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Electronic state of ^{57}Fe Mössbauer probe atoms in Cu(III) oxides with perovskite and perovskite-related structures

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Abstract : Mössbauer spectroscopy studies were developed in order to obtain an evaluation of different physico-chemical factors characterizing the electronic structure of the local sites (CuO_6) into three copper(III) oxides: LaCuO_3 having a three-dimensional (3D) perovskite structure; SrLaCuO_4 and $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ with a two-dimensional (2D) K_2NiF_4 -type structure. All these matrixes have been doped with ^{57}Fe (1 at.%) Mössbauer probe atoms. Such evaluation was based on analysis of the ^{57}Fe Mössbauer parameters (isomer shift and quadrupole splitting) characterizing the formal oxidation state and the local structure of the ^{57}Fe probe atoms. The obtained results underline that four main factors play an important role in the stabilization of formally trivalent " Cu^{3+} " ions: (i) the involved preparation process (in particular the oxygen pressure level able to impede the formation of oxygen vacancies); (ii) the dimensionality (3D or 2D) of the lattice; (iii) the chemical surrounding and (iv) the local structural distortion of the transition metal site (CuO_6), both last factors governing the local crystal field energy, orbital ordering and a possible charge transfer $\text{Cu}^{3+}-\text{O}^{2-} \leftrightarrow \text{Cu}^{2+}-\text{O}^-(\text{L})$.

Keywords : Oxides, Cu^{3+} oxides, High pressure synthesis, Perovskite structure, K_2NiF_4 structure, Mössbauer spectroscopy, Charge transfer phenomena

1. Introduction

In Solid State Chemistry, the high oxidation states M^{m+} of transition metals have been in the past the subject of numerous studies due to the correlations between the formal oxidation state value "m" and the strong increase of the covalency of the resulting $M^{m+}-\text{O}$ bond [1,2]. Trivalent copper oxides are obviously a very good example. Most physical properties of these compounds, including high T_C superconductivity [3,4], strongly depend on the electronic structure of the $\{\text{CuO}_x\}^{(2x-3)-}$ sites. Few oxides containing only trivalent " Cu^{3+} " ions have been prepared. As the corresponding $\text{Cu}-\text{O}$ bonds are strongly covalent, it is necessary, in the most cases, to stabilize them by interaction with a weak bond as $\text{A}-\text{O}$ ($\text{A}=\text{alkaline metal}$). Such ionic bonds $\text{A}-\text{O}$ allows the oxygen atoms to involve mainly their 2p orbitals in the σ -bonds with the " Cu^{3+} " ions. By this method, the compounds ACuO_2 ($\text{A}=\text{Na, K, Rb, Cs}$) were first prepared by Klemm and co-workers [5,6]. Structural investigations of these oxides developed by Hestermann and Hoppe [7] and Brese et al. [8] underline that Cu(III) is stabilized in a square planar envi-

ronment (CuO_4) with shared edges thus inducing the low spin (LS) electronic configuration ($t_{2g}^6 e_g^2 d_{x^2-y^2}^0$). Then Demazeau and co-workers [9,10], using high oxygen pressures, have stabilized Cu(III) in six-coordinated sites in perovskite-type or derived structures. In particular three oxides have been prepared: LaCuO_3 having a three-dimensional (3D) perovskite structure [9]; SrLaCuO_4 and $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ characterized by a two-dimensional (2D) K_2NiF_4 -type structure [9,10]. These oxides can be distinguished by chemical bonding factors versus the nature of the competing bond existing into the lattice: ($\text{Cu}-\text{O}$) bonds within the LaCuO_3 lattice and into the perovskite planes of the SrLaCuO_4 matrix or weak ($\text{Li}-\text{O}$) bond into the $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ structure (Fig. 1). All these factors can significantly affect local parameters characterizing the (CuO_6) sites: crystal field energy (Dq/B), structural distortion (θ) and electronic anisotropy versus the possible charge transfer $\text{Cu}^{3+}-\text{O}^{2-} \leftrightarrow \text{Cu}^{2+}-\text{O}^-(\text{L})$ [11,12]. If LaCuO_3 is metallic, SrLaCuO_4 is a semiconductor and $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ is an insulator. Consequently, in such Cu(III) oxides, copper ions adopt different electronic configurations.

