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Structural and magnetic properties of iron doped ZrO₂

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ABSTRACT

 $Zr_{1-x}Fe_xO_2$ samples were synthesized by a freeze-drying process, varying the iron concentration from x = 0 to x = 0.40. The solid solutions prepared were structurally and magnetically characterized. The results showed that the samples crystallized with the tetragonal structure of zirconia for low iron concentrations, with the respective cubic structure for intermediate iron concentrations, and that hematite is formed secondarily at the highest doping levels. It was also revealed that the lattice parameter of the zirconia solid solutions decreases almost linearly with increasing dopant concentration. All the monophasic samples are paramagnetic at room and low temperatures, except for the x = 0.25 sample, which revealed an incipient magnetization at 13 K. The fluctuations are antiferromagnetic throughout the temperature range and the exchange interaction was attributed to two mechanisms occurring simultaneously: a direct exchange interaction between nearest neighbors magnetic moments, dominant at the lowest temperatures. Both mechanisms are more active for higher iron concentrations.

1. Introduction

Diluted magnetic semiconductors (DMS) and diluted magnetic oxides (DMO) have been intensively investigated within the last decade [1–6]. II-VI, III-V and IV-VI family semiconductors, as well as $M^{4+}O_2$ -type oxides (e.g., TiO₂, ZrO₂ and SnO₂) [7–10] have been doped with magnetic transition metals (e.g., Co, Fe and Mn) in the search for ferromagnetic (FM) order. The driving force of this research field is the potential applications of such semiconductors in spintronics [11–13]; a device made with a diluted (ferro)magnetic semiconductor could, plausibly, transport a spin polarized current while still exhibiting all of the basic functions of an undoped matrix. Models and theories have been reported to foresee or even to explain the FM behavior of such systems [2,14,15]. However, there is still no general agreement on any of these models and theories.

Scientists in this area of research are faced with a complicated experimental challenge regarding phase formation in samples. Since researchers are handling diluted systems, small fractions of (magnetic) secondary phases can be present in the samples, which

* Corresponding author. E-mail address: paesano@wnet.com.br (A. Paesano). These undesirable phases may not be detected using ordinary X-ray diffraction methods. Despite the small size of crystallites and the low relative amount, minor phases can yield a magnetic response that is strong enough to result in incorrect interpretations about the true properties of the doped semiconductor. This situation explains why many reports in the literature pertaining to FM order for DMS and DMO must be interpreted with caution. Close attention must accordingly be paid to the phase identification of the doped samples before assertively classifying them as DMS or DMO. We recently developed a novel routine for doping oxide systeme which we appear to be a user efficient preadure for the the phase identification.

are commonly prepared using different chemical routes [10,16,17].

tems, which was shown to be a very efficient procedure for the preparation of single phases [18]. Several types of monoxides, dioxides and sesquioxides were prepared using different dopants. Given the determined concentration limits, the samples were undoubtedly monophasic after low-temperature thermal annealing.

Here, we report structural and magnetic results of zirconium dioxide (ZrO₂) doped with iron atoms prepared via the routine noted above. We focus on examining the presence or absence of magnetism in real solid solutions.

Zirconium oxide, or simply zirconia, is a wide-band gap metal oxide that may stabilize in three crystalline structures depending on temperature: monoclinic (m-ZrO₂), from room temperature (RT) up to 1170 °C, tetragonal (t-ZrO₂), between 1170 °C and 2370 °C, and





ADD CONTROL OF ADD CO cubic (c-ZrO₂), above 2370 °C [19]. In the cubic structure (shown in Fig. 1a), each cation is at the center of a perfect cube with eight oxygen atoms at the corners. In the tetrahedral structure (shown in Fig. 1b), the oxygen cube is distorted in such a way that the first-and second-nearest neighbors form two non-regular tetrahedra.

For the cubic/tetrahedral structure, the zirconium sub lattice is formed by regular/non-regular octahedra (i.e., the main axis is stressed along the <u>c</u> lattice axis) connected by edges, and the basal plane lies on the x-y plane (i.e., the main axis is parallel to the <u>c</u> lattice axis). The high-temperature phases, t-ZrO₂ and c-ZrO₂, can be stabilized at RT by doping ZrO₂ with suitable metal cations [20,21].

Zirconia is an n-type semiconductor with a wide band gap (5.0-5.5 eV) for all phases [22-24] and was characterized regarding the structural and magnetic properties after doping with various transition metals [1,3-5,7,8].

Other authors have carried out similar studies. For example, Okabayashi *et al.* characterized $Zr_{1-x}(Co,Fe)_xO_2$ and $Zr_{1-x}Fe_xO_2$ prepared via a sol-gel method [25] and observed that dilute Fe and Co co-doping exhibited FM behavior at RT.

Sahoo *et al.* reported the presence of RT FM in Zr_{1-x}Fe_xO₂ synthesized via combustion (via microwaves) [26].

