# Local Environment and Electronic Structure in $K_2NiF_4$-type $La_2Li_{0.50}Cu_{0.50}O_4$ Doped by $^{57}Fe$

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The $^{57}$Fe Mössbauer spectrum of the oxide $La_2Li_{0.50}Cu_{0.50}O_4$ doped with $^{57}$Fe (1 at.-%) underlines at 300 K the presence of three different components: two corresponding to the substitution of $^{57}$Fe probe atoms for respectively “$Cu^{3+}$” [Fe(1)] and $Li^+$ [Fe(3)] and the third [Fe(2)] attributed to $^{57}$Fe associated with oxygen vacancies. A decrease of the temperature down to 77 K does not lead to essential changes of the Mössbauer parameters corresponding to the Fe(1) and Fe(2) sub-spectra. On the contrary, a drastic change occurs in the Fe(3) sub-spectrum which has been interpreted by a displacement of the charge-transfer equilibrium $Fe^{4+}(3) + O^{2-} \rightarrow Fe^{3+}(3) + O(\underline{L})$ at the $Li^+$ sites.

*Key words:* Solid State, Electronic Structure, $^{57}$Fe Mössbauer Spectroscopy,
$K_2NiF_4$-type Compound

## Introduction

Few oxides derived from the perovskite structure containing formally $Cu^{3+}$ cations have been prepared [1, 2]. Due to the strong covalency of the $Cu^{3+}$–O bond different electronic phenomena can be induced in these matrices.

Among the $Cu^{3+}$ containing oxides, $K_2NiF_4$-type $La_2Li_{0.50}Cu_{0.50}O_4$ was prepared in 1972 under oxygen pressure (300 MPa) by Demazeau *et al.* [1] from a stoichiometric mixture of the precursors $La_2O_3$, $Li_2O$, and CuO. In such a structure, $Cu^{3+}$ is characterized by a $d^8$ low-spin electronic configuration ($t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^0$). More recently Rykov *et al.* [3], through the substitution of $Li^+$ for $Cu^{2+}$ in the parent compound $La_2CuO_4$, have prepared the solid solution $La_2Li_xCu_{1-x}O_4$ ($0 < x < 0.50$). Substitution of $Li^+$ for $Cu^{2+}$ was followed by magnetic, NMR and NQR measurements and the stabilization of the $d^9\underline{L}$ electronic configuration was proposed for this hole-doped compound. At composition $La_2Li_{0.50}Cu_{0.50}O_4$ (*i. e.* $x = 0.5$) the $Li^+$ and $Cu^{3+}$ ions form an ordered superstructure in which all $Cu^{3+}$ ions are surrounded by four in-plane $Li^+$ neighbors. Therefore, the perovskite layers of the $La_2Li_{0.50}Cu_{0.50}O_4$ structure can be described as an ordered network of isolated ($Cu^{3+}O_6$) and ($Li^+O_6$) octahedra (Fig. 1). In this compound the ionic character of the equatorial $(Li–O)_{eq}$ bonds increases the covalency of the competing $(Cu–O)_{eq}$ bonds, leading to their shortening, and enhancing the elongation of the ($CuO_6$) octahedral environment ($c/a > 1$). The ($CuO_6$) octahedra in the $K_2NiF_4$-type structure $La_2Li_{0.50}Cu_{0.50}O_4$ are strongly elongated as illustrated by a large ratio $c/a$ ($c/a = 3.54$) [1] in comparison with the $c/a$ value for the homologous oxide $La_2Li_{0.50}Ni_{0.50}O_4$ containing Jahn-Teller (JT) low-