In this paper we report results of comparative investigation of LaCuO_3 , SrLaCuO_4 and $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ matrix doped with ^{57}Fe (1 at.%) Mössbauer probe atoms. The objective of this work was to characterize, using Mössbauer spectroscopy, the electronic state and local surrounding of ^{57}Fe probe atoms through

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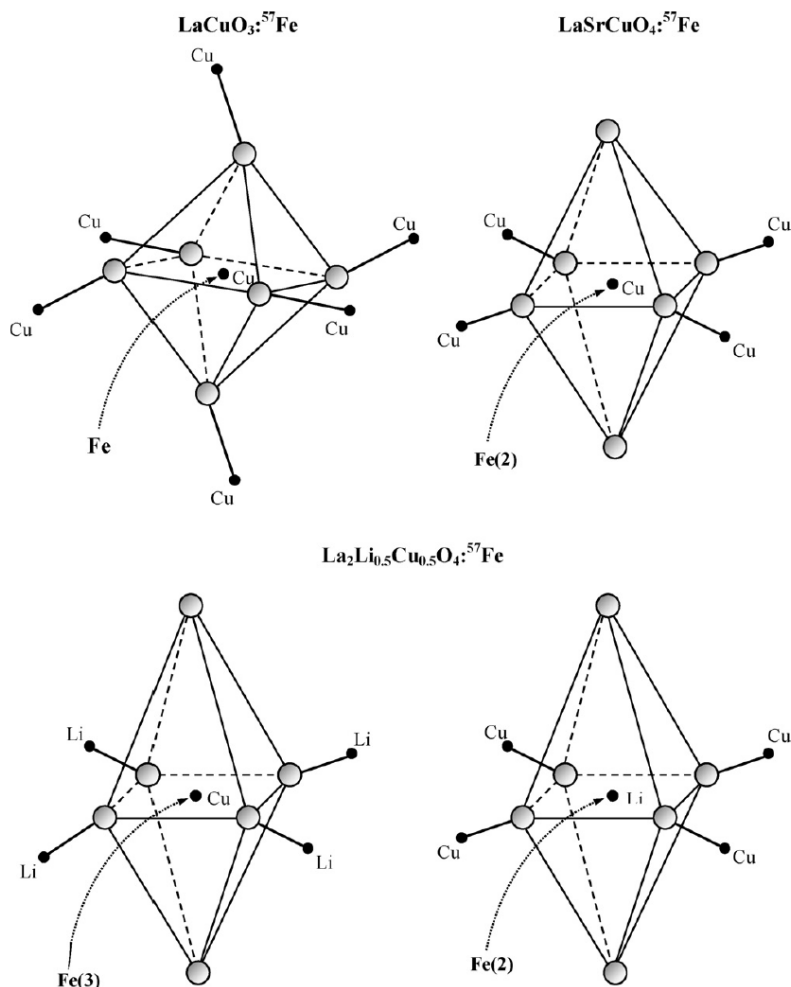


Fig. 1. Schematic representation of the local structure in the iron-doped: (a) 3D $\text{LaCu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_3$; 2D K_2NiF_4 -type, (b) $\text{LaSrCu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_4$ and (c) $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ lattices.

its observed isomer shift and quadrupole splitting values. This method was recently developed for the physical characterization of manganite $\text{CaMn}_7\text{O}_{12}$ containing in octahedral sub-lattices mixed valence $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions [13,14]. It has been shown that ^{57}Fe probe atoms reflect structural and chemical factors characterizing not only its local environment but also the electronic phenomena in the bulk. Moreover, the behaviour of iron atoms – as local probe in perovskite-type or derived matrixes – appears to be an interesting approach for studying the mechanisms of substitution on the different six-coordinated sites and the corresponding induced electronic phenomena characterizing the bulk.

2. Experimental

In all cases, instead of undoped CuO oxide, a $\text{Cu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}$ precursor was used for introducing the ^{57}Fe Mössbauer probe atoms into the corresponding lattices. This precursor was prepared through the thermal decomposition of the iron-doped hydroxide $\text{Cu}(\text{OH})_2:^{57}\text{Fe}$.

In the case of LaCuO_3 (^{57}Fe : 1 at.%), the preparation process developed for the undoped material [with La_2CuO_4 and CuO as reagents and KClO_3 as an in situ oxygen source, using a belt type equipment (6 GPa, 900 °C, 15 min)] was inoperative to get a pure perovskite phase. Consequently a new process was developed with monoclinic $\text{La}_2\text{Cu}_2\text{O}_5:^{57}\text{Fe}$ (2 at.%) as precursor, KClO_3 as in situ oxygen source but using more severe pressure conditions (11 GPa, 900 °C, 15 min) [15]. Such a strong difference in the preparation process was attributed to the metallic behaviour of LaCuO_3 , the corresponding band structure being perturbed by the ^{57}Fe probe substituting Cu^{3+} cations.