Garcia *et al.* focused on a $Zr_{0.9}Fe_{0.1}O_2$ solid solution prepared by a nitrate/urea combustion route [27]. These authors showed that using an appropriate amount of urea made it possible to obtain a completely stabilized $Zr_{0.9}Fe_{0.1}O_{1.95}$ solid solution without free iron oxide species.

Besides bulk and nanocrystalline samples, Zippel *et al.* [28] also analyzed Mn-doped and undoped ZrO₂ thin films grown by pulsed laser deposition. These authors detected FM related to defects in these systems.

More recently, Kuryliszyn-Kudelska *et al.* studied iron-doped ZrO_2 nanocrystals synthesized via the hydrothermal method [29] and observed that ZrO_2 samples doped with 2.8 wt% of Fe were paramagnetic.

Jiang *et al.* applied high-energy ball milling of $ZrO_2 - Fe_2O_3$ for preparing and studying iron-doped zirconia [30]. These authors showed that the maximum solubility of iron in c(or t)-ZrO₂ was approximately 18.5 mol%.

Guo *et al.* found FM order in Fe-doped nanotubes prepared via anodization of a Zr-Fe alloy [31].

Based on these and other investigations, it is clear that doped zirconia can stabilize in monoclinic, tetragonal or cubic structures depending on the specific doping process, the dopant concentration and the temperature of the thermal treatment.

Ferromagnetic order may appear depending on the specific conditions of the $(Zr.Fe)O_2$ sample preparation. Therefore, it is still unclear if the system is or is not a DMO. If it is a DMO, it remains to be understood how this property is connected with the stable structures of zirconia and their methodology of production.

It is also worthwhile noting that Mössbauer spectroscopy (MS) was used as a characterization technique in some studies in which iron was used as a dopant [25,26,29]. Indeed, MS is able to identify iron-containing phases, their magnetic state and their relative amount. In addition, valence information about the iron chemical environment (coordination symmetry) in the zirconia matrix may be extracted from MS data [25,29]. This spectroscopy technique is very selective to the specific nuclear probe (in this case, ⁵⁷Fe) and can detect nanostructured iron precipitates.

Here, we extensively used MS for the crystallographic and magnetic characterizations; we made use of X-ray diffraction (XRD) and magnetometry techniques for these investigations, respectively. We applied these techniques to very pure bulk samples prepared by significantly varying the doping concentration. However, we retained very good control over the phase(s) present in the samples. All of our results were effectively interconnected, which makes this study unique.

Our findings allow us to describe the $Zr_{1-x}Fe_xO_2$ system on the atomic level and demonstrate the absence of any RT magnetic order in monophasic samples. We estimated the solubility limit for iron doping in zirconia for samples in an equilibrium state.

2. Experimental details

2.1. Sample preparation

First, commercial salts containing zirconium acetate, $Zr(CH_3COO)_4$ (solution in dilute acetic acid, 15–16% Zr) and iron (II) acetate, $Fe(CH_3COO)_2$, were homogeneously diluted in 80 ml of distilled-deionised water, in prescribed concentrations. Thereafter this aqueous mixture was slowly frozen inside a glass flask, which rotated in contact with a refrigerant fluid (liquid nitrogen). After that, the flask was connected to a freeze-dryer, which consists of a vacuum pump and a water trap. During freeze-drying, the frozen sample was sublimed under low pressure (~250 μ m Hg) and temperature (-58 °C). The process for complete drying of the samples



Fig. 1. Cubic (a) and tetragonal (b) ZrO₂ crystalline structures. Blue balls = Oxygen; Green balls = Zirconium. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

took approximately 24 h. Finally, all powders were heat treated in air, first increasing the temperature at a rate of 10 °C/min up to 600 °C, where the samples remained for 3 h. Then, the furnace was switched off and the samples cooled naturally to RT. Following this routine, $Zr_{1-x}Fe_xO_2$ powder samples, with x = 0, 0.05, 0.07, 0.09, 0.15, 0.20, 0.25, 0.30, 0.35 and 0.40, were prepared and immediately characterized.

2.2. Characterization techniques

2.2.1. Scanning electron microscopy

The morphological aspects of doped and undoped materials were analyzed through the image formed by secondary electrons in a scanning electron microscopy.

2.2.2. X-ray diffraction

The XRD measurements were taken with an ordinary diffractometer, operating in the conventional θ -2 θ geometry (Bragg-Brentano). The X-ray radiation used came from a cooper tube (i.e., K_{α} emission lines with $\lambda = 1.5406$ Å) with 40 kV voltage and 30 mA filament current. Diffraction patterns were taken in the range of $20^{\circ} \le 2\theta \le 90^{\circ}$, with 0.02° angular step and 3 s acquisition time. Herein, the experimental diffractograms are presented with the vertical axis expressing the counts in logarithmic scale, because it shows the smallest peaks and better reveals the minor phases. The FULLPROF program [32] was applied to refine the c-ZrO₂ and t-ZrO₂ crystalline structures by the Rietveld method considering the Fm-*3m* and *P42/nmc* space groups, respectively, according to the symmetries usually attributed to these phases [33,34]. Pseudo-Voigt peak-shape functions were used to fit the experimental data. The data refined were the lattice parameter, the peak shape and thermal parameters.

