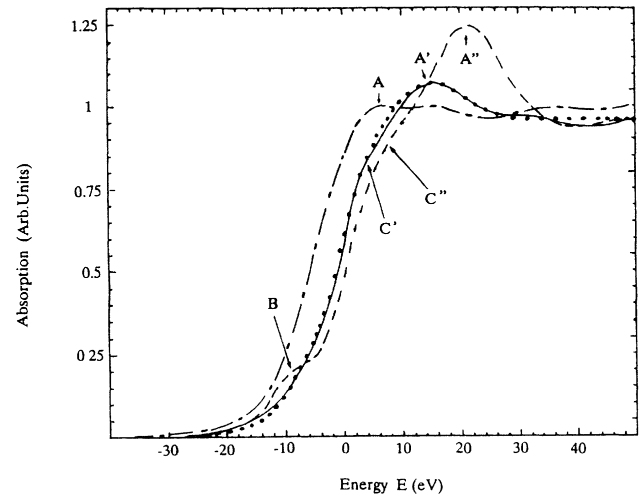

FIG. 2. Bismuth L_{III}-edge spectra for Bi metal (–·–), $Bi_2SrNb_2O_9$ (——), Bi_2O_3 (···), and $NaBiO_3$ (— — —).

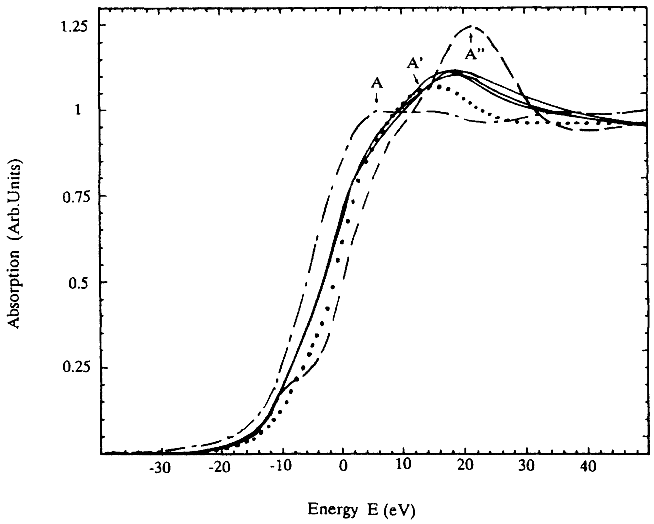

FIG. 3. Bismuth L_{III}-edge spectra for Bi metal (–·–), Bi_2O_3 (···), $NaBiO_3$ (— — —), and for bismuth superconductors 2:2:0:1, 2:2:1:2, 2:2:2:3 (solid lines).

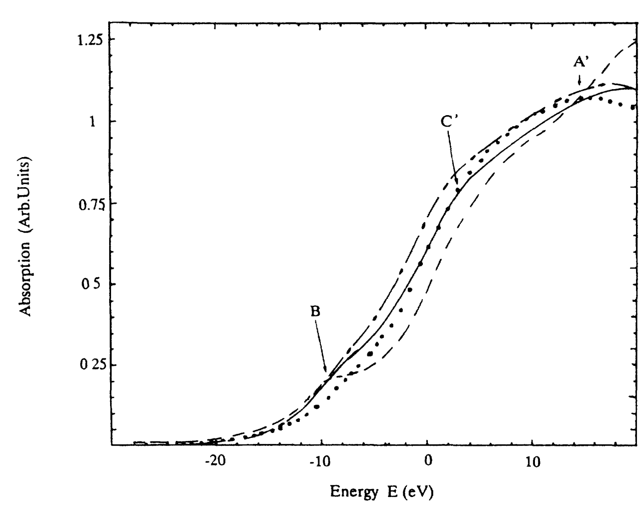

FIG. 4. Enlarged bismuth L_{III} edge for 2:2:0:1 (–·–), Bi_2O_3 (···), $Bi_2Sr_2CaFe_2O_9$ (——), and $NaBiO_3$ (— — —).

only. This structure has the same origin as for PbO_2 which was studied by J. Wong and co-workers[18] and corresponds to a $6p^{3/2} \rightarrow 6s$ transition, since the $6s$ levels are vacant in Bi (V) only. Such a feature which signifies the absence of the lone pair doublet allows an unambiguous determination of the highest valence states of these elements and to discriminate between Pb (II)/Pb (IV), Tl (I)/Tl (III), and Bi (III)/Bi (V).

