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*Strontium Doping Effects in
 $^{57}\text{Fe}:\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ Oxides*

by

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Abstract

A series of $^{57}\text{Fe}:\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ specimens (1% atomic of ^{57}Fe) with $x=0.0; 0.05; 0.10; 0.15; 0.20; 0.25; 0.30; 0.35$ and 0.40 were prepared by sintering in air and oxygen flow and studied by Mössbauer spectroscopy and X-ray diffraction. Taking into account the short range disorder two types of neighborhoods for iron in copper sites were proposed.

Key-words: Superconductors; Sr oxides; Mössbauer.

1 Introduction

At present, an important part of the investigation on high T_c superconducting ceramics is devoted to its characterization in a non-superconducting state, induced by an appropriate doping or deoxygenation.

In principle, La_2CuO_4 -based compounds has only one Cu site; however, the complexity of the crystal structure of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M=\text{Sr}, \text{Ba}, \text{Ca}$) system indicates that the actual situation is not so simple. In this p-type oxides, there is a broad maximum for the critical temperature T_c at $x=0.15$ [1,2] with Sr content, in contrast with the n-type $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ superconductors, where a narrow peak is detected when the Ce concentration is changed [3]. This behavior, is possibly revealing the coexistence of slightly different stoichiometries and/or the presence of an inhomogeneous electronic state for x far from the optimal value [4].

The size of the M^{2+} doping ions and their specific configuration of neighboring oxygen atoms are other points to be considered, as well as the low temperature transition (tetragonal to orthorhombic) in this system with its associated micro twin distribution [5]. Since all these facts point to the possibility of some local deformation or more than one type of neighborhood for copper in the lanthanum cuprate based compounds, it would be very important to obtain direct information concerning these local environments using a microscopic technique.

In this paper, we present a Mössbauer study of the $^{57}\text{Fe}:\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ doped system (LSCO) with $x = 0.0; 0.05; 0.10; 0.15; 0.20; 0.25; 0.30; 0.35$ and 0.40 , using the ^{57}Fe nucleus as a local probe.

The results can be described by two components which, in a first approach, have been assigned to iron species corresponding to different environments. Mössbauer results as a function of the Sr concentration are discussed taking into account previous reports on oxygen defects [6] and electron microscopy studies [7].

2 Experimental

Samples were obtained by using the standard ceramic technique. High purity La_2O_3 , SrCO_3 and CuO were well mixed in stoichiometric amounts, pressed and crushed successively after heat treatments in air at 900°C , 980°C and 1050°C (series I). This last treatment was repeated for a set of samples (series II) in flowing oxygen. The ^{57}Fe concentration was kept constant at 1% atomic (relative to copper) and the Sr content x covered a wide concentration range ($x = 0.0; 0.05; 0.10; 0.15; 0.20; 0.25; 0.30; 0.35$ and 0.40).

Lattice parameters were refined from X-ray powder patterns taken with Cu-K_α radiation.

Mössbauer spectra were collected at room temperature. The fits were performed assuming one, two or even three doublets in the Mössbauer spectra (the later case for high x concentration). In most of the cases the χ^2 values were lower for the proposal including two Fe sites with narrower line widths (ranging from 0.25 to 0.35 mm/s) in comparison to the fit with only one site. All the isomer shift (IS) values are relative to $\alpha\text{-Fe}$.

3 Results

X-ray powder diffraction patterns were obtained for all samples at room temperature. The lattice parameters dependence on the Sr concentration is shown in fig.1 for series I (a) and series II (b). The c axis length of the unit cell increases with Sr concentration in both series; however, it decreases for $x = 0.40$ as already observed [8].

Some typical Mössbauer spectra for samples from series II are shown in fig. 2. The asymmetry of the spectra becomes more evident as the strontium concentration increases. Some amount of iron can be present as two less intense doublets; the one observed for $x=0.25$ with quadrupole splitting $QS=0.40$ mm/s and isomer shift $IS=0.28$ mm/s (doublet C) is considered a spurious phase and is more intense in series I, disappearing after an appropriate heat treatment. The other one, ($QS= 0.70$ mm/s; $IS=0.12$ mm/s) present for $x=0.40$ (doublet D), may be due to a solubility limit for Sr in the structure. However, our attention was focused on the hyperfine parameters of the main absorption lines. Our conclusions were driven by following the variation of their hyperfine parameters.