2.2.3. Magnetization techniques

Specific magnetization (emu/g) *versus* temperature curves were measured in the 10 K–300 K temperature range, with the application of a 500 Oe magnetic field. For such measurements, the ZFC (Zero Field Cooling) and FC (Field Cooling) ordinary procedures were adopted. Magnetization *versus* applied magnetic field (kOe) cycles were also measured at 300 K and 10 K. All the magnetization measurements were performed using the vibrating sample magnetometer option in a Physical Property Measurement System (PPMS – Quantum Design – model Evercool II).

2.2.4. Mössbauer spectroscopy

 57 Fe Mössbauer transmission spectra were obtained at room and low temperatures, in a spectrometer operating with a $^{57}Co(Rh)$ source moved with constant acceleration. $Zr_{1-x}Fe_xO_2$ powder samples with about 20 mg cm $^{-2}$ were used as absorbers. The equipment was calibrated from the spectrum of an alpha-Fe thin foil, also measured at RT. The low temperature measurements were run in a closed cycle He cryostat.

The numerical fits were made considering a Lorentzian line shape and applying the minimum chi-square method. Each relevant and specific site was represented by an individual subspectrum and a hyperfine magnetic field distribution was used for the low temperature spectra.

3. Results and discussion

3.1. Scanning electron microscopy

Fig. 2 shows micrographs of some as-prepared samples and their morphology of flakes, structured in the sub micrometer scale. This result is quite different from those reported in literature



Fig. 2. SEM images of the microstructure for the x = 0 (a) and x = 0.20 (b) samples.

[35-37], in which ZrO₂ was obtained in the form of nanowires, spherical agglomerates or rounded particles (polyhedral). The thickness of the flakes remains practically the same with the iron doping, and their aspect ratio can be estimated to be ~0.01.

3.2. X-ray diffraction

Fig. 3 shows diffractograms for some representative samples. For the x = 0 sample (Fig. 3a) all the peaks belong to the t-ZrO₂ phase. Diffractograms for x = 0.05, 0.07 (not shown) reproduce qualitatively this result. However, a closer inspection of the x = 0.15 diffractogram (Fig. 3b) reveals that the peaks became narrower. This suggests the appearance of the c-ZrO₂ structure, because in the diffractometric profile of a cubic phase several peaks come from the collapse of pairs of neighboring peaks existing in the respective tetragonal phase. Further Rietveld refinements showed by a comparison of errors that this is correct.

Thus, from x = 0.15 (Fig. 3c) up to x = 0.25 (Fig. 3d) the cubic phase was assumed to be present, at least as the very major constituent. Obviously, this means that increasing the iron concentration up to these levels stabilizes the c-($Zr_{1-x}Fe_x$)O₂ phase, as previously pointed out [26].

The XRD patterns of the $x \ge 0.30$ samples reveal peaks of a second phase, initially of low intensity (Fig. 3e), but becoming more intense as the iron concentration reaches x = 0.40 (Fig. 3f). They belong to a pattern that can be unequivocally attributed to hematite, thus establishing a solubility limit for iron in c-ZrO₂, prepared by the synthesis method above described. This large limit for the formation of a second phase in a ZrO₂ matrix can be explained by



Fig. 3. X-ray experimental diffractograms for the x = 0 (a), 0.09 (b), 0.15 (c) 0.25 (d), 0.30 (e) and 0.40 (f) samples. Miller indexes in (a) and (c) are respective to the tetragonal and cubic zirconia structures, respectively. The red arrows in (f) indicate the peaks of the Fe₂O₃ phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the fact that the ionic radius of Fe³⁺ (the valence will be given by the Mössbauer results presented later in this paper) (0.92 Å) is smaller than that of Zr^{4+} (0.98 Å) in an eight-coordinated neighborhood [38]. Hematite was pointed out as the phase formed from the exceeding iron, also in samples prepared by other methods [26,29].

Fig. 4 shows refined diffractograms for the x = 0.05 (Fig. 4a) and x = 0.20 (Fig. 4b) samples. All the refinements were performed considering only one phase (i.e., tetragonal for $0 \le x \le 0.09$ and cubic for $0.15 \le x \le 0.25$) and resulted in lattice parameters (see Table 1) which are in good agreement with those previously obtained, either for undoped ZrO₂ or for iron doped zirconia [39–41]. Small differences observed between these and the present values may be attributed to different methods of refining the X-ray profiles (i.e., refinement programs used and parameters fixed initially in the



Fig. 4. Refined X-ray diffractograms, for the x = 0.05 (a) and x = 0.20 (b) samples.

refinement).

