Mössbauer investigation of hyperfine interactions in dilute Fe-SnO$_2$ nanoparticles

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Abstract. We present a Mössbauer (MS) analysis on the nanoparticle system $x$SnO$_2$-(1-$x$)α-Fe$_2$O$_3$, ($x \in [0.995 \div 0.925]$). The samples were prepared by a hydrothermal route and have been 50% enriched in $^{57}$Fe. The MS spectra were recorded at room (RT) and liquid nitrogen temperature (LNT). Below $x = 0.975$ the MS consist in a paramagnetic pattern, while at $x \geq 0.975$ magnetic hyperfine interactions were evidenced. The observed coexistence of paramagnetic and ordered magnetic phases is discussed by taking into account the role of oxygen vacancies ($\square$), Sn-O and Sn-$\square$ distances together with the iron-oxygen configurations.

1. Introduction
Diluted magnetic semiconductors (DMS) using doping transition metal (TM) ions become of great and extensive interest as materials for spintronic applications. SnO$_2$ is an attractive host lattice for the investigation of DMS, due to the high carrier density and natively n-type semiconducting properties. Recently, some of TM (Fe, Co, Ni)-doped semiconductors as TiO$_2$, GaN, ZnO, and SnO$_2$ obtained by different procedures (pulsed laser deposition, sol-gel, hydrothermal), were found to show room-temperature ferromagnetism [1-3]. It seems that critical TM-dilution and observable magnetic ordering temperature are dependent on preparing procedure and/or thermal treatments. Continuing the earlier investigations [4-9], this work aims at showing a Mössbauer analysis on the nanoparticle system $x$SnO$_2$-(1-$x$)α-Fe$_2$O$_3$ synthesized by a hydrothermal route [7], at very low iron concentrations ($1-x \in [0.005 \div 0.075]$).

2. Experimental aspects and results
A series of $x$SnO$_2$-(1-$x$)α-Fe$_2$O$_3$ ($x \in [0.995 \div 0.925]$) was prepared by hydrothermal route starting with an aqueous mixture of iron (III) chloride hexahydrate, FeCl$_3$.6H$_2$O, and tin (IV) chloride pentahydrate, SnCl$_2$.5H$_2$O, as raw materials. The samples have been 50% enriched in $^{57}$Fe. The suspension obtained by coprecipitation with ammonia (at pH=8) was heated in autoclave at 200 °C for 4 h and then quenched to room temperature. X-ray diffraction (XRD), $^{119}$Sn and $^{57}$Fe transmission Mössbauer spectroscopy (TMS) were utilised to examine the as resulted powders. The XRD patterns obtained using a Bruker D8 Advance diffractometer and CuK$_\alpha$ radiation ($\lambda$=1.540598 Å) have been analysed to study the phase structure in relation to iron concentration 1-$x$. In figure 1a, representative XRD patterns are displayed. All patterns correspond to tetragonal SnO$_2$ phase known as cassiterite

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Rietveld refinement of the XRD patterns indicates a decrease of lattice parameters $c$ and $a$ of SnO$_2$ structure, as the iron content in the investigated samples increases (figure 1b). This result supports our expectation because the six coordinated ionic radius of Sn is greater than the ionic radius of Fe ion [7]; this behaviour is an argument for the substitution of Sn$^{4+}$ ions by Fe$^{3+}$ ions in SnO$_2$ lattice. The mean particle size given by Scherer formula is as small as 8 nm.

![Figure 1](image)

**Figure 1.** a) XRD patterns for the xSnO$_2$-(1-x)$\alpha$-Fe$_2$O$_3$ system at x=0.925, x=0.950 and x=0.975; b) Lattice parameters $c$ and $a$ versus iron molar content (1-x).

TMS spectra were recorded at room (RT) and liquid nitrogen temperature (LNT) using $^{57}$Co: Rh and $^{119}$Sn:CaSnO$_3$ matrix sources and a constant acceleration spectrometer, in the velocity range $v \in [-12+12]$ mm/s. The $^{119}$Sn-spectra of the investigated samples consist in one resonance line with unchangeable line-shapes both at RT and LNT. The room temperature $^{57}$Fe-Mössbauer spectra of the same samples exhibit a doublet pattern with small quadrupole splitting. Relevant changes in Mössbauer line shape and the appearance of magnetic hyperfine structure, as the iron content in the samples decreases, were evidenced in $^{57}$Fe-spectra at LNT (figure 2a); basically, superposed paramagnetic and magnetic ordering contributions are displayed by all $^{57}$Fe spectra in the studied concentration range.