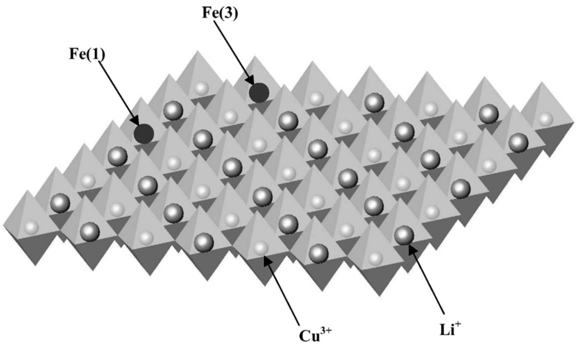

Fig. 1. Schematic representation of the anisotropic chemical bonding environment of the ($CuO_6$) and ($LiO_6$) octahedra in the iron-doped 2D $K_2NiF_4$-type structure of $La_2Li_{0.50}Cu_{0.50}O_4$.

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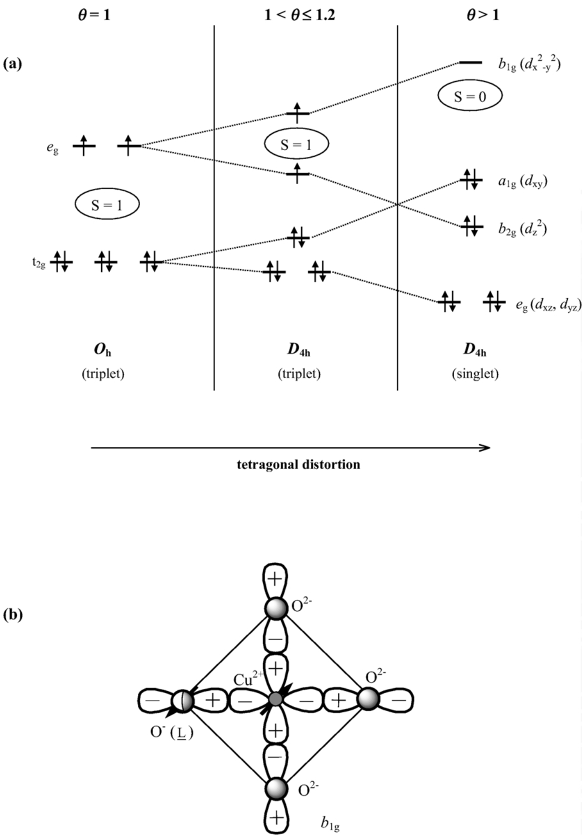

Fig. 2. Schematic representation of (a) crystal field splitting of $Cu^{3+}$ : $3d$ levels in the tetragonal ($y$) distorted ($CuO_6$) polyhedra; (b) $Cu^{3+}$ : $3d_{x^2-y^2}$ hybridization with $O^{2-}$ : $p_{x,y}$ orbitals (Zhang-Rice singlet).

spin $Ni^{3+}$ ($d_{xz,yx,zx} d^1_{z^2} d^0_{x^2-y^2}$) ions ($c/a$ = 3.43) [4]. From a single crystal X-ray analysis, Abou-Warda *et al.* [5] have confirmed an ordered distribution of $Li^+/Cu^{3+}$ on the octahedral sites with Cu–O bond lengths of 1.80 Å in the $xy$ plane and 2.47 Å along the $z$ axis. Using such values, the $\theta$ parameter evaluating the ($CuO_6$) elongation [$\theta \equiv (\text{Cu–O})_{\text{apic}}/(\text{Cu–O})_{\text{eq}}$] is close to 1.38.

Such a very strong local tetragonal distortion of the ($CuO_6$) polyhedra destabilizes the $d_{x^2-y^2}$ ($b_1$) orbital which corresponds to the two holes (Fig. 2a) and thus correlates well with the low-spin configuration of the $Cu^{3+}$ ($d^6_{xz,yx,zx} d^2_{z^2} d^0_{x^2-y^2}$) ions. This finding is consistent with results of (LDA+U) calculations [6] which have shown that the lowest energy excitation in the $La_2Li_{0.50}Cu_{0.50}O_4$ structure will be from the singlet $d^2_{z^2}$ (S = 0) configuration (ground state) to the triplet $d^1_{z^2} d^1_{x^2-y^2}$ (S = 1) configuration. However, if the copper-apical oxygen bond length $(\text{Cu–O})_{\text{apic}}$ is contracted by 17 %, the triplet $d^1_{z^2} d^1_{x^2-y^2}$ state becomes the ground state.

