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Evidence of the Anomalous Charge State $^{57}Fe^{4+}$ in the Nuclear Decay of $^{57}Co^{3+}$

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The first observation of the elusive Fe^{4+} charge state coming from the nuclear decay of $^{57}Co^{3+}$ has been found in the Mössbauer emission spectra of $^{57}Co:La_2Li_{0.5}Co_{0.5}O_4$. A Ti-doped sample was prepared in order to show that the Fe^{4+} fraction can be conveniently monitored. Both results were predicted on the basis of the electronic energy-band scheme of these oxides.

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Capture of an inner-shell electron by a ^{57}Co nucleus transforms the ^{57}Co species into $^{57}Fe^{m+}$ having an inner-shell hole in its electronic structure. Such an event is followed by an electron-vacancy cascade, which generates in turn an Auger-electron cascade that leaves the atom in an ionized state.[1]

The 14.4-keV γ ray emitted in the final step of the nuclear decay of the ^{57}Co probe can be analyzed by Mössbauer spectroscopy; the Mössbauer spectrum reveals the valence state and local environment of the ^{57}Co-atom probe about 10^{-7} s after its decay. If the Auger electrons ejected from the atom probe by the intra-atomic cascade are not recaptured in a time $\tau \leq 10^{-7}$ s, the probe atom exhibits the Mössbauer spectrum of a more positive ionic state. Such a situation may occur in an insulator, and both $^{57}Fe^{3+}$ and $^{57}Fe^{2+}$ daughter ions of $^{57}Co^{2+}$-ion probes have been observed in Mössbauer emission studies of *p*-type ^{57}CoO.[2] The appearance of the higher charge state has been related to the semiconducting properties of the oxide.[3]

In some recent papers,[4] we have reported the Mössbauer emission spectra from ^{57}Co probe atoms substituting for nickel in *p*-type $^{57}Co:La_2NiO_4$. In this case, the cobalt atoms capture the mobile holes of a narrow $Ni^{3+/2+}$ band, thereby becoming $^{57}Co^{3+}$-ion probes. Nevertheless, no higher-valent $^{57}Fe^{4+}$-ion daughter was observed. We pointed out that this finding was consistent with a predicted placement of the $Fe^{4+/3+}$ couple below the Fermi energy in this compound.

Several other studies of Mössbauer emission spectra from $^{57}Co^{3+}$-ion probes have similarly failed to observe any evidence of a $^{57}Fe^{4+}$-ion daughter,[5] but no physical reason was advanced as to why this should be so. Therefore we used our analysis of $^{57}Co:La_2NiO_4$ to predict that the Mössbauer emission spectra of *p*-type $^{57}Co:La_2Li_{0.5}Co_{0.5}O_4$ should exhibit a $^{57}Fe^{4+}$-ion daughter.[4] In this paper we present experimental data that establish the correctness of this prediction, and we show how Mössbauer emission spectroscopy can be used to study the semiconductor properties of some materials.

Following the procedure of Demazeau *et al.*,[6] we prepared $La_2Li_{0.5}Co_{0.5}O_4$ by dissolving stoichiometric proportions of the corresponding nitrates in diluted HNO_3. After decomposition at low temperature, the sample was annealed in air for 10 h at 800 °C. To compensate for the sublimation of Li_2O that takes place at about 800 °C, a 30% excess of $LiNO_3$ was added to the solution before calcining.

The radioactive probe atoms were introduced by adding a drop of diluted $^{57}CoCl_2$ on a pellet of the presynthesized oxide. After water evaporation under an infrared lamp, the pellet was again annealed at 800 °C for 6 h. Nonradiative samples were similarly prepared for x-ray analysis.

The x-ray pattern, obtained with Cu *Kα* radiation and a two-circle diffractometer, could be completely indexed in the tetragonal cell (*I4/mmm*) of the K_2NiF_4 structure. The cell parameters $a = 3.780(2)$ Å and $c = 12.604(2)$ Å are in close agreement with those previously reported[6] for this compound. No additional reflections indicative of Li^+, Co^{3+} ordering in the perovskite intergrowth layers were detected; by using a Guinier camera, Demazeau *et al.*[6] were able to observe very weak superstructure lines.

