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Paramagnetism and clustering in Fe-doped TiO_2 nanoparticles

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ABSTRACT

The magnetic behavior of Fe-doped TiO_2 anatase nanoparticles (2.8 and 5.4 at.%) was investigated throughout magnetizations versus applied field measurements between 2 and 300 K temperatures. The experimental results were well-fitted by using the Brillouin function, giving rise to a moment per isolated Fe atom of about 5 μ_B. The thermal evolution of the number of magnetic ions shows that a decrease of ions in paramagnetic state occurs below 50 K for the most diluted sample. However for the 5.4 at.% sample the fall even at room temperature is evident. These moments probably order antiferromagnetically via superexchange interactions. Taking into account the low concentration of dopant and the high fraction of interacting ions, a correlated substitution of Fe in cation sites of TiO_2 structure needs to be considered.

Systems consisting in the dilution of magnetic ions in semiconductor non-magnetic matrices (DMS) have attracted considerable interest in the last years due to their potential application in spintronic devices. Indeed, the search for this kind of materials has encouraged numerous investigations mainly motivated by the reported ferromagnetic behavior at room temperature found in some DMS [1]. However, contradictory results suggest that the intrinsic magnetic properties of DMS are far from being entirely understood.

Previously, we reported the absence of ferromagnetism in Fe-doped TiO_2 nanoparticles where iron (III) replaces titanium (IV) in the anatase structure [2]. Instead, our results showed a paramagnetic state of iron in Fe-doped anatase at room temperature. Furthermore, two kinds of magnetic entities were distinguished to explain the magnetic behavior: isolated magnetic Fe ions and short-range correlated Fe ions. In this work, to get insight into the magnetic behavior of these Fe-doped TiO_2 nanoparticles we extended the thermal evolution study of the magnetic ions in the semiconductor host.

Fe-doped TiO_2 anatase-type nanoparticles (grain sizes 10–13 nm) of composition 2.8 and 5.4 at.% Fe (samples SA and SB, respectively) were synthesized by a microemulsion method. Details of sample preparation and characterization were published elsewhere [2,3]. DC magnetic measurements were performed in a Physical Property Measurement System (PPMS) from Quantum Design.

Fig. 1 shows the hysteresis loops of SA and SB taken between 2 and 300 K with maximum applied field $H = 7$ T. We observe that all the curves are reversible and the samples seem to behave paramagnetically down to the lowest temperature. However, when plotting the magnetization as a function of H/T (Fig. 2) the curves overlap above 50 K for the most diluted sample (SA), as expected for a pure paramagnetic state but curves taken at 10 and 5 K do not scale. For the most concentrated sample (SB) the curves do not coincide at any measured temperature (Fig. 2).

We fitted the M–H curves by assuming the magnetization as:

$$M = NgJ\mu_B B_J(x) \qquad (1)$$

where $B_J(x)$ is the Brillouin function, $x = gJ\mu_B H/k_B T$, N is the number of magnetic entities per gram, g is the Landé-factor, μ_B Bohr magnetron, $J = L + S$ is the total quantum number and k_B is the Boltzman constant. For Fe ions, $J = S$ and then, $g = 2$ due to the quenching of the orbital angular moment by the crystalline electric field. Simultaneous fits were performed constraining the total quantum number to take the same value for all temperatures. For SA, J results to be about 1.80 ± 0.02, while the corresponding N values are shown in Fig. 3. From these results we observed that, between 50 and 300 K, the number of paramagnetic iron ions almost coincides with the number of iron ions derived from the atomic percentages determined by inductively coupled plasma atomic emission spectroscopy (ICP). Below 50 K, N decreases indicating a certain correlation between the magnetic ions. As no signs of ferromagnetism were detected in the hysteresis loops, the moment correlation can be due to an antiferromagnetic-like interaction, in agreement with what has been inferred from ac-susceptibility results and predicted by *ab initio* calculations [2].