The electronic structure of the "super" Jahn-Teller $Cu^{3+}(3d^8)$ ions has attracted great interest because it remains to be clarified whether their ground states are dominated by $d^8(Cu^{3+})$ or $d^9\underline{L}$ ("$Cu^{2+}$–$O^-$" state), where $\underline{L}$ is an oxygen hole. Spectroscopic measurements [7] and configuration interaction (CI) calculations [8] for the formally $Cu^{3+}$ oxides showed that positive holes predominantly occupy oxygen $2p_\sigma$ orbitals which hybridize with the copper $3d_\sigma(d_{x^2-y^2}, d_{z^2})$ orbitals to form a $d^9\underline{L}$ configuration and not a $d^8$ configuration as for a simple $Cu^{3+}$ ion. The key structural element of the crystal structure of the $K_2NiF_4$-type $La_2Li_{0.50}Cu_{0.50}O_4$ is the same as in the layered Cu oxides (for example $La_{2-x}Sr_xCuO_4$): the Cu atoms are located in the center of a quasi-square planar surrounding of oxygen atoms. Zhang and Rice [9] proposed for a planar coordinated $Cu^{3+}$ ion that, due to the strong Cu–O hybridization, the hole ($\underline{L}_{x^2-y^2}$) on each square of oxygen atoms forms with the central $Cu^{2+}$ ($d^2_{z^2} d^1_{x^2-y^2}$) ions a local singlet state (Zhang-Rice singlet) which involves the $3d_{x^2-y^2}$ (Cu) orbitals and a linear combination of the $2p_{x,y}$ orbitals of the four nearest neighbor oxygen atoms (Fig. 2 b).

Although the described Zhang-Rice (ZR) model is widely accepted, there is still a lack of experimental evidence that such a local singlet state exists within the copper oxide layers. For example, a Cu nuclear quadrupole resonance (NQR) study [10] revealed the existence of a low-lying excitation within the $(Cu/Li)O_2$ planes of the $La_2Li_{0.50}Cu_{0.50}O_4$ structure with an energy ($\sim$ 130 meV) which is much lower than that ($\sim$ 6 eV) predicted by the ZR model [9, 10]. In particular, it has been shown that below $T \approx 170$ K quadrupole relaxation is primarily due to fluctuations of the electric field gradient (EFG) with an anomalously slow rate. Though the physical mechanism of the EFG fluctuations is not yet understood, they could arise from distortions of the ($CuO_6$) octahedra or from charge-fluctuation involving the $Cu^{3+}$ ions [11].

In this paper we report results of $^{57}$Fe Mössbauer spectroscopy of $La_2Li_{0.50}Cu_{0.50}O_4$ doped with $^{57}$Fe. This method was recently developed for the physical characterization of oxides containing transition metals in high oxidation states such as $Fe^{4+}$ or $Ni^{3+}$ [12 – 16]. In the first case ($CaFeO_3$ or $SrFeO_3$), $Fe^{4+}$ is itself used as the Mössbauer cation but in the second one

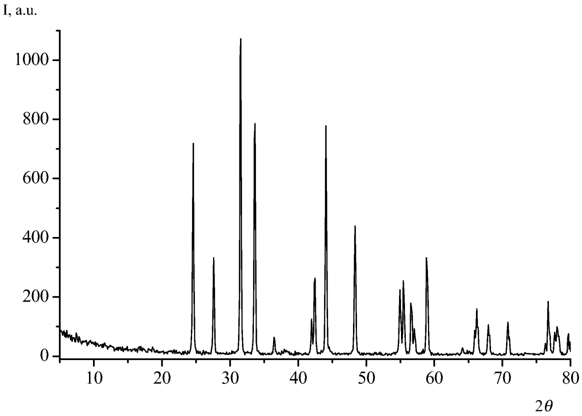

Fig. 3. Powder X-ray diffraction pattern of an iron-doped $La_2Li_{0.5}Cu_{0.5}O_4$ sample (Cu$K_\alpha$ radiation).