Fig. 5 shows the volume of primitive unitary cell (V_C) as a function of the iron concentration (x). The cell volume decreases almost linearly with the iron concentration, at a rate of $dV_C/dx \sim -0.06 \text{ Å}^3$ and -0.01 Å^3 , for the tetragonal and cubic structures, respectively.

This decrease may be explained based on the Fe³⁺ cation radius, smaller than that of the Zr⁴⁺ cation, and confirms that iron enters substitutional to zirconium in either the t-ZrO₂ matrix, or the c-ZrO₂ matrix, forming Zr_{1-x}Fe_xO₂ solid solutions. Vacancies generated by the doping (as shown below) may contribute to the volume decrease as well.

Compared to the data reported in Ref. [39], the present values for the volume of the tetragonal lattice differ only about 1%, but present the same rate of change under the dopant concentration variation. On the other hand, the results obtained by Ref. [40] differ from the ours not only in magnitude (~3%) but also regarding the range of stability of the c- $Zr_{1-x}Fe_xO_2$ (mono)phase.

3.3. Magnetization characterization

Fig. 6 shows the curves of magnetization and the respective reciprocal susceptibility as a function of temperature, for the x = 0.05, 0.07 and 0.09 samples.

For these concentrations, the magnetization grows monotonically with decreasing temperature. FC and ZFC curves overlap without evidence of magnetic irreversibility (i.e., a temperature, T_{irr} , which indicates the separation of ZFC and FC curves). Therefore, these samples show a feature typical of paramagnetic (PM) systems. However, the temperature dependence of reciprocal susceptibility curves reveals the possible existence of two Curie-Weiss (C-W) regimes, one at higher temperatures and another at lower temperatures.

In this sense, the χ^{-1} vs. T curves were fitted, using the $\chi = \chi_0 + (T - \theta)/C$ equation (i.e., a modified Langevin function), considering different temperature ranges. The temperatureindependent signal χ_0 was added to the Langevin fitting procedures in order to allow for magnetic contributions other than the specific Zr_{1-x}Fe_xO₂ solid solution phase, composing the specimen to be characterized (e.g., the sample holder). The parameters fitted specifically taking into account separately the T \geq 100 K and $T \le 100$ K ranges are listed in Table 2 (which also includes data for the x = 015 and 0.25 samples). For the lowest temperature range, all the C-W coefficients (θ 's) are small and negative, whereas for the highest temperature range they totalize some tens of negative Kelvin degrees. All these coefficients reflect AFM fluctuations, although a change in the magnetic regime is effectively revealed in going from RT to 10 K, for the three concentrations. This may be attributed to a variation with temperature of the molecular field constant, $\gamma (=\theta/\rho C)$ [42], which would weaken with decreasing temperature, until an "almost ideal" paramagnet. However, in every case the interactions between the magnetic moments are weak and are overcame by thermal fluctuations, even at low temperatures.

On the other hand, χ_0 presents typical values for frustrated oxide systems [43–45], increasing slightly with x and the T range, whereas the specific constant, C, does not show any noteworthy trend, as the concentration or the T range vary.

In principle, the AFM fluctuations should involve only iron magnetic moments, stabilized in trivalent state, as revealed by Mössbauer spectroscopy. Considering the concentrations used and a good dilution of the dopant in the ZrO₂ matrix, the nearest ferric cations are apart by two or three lattice parameters. Therefore, not close enough for an effective exchange interaction. In other words, a percolation threshold was not reached by the cations, somehow

Table 1	
Crystalline structure data for the Zr_1 "Fe ₂ O ₂ phases obtained from the Rietveld refinements"	

Sample (x)	Phase	Lattice	Edge length of the oxygen	Edge lengths (el1, el2)	Cation – O (<i>co</i>) bond length (Å)	Residues (%)		Rwp/Rexp
		parameter (A)	tetrahedra/cubes (A)	of the cation octahedra ^a (A)		R _{wp}	Rexp	S
0	t-ZrO ₂	a = 3.592	3.3018 (x4)	3.5920 (x4)	2.0828 (x4)	15.5	6.01	2.56
		c = 5.158	3.5920 (x2)	3.6197 (x8)	2.3556 (x4)			
			3.5920 (x2)					
			3.9679 (x4)					
0.05	t-Zr _{0.95} Fe _{0.05} O ₂	a = 3.590	3.2978 (x4)	3.5900 (x4)	2.0808 (x4)	7.56	4.45	1.70
		c = 5.147	3.5900 (x2)	3.6148 (x8)	2.3527 (x4)			
			3.5900 (x2)					
			3.9620 (x4)					
0.09	t-Zr _{0.91} Fe _{0.09} O ₂	a = 3.589	3.2900 (x4)	3.5890 (x4)	2.0775	10.3	5.15	2.00
		c = 5.119	3.5890 (x2)	3.6044 (x8)	(x4)			
			3.5890 (x2)		2.3470 (x4)			
			3.9488 (x4)					
0.15	c-Zr _{0.85} Fe _{0.15} O ₂	a = 5.071	2.5355 (x8)	3.5857 (x12)	2.1958 (x8)	10.9	5.17	2.11
0.20	c-Zr _{0.80} Fe _{0.20} O ₂	a = 5.061	2.5305 (x8)	3.5787 (x12)	2.1915 (x8)	12.6	6.19	2.03
0.25	c-Zr _{0.75} Fe _{0.25} O ₂	a = 5.056	2.5280 (x8)	3.5751 (x12)	2.1893 (x8)	13.7	6.17	2.22