In the case of SrLaCuO_4 simple doped with ^{57}Fe (1 at.%), the preparation process developed for preparing the undoped simple [10] (SrO , La_2O_3 and $\text{Cu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}$ as reagents; 300 MPa of oxygen gas pressure and 820 °C) was appropriated for obtaining a pure phase with the K_2NiF_4 -type structure.

The ^{57}Fe (1 at.%) doped $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}^{3+}\text{O}_4$ matrix was also synthesized using the previous process developed for preparing the undoped material [9] (200 MPa of oxygen gas pressure, 870 °C, 48 h using La_2O_3 , Li_2O and $\text{CuO}:^{57}\text{Fe}$ as reagents) [16].

XRD data were collected at 298 K using a STOE diffractometer ($K_{\alpha}\text{Cu}$ $\lambda = 1.5451 \text{ \AA}$).

The ^{57}Fe Mössbauer spectra were recorded at 300 K using a conventional constant-acceleration spectrometer. The radiation source $^{57}\text{Co}(\text{Rh})$ was kept at room temperature. All isomer shifts refer to the $\alpha\text{-Fe}$ absorber at 300 K.

Table 1
XRD data for iron-doped simples

Phase	Space group	$a = b$ (Å)	c (Å)	V (Å ³)
LaCu _{0.99} Fe _{0.01} O ₃	$R\bar{3}c$	5.498	13.211	345.8
LaSrCu _{0.99} Fe _{0.01} O ₃	$I4/mmm$	3.766	13.272	163.0
La ₂ Li _{0.5} Cu _{0.5} O ₄ : ⁵⁷ Fe	$I4/mmm$	3.736	13.238	160.0

3. Results

3.1. Structural characterization

The observed X-ray diffraction patterns underline that all diffraction peaks for iron-doped Cu(III) oxides can be indexed in the same space group respectively to those of the undoped LaCuO₃, La₂Li_{0.50}Cu_{0.50}O₄, and LaSrCuO₄ oxides. The calculated cell parameters are close to that observed, respectively for the undoped oxides (Table 1). Such result can be attributed to the small atomic rate of the ⁵⁷Fe Mössbauer probe atoms into the investigated matrixes in spite of the different ionic sizes: $r(\text{Fe}^{3+}) = 0.64 \text{ \AA}$, $r(\text{Cu}^{3+}) = 0.55 \text{ \AA}$ [17].

3.2. Mössbauer characterization

3.2.1. LaCu_{0.99}⁵⁷Fe_{0.01}O₃

The Mössbauer spectrum of the sample LaCu_{0.99}⁵⁷Fe_{0.01}O₃ measured at 300 K can be described as a single not resolved quadrupole doublet (see Fig. 2a). The full linewidth at half height ($\Gamma = 0.28 \text{ mm s}^{-1}$) for each component of this doublets was found to be close to the corresponding value for the calibration spectrum ($\Gamma = 0.27 \text{ mm s}^{-1}$), which evidences that only one type of crystallographic position is occupied by the dopant ⁵⁷Fe atoms in the LaCu_{0.99}Fe_{0.01}O₃ perovskite structure. The isomer shift value ($\delta \approx -0.11 \text{ mm s}^{-1}$) is in a range of corresponding values, characterizing tetravalent Fe(IV) cations in perovskite oxides [18].

3.2.2. SrLaCu_{0.99}⁵⁷Fe_{0.01}O₄

The Mössbauer spectra of the simple SrLaCu_{0.99}⁵⁷Fe_{0.01}O₄ at 300 and 77 K have been fitted using two Fe(1) and Fe(2) quadrupole doublets (Fig. 2b). The isomer shift value (δ_1) and quadrupole splitting (Δ_1) for the smallest doublet Fe(1) (Table 2) can be attributed to Fe³⁺ cations in a distorted six-coordinated oxygen environment [18]. For the most important doublet, the δ_2 value (Table 2) is characteristic of high spin Fe⁴⁺ in a perovskite-type structure as observed for SrFeO₃ ($\delta = 0.01 \text{ mm s}^{-1}$, at 300 K [19]). At 77 K, the δ_2 value is increased to 0.12 mm s^{-1} in agreement with the second order Doppler shift ($\partial\delta/\partial T \sim 7 \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$ [18]); while the quadrupole splitting value ($\Delta_2 \approx 0.62 \text{ mm s}^{-1}$) is temperature independent.

