Mössbauer study of the $(Ru_{1-x}Fe_x)Sr_2GdCu_2O_{8-\delta}$ system and two of its possible impurities: $SrRuO_3$ and Gd_2CuO_4

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Abstract Mössbauer spectra of a series of samples of the weak ferromagnetic $(Ru_{1-x}Fe_x)$ $Sr_2GdCu_2O_{8-\delta}$ system reveal the existence of three dissimilar sites where the Fe atoms can go into the structure. The Mössbauer parameters of the three observed quadrupole doublets, together with the relative population on each site, allow the following site assignment for the iron atoms: Fe^{3+} in four-fold planar coordination at Ru sites; Fe^{3+} in five-fold pyramidal coordination also at Ru sites and Fe^{2+} or Fe^{3+} in five-fold coordination at Cu sites. This assignment implies the formation of oxygen-vacancies at the charge reservoir (the RuO_2 planes) that affect the structure and the superconducting and magnetic properties of the undoped system. Moreover, a close correlation between the oxygen content, calculated through the Mössbauer data, and the measured cell volume is established. We also report the Mössbauer spectra of two compounds ($SrRu_{0.95}Fe_{0.05}O_3$ and $Gd_2Cu_{0.95}Fe_{0.05}O_4$) that could be formed as impurities during the synthesis of our samples.

Keywords Mössbauer spectra · Quadrupole doublets · Superconductor

1 Introduction

In the search for new high-T_c superconductors, the emergence of the ruthenate-cuprates $RuSr_2GdCu_2O_8$ (Ru-1212) and $RuSr_2(RE_{1-x}Ce_x)_2Cu_2O_{10}$, RE=Gd, Eu (Ru-1222), has raised much interest by virtue of the coexistence of two antagonistic phenomena: long-range ferromagnetic order and superconductivity (SC) [1–3]. Although there is widespread

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consensus in that SC originates in the CuO_2 planes and the magnetic order in the RuO_2 planes, details of the nature of both SC and magnetism require further understanding.

Our study refers only to compounds of the Ru-1212 type, so in what follows we will refer only to them.

The description of the tetragonal Ru-1212 type structure (space group: P4/mmm) is based on the well-known $(RE)Ba_2Cu_3O_\delta$ structure (RE-123, where RE stands for rare earth), and has been described elsewhere [4–5]. In the former, RuO_2 planes replace the CuO chains of the later in such a way that the Ru atoms occupy the centers of RuO_6 octahedra, which arrangements resemble that of the $SrRuO_3$ itinerant ferromagnet [6–7]. It is believed that the RuO_2 planes are the charge reservoir responsible for doping holes into the superconductive CuO_2 planes [4, 7], playing a role similar to that of the CuO chains in the RE-123 system.

The coexistence of a ferromagnetic transition (T_{CW}=132 K, associated with the Ru sublattice) and superconductivity (T_c=30 K) in Ru-1212 was established through magnetization and muon-spin rotation experiments [3]. However, by means of neutron diffraction experiments, it has been shown that the dominant magnetic interactions present in $RuSr_2(RE)Cu_2O_8$ are of the antiferromagnetic (AFM) type, with the Ru magnetic moments forming the *G*-type AFM structure [8–9]. Two schemes have been put forward to explain the observed ferromagnetism: (a) It has been suggested that the Ru magnetic moments tilt in such a way as to give a net magnetic moment perpendicular to the *c*-axis [10] and (b) a ferrimagnetic ordering of different magnetic moments of the Ru atoms due to a mixed 4+/5+ valence state [11].

In order to explain SC, McLaughin et al. [4, 7] propose a self-doping mechanism involving the Ru:t_{2g} and the Cu:$3d_{x^2-y^2}$ bands. Since the $RuSr_2GdCu_2O_8$ compound is found to be oxygen-stoichiometric, it is then assumed that the oxidation state of Ru should be 5+, and that of copper 2+. However, the proposed self-doping mechanism would imply a 4+/5+ mixed-valence state of Ru (as has been experimentally determined [12, 13]) and a 2+/3+ mixed-valence state of Cu. The distribution of holes between the two bands may then be written as $Ru^{5-2p}Sr_2Gd(Cu^{2-p})_2O_8$ [14].