In order to investigate the influence of donor impurities on the Mössbauer emission spectrum, 1% titanium substitutions for cobalt were prepared; x-ray analysis did not show any structural modification due to this substitution.

The Mössbauer spectra were recorded at room temperature with a constant-acceleration drive system, a single-line (SS) absorber, and a 200-channel analyzer.

As shown in Fig. 1, the Mössbauer emission spectrum of $^{57}Co:La_2Li_{0.5}Co_{0.5}O_4$ has been fitted with a single quadrupole doublet [$\Delta Q = 1.02(2)$ mm/s] having

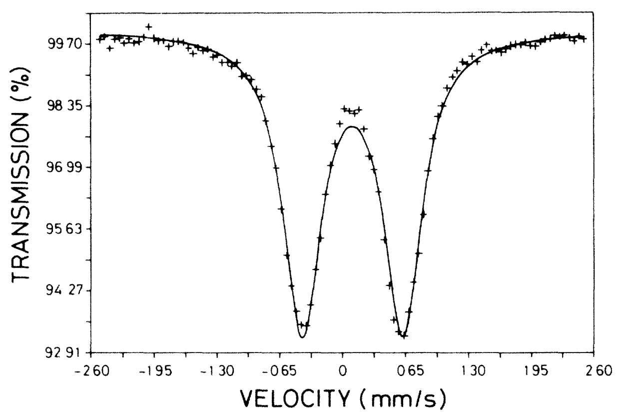

FIG. 1. Room-temperature Mössbauer emission spectrum of *p*-type ^{57}Co:$La_2Li_{0.5}Co_{0.5}O_4$ obtained with a SS absorber.

an isomer shift (IS) of $+0.18(1)$ mm/s with respect to α-Fe. That this isomer shift is characteristic of a localized, high-spin, octahedral-site $Fe^{4+}(t_2^3e^1)$ configuration is apparent from a comparison with the IS of -0.19 mm/s reported[7] for isostructural $La_{1.5}Sr_{0.5}Li_{0.5}Fe_{0.5}O_4$ (absorption experiment); the metallic perovskite $SrFeO_3$, which has delocalized *e* electrons and evidence of the onset of high-spin–low-spin crossover,[8] has an IS of 0.0 mm/s.[9] Therefore we conclude that in our nominal composition $La_2Li_{0.5}Co_{0.5}O_4$, which contains Co^{3+} ions, the $^{57}Co^{3+}$ ions are all transformed into $^{57}Fe^{4+}$ ions. In fact, some Li^+-ion loss is expected to convert a small fraction of the cobalt to Co^{4+} ions, but the probability that a ^{57}Co is in a $^{57}Co^{4+}$ state must be extremely small. Therefore, the $^{57}Fe^{4+}$ daughter ions must be higher-valent states derived primarily from $^{57}Co^{3+}$ ions.

The room-temperature spectrum from the Ti-doped sample is shown in Fig. 2. The best fit is obtained with a superposition of three quadrupole doublets. In order to avoid a strong correlation between the fitting parameters, the linewidths were constrained to be equal. Table I summarizes the data obtained from the fit. The most intense doublet is similar to the one we found in the pure sample; it corresponds to a high-spin, localized Fe^{4+}-ion state. The least intense doublet has a room temperature IS of 0.33 mm/s with respect to α-Fe, which is typical of the high-spin octahedral-site configuration $Fe^{3+}(t_2^3e^2)$.[10] The third doublet has an IS of -0.28 mm/s with respect to α-Fe at room temperature, which is a value intermediate between those of high-spin and low-spin Fe^{3+} ions[11]; it can therefore be assigned to the intermediate-spin Fe^{3+}-ion configuration $(d_{xy}d_{zx})^3d_{xy}^1d_{z^2}^1d_{x^2-y^2}$ made available by the important tetragonal distortion ($c/a > 1$) of the octahedral site.[6]