^a el1 = el2 = el, for the cubic phase.

arranged in the lattice of this p-doped wide gap semiconductor.

Possibly, the Zr³⁺ cations - having a 3 d¹ electronic configuration - formed in consequence of the presence of "original" oxygen vacancies in the undoped matrix, could contribute to the magnetism of the system [39,46]. However, they are not numerically significant, considering the present iron doping levels.

The magnetization and respective reciprocal susceptibility as a function of temperature curves for the x = 0.15, 0.20 and 0.25 samples are shown in Fig. 7. The magnetization still grows up towards the lower temperatures. However, for the x = 0.15 sample the ZFC and FC curves separate around 200 K. The presence of a T_{irr} for this iron concentration indicates a turning point in the magnetic behavior of the material. Furthermore, for the x = 0.20 and 0.25 samples, which show T_{irr} = 50 K and 100 K, respectively, it is noticeable that the ZFC curves saturate and, even, decrease at lower temperatures. Such a magnetic behavior cannot be found in a simple paramagnet, but should appear in a material with antiferromagnetic interactions or presenting magnetic frustration. In fact, it is expected that, beyond some doping concentration (say, $x \leq 0.15$), clusters of iron cations become so numerous that they may, eventually, behave as spin-glass at low temperatures.

Fits with a modified Curie-Weiss law were also applied to the reciprocal susceptibility curves of the x = 0.15 and 0.25 samples, as



Fig. 5. Primitive cell volume for the $Zr_{1-x}Fe_xO_2$ phases, as a function of the iron concentration: $t-Zr_{1-x}Fe_xO_2$ (blue balls)/ $(c-Zr_{1-x}Fe_xO_2$ (red balls). Empty symbols are values reported in Refs. [37] and [38] for t and c phases, respectively. The solid lines are the best linear fits of experimental points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

done before for the x = 0.05, 0.07 and 0.09 samples. The curve of the x = 0.20 sample was not fitted because its behavior is exceptional and we do not have yet any explanation yet for that. In addition, the part of the x = 0.25 curve, respective to the 10 K–100 K range, was also disregarded since its performance is not typical for a PM system. Some kind of magnetic order seems to take place at the lowest temperature range, according to the respective ZFC curve.

Fitting the x = 0.15 curve, again resulted in a small C-W coefficient for the lowest temperature range. However, the coefficient obtained for the highest temperature range is quite large, though of the same order of magnitude as those reported for some common oxides [42]. An even higher value for this parameter was found for the x = 0.25 sample, indicating its dependence on the iron concentration.

In our opinion, excluding a crystallographic transition at low temperatures, the change in the magnetic behavior of the studied samples, under temperature and concentration variations, may be interpreted based on the simultaneous occurrence of two types of exchange interactions. One is the superexchange interaction involving neighboring iron moments. This is more significant for the x > 0.09 samples, a concentration beyond which the percolation limit is reached. The other is the indirect exchange interaction, mediated by the charge carriers in the impurity (conduction) band and/or holes in the valence band of the Zr_{1-x}Fe_xO₂ system. Here, it is plausible to consider that the acceptor dopant creates a impurity band because of the relatively high concentration of Fe³⁺ cations in the ZrO₂ matrix. Indeed, it has been stated that the RKKY mechanism takes place in highly doped DMS and DMO systems [15,47–49].

Hypothetically, this indirect exchange could induce "stronger" AFM correlations at the highest temperatures, where the charge carrier concentration is higher, for every doping concentration. However, thermal fluctuations prevent AFM ordering and all the systems are non-ordered at RT. Under decreasing temperature, the concentration of charge carriers in the conduction band would decrease, weakening the carrier capability of mediating the interaction between the diluted (or not so much) iron moments. Throughout this (low) temperature range, the RKKY interaction significantly weakens and no significant interaction exists in the x \leq 0.09 samples – which remain close to a PM state (i.e., according to the small θ 's). On the other hand, the superexchange interactions persist at lower temperatures for the 0.15 \leq x \leq 0.25 samples, maintaining the systems with more coupled AFM fluctuations. The existence of regions with many iron atoms close to each other – i.e.,



Fig. 6. Temperature dependence of magnetization, M (left), and reciprocal susceptibility (taken from FC), $\chi^{-1}(T)$ (right), for the $Zr_{1-x}Fe_xO_2$ samples with 0.05 $\leq x \leq$ 0.09. Yellow/ green plots are the C-W fits for χ^{-1} vs. T curves, in the T \leq 100 K/T \geq 100 K temperature range. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2	
Parameters obtained by fitting the $\chi(T)^{-1}$	curves with a modified Langevin function.

