X-ray magnetic circular dichroism discloses surface spins disorder in maghemite hollow nanoparticles

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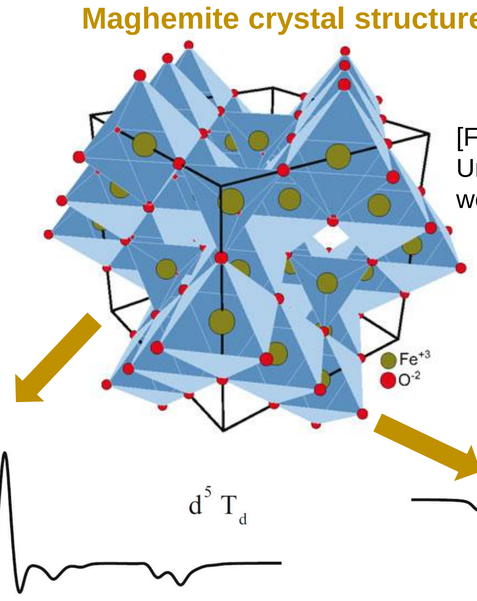
Introduction

Iron oxide magnetic nanoparticles (MNPs) have received increasing attention due to their expanding application fields, from catalysis [1] to biomedicine [2], where they are used as magnetic hyperthermia mediators or contrast agents for enhanced magnetic resonance imaging. A careful comprehension of the spin state and dynamics in such structures remains a key-point to understand and manipulate their magnetic behavior. Often the processes involving the surface spins depend not only on the uncompensated atomic structure, typical of the surface geometry, but also on a variation of the electronic state of the surface atoms related to processes like oxidation or contamination. The turn to element sensitive techniques like the x-ray absorption spectroscopy (XAS) and the x-ray magnetic circular dichroism (XMCD) offers to the scientist the capability of combining and explore these two aspects [3].
We have conceived a XMCD measurements procedure at low magnetic field (160 Oe) in **hollow and full maghemite NPs** in order to disclose the presence of a reduced magnetic correlation among the spins of the hollow NPs system compared to the full one.

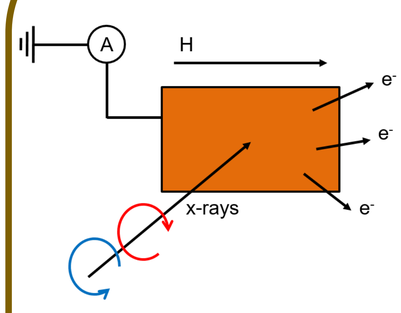
Maghemite crystal structure



[From theTechnische Universität Braunschweig website]

Calculated XMCD spectra for Fe3+ ions in octahedral (O_h) and tetrahedral (T_d) sites [4]

Experimental details of Fe $L_{2,3}$ XAS and XMCD measurements

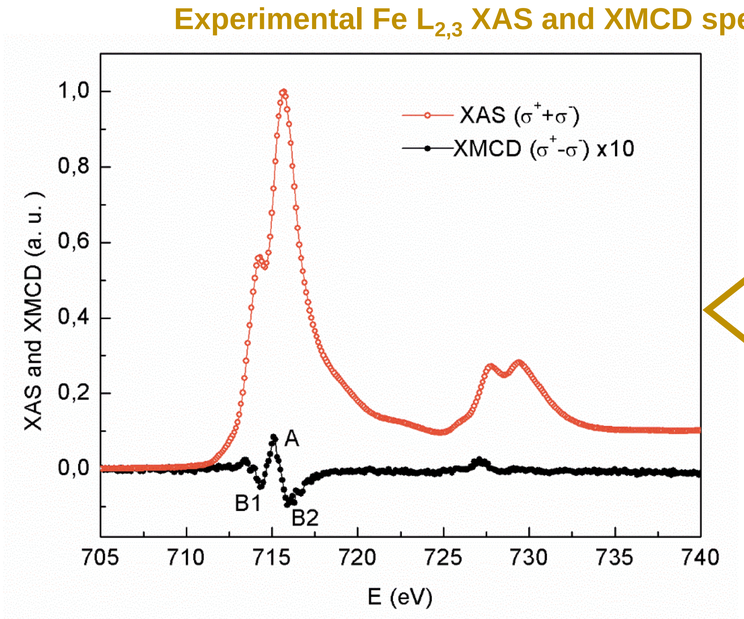


- Total electron yield (TEY) and partial electron yield (PEY) modes.
- Temperature of 70 K.
- Angle of incidence of 55° from the sample surface.
- Two different measurements procedures:

1. **Procedure #1**: external magnetic field fixed at 160 Oe, absorption measured in circular polarization, clockwise (σ+) and anti-clockwise (σ-). XAS is σ+ and σ-, XMCD is σ+-σ-.
2. **Procedure #2**: XMCD measured switching the magnetic field between + 160 Oe and - 160 Oe, at a fixed polarization of the light (σ+ or σ-). The measurement is taken at the remanence.

The spectra are normalized to the L_3 peak.

Experimental Fe $L_{2,3}$ XAS and XMCD spectra of maghemite NPs



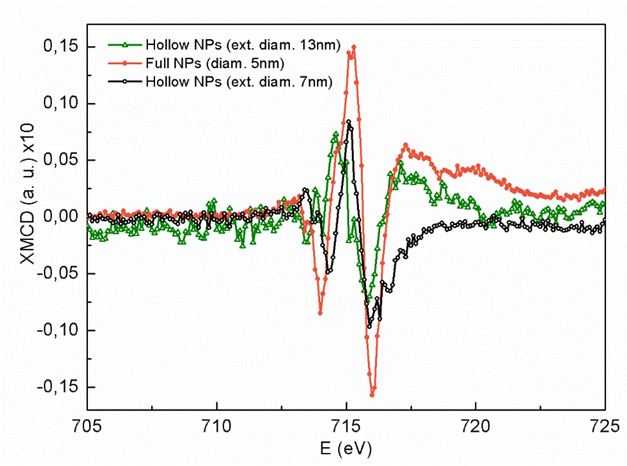
XAS/XMCD lineshape characteristic of the maghemite phase.

Three peaks in the XMCD L_3 spectrum: the positive peak A is mostly ascribable to the Fe^{3+} ions in T_d sites, the negative peaks B1 and B2 to the Fe^{3+} ions in O_h sites.

Experimental Fe L_3 XMCD spectra of maghemite NPs

Procedure #1

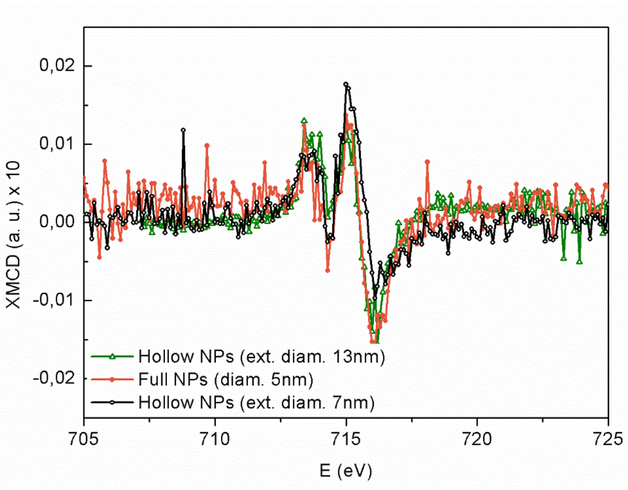
Procedure #1:
the **XMCD** intensity for the full NPs system is twice the one of the hollow NPs.