In the strive to find new superconductor materials, many studies have been done in which one or more of the elements present in the different superconductor families are substituted by others. It has been found that the substitution of a fraction of the Cu atoms by other 3d-metals rapidly downgrades the T_c of the RE-123 and RE-124 families, especially if the substitution takes place in the CuO_2 planes [7, 15–20], so it is important to determine where the 3d-metal atoms go to in the superconductor structure.

When some of the atoms of one of the elements are substituted by Fe atoms, Mössbauer spectroscopy (MS) provides a local-probe to determine the sites where the substitutions take place, by measuring the crystal symmetry distortions (quadrupole-splitting), the charge and spin-states of the Fe-ions (isomer-shift) and their magnetic surroundings (hyperfine-field). In particular, as the charge state of the Fe atoms can hardly be 5+, changes in the doping mechanism and even in the oxygen stoichiometry are to be expected, affecting the crystal structure and, hence, the magnetic and transport properties of the system [21].

The main objective of the present research is to extend and complement previous magnetization results obtained in the $(Ru_{1-x}Fe_x)Sr_2GdCu_2O_{8-\delta}$ [22] and to make a cross confirmation, between X-ray and Mössbauer results, of where do the iron atoms go into the structure of the Ru-1212 compound.

We report results obtained with Mössbauer spectroscopy in compounds of nominal composition $(Ru_{1-x}Fe_x)Sr_2GdCu_2O_{8-\delta}$ (x=0, 0.025, 0.05, 0.075, 0.1 and 0.2) and of $SrRu_{0.95}Fe_{0.05}O_3$ and $GdCu_{0.95}Fe_{0.05}O_4$, the two principal impurities that can be formed during the synthesis process. We complement our study with powder X-ray diffraction and resistance *vs.* temperature measurements.

2 Experimental details

Polycrystalline samples of $(Ru_{1-x}Fe_x)Sr_2GdCu_2O_{8-\delta}$ (x=0, 0.025, 0.05, 0.075, 0.1 and 0.2), $SrRu_{0.95}Fe_{0.05}O_3$ and $Gd_2Cu_{0.95}Fe_{0.05}O_4$ were synthesized by solid-state reaction of stoichiometric quantities of RuO_2, $^{57}Fe_2O_3$ (99.999%), Gd_2O_3, CuO and $SrCO_3$. After calcination in air at 900°C, the material was ground, pressed into pellets and annealed in oxygen at 1,000°C during 72 h. Phase-identification of the samples was done with a Siemens D5000 X-ray diffractometer, using $Cu-K_\alpha$ radiation and a Ni filter. The peak-intensities were measured in steps of 0.02° for 14 s in the 2θ range 20–100° at room temperature and the crystallographic phases were identified by comparison with the X-ray patterns in the JCPDS database. Crystallographic parameters were quantified using a Rietveld refinement program, Rietica v 1.7.7 with multi-phase capability. The resistance *vs.* temperature curves were determined by the standard four-probe technique in a closed-cycle helium refrigerator. The room temperature Mössbauer spectra (MS) were recorded in transmission geometry with a constant acceleration spectrometer, using a ^{57}Co in Rh source. The low-temperature spectra were recorded with the samples kept in a closed-cycle helium refrigerator. The spectra were fitted with the Recoil 1.05 program.

3 Results and discussion

Figure 1 shows the X-ray diffraction patterns for the $(Ru_{1-x}Fe_x)Sr_2GdCu_2O_{8-\delta}$ samples. The analysis of the data indicates that the spectra indeed correspond to the tetragonal Ru-1212 structure. The faint features (marked as + in Fig. 1) observed at $2\theta\approx32$ and 48° correspond to $SrRuO_3$ (IDDE n° 28-1,250) or Gd_2CuO_4 (IDDE n° 24-0422) [23]; there is also a very faint feature (marked as * in the same figure) associated with $Sr_3(Ru,Cu)O_7$. The X-ray diffraction patterns were Rietveld-fitted using a space group P4/mmm (n° 123). In the process of refinement, the substitution of Fe ions in the Ru and Cu sites and the presence of $SrRuO_3$, $Sr_3(Ru,Cu)O_7$ and Gd_2CuO_4 phases were considered. As an example, one of the fitted patterns (x=0.0) is shown in Fig. 2.