3.2.3. La₂Li_{0.50}Cu_{0.50}O₄:⁵⁷Fe (1 at%/Cu)

The ⁵⁷Fe Mössbauer spectrum of the La₂Li_{0.50}Cu_{0.50}O₄:⁵⁷Fe sample recorded at $T = 300 \text{ K}$ has been fitted using three quadrupole doublets (Fig. 3a). The Mössbauer parameters characterizing these doublets are given in Table 3.

Table 2
⁵⁷Fe Mössbauer parameters for LaSrCu_{0.99}Fe_{0.01}O₃

T (K)	Spectra	δ (mm s ⁻¹)	Δ (mm s ⁻¹)	S (± 2) (%)
300	Fe(1)	0.34(1)	0.46(1)	9
	Fe(2)	0.05(1)	0.62(1)	91
77	Fe(1)	0.46(1)	0.45(1)	10
	Fe(2)	0.12(1)	0.62(1)	90

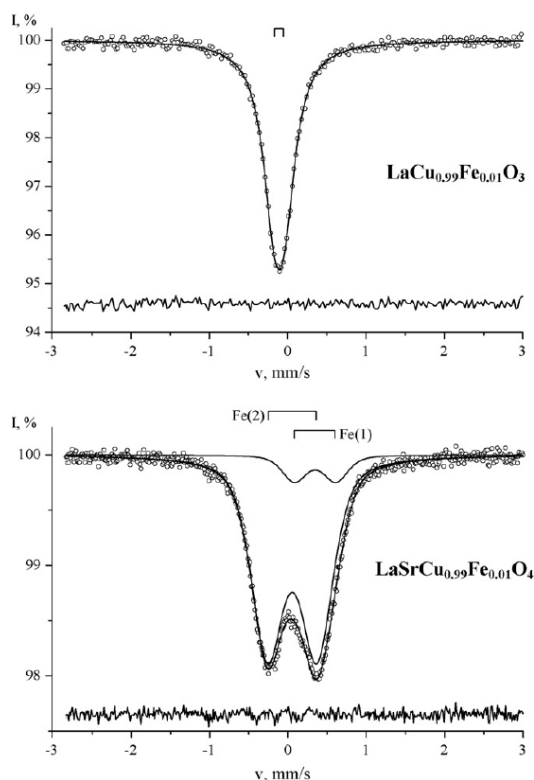


Fig. 2. ⁵⁷Fe Mössbauer spectra of LaCu_{0.99}⁵⁷Fe_{0.01}O₃ and LaSrCu_{0.99}⁵⁷Fe_{0.01}O₄ at $T = 300 \text{ K}$.

The first doublet Fe(1) is characterized by a positive isomer shift value (δ_1) and strong quadrupole splitting (Δ_1) corresponding to high-spin Fe³⁺ ions with a distorted oxygen surrounding [18]. The δ_2 value for the second doublet Fe(2) is close to that characterizing high spin Fe⁴⁺ in a six-coordinated site with a Jahn-Teller distortion ($\Delta_2 = 0.98 \text{ mm s}^{-1}$) as observed for the series A_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O₄ (A = Ca, Sr, Ba) [20].

The Mössbauer parameters (δ_3 and Δ_3) of the third doublet Fe(3) are comparable with those ($\delta = -0.20 \text{ mm s}^{-1}$ and $\Delta = 1.07 \text{ mm s}^{-1}$ [20]) observed for the (Ca_{0.50}La_{1.50})Li_{0.50}Fe_{0.50}O₄ ferrate containing high-spin Fe⁴⁺ ions in D_{4h} distorted octahedral (FeO₆) polyhedra. Due to 1/1 Li/Fe ordering in the perovskite layers each (Fe⁴⁺O₆) octahedron is surrounded by four Li–O bonds.

The spectra at $T = 77 \text{ K}$ (Fig. 3) can be also fitted using three doublets with parameters given in Table 3. The thermal evolution of δ_1 and δ_3 values for the Fe(1) and Fe(3) sub-spectra, respectively, are in agreement with the second order Doppler shift. On the contrary a drastic change for δ_2 and Δ_2 values is observed for the third Fe(2) sub-spectrum. The $\delta_2^{300 \text{ K}}$ value was transformed to the $\delta_2^{77 \text{ K}}$ value (Table 3) which corresponds to Fe³⁺ ions in a six-coordinated site. The unusual large quadrupolar splitting ($\Delta_2^{77 \text{ K}}$) reflects probably strong structural and electronic anisotropies in its anionic surrounding. Such strong modifications suggest a change of the oxidation state adopted for ⁵⁷Fe substituted for Li⁺ into (LiO₆) polyhedra [Fe³⁺(2) instead of Fe⁴⁺(2)] and an important anisotropy in the near Fe³⁺(2) surrounding.