($R$NiO$_3$, $R$ = rare earth element) $^{57}$Fe doping was employed ($R\mathrm{Ni}_{0.99}{}^{57}\mathrm{Fe}_{0.01}\mathrm{O}_3$) as the Mössbauer probe. It has been shown that Mössbauer spectra of $^{57}$Fe probe atoms reflect structural and chemical factors characterizing not only the local environment but also the electronic phenomena in the bulk. Recently, a first Mössbauer study [17] using $^{57}$Fe as a probe was carried out for comparing the isostructural perovskites $LaNiO_3$ and $LaCuO_3$, both characterized by a metallic character [18].

The behavior of high-spin $Fe^{3+}(3d^5)$ ions – characterized by an isotropic electronic configuration – as local probe in $La_2Li_{0.50}Cu_{0.50}O_4$ appears to be an interesting approach for studying the mechanisms of substitution on the different six-coordinated sites and the corresponding induced electronic phenomena. Temperature-dependent Mössbauer measurements have been made to investigate the electronic behavior of $^{57}$Fe probe atoms *versus* the structural and chemical bonding factors characterizing the $La_2Li_{0.50}Cu^{3+}{}_{0.50}O_4$ matrix.

## Experimental Section

Polycrystalline iron-doped $La_2Li_{0.50}Cu_{0.50}O_4 : {}^{57}Fe$ (1 at.-% ratio for cations in coordination number 6) was prepared using the method developed for the synthesis of the undoped sample [1]. However, instead of undoped CuO oxide, a $\mathrm{Cu}_{0.99}{}^{57}\mathrm{Fe}_{0.01}\mathrm{O}$ precursor was prepared through the thermal decomposition of the iron-doped hydroxide $Cu(OH)_2$: $^{57}$Fe with a $^{57}$Fe doping atomic ratio equal to 1 %.

XRD data were collected at 298 K using a Stoe powder diffractometer (Cu$K_\alpha$ radiation).

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

Table 1. XRD pattern of $La_2Li_{0.50}Cu_{0.50}O_4$: $^{57}$Fe (1 at%)[a].

| $d$ (Å) | $h$ | $k$ | $l$ | $I$ (%) |
|---|---|---|---|---|
| 3.600(2) | 1 | 0 | 1 | 65.4 |
| 3.309(6) | 0 | 0 | 4 | 31.8 |
| 2.850(4) | 1 | 0 | 3 | 100.0 |
| 2.640(5) | 1 | 1 | 0 | 72.7 |
| 2.203(6) | 0 | 0 | 6 | 17.6 |
| 2.062(1) | 1 | 1 | 4 | 69.3 |
| 1.867(8) | 2 | 0 | 0 | 40.9 |
| 1.691(7) | 1 | 1 | 6 | 20.0 |
| 1.561(3) | 2 | 1 | 3 | 33.7 |
| 1.422(2) | 2 | 0 | 6 | 15.8 |

[a] Space group $I4/mmm$ with $a = b = 3.736$, $c = 13.238$ Å, $V = 160.0$ Å$^3$, $c/a = 3.543$.