The cell-parameters, cell-volume and Fe occupation numbers obtained from the results of the structural refinement are listed in Table 1.

Figure 3 shows the room-temperature evolution of the lattice parameters for the $(Ru_{1-x}Fe_x)Sr_2GdCu_2O_{8-\delta}$ samples as a function of Fe-content (x). We observe that, as x grows, the *a*-axis lattice parameter increases slightly and *c*-axis lattice parameter decreases at a higher rate. As a result, the unit-cell volume diminishes slightly.

Figure 4 shows the normalized resistance as a function of temperature for the studied samples. For x=0, the sample shows a T_c-onset at 40.5 K and zero resistance at 19 K, with a slightly metallic behavior at high temperatures. When x=0.025, the onset appears at T_c=26.3 K but zero resistance cannot be accomplished up to 14 K (T_c=10 K is an extrapolated value). A small kink at 135 K is also observed, similar to that reported in Fang et al. [24] which origin could be associated with the magnetic transition. For $x>0.025$, the resistance curves show a strong semiconductor behavior, with no sign of a superconducting transition.

No significant qualitative changes were observed in the shape of the MS of the Ru_{1-x} Fe_x-1212 series, so we present, in Fig. 5a and b, the spectra of only the lowest and

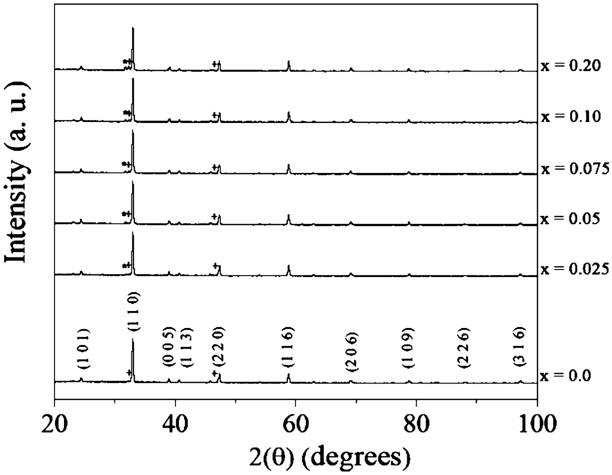


Fig. 1 X-ray diffraction patterns for the $(Ru_{1-x}Fe_x)Sr_2GdCu_2O_8$ samples. The symbols + and * point out peaks of $SrRuO_3$ or Gd_2CuO_4 and $Sr_3(Ru,Cu)O_7$ impurity phases, respectively

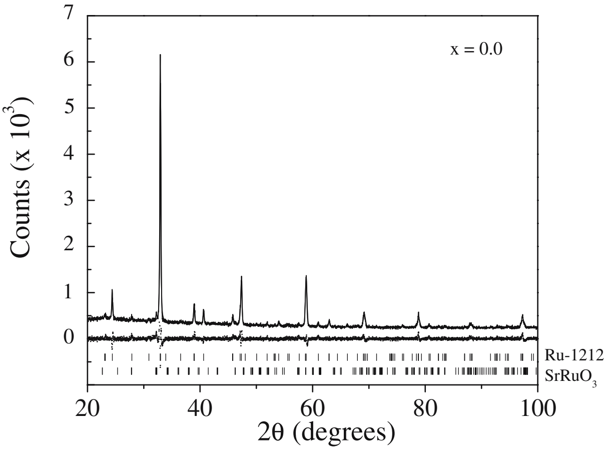


Fig. 2 Rietveld refinement of the X-ray diffraction pattern for the x=0.0 sample. Experimental spectrum (*dots*), calculated pattern (*continuous line*), their difference (*middle line*) and the calculated peak positions (*bottom*)

highest Fe concentrations, including the fitted curves and the corresponding sub-spectra. In all cases, good quality fitting could only be achieved with three quadrupole doublets (labelled A, B, and C in Table 2).