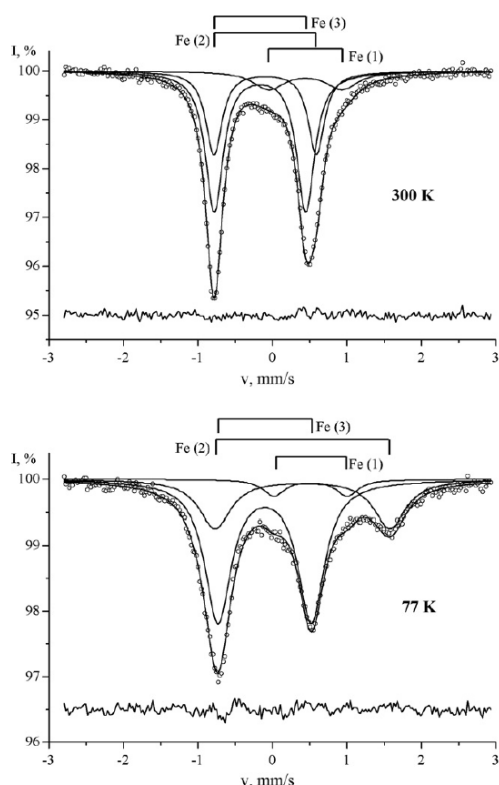


Fig. 3. ^{57}Fe Mössbauer spectra of iron-doped $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ sample at (a) $T=300\text{ K}$ and (b) $T=77\text{ K}$.

4. Discussion

Three main factors characterize these three Cu(III) perovskite-type oxides:

- (i) The preparation process involving different pressure levels, if the highest oxygen pressures (11 GPa) were required for stabilizing $\text{LaCu}_{0.99}\text{Fe}_{0.01}\text{O}_3$, on the contrary lowest pressures level (200–300 MPa) was used for the elaboration of oxides with two-dimensional K_2NiF_4 -type structure. Consequently, few amounts of oxygen vacancies can be stabilized into the $\text{SrLaCu}_{0.99}\text{Fe}_{0.01}\text{O}_4$ and $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$: ^{57}Fe matrixes.
- (ii) The local distortion which is closely dependent on two factors: the global structure of the host 3D or 2D matrix and the chemical bonding environment for copper ions.

Table 3
 ^{57}Fe Mössbauer parameters for $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$: ^{57}Fe

T(K)	Spectra	δ (mm s $^{-1}$)	Δ (mm s $^{-1}$)	S(± 2) (%)
300	Fe(1)	0.44(1)	0.98(1)	12.1
	Fe(2)	-0.09(1)	1.39(1)	23.2
	Fe(3)	-0.16(1)	1.23(1)	64.7
77	Fe(1)	0.50(1)	0.99(1)	6.6
	Fe(2)	0.40(1)	2.34(1)	27.4
	Fe(3)	-0.11(1)	1.25(1)	65.5

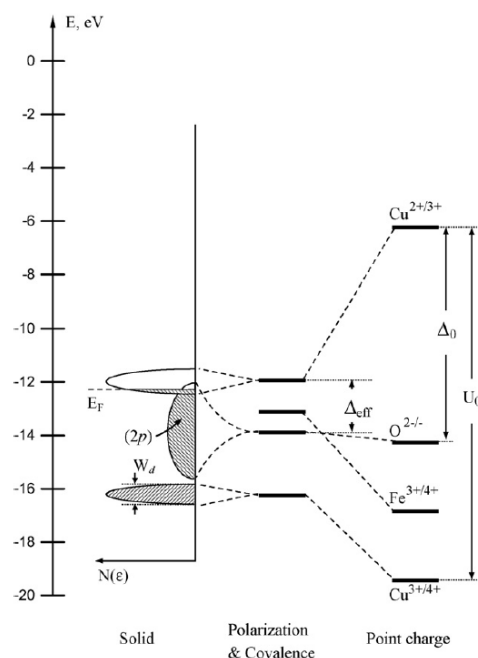


Fig. 4. Schematic representation of various steps in the constructions of a band diagram for iron-doped LaCuO_3 perovskite.

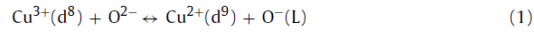
- (iii) The competing chemical bond of the Cu–O ones, such a factor playing in particular an important role on the Cu–O covalence.