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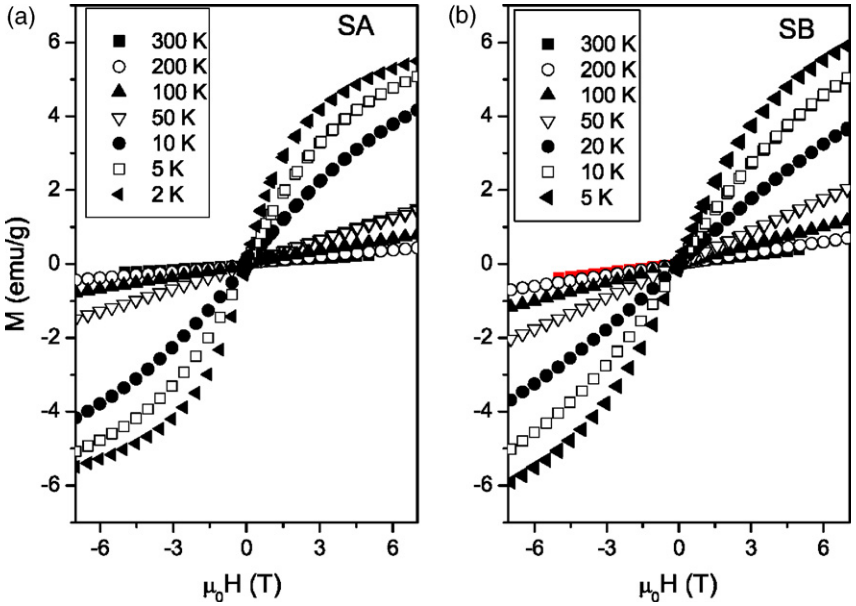

Fig. 1. Magnetization versus applied magnetic field curves taken at different temperatures for Fe-doped TiO_2 samples, SA (a) and SB (b).

In the case of SB, although equivalently satisfactory fits were obtained for J ranging from 2.1 to 2.5 (see Fig. 4), the lowest J value (2.1) gives an N value at room temperature which is in agreement with the N number estimated considering the sample stoichiometry (see Fig. 3). As a general trend, no matter the J value within that range is, N decreases with decreasing temperature. The N decrease observed at 300 K would indicate that the spin correlation begins at relatively high temperatures.

These J values 1.8 and 2.1 for SA and SB, respectively, lead to magnetic moments of about 4.5 and 5 μ_B, respectively. On the other hand, the fraction of magnetic ions remaining in a paramagnetic state at $T = 5$ K are NA = 0.6 and NB = 0.3 for SA and SB, respectively. It is worth noticing that the NA/NB ratio coincides with the ratio found considering Mössbauer results at 4.2 K [2], even though the NA and NB values double the values obtained by Mössbauer spectroscopy (0.30 and 0.15, respectively). The mismatch between these results can probably be related to the influence of relaxation effects present in the Mössbauer spectra. The paramagnetic fraction resulting from the Mössbauer fittings is probably underestimated because a broad single line component that represents relaxation effects overlaps the paramagnetic one.

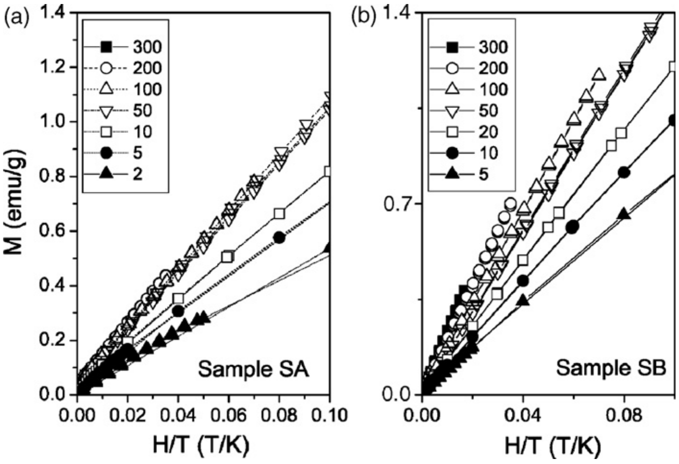

Fig. 2. M versus H/T curves corresponding to samples SA (a) and SB (b). For clarity, only the first quadrant is shown.