Considering the possible valence-states and ionic-radii of the Fe atoms, there are only two sites where the Fe-atoms can substitute in the structure: the Ru and the Cu sites. The fact that we observe three doublets must be associated with different charge-distribution environments around these sites. In Table 2, we summarize the Mössbauer parameters (quadrupole-splitting ΔQ, isomer-shift IS and line-width Γ) for all the studied samples; and the relative intensity of each site (% occupancy).

Previous results in the related Y123 and Y124 structures [25–28] also reported Mössbauer spectra with three quadrupole doublets whose ΔQ values are approximately 1.9, 1.1 and 0.6 mm/s.

Sufficient arguments have been put forward to sustain that the ΔQ≈0.6 mm/s doublet (doublet B in our case) must be associated with Fe in the Cu(2) sites of the structure, in five-fold pyramidal coordination [29] and, although the small value of its IS suggests that

Table 1 Rietveld refinement results for the $(Ru_{1-x}Fe_x)Sr_2GdCu_20_8$ system

Rietveld refinement results

	X	0.0	0.025	0.05	0.075	0.10	0.2
	a(Å)	3.8369(3)	3.8373(2)	3.8385(2)	3.8393(4)	3.8395(4)	3.8412(4)
	c(Å)	11.563(3)	11.557(2)	11.555(3)	11.542(3)	11.539(4)	11.528(4)
	V($Å^3$)	170.23(3)	170.18(2)	170.25(2)	170.13(4)	170.11(4)	170.09(4)
Ru	N(Fe)	–	0.01(1)	0.04(2)	0.06(2)	0.07(1)	0.10(1)
Cu	N(Fe)	–	0.02(2)	0.01(3)	0.02(2)	0.03(2)	0.08(2)

Space group: P4/mmm; cell parameters: *a* and *c*; cell-volume *V*; iron occupancy parameters: N(Fe)

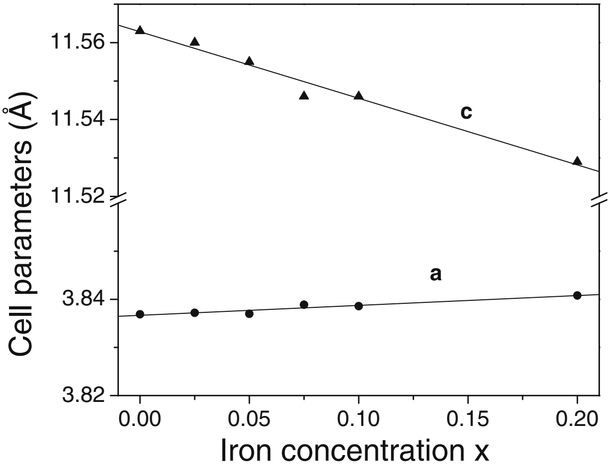


Fig. 3 Crystal lattice parameters as a function of Fe content x

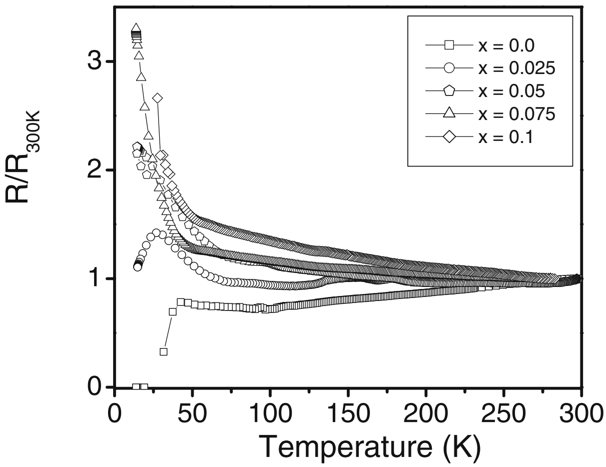
the charge state of iron in this site should be +2, the joint values of the IS and ΔQ do not allow a conclusive assignment of the charge-state of Fe.