### 3. Discussion

For the Mössbauer spectra fitting we have to consider that in our system at least three different nearest-neighbour cation interactions could exist: iron-iron, iron-tin and iron-oxygen vacancy. These possible interactions imply that at least three magnetic sublattices have to be taken into account in the computing run. The fit obtained with this approximation was far from satisfactory. The best fit has been obtained considering quadrupole patterns (paramagnetic contribution) together with magnetic hyperfine field distribution (MHFD). For example, at x=0.995 (LNT spectrum) the central quadrupole pattern was deconvoluted in two doublets. The first one, a symmetric doublet with quadrupole splitting ($\Delta_Q$) of 0.74(3) mm/s and isomer shift ($\delta_{\text{Fe}}$) of 0.44(5) mm/s can be assigned to Fe$^{3+}$ substituting for Sn$^{4+}$ in the SnO$_2$ lattice [7]. The second one with $\Delta_Q=0.85(4)$ mm/s and $\delta_{\text{Fe}}=0.49(8)$ mm/s could represent iron ions in more distorted neighbouring due to the close defects. These findings are in good agreement with the data reported in [13]. The relative areas of the paramagnetic / magnetic patterns
slightly decrease/increase from ~ 33%/67% to ~ 29%/71% as the iron molar concentration 1-x decreases. The paramagnetic contribution is strongly dependent on the molar concentration x, as stated also in [10]. In figure 2a the computer fit of LNT spectrum at x=0.995 is presented. The magnetic hyperfine filed distribution is plotted for the samples at x=0.990 and x=0.995 at LNT. Depending on molar concentration x, three magnetic field relative maxima can be observed: at B < 15.0 T, 15.0 T < B < 35.0 T and 35.0 T < B < 55.0 T. The increase of Fe-dilution induces an enlargement of the second range of B-values, a shift of MHFD through higher magnetic field and a more intense contribution at B > 45 T. In figure 2b, given by the fit, a tentative-deconvolution of MHFD into several Gauss peaks is depicted.

Based on XRD data, we consider that the magnetic behaviour observed in TMS spectra is correlated with the presence of Fe ions in SnO2 – tetragonal structure. Our TMS data revealed that at x > 0.975 the samples are magnetically inhomogeneous. In the case of low Fe-diluted sample (x = 0.975), the LNT spectrum indicates only one iron ion in four as being magnetically ordered, in acceptable agreement with [3]. The LNT-spectra of high Fe- diluted samples (x ≥ 0.990) evidenced a more important contribution of magnetic ordering (~67÷71 %).

As it was suggested by Coey et al. [11, 12] the Fe3+ ions in SnO2 could experience the following magnetic type interactions: a ferromagnetic exchange mechanism (FM) involving oxygen vacancies which form F-centres with trapped electrons; a paramagnetic behaviour coming from the isolated spin systems where the F-centre mediated ferromagnetic coupling is not achieved due to lack of Fe3+ neighbours; an antiferromagnetic (AM) behaviour given by Fe3+ – O2– –Fe3+ superexchange interactions. Consequently the hyperfine magnetic fields or magnetizations should increase as the iron content in the samples increases. In our samples the reverse effect is observed. Nomura et al [13] reported that the ferromagnetism in DMS material could originate both from ions and defects generated by the presence of the magnetic iron ions; this new magnetic contribution could explain the increase of magnetic hyperfine component by decreasing the iron content in our samples. The balance between the AM and FM interactions depends on the distance of attached Sn4+– O2−, Sn4+- groups to Fe3+ - O2− - Fe3+ or Fe3+ - O2− - Fe3+ configurations; that might influence the overlap of the electronic orbitals and can be favourable to the FM and AM interactions respectively [13, 14]. The present Mössbauer results cannot distinguish between the two magnetic ordering behaviours, however
considering the statements in ref. [3], one can suppose that the iron sites with high B-values (B > 45 T) correspond to AF interaction and those with smaller B-values to FM interaction.

4. Conclusions
The magnetic dilute nanoparticle system xSnO$_2$-(1-x)\(\alpha\)-Fe$_2$O$_3$, (x \in [0.995 ÷ 0.925]) obtained under hydrothermal conditions was investigated by Mössbauer spectroscopy at room and liquid nitrogen temperatures. In the studied tin molar concentration range, the TMS on $^{119}$Sn consist in a characteristic SnO$_2$ -single lorentzian line at both RT and LNT. Dramatic changes in the line shape and pattern were observed in the TMS spectra on $^{57}$Fe mainly at LNT. At x > 0.975 the onset of magnetic hyperfine interaction was evidenced. The complex spectra were fitted in terms of magnetic hyperfine distributions. Three types of magnetic sites relative to three ranges of the magnetic field intensity (B < 15.0 T, 15.0 T < B < 35.0 T and 35.0 T < B < 55.0 T) were identified in the distribution diagram. The magnetic sextets higher than 45 T have been ascribed to AF interaction. The increase of magnetic hyperfine component in MS, as the iron content in the samples decreases, suggests a more complex phenomenology regarding the contribution to the magnetic ordering in DMS, the direct involvement of defects having to be considered as a real possibility. The explanation for the appearance of ferromagnetism in iron doped SnO$_2$ is still an open issue. Further studies on annealed samples are in progress.

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