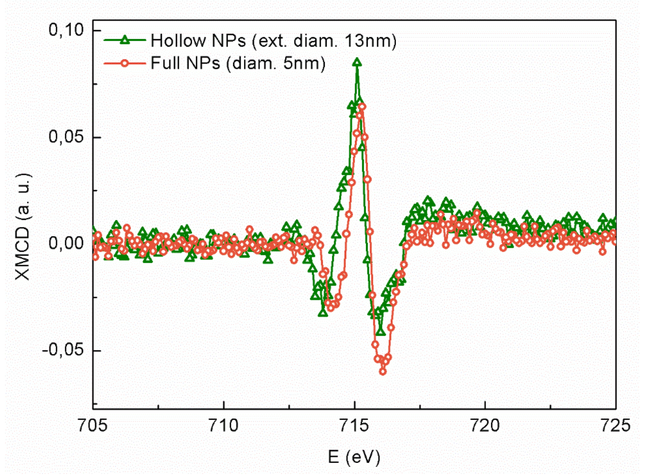
Procedure #2

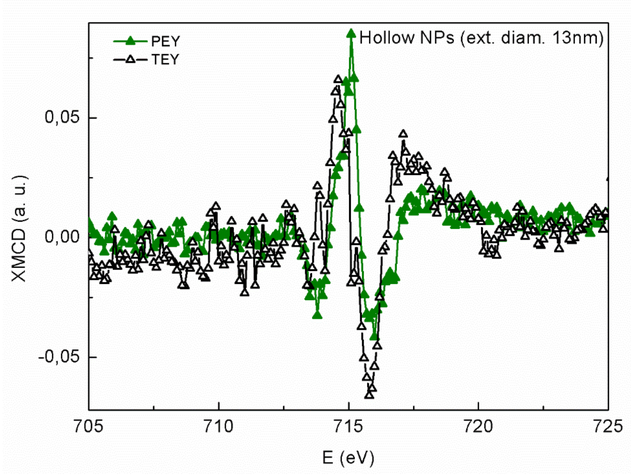
Procedure #2:
no differences in the **XMCD** intensity are measured among the three samples spectra.

The intensity of the XMCD signal decreases at least 5 times from procedure #1 to procedure #2.

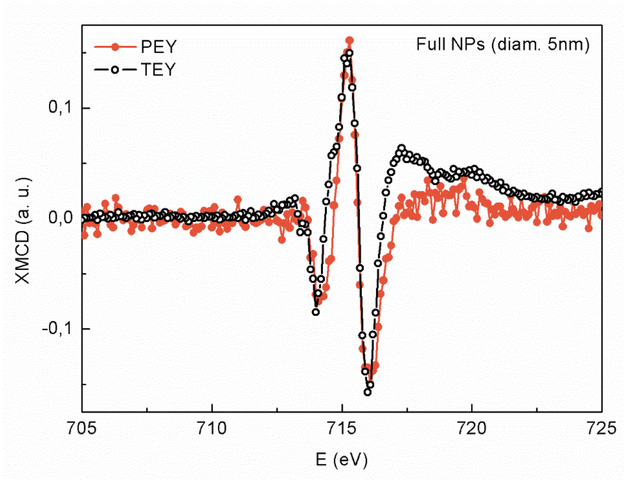


Total electron yield (TEY) vs partial electron yield (PEY)





The **PEY** method allows being even more surface sensitive than **TEY** due to a retarding potential applied to the sample, which reduces the probing length of the absorption to a few nanometers.
Rescaling the spectra according to the overlapping of the A peak, a reduction in intensity of the B2 peak is observed in PEY mode for the hollow NPs.
The same reduction emerges comparing the PEY and the TEY measurements for the hollow NPs but not in the case of the full NPs.



Conclusions

The results show that the state of oxidation in the maghemite NPs is preserved in both the full and the hollow structures. However the XMCD spectra reveal a decreased local magnetic moment in the hollow NPs compared to the full NPs.
Moreover, a reduction in the relative intensities of the XMCD peaks at the Fe L_3 edge emerges in the partial electron yield measurements of the hollow NPs. This result can be associated to a reduced correlation among the spins of the external surface of the hollow NPs.

[1] M. Hermanek, R. Zboril, I. Medrik, J. Pechousek, and C. Gregor, J. Am. Chem. Soc. 129, 10929 (2007). [2] A. Figuerola, R. Di Corato, L. Manna, and T. Pellegrino, Pharmacol. Res. 62, 126 (2010). [3] S. Brice-Profeta, M.-A. Arrio, E. Tronc, N. Menguy, I. Letard, C. Cartier dit Moulin, M. Noguès, C. Chanéac, J.-P. Jolivet, and P. Sainctavit, J. Magn. Magn. Mater. 288, 354 (2005). [4] R. A. D. Pattrick, G. van der Laan, C. M. B. Henderson, P. Kuiper, E. Dudzik, D. J. Vaughan, Eur. J. Mineral., 14, 1095 (2002).

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