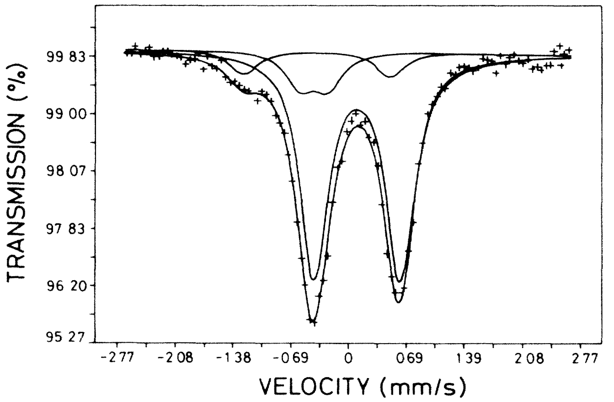

FIG. 2. Room-temperature Mössbauer emission spectrum of ^{57}Co:$La_2Li_{0.5}Co_{0.5-x}Ti_xO_4$, $x \approx 0.005$, obtained with a SS absorber.

TABLE I. Mössbauer emission data from $^{57}Co^{3+}$ decay. IS, ΔQ, Γ, A, and χ^2 are the isomer shift, the quadrupole splitting, the linewidth, the percentage of the total area, and the quality-of-fit parameter, respectively. The usual convention of positive velocity for source and absorber approaching each other is used.

Sample	IS (mm/s)	ΔQ (mm/s)	Γ (mm/s)	A (%)	χ^2
p-$La_2Li_{0.5}Co_{0.5}O_4$	+0.18(1)	1.02(1)	0.44(1)	100	2.3
Ti doped	+0.18(1)	1.02(1)	0.40(0)	79	2.1
	−0.28(4)	1.72(4)	0.40(0)	9	
	−0.33(4)	0.40(10)	0.40(0)	12	

Demazeau *et al.*[6] have reported a Mössbauer absorption spectrum for ^{57}Fe:$La_2Li_{0.5}Co_{0.5}O_4$ with IS of $-0.19(1)$, 0.25(2), 0.37(5) mm/s and $\Delta Q = 1.08(2)$, 1.84(9), 0.61(9) mm/s that is similar to the spectrum of our Ti-doped sample in which $^{57}Fe^{3+}$ daughter ions are established. The coexistence of high-spin and intermediate-spin $^{57}Fe^{3+}$ ions with high-spin $^{57}Fe^{4+}$ ions is a consequence of the D_{4h} distortion of the coordination polyhedron of a Co^{3+} ion in the ordered $La_2Li_{0.5}Co_{0.5}O_4$ structure[6] (see Fig. 3); the relative concentrations of the species depend upon tempera-

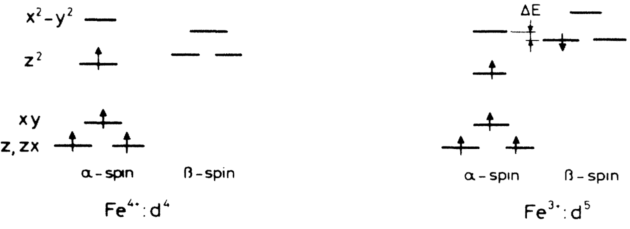

FIG. 3. Schematic crystal-field splitting of one-electron $3d$ energy levels of Fe^{3+} and Fe^{4+} ions in D_{4h} point symmetry.

ture and the relative position (ΔE) of the majority-spin $d_{x^2-y^2}$ and the minority-spin $d_{yz}d_{zx}$ orbitals.

Of particular interest for the discussion of this paper is the mechanism responsible for the appearance of the higher-charge state $^{57}\mathrm{Fe}^{4+}$ and the introduction of $^{57}\mathrm{Fe}^{3+}$ daughters by tatanium impurities. We begin the discussion with a summary of the relevant features of the band structure of $^{57}\mathrm{Co}$:$\mathrm{La_2NiO_4}$ in which no $^{57}\mathrm{Fe}^{4+}$ daughters were observed.[4]