The two peaks A', C' and A'', C'' for Bi_2O_3 and $NaBiO_3$ respectively correspond to *p-d* transitions. Since the environments are similar, the schematic energy level diagram proposed by J. Wong *et al.* for PbO and PbO_2 and based on crystal field effects is still applicable:

$$\text{peak } A: 6p^{3/2} \rightarrow 6d\,(e_g \text{ antibonding})$$

$$\text{peak } C: 6p^{3/2} \rightarrow 6d\,(t_{2g} \text{ nonbonding}) .$$

Note that the distribution of Bi-O distances is larger in Bi_2O_3 than in PbO, which results in an enlargement of peak A. However, the regular oxygen octahedra found in $NaBiO_3$ will allow a direct comparison with PbO_2.

The Bi L_{III} XANES spectra of the superconducting cuprates are presented in Fig. 3 with three reference compounds, Bi metal $NaBiO_3$ and Bi_2O_3, in order to visualize the shift of the superconductor edges to the lower energies with respect to Bi_2O_3. Values of these shifts are reported in Table II.

The question arises whether or not these shifts in the superconducting Bi L_{III} edges are a characteristic of the superconducting phases. In other words, will similar shifts be observed in other bismuth layered compounds which are not superconductors?

The $Bi_2SrNb_2O_9$ spectrum is shown in Figs. 2 and 4 whereas the $Bi_2Sr_2CaFe_2O_9$ Bi L_{III} edge has been plotted in Fig. 4; the edge of the first phase fits properly with the one of Bi_2O_3 and the edge of the latter compound shows no shift with respect to Bi_2O_3 at the midpoint of the main step. Again in $Bi_2Sr_2CaFe_2O_9$ in which modulations of the Bi-O planes have been clearly identified by several authors,[16–17] a clearly visible shoulder appears at the same energy as prepeak B in $NaBiO_3$ (Figs. 2–4). This feature, which corresponds to partially empty $6s$ levels, leads us to the conclusion that a concentration of Bi (V) is present in the iron compound which can explain the oxygen overstoichiometry with respect to the formula.

Although less pronounced, a similar shoulder appears also on the superconductors curves (Figs. 3–4) and leads to the conclusion that some amounts of Bi (V) (less than 10%) are also present in the Bi-O layers of the superconducting phases.

Thus, at the Bi L_{III} edge, the bismuth superconductors present a unique feature which can be described as the simultaneous presence of two oxidation states of bismuth, one state smaller than 3, larger than the other state, the Bi (V) state. As no bismuth valency lower than 3 is known, we will discuss the bismuth state in terms of charge in the discussion paragraph.

2. Bi L_I edge

The spectra of some reference compounds, Bi_2O_3, $NaBiO_3$ and Bi metal, and of the bismuth superconductors have been recorded at the Bi L_I edge. No prepeak is visible in these spectra since the $2s \rightarrow 6s$ transition is forbidden. Since the crystal field is less effective on $6s$ levels, the valence shifts should be smaller than at L_{III} edge. Actually, no shift is visible between Bi metal and Bi_2O_3 and as a consequence the superconductors spectra appear superimposed on the Bi_2O_3 metal.

3. Copper K edge

XANES spectra of Cu_2O, CuO, Nd_2CuO_4, and $Bi_2Sr_2CuO_6$ are shown in Fig. 5(a) whereas the same reference compounds with $Bi_2Sr_2CaCu_2O_8$ and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ superconductors are shown Fig. 5(b): we observe the following: No trace of the Cu (I) valence state ($|3d^{10}\rangle$ configuration: peak A on the Cu_2O spectrum are visible in the spectra of the superconductors; the CuO spectrum, as well as the $NaCuO_2$ spectrum [Cu (III) standard],[14] presents two shoulders noted B and C which are found also in the $Bi_2Sr_2CuO_6$ edge and correspond to the $|3d^{10}\underline{L}\rangle$ and $|3d^9\rangle$ configurations characteristic of the Cu II valence state in a distorted octahedral or pyramidal environment. The only difference between both the spectra of CuO and $NaCuO_2$ is an edge shift towards higher energies for the highest copper valence state; this edge shift is also found between the CuO and $Bi_2Sr_2CuO_6$ spectra and supposes large amounts of Cu (III) valence state in this last compound; the two

TABLE II. Edge energies at the Bi L_{III} edge and bismuth formal valency of bismuth references and the superconducting cuprates. The mean valence state of bismuth ions in the cuprates has been determined assuming a linear variation of the formal valency as a function of edge shifts between Bi metal and $NaBiO_3$ [formal Bi (V)].

