The Insight into $T_d^{3+}/O_h^{2+/3+}$ Fe Site Distribution in Iron Oxide Magnetic Nanoparticles for Medical Applications.

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Due to the tuneable size, biocompatibility and remarkable magnetic properties, iron oxide magnetic nanoparticles (IOMNPs) attract particular interest and are widely used as contrast agents in MRI [1] and for local hyperthermia in therapy [2]. An inverse spinel structure of magnetite hosts Fe T_d^{3+} cations in the tetrahedral sites and both Fe O_h^{3+} and O_h^{2+} cations in the octahedral sites. Despite of knowing magnetite atomic structure for more than a hundred years [3] a new insight on charge distribution in bulk magnetite is now in focus of the scientific community [4]. A number of studies was devoted to IOMNPs structure based on a set of different method including XRD, TEM, FTIR, Mössbauer, etc [5, 6]. However, such studies are complicated by the similarity of magnetite and maghemite structures, small particles sizes, and a large number of surface atoms that give rise to edge effects. Due to the fact that XANES is sensitive to both local symmetry and charge of the absorbing atom, it is possible to separate and quantify the amount of inequivalent Fe positions in IOMNPs.

We use a combination of Mössbauer and Fe *K*-edge XANES spectroscopy to study local atomic and electronic structure of a set of IOMNPs. High energy resolution fluorescence detected *K*-edge XANES spectra for IOMNPs were measured on ID26 beamline of European Synchrotron Radiation Facility. Theoretical XANES spectra for different Fe positions in magnetite structure were simulated by means of FDMNES code [7] and a linear combination fit of the experimental XANES spectra by the simulated ones, corresponding to O_h^{3+}, O_h^{2+}, and T_d^{3+} Fe sites, was then performed. Transmission electron microscopy was employed to determine the size and morphology of IOMNPs, XRD was performed to identify the symmetry of the phase, cell parameters and crystalline sizes of IOMNPs.

Simulated spectra for O_h^{3+} and T_d^{3+} Fe sites clearly display different spectral shape, that allows to quantify the amount of Fe ions in tetrahedral positions. O_h^{2+} substantially shows spectral shift compared to O_h^{3+}. The general trend is that spectra for smaller nanoparticles show higher number of tetrahedral coordination that is consistent with Mossbauer data.

By means of Fe *K*-edge XANES spectroscopy we found the size dependence of the fraction of tetrahedrally coordinated Fe in small IOMNPs. Such approach can be extended for a large number of rare earth-doped IOMNPs.

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