Stoichiometric $\mathrm{La_2NiO_4}$ is a narrow-gap semiconductor; placement of E_F above the O^{2-} ($2p^6$) band defines formal nickel valence states. A tetragonal ($c/a > 1$) distortion of the Ni^{2+}-ion octahedral sites and the Ni-O-La-La-O-Ni c axis coupling vs Ni-O-Ni basal-plane coupling splits and half-filled e_g orbitals of Ni^{2+} ions into strongly correlated d_{z^2} orbitals oriented along the c axis and an itinerant $\sigma^*_{x^2-y^2}$ band of $d_{x^2-y^2}$-orbital parentage. The basal-plane Ni-O-Ni interactions are of sufficient magnitude that only a small correlation gap is anticipated in the $\sigma^*_{x^2-y^2}$ band; a larger correlation splitting of the d_{z^2} orbitals places the filled $d^1_{z^2}$ level discretely below the top of the lower $\sigma^*_{x^2-y^2}$ band and the empty $d^2_{z^2}$ level discretely above the bottom of the upper $\sigma^*_{x^2-y^2}$ band. As normally prepared, $\mathrm{La_2NiO_4}$ contains native defects that render it p type, and so the Fermi energy E_F is displaced toward—if not into—the lower $\sigma^*_{x^2-y^2}$ band and away from the upper $\sigma^*_{x^2-y^2}$ band. This displacement introduces mobile $\sigma^*_{x^2-y^2}$-band holes to make $\mathrm{La_2NiO_4}$ a p-type conductor.[12]

Substitutional Co impurities should have a $\mathrm{Co}^{3+/2+}$ ($3d^7$) redox energy some 0.5 eV above E_F.[13] Therefore, a $^{57}\mathrm{Co}$ impurity would not exist as Co^{2+} in p-type Co:$\mathrm{La_2NiO_4}$; it loses an electron to the holes in the lower $\sigma^*_{x^2-y^2}$ band to become $^{57}\mathrm{Co}^{3+}$. On the other hand, an octahedral-site $\mathrm{Fe}^{4+/3+}$ redox level lies discretely below the octahedral-site $\mathrm{Ni}^{3+/2+}$ level in an oxide,[13] and so any $^{57}\mathrm{Fe}^{4+}$ daughter state formed by nuclear decay of a $^{57}\mathrm{Co}^{3+}$ ion in Co:$\mathrm{La_2NiO_4}$ would capture a $\sigma^*_{x^2-y^2}$-band electron within 10^{-7} s to give only a $^{57}\mathrm{Fe}^{3+}$ Mössbauer emission spectrum. In fact, only the $^{57}\mathrm{Fe}^{3+}$ daughter ion was found in this case.[4]

In $\mathrm{La_2Li_{0.5}Co_{0.5}O_4}$, ordering in the basal planes creates Co-O-Li linkages and hence a localization of the $d_{x^2-y^2}$ electrons. In this case, oxidation of the material creates Co-trapped holes that introduce discrete, Co^{4+}-ion centers. If the high-spin $\mathrm{Fe}^{4+/3+}$ redox energy lies above the $\mathrm{Co}^{4+/3+}$ redox energy, as predicted,[4] then any Auger electron ejected from the daughter $^{57}\mathrm{Fe}^{3+}$ ion will become trapped at a Co^{4+} ion, thus producing a $^{57}\mathrm{Fe}^{4+}$ daughter ion:

$$^{57}\mathrm{Fe}^{3+} + \mathrm{Co}^{4+} \rightarrow {}^{57}\mathrm{Fe}^{4+} + \mathrm{Co}^{3+}.$$

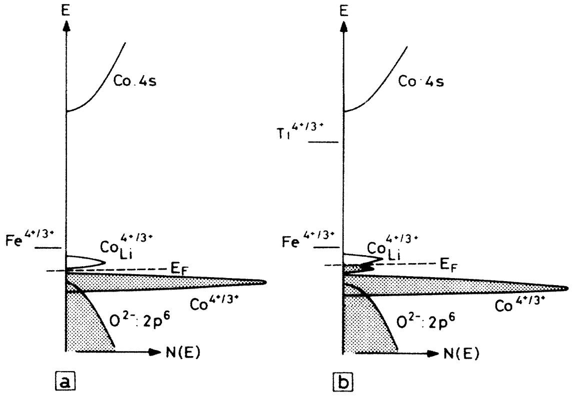

FIG. 4. Schematic energy diagrams illustrating the Auger-electron capture process at Co^{4+} associated with a native defect (Li^{+}-ion vacancy) in a (a) p-type sample, and (b) Ti-doped sample.