Compounds	Edge energies (eV)	Bi formal charges
Bi metal	−4.10±0.25	0
Bi_2O_3	0	3.20±0.25
$NaBiO_3$	2.20±0.25	5
$Bi_2SrNb_2O_9$	0	3.20±0.25
$Bi_2Sr_2CaFe_2O_{9.2}$	0	3.20±0.25
$Bi_2Sr_2CuO_6$	−1±0.25	2.50±0.25
$Bi_2Sr_2CaCu_2O_8$	−1±0.25	2.50±0.25
$(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_{2.4}Cu_3O_{10}$	−1±0.25	2.50±0.25

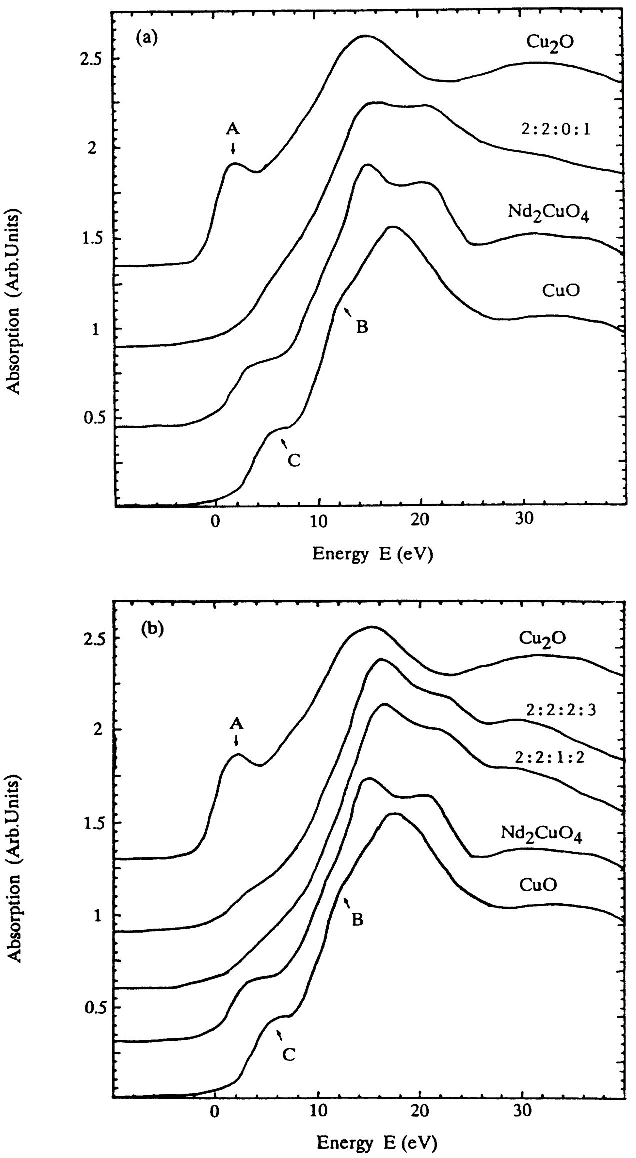

FIG. 5. (a) Copper *K*-edge spectra for CuO, Nd_2CuO_4, $Bi_2Sr_2CuO_6$, and Cu_2O; (b) Copper *K*-edge spectra for CuO, Nd_2CuO_4, $Bi_2Sr_2CaCu_2O_8$, and $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_{2.4}Cu_3O_{10}$.

shoulders noted *B* and *C* appear again on the $Bi_2Sr_2CaCu_2O_8$ and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ spectra, which correspond to the mixture of $|3d^{10}\underline{L}\rangle$ and $|3d^9\rangle$ configurations in the final configuration state, but in a way clearly observed in the $YBa_2Cu_3O_{7-\delta}$ superconductor and square planar copper compounds such as Nd_2CuO_4 [Figs. 5(a) and 5(b)], Gd_2CuO_4, Sr_2CuO_3, and Ca_2CuO_3.

IV. DISCUSSION

The charge balance in the superconducting cuprates, determined by the cation valencies and the oxygen stoichiometry, has been shown to be one of the main parameters which govern superconductivity in these oxides. The number of hole per copper in the oxygen *p* band, i.e., the mean copper valence in the CuO_2 layers, determines the semimetallic conduction of these materials and their superconducting properties. A recent XANES investigation of lead superconductors at the Pb L_{III} and Cu *K* edges has raised the possibility of a link between the mean formal copper valence and the critical temperature:[14] there seems to be an optimum number of holes per copper in CuO_2 layers, 0.17, to observe the highest T_c's. Such an optimum number has been also proposed for the "1:2:3" compound.[19]

Thus, a reduced valence state of bismuth will result in an increase of the copper valency by charge transfer from Cu-O to Bi-O planes. The evaluation of this charge transfer has been performed by evaluating the bismuth charges on the Bi L_{III} edge spectra from the midpoint of the main step for each reference and superconducting compounds. Table II gives the edge energies of the reference and the bismuth formal charges. Assuming a linear dependence of the edge shifts versus the charges between Bi (V) and the metal, a mean bismuth charge for the three superconducting cuprates can be estimated. But, as shown by the edge position of the Bi (III) and Bi (V) states, the relation between edge shifts and formal valencies is not completely linear leading to an error in estimating the bismuth charges in the superconductors which can lie between 2.3 and 2.5±0.2.