Sample (x)	Range	θ(Κ)	$\chi_o \times 10^{-5} (emu/g \ \text{Oe})$	$C \times 10^{-4} (K \; emu/g \; Oe)$
0.05	$T \ge 100 \text{ K}$	-56.1	0.8	18
	$T \leq 100 \ K$	-2.8	1.2	8
0.07	$T \ge 100 \ K$	-20.2	1.9	14
	$T \leq 100 \ K$	-2.6	2.1	10
0.09	$T \ge 100 \ K$	-86.5	2.3	29
	$T \leq 100 \ K$	-1.8	2.9	10
0.15	$T \ge 100 \ K$	-1,656	-9.9	4,200
	$T \leq 100 \ K$	-4.7	12.8	15
0.25	$T \ge 100 \ K$	-2,095	-54.0	23,500
	$T \leq 100 \ K$	-	-	-

forming clusters — is predictable. Of course, the magnetic behavior changes progressively with doping concentration and the coexistence of a paramagnetic fraction with the spin-glass behavior of the clusters may be expected nearby and above $x \approx 0.15$.

It is attractive to analyze the present results under the model of *Bound Magnetic Polarons* (BMP's), as proposed by Coey *et al.* [15]. However, the situation here seems to be more complex than that considered by those authors, since the presence of magnetic dopants comes together with (numerous) vacancies, as pointed out above and established ahead. Like acceptors dopants (i.e., not just magnetic isovalent dopants, as in Ref. [15]), the iron cations may trap holes in hydrogenic orbits [50], whereas the vacancies have donor electrons available to trap. Each iron cation/oxygen vacancy exerts a proper central force under which the carrier charge (i.e., the hole/the electron) is bound. Thus, when they are "close" to each other, say, apart by some lattice parameters, the mutual interaction between the moment carriers is not mediated by a vacancy (as assumed in Ref. [15]), but by the holes in the band formed by

overlapped orbitals. Presumably, these are shallow orbitals, placed right above the top of the valence band. Analogously, the oxygen vacancies may generate shallow orbitals right below the bottom of the conduction band. The number of donor and acceptor orbitals is the same, since for each pair of dopants a vacancy is created. Thus, magnetic cations and vacancies, sharing the same region in the zirconia matrix, form a "two-bands" construction inside the gap. The donors electrons will not stay at the more energetic levels but will occupy the less energetic (acceptor) levels, in a configuration with null spin polarization at 0 K (i.e., two antiparallel spins in each orbital). In this condition, half of the levels is fully occupied and half is completely empty. This explain why the charge carriers have a negligible effect on the cation moments orientation, at low temperatures. When the temperature increases, more energetic levels in the acceptor impurity band become occupied by electrons, whereas holes may also form in the valence band. Both charge carriers provide the conductivity for an indirect interaction between the localized moments. Thus, the BMP model seems to be



Fig. 7. Temperature dependence curves of magnetization, M (left), and reciprocal susceptibility (taken from FC), $\chi^{-1}(T)$ (right), for the $Zr_{1-x}Fe_xO_2$ samples ($0.15 \le x \le 0.25$). Yellow/ green plots are the C-W fits for χ^{-1} vs. T curves, in the T ≤ 100 K/T ≥ 100 K temperature range. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

not applicable to the present situation.

The isothermal magnetization (M) *versus* applied magnetic field (H) curves for the $Zr_{1-x}Fe_xO_2$ samples is shown in Fig. 8. As seen in the measurements performed at 300 K (Fig. 8a), all curves reveal a paramagnetic-like behavior and no significant magnetic hysteresis. Thus, it is clearly indicated that the AFM couplings are not of the long-range type and fluctuations of the magnetic moments predominate. Qualitatively similar results were previously reported in the literature by some authors [26,29,40]. The low temperature $M \times H$ curves (Fig. 8b) reveal a stronger PM moment than at RT, but it still was not possible to observe any magnetic hysteresis.

Attempts to fit M vs. H curves using a Langevin function, L(a), a behavior which would be expected for an ideal paramagnet (i.e., composed by individual magnetic moments, non-interactive between themselves), resulted in a poor quality for all the 300 K measurements, particularly for the higher iron concentration samples (Fig. 9a). This may be attributed to the "strong" (AFM) interactions between moments induced by the conduction electrons, numerous enough to indirectly connect magnetic cations. On the other hand, fits for the 10 K curves are very reasonable, mainly for the lower iron concentration samples (Fig. 9b). The relevant magnetic parameters, resultant from the Langevin fits, are listed in Table 3.