The absence – in the ^{57}Fe Mössbauer spectra of $\text{LaCu}_{0.99}\text{Fe}_{0.01}\text{O}_3$ – of noticeable quadrupole interactions and also the presence of iron probe atoms of unique type for crystallographic positions correspond to the perovskite structure of LaCuO_3 containing nearly non-distorted octahedral (CuO_6) polyhedra resulting from the itinerant character of the $e_g(\text{Cu})$ electrons (σ^* -band) which does not lead to a local Jahn-Teller distortion or charge disproportionation (as in the case of the SrFeO_3 ferrate [19]). However, the main interest for the discussion of the above results is the mechanism responsible for the stabilization of formally tetravalent Fe(IV) ions in the Cu(III) perovskite-like oxides (Fig. 4).

The most important peculiarity for diagrams of the energy levels corresponding to discussed oxides concerns the relative positions of energy levels $\varepsilon(\text{O}^{2-/})$ and $\varepsilon(\text{Cu}^{3+/4+})$, which influences the covalence degree of the corresponding Cu–O bonds. The lowest unoccupied $\text{Cu}^{2+/3+}$ redox level lies at an energy U_0 above the highest occupied $\text{Cu}^{3+/4+}$ level, as shown in Fig. 3 (point charge approximation). The $\text{O}^{2-/}$ and $\text{Cu}^{2+/3+}$ levels are separated by the energy Δ_0 , which corresponds to the charge transfer ($\text{O}^{2-} \rightarrow \text{Cu}^{3+}$) gap in the Zaanen-Sawatzky-Allen (ZSA) model [11,12]. The subscripts “zero” on U_0 and Δ_0 have been introduced to remind that these values are calculated using the simple ionic model.

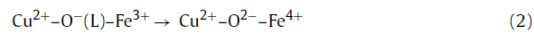
In the case of Cu(III) perovskite-type oxides the $\text{Cu}^{3+/4+}$ redox couple lies below the top of the $\text{O}:2p_r$ band, so an oxidation of the “ CuO_6 ” sites should introduce holes into the σ^* antibonding states pinned at the top of the valence $\text{O}:2p_r$ band. In other words, the representation of the ground-state properties of LaCuO_3 (SrLaCuO_4 or $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$) requires introduction of a strong hybridiza-

tion of $O:2p_{\sigma}$ and $Cu:3d_{\sigma}$ orbitals in the itinerant-electron σ^* -band states corresponding to an equilibrium charge transfer reaction:



that is biased strongly to the right. For example, according to photoemission and X-ray-absorption spectroscopy [11,12], the ground electronic state of copper ions in $LaCuO_3$ structure is preferentially describe as superposition of two configurations: 34% (d^8) and 66% (d^9L), dominated by the d^9L configuration (where L is an oxygen hole). The charge-transfer phenomenon had been also pointed out through “*ab initio*” calculations of the electronic structure based on the A.S.W. method [21].

The obtained results evidence that in case of $LaCu_{0.99}Fe_{0.01}O_3$, the probe Fe^{3+} cations will appear in an anionic environment “ $O^{(2-\sigma)-}$ ” with lower value of a negative charge. As the electronegativity of oxygen sharply increases within downturn of its negative charge, the $Fe-O$ bonds will be characterized by a very high ionicity degree that can be possible to present schematically as a displacement of the following reaction balance:



that is biased strongly to the right.

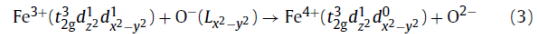
The absence in the ^{57}Fe Mössbauer spectra of the formally tetravalent Jahn-Teller “ Fe^{4+} ” ions of noticeable quadrupole interactions can be reconciled taking into account the fact that the ground state of this ions in the $LaCu_{0.99}Fe_{0.01}O_3$ perovskite is described by the relatively large occupancy of the $3d^5L$ (~64%) configuration and not of the $3d^4$ configuration (~36%) [22]. The $3d$ component of the $3d^5L$ configuration is given by the high-spin $t_{2g}^3e_g^2$ ($^6A_{1g}$ ground term) state which inhibits the Jahn-Teller distortion.

The $SrLaCuO_4$ and $La_2Li_{0.50}Cu_{0.50}O_4$ matrixes are both characterized by a K_2NiF_4 structure and a comparable preparation method (in terms of oxygen pressure levels). The moderated oxygen pressures developed for the synthesis of these 2D oxides can induce few amounts of oxygen vacancies. Consequently, in both ^{57}Fe doped matrixes, a small component (~10%) corresponding to $^{57}Fe^{3+}$ cations stabilized in the vicinity of oxygen vacancies, is observed. In addition, the intensity of $Fe(1)$ sub-spectrum for both matrixes seems to be independent of the temperature, the corresponding substitution being mainly governed by the experimental conditions during the synthesis of these iron-doped compounds.