Confronted with such a reduced bismuth valence state, the problem arises in which orbitals to place the 0.5 extra electrons per bismuth. Owing to the quasiabsence of the prepeak, which means the 6*s* levels are full, one must fill the 6*p* levels. This can be achieved by considering the splitting of the 6*p* levels in the very anisotropic crystal field around the bismuth atoms in the rock salt-type layers observed by the crystallographic works.[4,5] As shown by these works, 2 to 3 oxygen neighbors are close to the bismuth centers (2.16 Å) whereas the other oxygen neighbors are further away. The resulting decrease in energy of some 6*p* orbitals and their hybridization with 6*s* levels could induce a 6*s*-6*p* band by overlapping with the oxygen 2*p* levels in the Bi-O layers. Such a band could be responsible for the stabilization of reduced valence state of the bismuth cations and could be induced by the Bi-O layers modulations which offer a way to create large distortions of the oxygen polyhedra.

Estimations of the copper formal charge in the superconductors can be obtained from the charges observed for the other cations (2.5 for bismuth and 2 for lead): high values of copper charges are deduced especially in the compounds with small number of copper layers 2:2:0:1 and 2:2:1:2 since complete charge formulations for these compounds can be written $Bi_2^{2.5+}Sr_2Cu^{3+}O_6$, $Bi_2^{2.5+}Sr_2CaCu_2^{2.5+}O_8$ and $(Bi_{1.6}^{2.5+}Pb_{0.4}^{2+})Sr_{1.6}Ca_{2.4}Cu_3^{2.4+}O_{10}$. These copper formal charges are not absolute ones at all and must be considered only as indications since they are based on -2 charge for the oxygen anions and the assumption the oxygen stoichiometry is the proper one, however in agreement with neutron and x-ray diffraction structure calculations.

In Table III are summarized the characteristics at Cu *K*-edge energies of some copper reference compounds and the superconductors. Edge energies have been measured on the first step of the derivative spectra and peak posi-

TABLE III. Copper K edges and XANES peak energies (in eV) for some copper references and bismuth cuprates. Letters refer to the peaks in Fig. 5. NB: $1s$ to $4p\pi$ nonbonding level transitions for copper in a given configuration.

Compounds	K edge	$\|3d^{10}\rangle$	NB ($\|3d^{10}\underline{L}\rangle$)	NB ($\|3d^{9}\rangle$)
		A	B	C
Cu_2O	0	1.7		
Nd_2CuO_4	1.7		4	10.8
CuO	3.7		5.1	11.8
$NaCuO_2$	4.1		4.9	11.5
$Bi_2Sr_2CuO_6$	4.8		6	
$Bi_2Sr_2CaCu_2O_8$	2.3		3.8	11
$(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_{2.4}Cu_3O_{10}$	1.7		3.8	11.2

tions on the second derivative.

The edge energy of the 2:2:0:1 compound is higher than that of $NaCuO_2$, the reference for formal Cu (III), and thus in good agreement with the high valency deduced above. The XANES spectra [Fig. 5(a)] of the compounds, $NaCuO_2$, CuO, and 2:2:0:1 are similar except for the edge positions and the double peak at the top of the 2:2:0:1 edge which signifies the presence of the largely distorted octahedra around copper (two oxygens at 1.98 Å and four at 2.52 Å).

The edge energies of the 2:2:1:2 and 2:2:2:3 compounds and the shape of the XANES spectra [Fig. 5(b)] are close to that of Nd_2CuO_4. The 2:2:1:2 edge energy is a little higher than the 2:2:2:3 and Nd_2CuO_4 edge energy in agreement with the higher formal valency of copper deduced from charge balance considerations. The shapes of the XANES spectra are compatible with a square planar or elongated pyramidal oxygen copper environment present in the structure of these compounds (Fig. 1).