Previous works on Mössbauer studies on the LSCO system [9,10] only report one Fe species; however, our best fits give two main doublets A and B with QS values varying with Sr concentration in the range of 1.81-1.19 mm/s and 1.55-0.88 mm/s, respectively. The dependence of the QS values with Sr concentration for species A is illustrated in fig. 3 for series I and II, showing a smooth decrease for both series. The behavior for-doublet B is similar but with lower absolute values (1.55 - 0.88 mm/s); The reported values of QS for samples with low Sr content move around 1.7-1.5 mm/s, when the one doublet fitting proposal is used [9]; so it seems to be really an average over the contributions coming from species A and B. The IS values (relative to iron) move close to 0.30 mm/s, evidencing a high spin Fe^{3+} state.

The dependence of the relative area for species A with strontium concentration (fig. 4), series I and II, exhibits fluctuations in both cases (from 80% to 20%), considering the remaining area corresponding to species B. Such fluctuations are rather unexpected despite it has also been observed by us in other batches of LSCO. For Ba and Ca doped samples it has been observed a rather different behavior [11,12]; in addition, the variation of the oxygen content and T_c with Ba and Ca doping is relatively different than those observed with strontium [1,13].

The presence of essentially two slightly different QS values reflects the existence of two or several types of environments, with possibly related different origins, as considered below.

4 Discussion

The observation of at least two Fe species (A and B) in LSCO is probably related to specific features of the K_2NiF_4 structure, as low temperature structural phase transitions, deformations and tilting of the oxygen octahedra surrounding the Cu or Ni sites and oxygen vacancies and interstitials, either in the La [14] or Pr [15] based compounds. In particular, as shown by XANES analysis [8], one source of distortion in strontium doped La_2CuO_4 is related to the removal of the apical oxygen and the existence of an interstitial oxygen defect trapped near the strontium atom. Tilting of oxygen octahedra, as suggested by

Imbert et al. [16] in strontium doped La_2CuO_4 , could be due to an association of the iron ions with a neighbouring charge defect. The fluctuations of the relative areas of A and B contributions show that these tiltings and deformations surrounding the Cu sites are associated to the content and location of the oxygen defects and also closely related to the thermal history of the sample.

The low temperature tetragonal-orthorhombic transitions are quite relevant to the microstructure. The strain energy associated with these transitions is minimized by the presence of coherent twin domains, and the temperature at which they take place depends on the size of the alkaline-earth ion used and its concentration [17]. A Convergent Beam Electron Diffraction (CBED) study [7] in quite homogeneous samples, free from the presence of second phases, revealed that there were short-range lattice variations at a scale of 100\AA .

The different types of defects mentioned above can take account of these variations. Whether or not this local disorder has a displacive and/or a chemical nature, it represents a source of different surroundings for the Cu sites. The attractive explanation that the perturbation of the local electronic structure at the Cu sites due to the presence of holes only induced by Sr doping is the source of a different environment cannot be kept, since these two species are also present in the undoped La_2CuO_4 parent compound. In addition, the different behavior of the hyperfine parameters and the relative areas of the Mössbauer spectra in the Sr-doped system in comparison with those reported for the Ba- and Ca doping [11,12], which also induce mobile holes at the Cu-O₂ planes, reflects that there are differences at microscopic scale.

Since in undoped La_2CuO_4 the appearance of microtwins is much less common [7], studies on this parent compound are particularly important. Jha et al [18] have reported a ^{57}Fe emission Mössbauer study on single crystals of La_2CuO_4 with very low ^{57}Co concentration (ppm). They succeeded to fit the spectrum with a single doublet with $QS = 1.76$ mm/s and $IS = 0.30$ mm/s, i.e., close to our values for species A. Ceramic polycrystalline samples, which inherently have higher strains, generally exhibit a more homogeneous size distribution of microtwin density than single crystals [7,18]. The fact that we have in our polycrystalline samples two iron species, even for the undoped compound, suggests that species B, with lower QS, is associated to structural defects.