In both 2D matrixes (at $T=300K$), the second $Fe(2)$ sub-spectrum is characterized by an isomer shift (δ_2) value (Tables 2 and 3) very close to that observed for the $LaCu_{0.95}Fe_{0.01}O_3$ perovskite. This result has allowed us to propose that for $SrLaCuO_4$ the $Fe(2)$ sub-spectrum would correspond to the iron probe atoms ions stabilized in an environment of six formally trivalent Cu^{3+} ions. As in the case of $LaCu_{0.95}Fe_{0.01}O_3$, a large amount of charge is transferred via $Cu-O$ bonds from the $2p_{\sigma}(O^{2-})$ to the $3d(Cu^{3+})$ orbitals (see Eq. (1)) and the ground state of copper ions is dominated by the d^9L configuration (“ $Cu^{2+}-O^-(L)$ ” state). The presence of electron holes on oxygen sub-lattice would lead, in the near environment of the ^{57}Fe probe cations, to a charge transfer (see Eq. (2)), transforming “ Fe^{3+} ” into “ Fe^{4+} ” state.

The case of $La_2Li_{0.50}Cu_{0.50}O_4$ appears more complicated. The stabilization of ^{57}Fe atoms in this compound could take place on the two different six-coordinated (CuO_6) and (LiO_6) sites. However, the difference in sizes of $Cu^{3+}(LS)$ state and $Fe^{3+}(HS)$ state ions [17] would limit the isovalent $Fe^{3+} \rightarrow Cu^{3+}$ substitution. Consequently, a partial $Fe^{3+} \rightarrow Li^+$ substitution would be induced (the corresponding excess of oxygen resulting in the difference of charges being compatible with the K_2NiF_4 -type structure). The analysis of these data has led us to propose that $Fe(2)$ sub-spectrum (at $T=300K$) would correspond to the iron probe atoms substituted for Li^+

cations in distorted (LiO_6) polyhedra. In this case its surrounding should be constituted of four very covalent $Cu^{3+}-O$ bonds located in the xOy plane (Fig. 1). Zhang and Rice [23] proposed, a planar coordinated Cu^{3+} ions, that due to the strong $Cu-O$ hybridization the hole ($L_{x^2-y^2}$) on each square of oxygen atoms forms with the central $Cu^{2+}(d_{z^2}^1d_{x^2-y^2}^1)$ ions a local singlet state (Zhang-Rice singlet) which involves the $3d_{x^2-y^2}(Cu)$ orbitals and a linear combination of the $2p_{xy}$ orbitals of the four nearest neighbor oxygen’s. The presence of electron hole ($L_{x^2-y^2}$) on oxygen (CuO_4) sub-lattice induces in the environment of the ^{57}Fe probe cations a charge transfer equilibrium, which at $T=300K$ is significantly displaced to the right:



The strong difference between the quadrupole splitting of $Fe(2)$ sub-spectrum for $La_2Li_{0.50}Cu_{0.50}O_4$ ($\Delta_2 \approx 1.39 \text{ mm s}^{-1}$) compared to $SrLaCuO_4$ ($\Delta_2 \approx 0.66 \text{ mm s}^{-1}$) would be attributed to the proposed local structural distortion for the (CuO_6) polyhedra in these two 2D matrixes. In $La_2Li_{0.50}Cu_{0.50}O_4$ the (CuO_6) polyhedra can be described as a strong elongated octahedral along the Oz axis (Fig. 1). On the contrary for $SrLaCuO_4$ in order to stabilize two strong “ $Cu^{3+}-O$ ” bonds sharing the same $2p$ oxygen orbital in the xOy plane, an orbital $d_{x^2-y^2}/d_{y^2}$ ordering was postulated [10,24].

A drastic change for the $Fe(2)$ component is observed in Mössbauer spectrum of $La_2Li_{0.50}Cu_{0.50}O_4$ at $T=77K$ (Fig. 3). If at 300K isomer shift value of the $Fe(2)$ sub-spectrum corresponds to the Fe^{4+} ions, at liquid nitrogen temperature the δ_2^{77K} value (Table 3) corresponds to six-coordinated high spin Fe^{3+} [17]. In parallel, an unusual high value is observed for the quadrupole splitting (Δ_2^{77K}). Such an unusual Δ value is consistent with a very strong anisotropy (structural and electronic) in the vicinity of Fe^{3+} . These drastic changes for Mössbauer parameters could be related to a modification of the charge transfer equilibrium (3) versus temperature from the stabilization of the high-spin $Fe^{4+}(Li^+)$ at 300K to that of the $Fe^{3+}(Li)$ ions at $T=77K$. This result suggests that the energy corresponding to the ($Fe^{3+}-O^-(L)$) state would be more stable than the ($Fe^{4+}-O^{2-}$) state at a low temperature. The high Δ_3 value would be induced both by the strong elongation of the host (LiO_6) polyhedra (structural distortion) and the presence of electron hole in the oxygen coordination (electronic anisotropy). However, for more comprehensive analysis of the local structure of ^{57}Fe probe atoms within the $La_2Li_{0.50}Cu_{0.50}O_4$ lattice, Mössbauer experiments at intermediate temperatures are in progress.