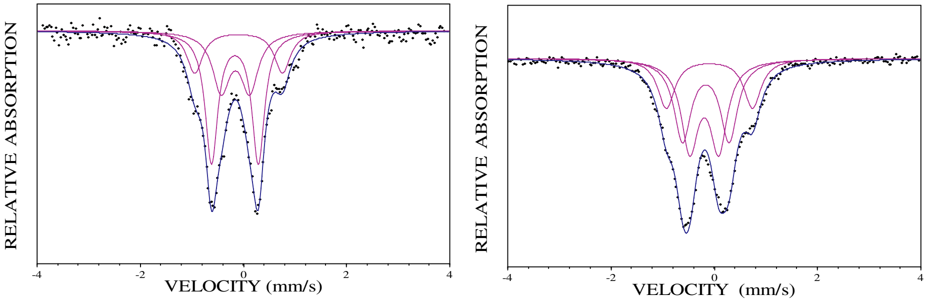
The guiding lines that we will use for the site assignment of the other two sites will be: a) the relative intensity of the quadrupole doublets in the Mössbauer spectra and b) the measured Fe occupation numbers, obtained from the Rietveld refinements.

There is a slight correspondence between the percent populations of doublets A+C with the occupation numbers N(Fe)-Ru, and the percent population of doublet B with the occupation numbers of N(Fe)-Cu. Considering the small iron content and the intrinsic sensitivity of X-ray diffraction and the high sensitivity of Mössbauer spectroscopy to detect minute changes in the ^{57}Fe content, we only take the X-ray occupation numbers as a sort of confirmation of the Mössbauer results. In Fig. 6 we show the percent population, obtained from the Mössbauer data, associated with the different doublets of the $(Ru_{1-x}Fe_x)\,Sr_2GdCu_2O_{8-\delta}$ system, where a tendency to a 50–50% occupation between doublets A + C and B can be observed as the iron content increases. That is, the population of the doublet A diminishes due to the growth of the populations of the other two doublets.

These facts and previous results and calculations [29] for different oxygen environments of Fe atoms in the Y123 and Y124 structures allow the following proposal for the Fe site assignment in the Ru1212 structure: Doublet A, that has a similar ΔQ (≈ 0.9 mm/s) to the ΔQ value of the doublet associated with Fe^{3+} with five-fold pyramidal coordination in the Cu(1) sites of the Y123 or Y124 structures, can be reasonably associated with the

Fig. 4 Normalized resistance as a function of temperature of the $Ru_{1-x}Fe_x$-1212 samples





a

b

Fig. 5 Room temperature Mössbauer spectra of $(Ru_{1-x}Fe_x)Sr_2GdCu_2O_8$ **a** $x=0.025$ and **b** $x=0.2$

corresponding Ru site of the Ru1212 structure, considering that the O-Ru bond-lengths of the later do not significantly differ from either of the former. On the other hand, the only surroundings compatible with the high ΔQ (≈ 1.70 mm/s) value of doublet C would turn out to be Fe^{3+} in four-fold (planar) coordination in the Ru sites.

The assigned Fe coordination is understood from the fact that while the charge character of the Ru ions in the structure is a 4+/5+ mixed-valence state [12, 30], that of the Fe atoms tends to be 2+/3+ ionic state. Therefore, in order to keep the charge valence of the system, the oxygen environment around the Fe ions in the Ru sites tends to a five-fold pyramidal coordination with the apical oxygen atoms of the SrO planes (doublet A), or to a four-fold planar coordination with two apical oxygen atoms (doublet C).

It is important to point out that these proposed assignments imply a loss of oxygen atoms in the RuO_2 planes that would create vacancies in the structure. The overall oxygen-content for each x value can be straightforwardly calculated with the proffered arrangement (using the relative Fe occupations obtained from the Mössbauer spectra), taking into account that the original compound is oxygen-stoichiometric, albeit the 4+/5+ valence state of the Ru atoms. In fact, the oxygen content $O_{content}$ is calculated as