To make an assignment for the two Fe species we have to discuss the local symmetry of the microstructures. At first glance, one would expect a higher value of QS for the contribution associated with short-range disorder. However, it should be reminded here that in this system the original oxygen octahedra surrounding the Cu sites are elongated significantly along the c-axis with the increase of Sr doping, as revealed through the systematic increase of the c/a ratio, measured by X-ray diffraction (fig.1). This intrinsic reduction of the cubic symmetry of the sites generates a high electric field gradient, even for a Fe^{3+} ion. A configuration with oxygen vacancies does not necessarily imply a still higher QS; actually, it would represent a local relax of the structure.

Information obtained from transport measurements can bring a further insight in connection with the nature of the short-range disorder. If oxygen vacancies appear associated to the onset of the interwoven twin domain structure, it would represent some kind of deoxygenated network generated through the crystal, surrounding not affected "islands". This was just the result obtained by resistivity measurements in intentionally deoxygenated samples in the LSCO system [19].

By considering all the facts discussed above, we propose that species B is sensing environments of the Cu sites affected in a larger extent by the different types of microscopic defects, while species A corresponds to less affected surroundings.

Really, the oxygen defects and the microstructure could probably generate more than two types of environments, but there is not enough resolution in the spectra to detect them.

5 Conclusions

Two types of neighborhoods for iron ions located at the Cu sites in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system are proposed using Mössbauer spectroscopy. The relative areas of the corresponding doublets fluctuate with Sr content ($0 \leq x \leq 0.40$) for samples annealed separately in air and oxygen, albite the respective absolute values differ from one batch to the other. Although the iron nuclei used as local probe can, of course, generate by themselves specific oxygen environments, we believe that the conclusions driven in this study are representative of the actual situation of the copper sites.

The discussion of recently reported results of microstructural and transport porperties studies, together with measurements on single crystals and oxygen defects are in agreement with the presence of two Fe species corresponding to doublets A (larger QS) and B (lower QS). The origin of these two contributions is related to the deformation of the copper site associated to octahedron tilting and oxygen defects and, consequently, to the microtwinned structure. Even if the average structure give only one Cu site, Cu atoms have slightly different environments, one of them more affected by defects (species B) than the other one (species A). The relative proportion depends on oxygen and strontium content and their distribution and related to the thermal history of the sample. A definitive interpretation in terms of specific oxygen configurations, however, can not be done yet.

A more detailed study correlating the microstructure of LSCO with the oxygen content and magnetic and electrical transport measurements is in course.

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Figure Captions

Figure 1 - Lattice parameters dependence on the Sr content (x) in the $^{57}\text{Fe}:\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ system for series I (air) and II (O_2).

Figure 2 - Mössbauer spectra for samples of $^{57}\text{Fe}:\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ series II (O_2) with different Sr contents. The different subspectra are indicated (see text for identification).

Figure 3 - Quadrupole splitting for species A as a function of Sr content (x) for series I (air) and II (O_2). Lines are a guide for the eye.

Figure 4 - The dependence of the relative area on Sr content (x) for species A, series I (air) and II (O_2). Lines are a guide for the eye.