As general trends, it is observed that M_S increases with the iron concentration, whereas μ shrinks, revealing an increasing degree of AFM coupling between (neighboring) moments, plausibly two. Indeed, this suggests a progressive pairing between couples of iron atoms in the zirconia matrix as long as their number rises, while the average distance separating them diminishes. In contrary direction, the major presence of isolated Fe³⁺ ions in high-spin states (as it will be seen in the Mössbauer analyzes) for low x contributes to increasing the individual magnetic moment. Their paramagnetic

response is accompanied by the AFM fluctuations resulting from the Fe^{3+} pairs that are somehow magnetically coupled.

3.4. Mössbauer spectroscopy

RT Mössbauer spectra of some selected samples are shown in Fig. 10. For the $x \le 0.25$ samples the spectra were fitted with one doublet and for $x \ge 0.30$ with a doublet and a sextet. The hyperfine parameters for all samples are listed in Table 4.

Despite different theoretical fitting procedures, the present experimental spectra for iron diluted in zirconia are, in general, similar to those found for cubic and tetragonal phases [26,40].

The doublet may be associated either to a t-(Zr_{1-x}Fe_x)O₂ phase (for x \leq 0.09) or to a c-(Zr_{1-x}Fe)O₂ phase (for 0.15 \leq x < 0.30), consistent with the X-ray diffraction results. Based on the values of the isomeric shifts (δ) it follows that iron is in the trivalent state (high-spin) and that the quadrupole splittings (Δ Eq) show a highly distorted site for the ferric iron, in both ZrO₂ matrices. The values found here for Δ Eq are comparable to the <u>mean</u> values found in Refs. [25,26,29], which authors considered two doublets for fitting the spectra of (Zr,Fe)O₂ phases.

The large quadrupole splitting and, therefore, the non-cubicity of the iron site may be associated with a certain amount of lattice disorder caused by replacement of zirconium by iron. This is particularly striking for the cubic phase, where the iron site should be cubic in a perfect lattice and, hence, $\Delta E_Q \cong 0$. However, because of the difference between the valence states of iron (3+) and zirconium (4+) ions, it follows that the cation replacement generates vacancies of oxygen atoms in the zirconia matrix. It is plausible to suppose that for each pair of substitutional iron atoms an oxygen vacancy is generated to preserve the local electroneutrality in the lattice. In fact, we believe that substitutional solute atom-vacancy



Fig. 8. Temperature dependence curves of magnetization (M) vs. applied magnetic field (H) measured at RT (a) and 10 K (b), for the $Zr_{1-x}Fe_xO_2$ samples.

complex formation — formed by two iron atoms (as suggested above) plus an oxygen vacancy, all of them separated by one bond length - is a predominant configuration resulting from the iron doping. Actually, Li *et al.* previously depicted a similar picture, for a vacancy-undersized dopant association [51].

Fig. 11 shows the configuration of iron atoms separated by one edge length (el), with an oxygen vacancy equidistant from them, the three point defects constituting a triangle. A close oxygen (O_1) – also equidistant from the iron atoms - may be the mediator of the superexchange interaction, responsible for the AFM fluctuations in the doped systems. Other configurations forming a similar clustered defect are also plausible considering, e.g., the substitutional iron atoms in the octahedron basal plane (*i.e.*, also separated by *el*) plus an oxygen vacancy placed not symmetrically from them. Very probably, this clustered defect has more energy relative to that of Fig. 11, but may exist as fluctuations. This means that fittings considering a distribution for the quadrupole interaction would also be plausible for the Mössbauer spectra. Actually, the relatively large linewidth found in the present spectra reveals the existence of some distribution in the quadrupole splitting. However, using only two subspectra, as often reported in the literature, is rather arbitrary. In summary, whatever the fit procedure, the picture is justified by the existence of a quadrupole interaction for iron in a site that otherwise should be cubic, or slightly distorted, in $c-Zr_{1-x}Fe_xO_2$.

It is also worthwhile to note that $Zr_{1-x}Fe_xO_2$ solid solutions did not show any magnetic hyperfine pattern at RT, whatever the iron concentration. In other words, possible direct (super-exchange) or



Fig. 9. Langevin fits of the magnetization vs. applied magnetic field curves (1st. quadrant), at RT (a) and 10 K (b), for the x = 0.15 and 0.09 samples, respectively.

indirect (mediated by carriers) interactions are not able to freeze the iron moments, at least in time intervals large enough to be "seen" by the Mössbauer spectroscopy. This result reinforces the earlier assumption of a PM state for the Zr_{1-x}Fe_xO₂ system, in spite of observable AFM correlations.

The x = 0.09 and 0.25 samples were measured also at 13 K and their spectra are shown in Fig. 12. The spectrum of the former was fitted with a doublet and the one of the later with a doublet and a B_{hf} distribution.