$$O_{content} = 8 - [N_A(x) + 2N_C(x)]x$$

Table 2 Mössbauer parameters of the $(Ru_{1-x}Fe_x)Sr_2GdCu_2O_8$ series

	x	0.025	0.05	0.075	0.1	0.2
A	IS_A (mm/s)	−0.05	−0.05	−0.05	−0.05	−0.04
	ΔQ_A (mm/s)	0.90	0.91	0.90	0.91	0.90
	Γ_A (mm/s)	0.31	0.27	0.29	0.32	0.40
	% occupancy	54.0	52.3	49.6	47.1	37.0
B	IS_B (mm/s)	−0.04	−0.05	−0.06	−0.07	−0.07
	ΔQ_B(mm/s)	0.54	0.58	0.58	0.58	0.56
	Γ_B (mm/s)	0.40	0.40	0.40	0.40	0.40
	% occupancy	28.0	29.8	30.8	33.7	40.3
C	IS_C (mm/s)	0.02	0.00	0.00	0.00	0.03
	ΔQ_C (mm/s)	1.70	1.70	1.70	1.69	1.67
	Γ_C (mm/s)	0.34	0.40	0.40	0.38	0.40
	% occupancy	18.0	17.9	19.6	19.3	22.7

Isomer shift: *IS* (respect to iron); quadrupole splitting: ΔQ; line with Γ.

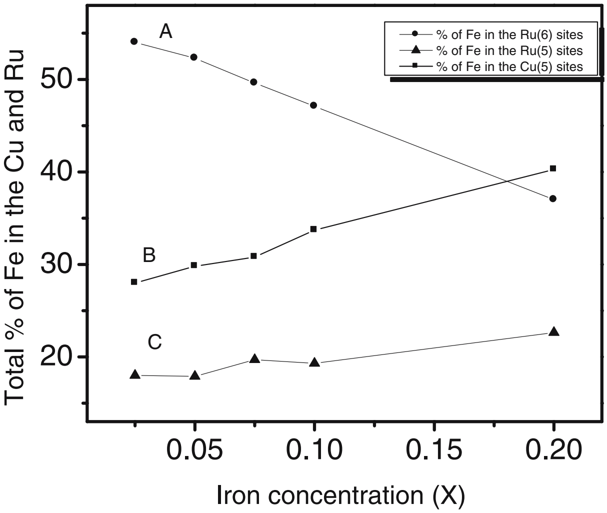


Fig. 6 Total Fe percent population in the different sites of the structure

where the 8 comes from the original oxygen content, the factor 2 in $N_C(x)$ is due to the fact that these Fe atoms are coordinated to only four O atoms (instead of six) and x is the overall Fe content. The results of this calculation are shown in Fig. 7, together with a linear regression fit of the data. That this could be true must be again associated with the inability of Fe to accomplish high ionic states (like the 5+ of Ru in those sites) and the formation of oxygen-vacancies would be necessary to keep the charge balance of the system.

Moreover, the formation of oxygen-vacancies would provoke a slackening in the rigidity of the structure that would diminish the *c* lattice parameter and slightly increase the average *a* parameter, with a concomitant reduction in the volume of the unit-cell. Likewise, the presence of vacancies in the charge reservoir would diminish the charge carrier population in the CuO_2 plane and, together with the presence of iron atoms in the Cu sites, would rapidly decrease T_c. In Fig. 8 we show the variation of the unit-cell volume as a function of