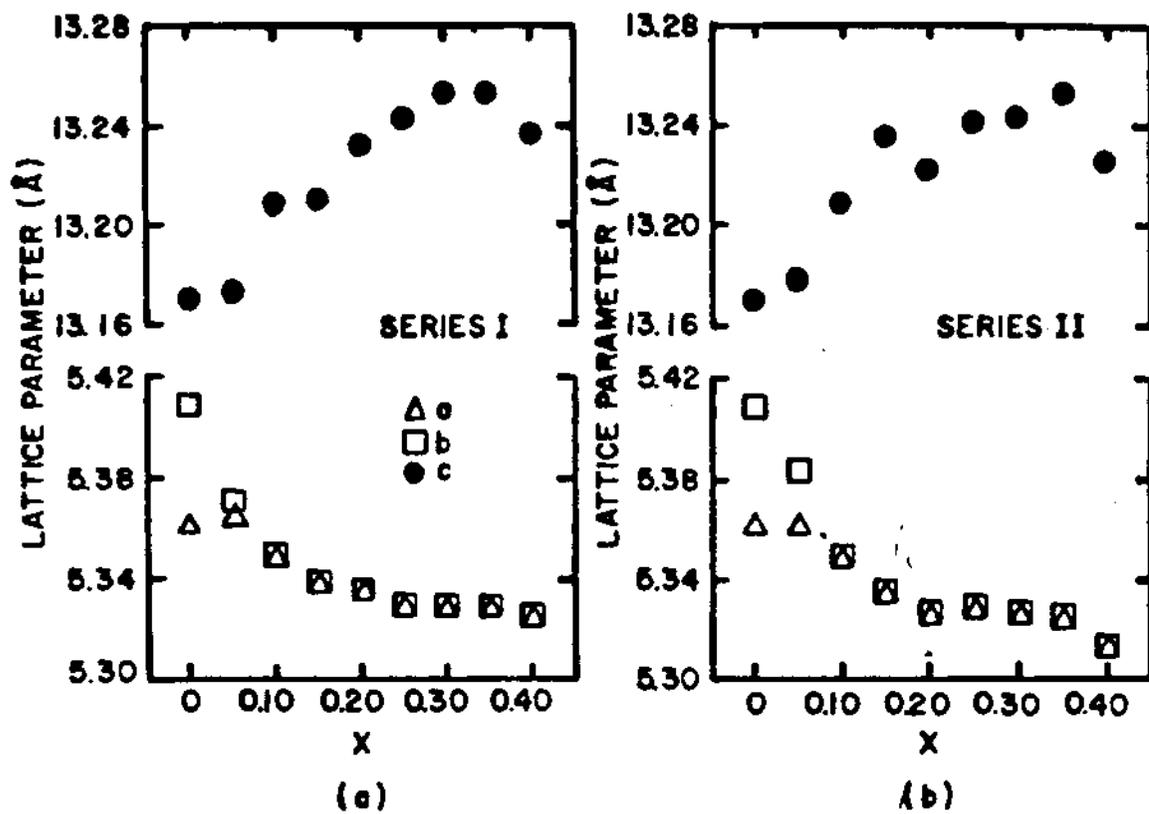


FIG. 1

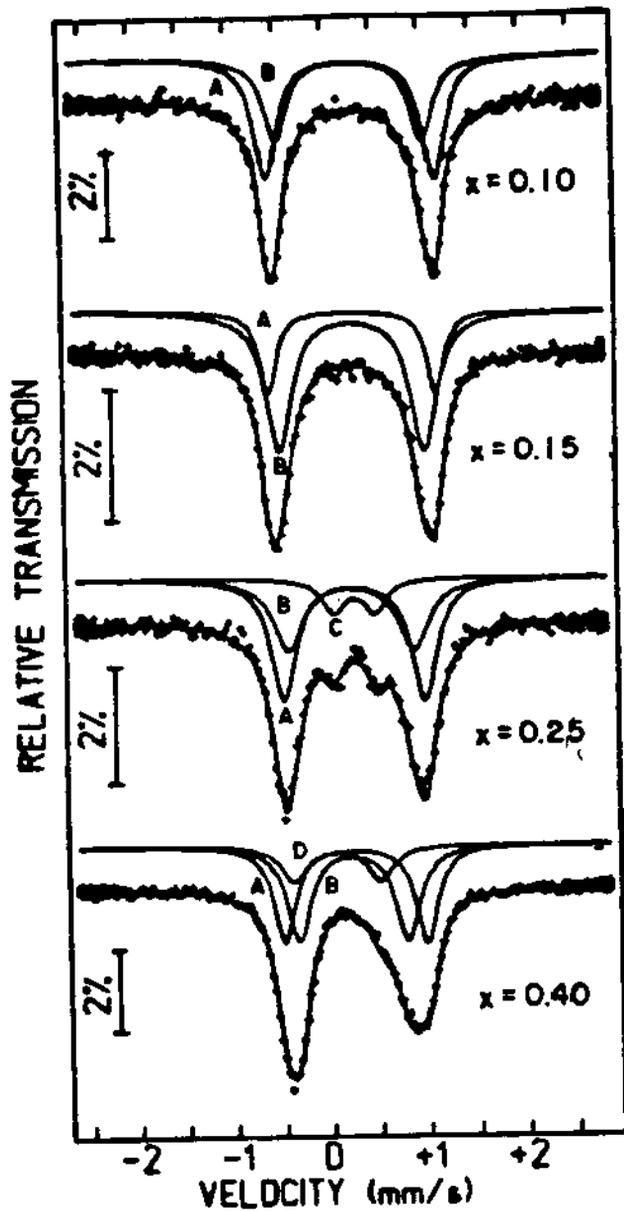


FIG. 2

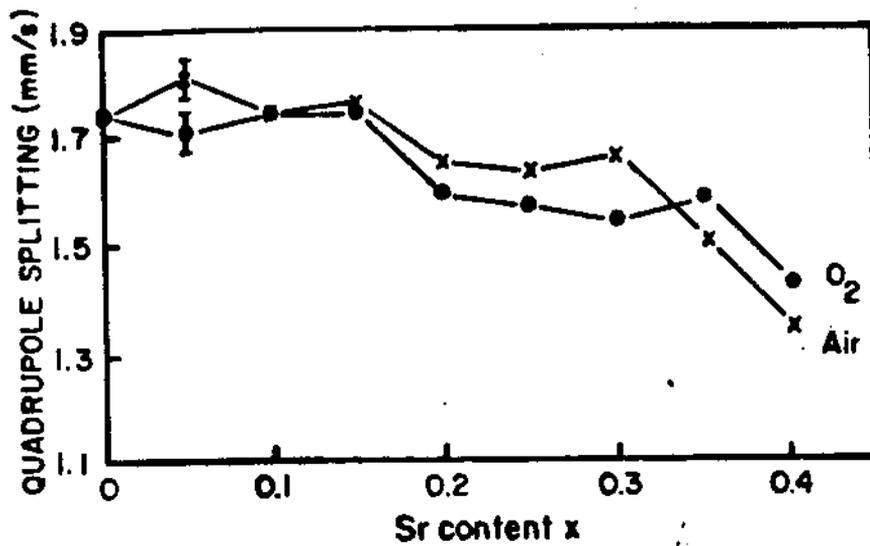