## Results

### *Structural characterization of $La_2Li_{0.50}Cu_{0.50}O_4$ (1 at.-% $^{57}Fe$)*

The X-ray diffraction pattern given in Fig. 3 underlines that all diffraction peaks for the iron-doped oxide $La_2Li_{0.50}Cu_{0.50}O_4$:$^{57}$Fe can be indexed on the basis of a tetragonal $K_2NiF_4$ lattice (space group $I4/mmm$). The indexation of the XRD pattern is given in Table 1. The calculated parameters for $La_2Li_{0.50}Cu_{0.50}O_4$:$^{57}$Fe ($a$ = 3.736, $c$ = 13.238 Å) are slightly higher than those observed for the undoped sample ($a$ = 3.731, $c$ = 13.20 Å) [1]. Such a result can be attributed to the small atomic ratio of the $^{57}$Fe Mössbauer probe atoms (1 at.-%) in the investigated matrices and the different ionic sizes: $r(Fe^{3+}) = 0.64$ Å, $r(Cu^{3+}) = 0.55$ Å [19].

### *Mössbauer spectroscopic results*

The $^{57}$Fe Mössbauer spectrum of the $La_2Li_{0.50}Cu_{0.50}O_4$:$^{57}$Fe sample recorded at $T$ = 300 K has been fitted using three quadrupole doublets (Fig. 4a). The Mössbauer parameters characterizing these doublets are given in Table 2.

The Mössbauer parameters [isomer shift ($\delta$) and quadrupole splitting ($\Delta$)] of the first doublet Fe(1) are comparable with those ($\delta = -0.20$ mm s$^{-1}$ and $\Delta = 1.07$ mm s$^{-1}$ [20]) observed for the ferrate $(Ca_{0.50}La_{1.50})Li_{0.50}Fe_{0.50}O_4$ containing high-spin $Fe^{4+}$ ($t_{2g}^3e_g^1$) ions in $D_{4h}$ distorted octahedra ($FeO_6$). 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).

Table 2. $^{57}$Fe Mössbauer parameters for $La_2Li_{0.50}Cu_{0.50}O_4$: $^{57}$Fe (1 at.-%).

| $T$ (K) | Spectra | $\delta$ (mms$^{-1}$) | $\Delta$ (mms$^{-1}$) | S ($\pm$2) (%) |
|---|---|---|---|---|
| 300 | Fe(1) | −0.16(1) | 1.23(1) | 64.7 |
| | Fe(2) | 0.44(1) | 0.98(1) | 12.1 |
| | Fe(3) | −0.09(1) | 1.39(1) | 23.2 |
| 77 | Fe(1) | −0.11(1) | 1.25(1) | 65.5 |
| | Fe(2) | 0.50(1) | 0.99(1) | 6.6 |
| | Fe(3) | 0.40(1) | 2.34(1) | 27.4 |

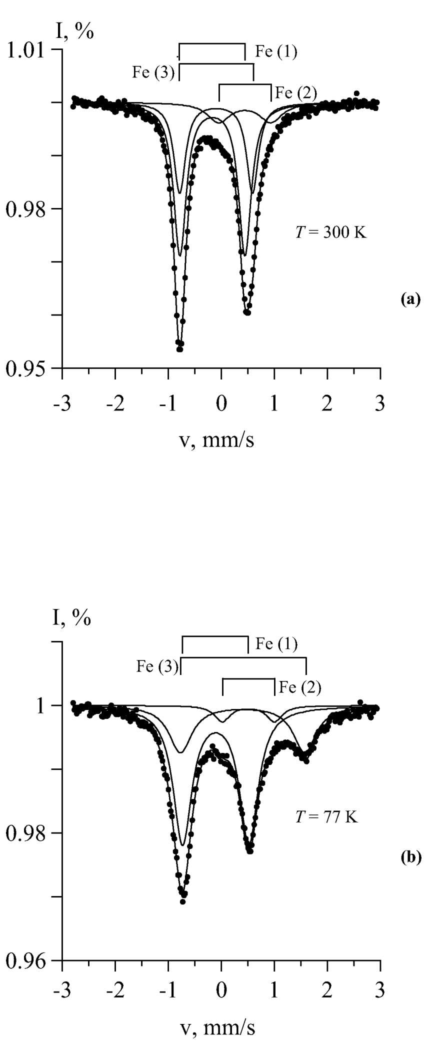

Fig. 4. $^{57}$Fe Mössbauer spectra of an iron-doped $La_2Li_{0.50}Cu_{0.50}O_4$ sample at (a) $T$ = 300 K and (b) $T$ = 77 K.