Fig. 7 Oxygen content as a function of iron concentration

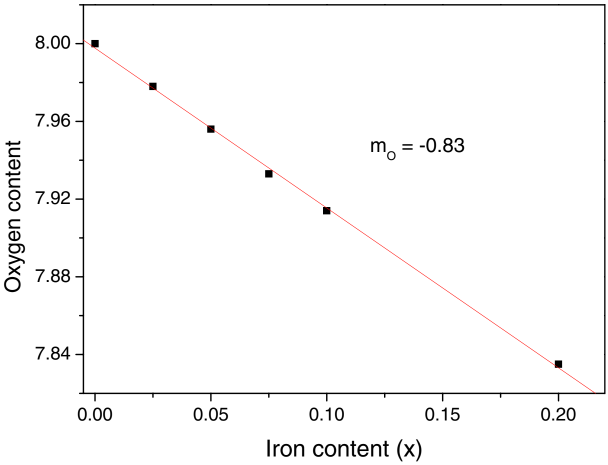
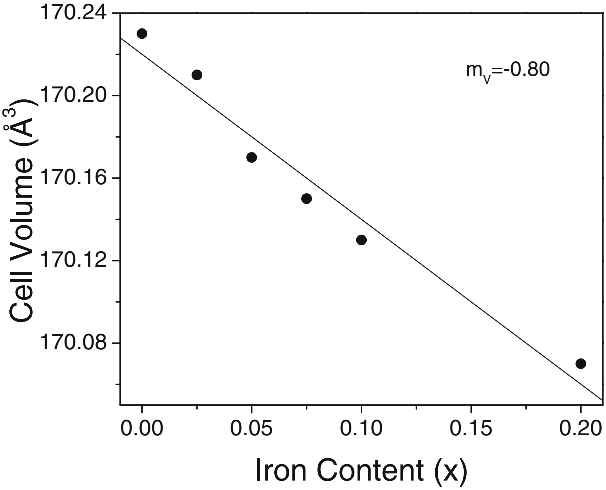


Fig. 8 Cell volume as a function of iron concentration x

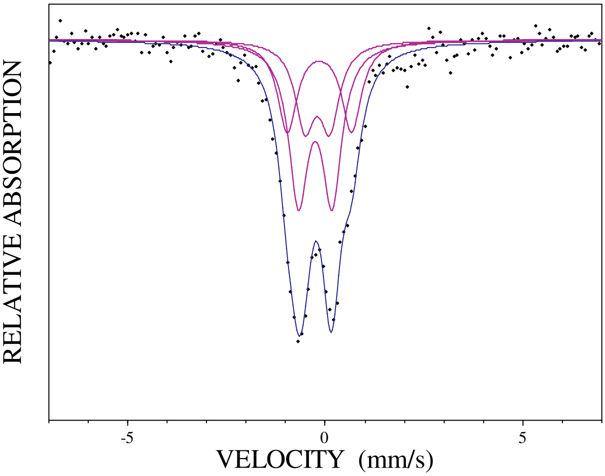


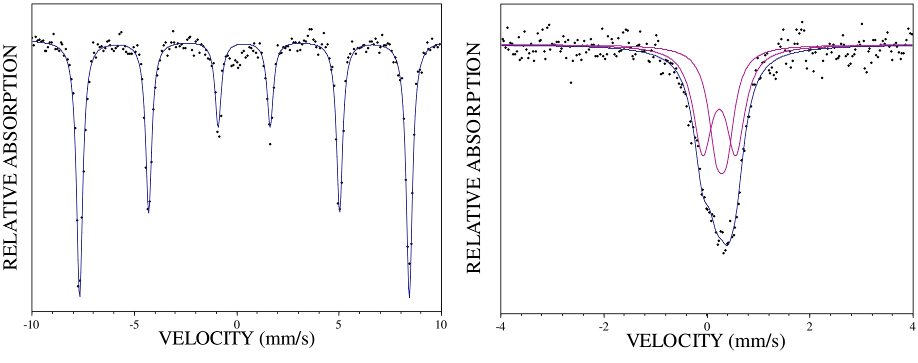
x, obtained from the Rietveld refined cell parameters, also with a linear regression fit. As can be seen, its behaviour much resembles that of the oxygen content.

It is interesting to note the results obtained by Awana et al. [31] on neutron-diffraction refinement and Mössbauer spectroscopy made in the $FeSr_2YCu_2O_{7.30}$ 1212 system. They also obtain three quadrupole doublets with quadrupole-splitting of $\Delta Q \approx 1.61$, 0.71 and 0.60 mm/s. They report that the total population of iron in the Cu(1) sites of the Cu1212 system is only of 54%, notwithstanding the fact that they attempted a complete substitution of Cu(1) by Fe. The consistency between Awana's results and ours suggest that, at high iron concentrations, the populations of Ru and Cu sites tend to be equal. We would like to point out that, with the Fe-oxygen environment that we propose, the same simple calculation mentioned above ($O_{content} = 7 - \delta + 0.44$, where the 0.44 comes from their fraction of Fe atoms in five-fold coordination) yields total oxygen occupancy in close agreement with their Rietveld results (7.30).