This situation is illustrated in Fig. 4(a). In this figure the $\mathrm{Co}^{4+/3+}$ level corresponds to a Co($3d^6$) configuration; it is the energy of a Co^{3+}-ion configuration when occupied, of an acceptor level at the Co^{4+} if empty. The $\mathrm{Co}_\mathrm{Li}^{4+/3+}$ level is shown empty and raised above the occupied $\mathrm{Co}^{4+/3+}$ by both the electrostatic attraction between the hole and the Li impurity and the local reorganization energy at a Co^{4+} ion.

The relative fraction (A_4/A_3) of Fe^{4+} and Fe^{3+} in the emission Mössbauer spectrum will be given by the ratio of the probabilities (P_4 and P_3) of electronic-capture process in the $\mathrm{Co}_\mathrm{Li}^{4+/3+}$ levels and in the $\mathrm{Fe}^{4+/3+}$ levels, respectively. The probability P_4 (P_3) depends linearly on the concentration of Co^{4+}-ion (Fe^{4+}-ion) centers and its cross section σ_Co (σ_Fe) for electronic capture. Therefore,

$$A_4/A_3 = P_4/P_3 = [\mathrm{Co}^{4+}]\sigma_\mathrm{Co}/[\mathrm{Fe}^{4+}]\sigma_\mathrm{Fe}. \qquad (1)$$

For a given value of the ratio $\sigma_\mathrm{Co}/\sigma_\mathrm{Fe}$, the fraction of Fe^{4+} in the Mössbauer spectrum should rise if the $[\mathrm{Co}^{4+}]$ concentration is increased. Indeed, only the $^{57}\mathrm{Fe}^{4+}$-ion resonance should be observed if $P_4 >> P_3$.

Figure 4(b) illustrates the energy-band scheme if substitutional titanium impurities are present in Ti:$\mathrm{La_2Li_{0.5}Co_{0.5}O_4}$. The $\mathrm{Ti}^{4+/3+}$ level lies about 3 eV above the $\mathrm{Fe}^{4+/3+}$ level,[12] and so the titanium enters the structure as a donor ion compensating for the defects that create Co^{4+} ions:

$$\mathrm{Ti}^{3+} + \mathrm{Co}^{4+} \rightarrow \mathrm{Ti}^{4+} + \mathrm{Co}^{3+}.$$

It follows that Ti doping decreases the concentration of the neutral acceptor centers Co^{4+} and lowers the P_4/P_3 ratio. Therefore, a mixture of $^{57}\mathrm{Fe}^{4+}$ and $^{57}\mathrm{Fe}^{3+}$ should be observed in the Mössbauer spectrum. The data of Table I are consistent with such a relationship, which indicates that the introduction of about 1% of Ti into the structure only partially compensates for the Co^{4+}-ion population.

In earlier experiments[14] on Mössbauer emission spectroscopy of Ti-doped $^{57}Co_{1-x}O$ sources, the concentration of the higher-valent $^{57}Fe^{3+}$ daughter ion was found to decrease with increasing Ti concentration, and this finding can be rationalized with similar arguments.

In summary, we have confirmed our prediction[4] that the higher-charge-state $^{57}Fe^{4+}$ daughter ion of a $^{57}Co^{3+}$-ion decay could be found in *p*-type $La_2Li_{0.5}Co_{0.5}O_4$ and that the concentration ratio $[^{57}Fe^{4+}]/([^{57}Fe^{4+}]+[^{57}Fe^{3+}])$ can be reduced to less than 1 by doping with a donor cation. In addition, we have demonstrated that Mössbauer emission spectroscopy can be successfully used to monitor the electronic properties of some solids.

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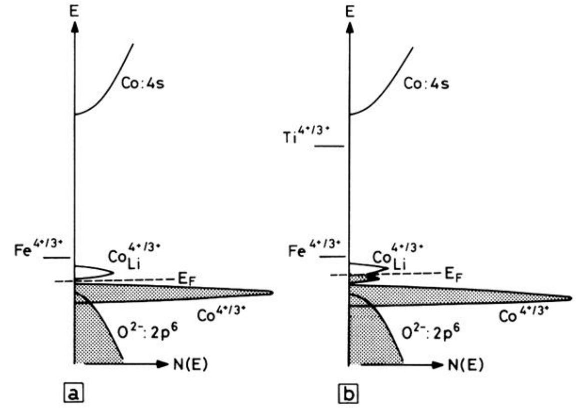

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