These spectra are also consistent with the magnetometry results, which showed that at low temperatures the x = 0.09 sample is PM and the x = 0.25 sample exhibits AFM fluctuations, derived from the direct exchange interaction (and not because of an indirect interaction, mediated by charge carriers). Therefore, the hyperfine

Table 3

Magnetic parameters obtained from Langevin fits of the M vs. H curves, for some of the $Zr_{1-x}Fe_xO_2$ samples measured at 10 K.

Sample (x)	M _s (emu/g)	μ (μ _B)
0.05	5.71	2.49
0.07	7.16	2.22
0.09	6.72	1.61
0.15	7.14	1.01
0.20	6.80	0.71
0.25	11.42	0.94

 $M = M_S L(a) = M_S [coth(a) - (1/a)]; a = \mu H/kT.$



Fig. 10. RT Mössbauer spectra for the x = 0.09 (a), 0.25 (b) and 0.30 (c) samples.

Table 4Hyperfine parameters for the $Zr_{1-x}Fe_xO_2$ samples.

Sample (x)	Site	δ (mm/s)	$\Delta E_Q (mm/s)$	$B_{hf}(T)$	Γ (mm/s)			
0.05	Doublet	0.34	1.03	-	0.67			
0.07	Doublet	0.34	1.05	-	0.66			
0.09	Doublet	0.34	1.06	-	0.65			
0.15	Doublet	0.35	1.11	-	0.77			
0.20	Doublet	0.35	1.14	-	0.72			
0.25	Doublet	0.35	1.12	_	0.70			
0.30	Doublet	0.34	1.12	_	0.69			
	Sextet	0.36	-0.21	51.3	0.60			
0.40	Doublet	0.33	1.13	-	0.73			
	Sextet	0.38	-0.21	51.7	0.42			
13 K								
0.09	Doublet	0.43	1.11	-	0.70			
0.25	Doublet	0.45	1.07	-	1.34			
	Bhf Dist.	0.46	-0.21	32.8 ^a	0.28 ^b			

^a Average value of B_{hf} Dist.

^b Value fixed in the fitting process.

magnetic field distribution observed for the latter is due to an insipient spin freezing of a pair of moments, aligning antiferromagnetically in a direction determined by the local crystalline field. This is opposed to the possibility of FM alignment between two



Fig. 11. Cationic octahedra in the cubic structure, with a pair of iron atoms (red balls) substituting two nearest neighbors zirconium atoms (green balls), and an oxygen vacancy (white ball) placed symmetrically to them. Other oxygens (blue balls) remain nearby. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 12. 13 K Mössbauer spectra for the x = 0.09 (a) and 0.25 (b) samples.

nearest neighbor magnetic moments at very low temperatures. In this sense, Archer *et al.* [52] calculated theoretically the energy of magnetic coupling between nearest-neighbors iron atoms (apparently without considering any vacancy presence) and concluded for a ferromagnetic alignment. Nonetheless, at this time, we do not have elements to depict assertively the situation and more experiments are needed to make this clear.

4. Conclusions

Zr_{1-x}Fe_xO₂ solid solutions were successfully prepared with flaked-nanostructures, by a chemical routine involving freezedrying and thermal treatment.

The x \leq 0.0.9 samples crystallized with the tetragonal structure of zirconia and for 0.15 \leq x \leq 0.30 with the respective cubic structure. Throughout all the studied iron concentration range, the samples were found to be virtually monophasic, and the lattice parameter of the solid solutions decreases almost linearly with increasing dopant concentration.

Iron is very well dissolved but constitutes clustered defects composed by a pair of substitutional iron atoms, separated by an edge distance, plus an oxygen vacancy one bond length far from both.

The solubility limit for iron in $c-Zr_{1-x}Fe_xO_2$ for samples prepared by the synthesis method above pointed out is $x \approx 0.30$, beyond which hematite is formed as a second phase. The hematite fraction increases with the iron concentration, although up to x = 0.40 the major phase is always the $c-Zr_{1-x}Fe_xO_2$ solid solution.

Monophasic Fe-doped zirconia with tetragonal and cubic structures exhibits an overall paramagnetic behavior from 10 K to 300 K, with AFM fluctuations of the magnetic moments throughout the entire temperature range.

Two mechanisms are responsible for the AFM fluctuations: first, a superexchange interaction, coupling two close iron cations, mediated by a common neighbor oxygen (and/or a vacancy). Second, a RKKY interaction involving charge carriers in the impurity conduction and valence bands. The former mechanism is more significant at lower temperatures and high iron concentrations. The latter may exist near RT, but is negligible at lower temperatures and for low-doped samples, due to the small population of charge carriers.

The concept of a clustered defect based on the hypothesis of *local electronic neutrality* may be extended to other doped oxide systems and is currently under intense investigation in our research

group.

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