The main difference between $SrLaCuO_4$ and $La_2Li_{0.50}Cu_{0.50}O_4$ doped with ^{57}Fe is the existence of only one six-coordinated site for the first matrix (CuO_6) and two for the second [(CuO_6) and (LiO_6)]. Consequently a substitution $^{57}Fe^{3+} \rightarrow Cu^{3+}$ can take place for the $La_2Li_{0.50}Cu_{0.50}O_4$ matrix. Mössbauer parameters of the $Fe(3)$ component corresponding to such substitution are comparable with those ($\delta = -0.20 \text{ mm s}^{-1}$ and $\Delta = 1.07 \text{ mm s}^{-1}$ [20]) observed for the ($Ca_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ ferrate containing high-spin $Fe^{4+}(t_{2g}^3e_g^1)$ ions in D_{4h} distorted octahedral (FeO_6) polyhedra. Due to a 1/1 Li/Fe ordering in the perovskite layers each ($Fe^{4+}O_6$) octahedron is surrounded by four $Li-O$ bonds (Fig. 1). The stabilization of the iron oxidation state “+4” would be induced by the high Dq/B value (Dq and B are the crystal field and Racah parameters, respectively) characterizing the Cu^{3+} local site. If, due to the energy value of the $3d$ orbitals corresponding to Fe^{4+} a partial charge transfer phenomenon $O(2p_{\sigma}) \rightarrow Fe^{4+}(3d_{\sigma})$ could be involved, the $Li-O$ surrounding induces no electronic transfer from lithium.

5. Conclusion

The comparative Mössbauer study of three cop-per(III) oxides: $LaCu_{0.99}^{57}Fe_{0.01}O_3$, $SrLaCu_{0.99}^{57}Fe_{0.01}O_4$ and

$\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$: ^{57}Fe , was developed in order to obtain an evaluation of different physico-chemical factors playing an important role on the electronic structure of the local (CuO_6) sites. The obtained results underline that four main factors are predominant in the stabilization of formally trivalent “ Cu^{3+} ” ions: (i) the involved preparation process (in particular the oxygen pressure level able to impede the formation of oxygen vacancies); (ii) the dimensionality (3D or 2D) of the lattice; (iii) the chemical surrounding and (iv) the local structural distortion of the transitional metal site governing the local crystal field energy, orbital ordering and a possible charge transfer $\text{Cu}^{3+}-\text{O}^{2-} \leftrightarrow \text{Cu}^{2+}-\text{O}^-(\text{L})$.

In the case of $\text{LaCu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_3$, $\text{SrLaCu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_4$, having only one type of octahedral sites, the dominant $d^9\text{L}$ ($\approx 70\%$) ground state for the (CuO_6) sub-lattice induces – in the environment of the iron probe cations – a charge transfer $\text{Fe}^{3+} + \text{O}^-(\text{L}) \rightarrow \text{Fe}^{4+} + \text{O}^{2-}$, leading to the stabilization of the “ Fe^{4+} ” state. The comparative analysis of the isomer shift and quadrupole splitting values for “ Fe^{4+} ” cations clearly underlined the different local structure of (CuO_6) polyhedra in these 3D and 2D lattices.

In the oxide $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$, with the K_2NiF_4 -type structure and with a cationic 1/1 (Cu/Li) ordering in the $x\text{Oy}$ planes, three different sub-spectra have been observed: the first [Fe(1)] representing the Fe^{3+} trapped near the surface of the crystallites and correlated to the preparation process; the second [Fe(2)] associated to Fe^{3+} substituted to the Li^+ sites due to the small local crystal field energy; and the third [Fe(3)] corresponding to Fe^{4+} substituted to “ Cu^{3+} ” in the (CuO_6) sites. Drastic thermal evolution observed for iron substituted for lithium [Fe(2)] has been interpreted by the charge transfer equilibrium $\text{Fe}^{3+} + \text{O}^-(\text{L}) \leftrightarrow \text{Fe}^{4+} + \text{O}^{2-}$, which is biased to the left at decrease of temperature.

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