The second doublet Fe(2) is characterized by a positive isomer shift value and strong quadrupole splitting (Table 2) corresponding to high-spin $Fe^{3+}$ ($t_{2g}^3e_g^2$) ions with a distorted oxygen surrounding [21].

A $\delta_3$ value for the third doublet Fe(3) is close to that characterizing high-spin $Fe^{4+}$ in a six-coordinated site with a Jahn-Teller distortion ($\Delta$ = 0.98 mm s$^{-1}$). This $\delta$ value appears slightly higher than the previous one corresponding to the first Fe(1) component and suggests a local surrounding inducing a smaller local crystal field energy.

The spectra at 77 K (Fig. 4b) can also be fitted using three doublets with parameters given in Table 2. The first Fe(1) sub-spectrum corresponds to high-spin $Fe^{4+}$, with parameters attributed also to that observed for $Fe^{4+}$ in $(Ca_{0.50}La_{1.50})Li_{0.50}Fe_{0.50}O_4$. The thermal evolution of the $\delta_1$ value ($\delta_1^{77\,K} - \delta_1^{300\,K}$ = 0.13 mm s$^{-1}$) is in agreement with the temperature shift ($\partial\delta/\partial T \sim 7 \times 10^{-4}$ mm s$^{-1}$ · K$^{-1}$ [21]). The second Fe(2) component is characteristic of high-spin $Fe^{3+}$ with approximately the same parameters as those ($\delta_2$) observed at 300 K (Table 2).

On the contrary, a drastic change of the $\delta_3$ and $\Delta_3$ values is observed for the third Fe(3) sub-spectrum. The $\delta_3^{300\,K}$ value was transformed to the $\delta_3^{77\,K}$ value (Table 2) which is in agreement with $Fe^{3+}$ ions in a six-coordinated site. The unusually large quadrupole splitting ($\Delta_3^{77\,K}$) probably reflects strong anisotropies, both structural and electronic, in the anionic surrounding.

## Discussion

The stabilization of $^{57}$Fe atoms in the $La_2Li_{0.50}Cu_{0.50}O_4$ matrix could take place on the two different six-coordinated ($CuO_6$) and ($LiO_6$) sites. The essential difference in the sizes of $Cu^{3+}$(LS state) and $Fe^{3+}$(HS state) ions [19] would limit the isovalent $Fe^{3+} \rightarrow Cu^{3+}$ substitution. As a consequence, a partial $Fe^{3+} \rightarrow Li^{+}$ substitution may be induced (the corresponding excess of oxygen resulting from the difference of charges being compatible with the $K_2NiF_4$-type structure). Due to the small $^{57}$Fe contents, the equilibrium of charge would be realized either by an excess of oxygen or a few lanthanum vacancies.

Due to the fact that the $\delta_1$ value of the sample is comparable to the $\delta$ value observed for $(Ca_{0.50}$-$La_{1.50})Li_{0.50}Fe^{4+}_{0.50}O_4$, the first Fe(1) sub-spectrum corresponds to high-spin $Fe^{4+}$ ions with a surrounding of four (Li–O) bonds in the *xy* plane. Consequently, this sub-spectrum results from the partial heterovalent $^{57}Fe^{4+} \rightarrow Cu^{3+}$ substitution. The stabilization of the oxidation state "4+" is 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 3$d$ orbitals corresponding to $Fe^{4+}$, a partial charge transfer phenomenon $O(2p_\sigma) \rightarrow Fe^{4+}(3d_\sigma)$ is involved, the Li–O surrounding induces no electron transfer from lithium.