In the magnetization measurements of Escamilla et al. [22], the samples showed ferromagnetic transition temperatures that decrease with increasing iron content. The

Fig. 9 Mössbauer spectrum of $(Ru_{0.975}Fe_{0.025})Sr_2GdCu_2O_{8-\delta}$ at 25 K





a

b

Fig. 10 Room temperature Mössbauer spectra of **a** $Gd_2Cu_{0.95}Fe_{0.05}O_4$ and **b** $SrRu_{0.95}Fe_{0.05}O_3$

observed broadening of the transition and the reduction of the magnetic ordering temperature as the Fe content was increased were associated with a weakening of the magnetic interactions among the Ru moments of the Ru sublattice caused by Fe doping. In order to corroborate that the magnetic moments of the Fe ions are not ordering at low temperatures to form a magnetic structure that affects in any sense the magnetic moment of the sample, Mössbauer studies at low temperatures were done. No significant changes were observed in the low temperature spectra with respect to those taken at room-temperature. In Fig. 9 we show the spectrum of the $x=0.025$ sample taken at $T=25$ K.

The absence of magnetic features could also be associated to the structural changes provoked by the oxygen vacancies. It has been pointed out [21] that the deformation and relative orientation of the octahedral surrounding the Ru atoms determines the crystal-field splitting, the band structure and, hence, the magnetic and transport properties of the compound. If there is, in addition, a lack of oxygen atoms in the octahedral, the doped compound can show a different magnetic behaviour. This point, however, requires further study to clarify it.

In order to ensure that the observed features were due to the iron atoms in the $Ru_{1-x}Fe_x$-1212 structure, we synthesized $SrRu_{0.95}Fe_{0.05}O_3$ and $Gd_2Cu_{0.95}Fe_{0.05}O_4$ samples that were observed in the X-ray diffraction (XRD) patterns. The Mössbauer spectra of these phases are shown in Fig. 10a and b. As can be seen, $Gd_2Cu_{0.95}Fe_{0.05}O_4$ is magnetic with a hyperfine field H_{hf}=499.1±0.4 kOe and isomer shift of 0.491±0.006 mm/s whereas the ferromagnetic perovskite $SrRu_{0.95}Fe_{0.05}O_3$ shows two quadrupole doublets with isomer shifts of 0.238 and 0.283 mm/s and quadrupole splittings of 0.64 and 0.20 mm/s, similar to the spectrum observed by Felner et al. [32]. From the comparison of the Mössbauer parameters of these compounds respect to those shown in Table 2, it is clear that none of them contribute to spectra of the original system.

4 Conclusions

The present study on the $(Ru_{1-x}Fe_x)Sr_2GdCu_2O_{8-\delta}$ system shows a sharp drop of T_c with increasing iron concentration. The tetragonal structure does not change with increasing x, although the unit-cell volume diminishes. The Mössbauer spectra consist of three quadrupole doublets, two of them associated with Fe^{3+} in the Ru sites with different coordination: four-fold planar and five-fold pyramidal, and the other one with Fe in the Cu sites of the structure, with five-fold pyramidal coordination. From these results we corroborate that Fe substitutes both Ru and Cu atoms, and we found that at high iron concentration the population between the Ru and Cu sites tends to get even. The presence of the four-fold and five-fold coordinated iron atoms in the RuO planes implies a loss of oxygen atoms in the structure that explains the diminishing cell-volume, without changing its tetragonal structure. Also, the loss of oxygen atoms could be related with the sharp drop of T_c with increasing iron concentration, due to a lower number of charge carriers in the charge reservoir. The results obtained with the occupancy of the Fe atoms in the Ru sites and the cell volume behavior as function of iron content, can be used as an alternative to determine the overall oxygen content of the compounds. We also prove that the impurity phases of the samples are not responsible of the features found in the Mössbauer spectra of the studied compounds, finding out that $Gd_2Cu_{0.95}Fe_{0.05}O_4$ is magnetic and $SrRu_{0.95}Fe_{0.05}O_3$ is paramagnetic with different Mössbauer parameters.

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