These latter edge shifts lead us to believe that the formal copper valency in the superconductors is not so high as the one deduced from the charge balance. To account for this, one can think of two main hypothesis. (1) The Bi formal charge is underestimated: it is closer to III than the value measured on the Bi L_{III} edge probably because of geometrical effects. (2) The oxygen stoichiometry is lower than in the theoretical formula: an oxygen loss can induce a decrease of copper valency especially in the case of the 2:2:0:1 compound in which copper ions are in an octahedral environment.

Nevertheless, although formal copper charges appear too high in the bismuth superconductors, critical temperatures T_c (Table I) follow the same rule as in both lead and lead substituted thallium compounds:[14] they increase when the copper valence state decreases, i.e., when the number of holes per copper in the oxygen-like p-band decreases.

In conclusion, this first investigation of the bismuth valency in the high T_c cuprates, shows that bismuth cations appear in a reduced formal valence state, less than III. This result seems characteristic of the superconductors since other layer structures with bismuth in an Aurivillius type environment such as $Bi_2SrNb_2O_9$, or the intergrowth compound where iron completely substituted copper $Bi_2Sr_2CaFe_2O_9$ and where Bi-O layers are still effected by incommensurate modulations do not present the same reduced valence state of bismuth. Thus, in the bismuth superconducting cuprates, the Bi-O layers appear to play the role of electron reservoir for the Cu-O planes.

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[1] C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987).

[2] M. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. Lett. **27**, L209 and L548 (1988).

[3] M. Hervieu, C. Michel, B. Domengès, Y. Laligant, A. Lebail, G. Ferey, and B. Raveau, Modern Phys. Lett. B **2**, 491 (1988).

[4] C. C. Torardi, M. Subramanian, J. C. Calabrese, J. Gopalakrishnan, E. M. C. McCarron, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, Phys. Rev. B **38**, 225 (1988).

[5] J. M. Tarascon, Y. Le Page, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Huang, Phys. Rev. B **37**, 9382 (1988).

[6] M. A. Subramanian, C. C. Torardi, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, Science **239**, 1015 (1988).

[7] M. Hervieu, B. Domenges, C. Michel, and B. Raveau, Modern Phys. Lett. **2**, 835 (1988).

[8] U. Endo, S. Koyama, and T. Kawai, Jpn. J. Appl. Phys. **27**, L1225 (1988).

[9] R. Retoux, V. Caignaert, J. Provost, C. Michel, M. Hervieu, and B. Raveau, J. Solid State Chem. **79**, 157 (1989).

[10] T. Brousse, R. Retoux, G. Poullain, J. Provost, H. Murray, D. Bloyet, and B. Raveau, Appl. Phys. A **42**, 217 (1989).

[11] N. Kijima, H. Endo, J. Tsuchiya, A. Sumiyama, M. Misuno, and Y. Oguri, Jpn. J. Appl. Phys. **27**, 10 (1988); **27**, L1852 (1988).

[12] B. Raveau, C. Michel and M. Hervieu, in *Advances in Superconductivity,* Proceedings of the International Symposium on Superconductivity, Nagoya, 1988, edited by K. Kitazawa and T. Ishiquro (Springer-Verlag, Berlin, 1988), p. 151.

[13] F. Studer, R. Retoux, C. Martin, C. Michel, B. Raveau, E. Dartyge, A. Fontaine, and G. Tourillon, Mod. Phys. B **7**, 1085 (1989).

[14] F. Studer, D. Bourgault, C. Martin, R. Retoux, C. Michel, B. Raveau, E. Dartyge, and A. Fontaine, Physica C **159**, 609 (1989).

[15] B. Raveau, C. Michel, M. Hervieu, D. Groult, and J. Provost (unpublished).

[16] J. M. Tarascon, P. F. Miceli, P. Barboux, D. M. Hwang, G. W. Hull, M. Giroud, L. H. Greene, Y. Le Page, W. R. McKinnon, E. Tselepis, G. Pleizier, M. Eibschutz, D. A. Neumann, and J. J. Rhyne, Phys. Rev. B **39**, 11587 (1989) and references therein.

[17] M. Hervieu, C. Michel, N. Nguyen, R. Retoux, and B. Raveau, Eur. J. Solid State Inorg. Chem. **25**, 375 (1988).

[18] K. J. Rao and J. Wong, J. Chem. Phys. **81**, 4832 (1984).

[19] H. Tolentino, E. Dartyge, A. Fontaine, G. Tourillon, T. Gourieux, G. Krill, M. Maurer, and M-F. Ravet, in International Symposium on the Electronic Structure of High T_c Superconductors, Rome, 1988, edited by A. Bianconi and A. Marcelli (unpublished), p. 245.