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About the ionic state of iron in the Cu sites of the $Nd_{2-x}Ce_xCu_{2-y}Fe_yO_{4-\delta}$. superconductor.

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The substitution of a small fraction of Cu atoms by Fe atoms in the cooper oxide superconductors has proven to be useful in sensing, with Mössbauer spectroscopy, the local surroundings of the Cu sites of their structures. In this work we report the results of such substitution in the $Nd_{1.85}Ce_{0.15}Cu_2O_{4-\delta}$ system. After annealing in argon at high pressure and temperature, a strong quadrupole doublet is observed indicating that the iron atoms have been incorporated into the superconductor structure.

Despite the great interest in n-type superconductors, very few studies have been made regarding the effect that substitution of part of the cooper atoms by other metallic atoms has on the properties and structure of these type of superconducting systems. This lack of work has its origin in the difficulty to incorporate metallic atoms to the T' structure of these systems. In particular, the substitution of Cu atoms by Fe atoms would allow the use of Mössbauer spectroscopy in the study of the electric and magnetic local properties around the sites where the Fe atoms go to. The attempts to incorporate Fe (or Co) atoms to the $Nd_{1.85}Ce_{0.15}Cu_2O_{4-\delta}$ system have failed due to the tendency of iron (and Co) to form $NdFeO_3$ and $CeFeO_3$ orthoferrites[1]. In this work, we report the first successful procedure to attain this incorporation, together with the Mössbauer parameters of the resulting spectra. With this information, we propose that iron atoms do substitute Cu atoms and we compare the present results with those obtained in the closely related $La_{2-x}Sr_xCu_{2-y}Fe_yO_{4-\delta}$ system.

The sample was prepared by solid state reaction, starting from stoichiometric quantities of high purity oxides; the iron oxide used was 73% enriched $^{57}Fe_2O_3$ in such a quantity as to make $y = 0.01$. Due to the difficulty of obtaining a pure phase, the sample was grounded, pressed and calcinated many times until a pure phase was obtained, as judged by X-ray diffractogram. In order to attain superconductivity, the sample was finally annealed 36 hours at 1000 °C in flowing argon.

The Mössbauer sample was prepared by grinding a small piece of the pellet and fitting the resulting powder into a sample holder. All spectra were taken at room temperature in transmission geometry with a constant acceleration spectrometer. The Mössbauer spectrum of the as-sintered sample consist of two magnetic subspectra due to $NdFeO_3$ and $CeFeO_3$ orthoferrites that were not detected by X-rays, due to the sensibility of this technique. The pathfinder to achieve the incorporation of iron to the structure was to anneal the sample in a reductive atmosphere at a temperature higher than the decomposing temperature of the orthoferrites. After annealing in argon, a small quadrupole doublet starts to appear, superimposed to the two sextets (Figure 1). It is only when the sample is annealed at 970 °C in argon at high pressure (10 MPa) that the magnitude of the quadrupole doublet increases with a concomitant decrease of the magnitude of the magnetic subspectra, until they almost disappear (Figure 2). When a low velocity scan is done, what seem to be a single quadrupole

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doublet is actually composed by two doublets that can be related to different environments of the iron atoms. Actually, van Aken et al[2] have detected orthorhombic and tetragonal phases in the NdCe system with different Nd/Ce distributions, the first being poor and the last rich in Ce. They also found out that, in the reduction process, the Ce poor phase losses more oxygen than the tetragonal phase.

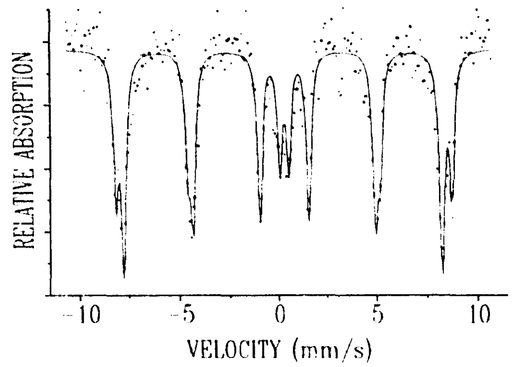

Figure 1. Sample annealed in argon at low pressure.

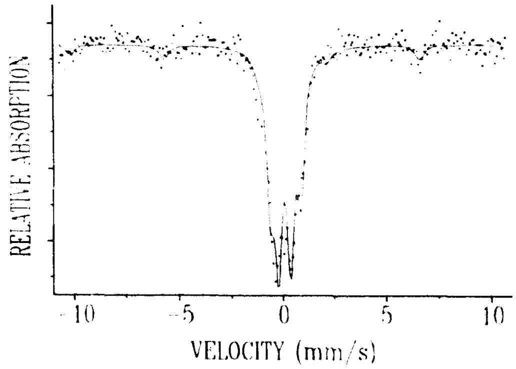

Figure 2. Sample annealed in argon at high pressure. The two magnetic subspectra have almost disappear.

The fitting of the spectra was done with a least squares restricted program using one magnetic sextet and two quadrupole doublets. The line widths were fixed to the smallest values that gave a good fit. Both isomer shifts (IS) are of the same order (0.17 and 0.14 mm/s), as they should, but their quadrupole doublets (ΔQ) have substantial differences (1.35 and 0.53 mm/s), indicating strong changes in the local surroundings of each site. On the basis of the ionic sizes and combined values of the IS and ΔQ of the doublets, we propose the following assignment: The weaker doublet (ΔQ = 1.35 mm/s and about half of the relative intensity of the other one) is to be associated with Fe(III), specially because its Mössbauer parameters are similar to those observed in the LaSrCu system[3]; on the other hand, we assign the strongest one, with ΔQ = 0.53 mm/s, with Fe(II). The observed ionic states of cooper in Fe undoped NdCe system are Cu^{2+} and Cu^{1+}, depending on the reduction process[4]. The tendency of iron to be in a 3+ state manifests itself by the formation of the Nd and Ce orthoferrites. It is only when a strong reduction at high temperature is done that these orthoferrites decompose and allow for the incorporation of the iron atoms into the structure. Nevertheless, changes must occur in the oxygen content of the system (as has been seen in the 1-2-3 system) so the possibility exists that a small fraction of the iron atoms in the cooper sites are surrounded by more oxygen atoms. This would explain that part of the iron atoms are in the +3 state, even if they are in the Cu sites. However, the higher oxygenation of the system would produce changes in the structure that must be investigated.

In conclusion, we have shown that by strong reduction of the NdCeCuFeO system, the iron atoms can be incorporated to the superconductor structure. The Mössbauer results are compatible with known previous results regarding to the oxygen mobility in this system. Further investigations are necessary in order to unambiguously decide the ionic states of the iron atoms and the influence that a higher oxygen content, due to the incorporation of Fe, would have in the structure of this system.

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