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Report :

Among the promising bio-nanotechnical applications of Magnetic Nanoparticles, a route towards "nanoradiotherapy" has been proposed [1] by incorporating Sm atoms into biofunctionalized and dispersable maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles. In order to investigate the local structure of such nanoparticles, doped or not with rare earth atoms, a series of XAS experiments have been performed at the iron K-edge and at the rare earth K- and L_3 - edges. Sm-, Y-doped maghemite and pure maghemite nanoparticles, of typical magnetic diameter between 4 and 10 nm, chemically synthesized in our laboratory by hydrothermal coprecipitation of a mixture of metallic salt solutions in alkaline medium [1], have been probed. Then, in order to elaborate magnetic fluids, these particles are hydrothermally treated with a boiling ferric nitrate solution before their peptization: (a) to prevent from acid attack when dispersed in acidic medium in the case of doped samples and (b) to induce the oxidation from magnetite to maghemite when dispersed in neutral medium for pure maghemite samples. The aim of this work was to determine the valence states of iron and rare earth elements in the nanoparticles by XANES and to extract the local geometric structure, such as coordination number, disorder and distribution in tetrahedral and octahedral sites of the spinel-type nanocrystal, by EXAFS.

The analysis of XANES data is done by comparison to pure standard materials of different oxidation states, here Y_2O_3 , Sm_2O_3 and $\gamma\text{-Fe}_2\text{O}_3$. The XANES data of nanosamples and of oxide references have very sharp spectral features at the Fe edge. The position of the absorption edge, taken as the maximum of the first derivative spectra, indicates that the valence state is +3 for the majority of iron atoms inside the various nanostructures. The XANES spectra at the Y and Sm edges also present sharp spectral features and the determined oxidation state of doping ions is also +3.

Figure 1a presents for pure maghemite samples the Fourier transform (FT) of the EXAFS spectra for Fe K-Edge. This spectrum illustrates Fourier features which are characteristics of tetrahedral and octahedral sites environments. The first peak, centered near to 1.5 Å, is due to the contribution of the first shell with the oxygen ions around the Fe atoms. The second one, centered near to 2.8 Å, corresponds to a second shell neighboring the Fe atoms and arises from multiple and

single scattering contributions of iron ions localized at A and B sites. Contrary to the spectrum of the bulk, for the nanosample spectra a shoulder develops on the right side of this second peak. We can attribute this behavior to the different quantity of vacancies inside the nanostructures when compared to the bulk. Moreover, we can observe an overall reduction of the FT amplitude of the nanosized samples in comparison to the standard sample. This is the signature of structural disorder and reduction of the average coordination number due to boundary effects at the surface of the nanoparticle [2].

Figure 1b presents for doped samples some of our fits, of the EXAFS data, in k-space. At the Fe K-edge (figure not shown), we obtain approximately the same interatomic distance value for the nanosized samples as for bulk standard, between the absorbing iron atoms and their respective neighbours. At their absorption edge, (figure 1b), we find the doping ions only at octahedral sites and none at tetrahedral sites, probably because of the physical space which is larger inside octahedral sites than tetrahedral ones (the ionic radii of the doping atoms are larger than for iron atoms). For the same reason, the interatomic distances between rare earth ions and their neighbours are larger than the interatomic distances between iron ions and their neighbours.

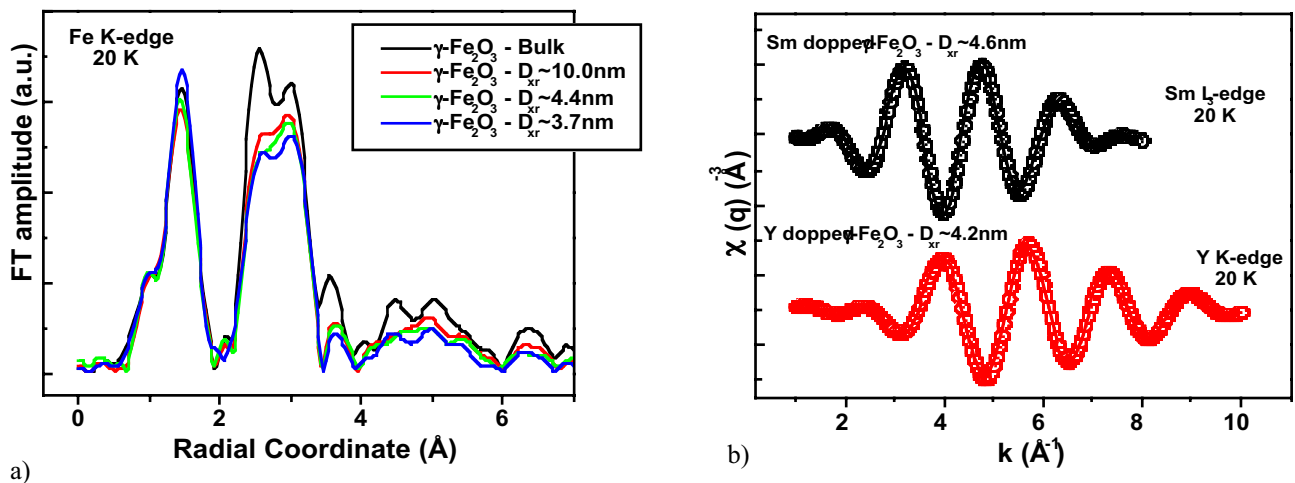


Figure 1. (a) FT at 20K of nanosized samples and bulk standard $\gamma\text{-Fe}_2\text{O}_3$ EXAFS spectra as a function of the radial coordinate, (b) filtered contribution, in k space, of the first shells of coordination (disks) and their fits (full line) for the nanostructures at Sm L₃-edge and Y K-edge.

In pure maghemite nanoparticle samples, the coordination number decreases as the nanoparticle size is decreasing. Moreover, this decrease is steeper as the nanoparticle sizes is reduced: as an example, it reaches 76% of the bulk value in undoped sample of $d_{xr} \sim 3.7\text{nm}$ and 84% for sample of $d_{xr} \sim 10\text{nm}$. This effect can be only attributed to the contribution of surface atoms since the surface disorder reduces the coordination number. For doped nanostructures, this decrease is more marked (57% to Sm doped sample of $d_{xr} \sim 4.2\text{nm}$) probably due : (a) to the large difference between iron and rare earth ionic radii that induces for doped samples a strong distortion that adds to the disorder contribution and (b) to the hydrothermal treatment with ferric nitrate solution that gives rise, only for doped samples, to the formation of a layer richer in iron on the particle surface that contribute to more surface disorder and thus to a larger reduction in the coordinate number.

[1] R. Aquino, J. A. Gomes, F.A. Tourinho, E. Dubois, R. Perzynski, G.J. da Silva, J. Depeyrot. *J. Magn. Magn. Mater.* **289** (2005) 431.

[2] J.A. Gomes, M.H. Sousa, G.J. da Silva, F.A. Tourinho, J. Mestnik-Filho, R. Itri, G. de M. Azevedo and J. Depeyrot. *J. Magn. Magn. Mater.* **300** (2006) e213.