FIG. 3

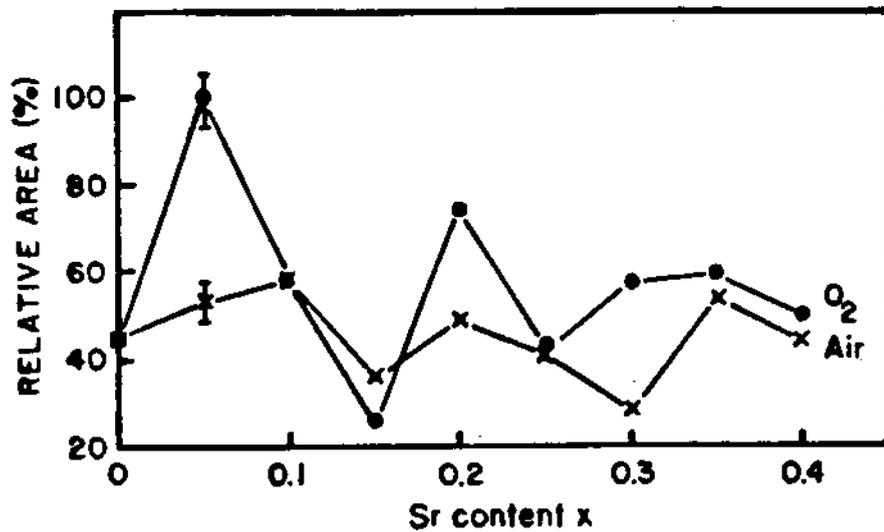


FIG. 4

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