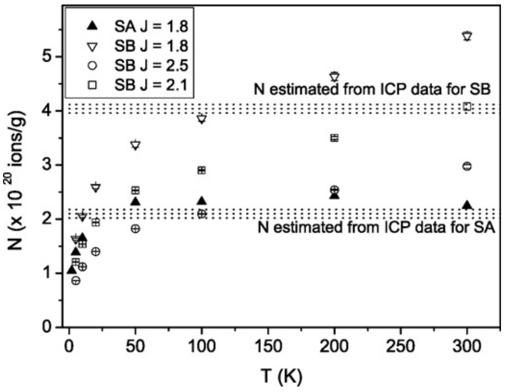

Fig. 3. Thermal evolution of the number of paramagnetic ions per gram (that results form the fitting procedure as explained in the text) as a function of temperature for samples SA and SB. Dot lines represent the iron ions per gram determined from ICP for SA and SB.

Our results seem to indicate that the magnetic behavior of Fe-doped TiO_2 nanosized samples can be attributed to localized magnetic moments from iron (III) replacing Ti(IV) in the anatase host. In accordance with our findings, these moments probably

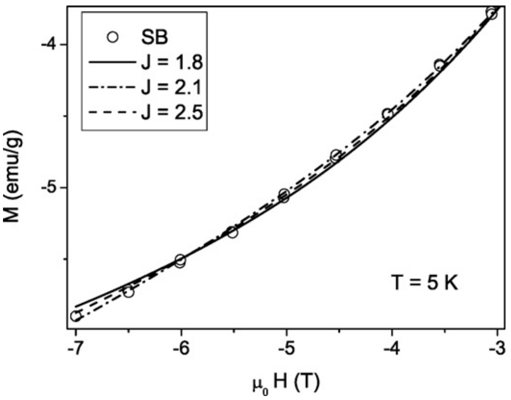

Fig. 4. Third quadrant of magnetization versus applied field (M–H) for sample SB (symbols) and the corresponding fits using different J values (lines).

are ordered antiferromagnetically. Then, as expected for iron oxide compounds the type of interaction that gives rise to the long range magnetic ordering is of superexchange-type. The large fraction of magnetic ions that is ordered at low temperature (0.4 and 0.7 for SA and SB, respectively) implies that the number of iron ions having also iron as second neighbors would be higher than those expected assuming a random distribution of iron ions in cation sites of TiO_2 structure (0.15% and 0.2%). Then, a correlated substitution needs to be considered as proposed for (GaMn)As system [4] and Co-doped ZnO [5]. The fact that the spin correlation starts to be noticeable at relatively low temperatures (25–50 K) would indicate that the interaction energy is lower than that usually found in iron oxides magnetically ordered at room temperature, but also due to the bond angle determined by the feasible Fe–O–Fe paths in the anatase lattice (near 90°). Future investigations will be carried out to clarify this point.

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References

[1] T. Fukumura, H. Toyosaki, Y. Yamada, Semicond. Sci. Technol. 20 (2005) S103–S111 (and references therein).
[2] C.E. Rodríguez-Torres, et al., J. Phys.: Condens. Matter 20 (2008) 135210.
[3] C. Adán, A. Bahamonde, M. Fernández-García, A. Martínez-Arias, Appl. Catal. B: Environ. 72 (11) (2007) 11–17.
[4] B.W. Wessels, New J. Phys. 10 (2008) 055008.
[5] A. Ney, K. Ollefs, S. Ye, T. Kammermeier, V. Ney, T.C. Kaspar, S.A. Chambers, F. Wilhelm, A. Rogalev, Phys. Rev. Lett. 100 (2008) 157201.