The second component, Fe(2), characterized by a $\delta_2$ value (Table 2), can be attributed to $Fe^{3+}$ ions located at the surface of crystallites or to a small oxygen non-stoichiometry due to the lower oxygen pressure used for the synthesis of $La_2Li_{0.50}Cu_{0.50}$:$^{57}$Fe (oxygen pressure: 300 MPa) compared to that required for preparing $LaCuO_3$:$^{57}$Fe (oxygen pressure: 11 GPa), where such a component is not observed [17]. In both cases $^{57}$Fe is associated with oxygen vacancies. In addition, it should be noted that the intensity of the Fe(1) and Fe(2) sub-spectra seems independent of the temperature, the corresponding substitution being mainly governed by the experimental conditions during the synthesis of the $La_2Li_{0.50}Cu_{0.50}O_4$ matrix doped with $^{57}$Fe.

At $T$ = 300 K the third Fe(3) sub-spectrum is characterized by an isomer shift ($\delta_3$) value (Table 2) very close to that observed earlier for the $LaCu_{0.99}Fe_{0.01}O_3$ perovskite ($\delta = -0.11$ mm s$^{-1}$) [17] containing high-spin $Fe^{4+}(d^4)$ ions in an environment of six formally trivalent $Cu^{3+}$ ions. The $\delta_3$ value appears slightly higher than $\delta_1$ corresponding to the first Fe(1) sub-spectrum (Table 2) and consequently suggests a lower covalent character of the corresponding Fe(2)–O bonds. The analysis of these data has allowed us to suppose that the Fe(3) sub-spectrum (at 300 K) corresponds 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 $xy$ plane (Fig. 2). As in the case of $LaCu_{0.99}Fe_{0.01}O_3$ [17], a large amount of charge is transferred *via* Cu–O bonds from the $2p_{x,y}$(O) to the $3d_{x^2-y^2}$(Cu) orbitals (Fig. 2b), and the ground state of the copper ions is dominated by the $d^9\underline{L}$ configuration (“$Cu^{2+}$–$O^-(\underline{L})$” state). The presence of an electron hole ($\underline{L}_{x^2-y^2}$) on the oxygen substructure leads, in the near environment of the $^{57}$Fe probe cations, to a charge transfer $Fe^{3+} + O^-(\underline{L}_{x^2-y^2}) \rightarrow Fe^{4+} + O^{2-}$, which transforms the “$Fe^{3+}$” into an “$Fe^{4+}$” state.

The large values of the quadrupole splitting ($\Delta$) for the Fe(1) and Fe(3) sub-spectra (Table 2) are consistent with the strong distortion of the ($CuO_6$) and ($LiO_6$) polyhedra in the $La_2Li_{0.50}Cu_{0.50}O_4$ structure. A previous $^7$Li NMR investigation of $La_2Li_{0.50}M^{3+}_{0.50}O_4$ (with $M^{3+}$ = Co, Ni, Cu) confirmed a high value for the quadrupolar coupling constants in particular for $Li^+$ in the “$Cu^{3+}$” oxide ($\gamma = 50$ kHz) [22].

The analysis of the Mössbauer spectrum at 77 K confirmed also the presence of three components (Fig. 4b). The $^{57}$Fe Mössbauer parameters characterizing the Fe(1) and Fe(2) sub-spectra are only slightly changed (Table 2). In the latter case [Fe(2)], this result is in agreement with $Fe^{3+}$ species resulting from the preparation process (associated with oxygen vacancies).

On the contrary, a drastic change of the Mössbauer parameters is observed for the Fe(3) component. If at 300 K the isomer shift value of the Fe(3) sub-spectrum corresponds to the $Fe^{4+}$ ions, however, the $\delta_3^{77\,K}$ value at liquid nitrogen temperature (Table 2) is in agreement with six-coordinated high-spin $Fe^{3+}$ [20]. In parallel, an unusually high value is observed for the quadrupole splitting ($\delta_3^{77\,K}$). Such an unusual $\Delta$ value is consistent with a very strong anisotropy (structural and electronic) in the vicinity of $Fe^{3+}$. This drastic change ($\delta$, $\Delta$) can be related to a modification of the charge-transfer equilibrium *versus* temperature:

$$\begin{aligned} &Fe^{3+}(d^3_{xz,yz,xy}d^1_{z^2}d^1_{x^2-y^2}) + O^-(\underline{L}_{x^2-y^2}) \\ &\leftrightarrow Fe^{4+}(d^3_{xz,yz,xy}d^1_{z^2}d^0_{x^2-y^2}) + O^{2-} \end{aligned}$$

from the stabilization of the high-spin $Fe^{4+}$ ($Li^+$) at 300 K to that of the $Fe^{3+}$ (Li) ions at 77 K.

Consequently, the above result suggests that the energy level corresponding to the [$Fe^{3+}$–$O^-(\underline{L})$] state would be lower than that of the ($Fe^{4+}$–$O^{2-}$) state at low temperature. The high $\Delta_3$ value is induced both by the strong elongation of the host ($LiO_6$) polyhedra (structural distortion) and the presence of an electron hole in the oxygen environment (electronic anisotropy).

Compared to the compounds $A_{0.50}La_{1.50}Li_{0.50}$-$Fe^{4+}_{0.50}O_4$ ($A$ = Ca, Sr, Ba) prepared under oxygen pressures [20], where two different transition metal sites ($FeO_6$) have been detected *versus* the stacking of the perovskite planes along the $c$ axis, in the related $Cu^{''3+''}$ oxide $La_2Li_{0.50}Cu_{0.50}O_4$:$^{57}$Fe only one $Cu^{''3+''}$ site was detected. This difference is due to the variation in the covalency between ($Cu^{''3+''}$–O) and

($Li^+$–O) bonds compared to that between ($Fe^{4+}$–O) and ($Li^+$–O) bonds.

For a more comprehensive analysis of the local structure of $^{57}$Fe probe atoms within the $La_2Li_{0.50}Cu_{0.50}O_4$ structure, Mössbauer spectroscopy experiments at intermediate temperatures (from 77 K to 300 K) are in progress.

## Conclusions

In the oxide $La_2Li_{0.50}Cu^{3+}{}_{0.50}O_4$ with the $K_2NiF_4$-type structure and with a 1/1 (Cu/Li) cation ordering in the *xy* planes, the formal "$Cu^{3+}$" ions adopt a $d^9\underline{L}$ electronic configuration inducing both a very strong elongation of the ($CuO_6$) polyhedra and a significant value of the local crystal field energy.

The Mössbauer spectroscopic study of the cation substitution by $^{57}$Fe probe atoms has allowed to demonstrate two important phenomena: (i) due to the existence of both ($CuO_6$) and ($LiO_6$) polyhedra ($M$ = Cu, Li), it is necessary to take into account two cation substitutions: ($^{57}Fe \rightarrow Cu^{3+}$) and ($^{57}Fe \rightarrow Li^+$), (ii) three different sub-spectra have been observed: the first [Fe(1)] corresponding to $Fe^{4+}$ substituted for "$Cu^{3+}$" in the ($CuO_6$) sites, the second [Fe(2)] representing $Fe^{3+}$ trapped near the surface of the crystallites and correlated with the preparation process, and the third [Fe(3)] associated with $Fe^{3+}$ substituted in the $Li^+$ sites due to the small local crystal field energy.

Although the Mössbauer parameters of the Fe(1) and Fe(2) sub-spectra do not change with temperature, on the contrary a drastic modification is observed for iron substituted for lithium [Fe(3)]. The thermal evolution of this component has been interpreted by the charge transfer equilibrium $Fe^{3+} + O^-\underline{L} \leftrightarrow Fe^{4+} + O^{2-}$, which is shifted to the right with increasing temperature.

Mössbauer spectroscopy with $^{57}$Fe as a local probe appears very appropriate to follow the local electronic phenomena induced by the coexistence of very different chemical bonds in the same structure.

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