Structural and magnetic deconvolution of FePt/FeO\textsubscript{x}-nanoparticles using x-ray magnetic circular dichroism

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Abstract. Recently, magnetite nanoparticles have attracted much attention, due to their technological potential based on different optic, magnetic and catalytic sections. In particular, the magnetic properties of hybrid nanocrystals can be tailored by the combination of complementary magnetic materials like for example magnetite and FePt. In order to analyse the related magnetic and structural properties of the resulting bi-component systems, we present x-ray absorption and x-ray magnetic circular dichroism studies at the Fe L\textsubscript{2,3} edges simultaneously performed in total electron yield and transmission mode, done at room and low temperatures. This provides in particular the separation of volume- and surface-related properties. The investigated system was made up of FePt/FeO\textsubscript{x} hybrid nanocrystals, which could be uniquely tuned in size and volume ratios. These measurements have been combined with magnetometry and high-resolution transmission electron microscopy studies. The separation between surface and bulk has been done by a deconvolution of the absorption spectra in terms of a linear superposition of reference spectra. With this universally applicable technique we are able to experimentally determine that

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the outer FeO$_x$ shell fraction at the surface has a strongly reduced magnetization and is of maghemite character, while the inner part is more magnetite like. So the technique shown here can be used to characterize nanoparticular systems and determine their structural and magnetic properties.

1. Introduction

In the past few years, new synthesis routes for inorganic nanocrystals (NCs) have provided a large variety of particulate matter. Large amounts of these new monodispersed nanosystems can be produced in a range between 2 and 20 nm in size. Recently, there has been the interesting development of the synthesis of hybrid nanocrystals (HNCs) where domains of different materials with individually tailored geometric parameters are joined through epitaxial interfaces. This type of structure allows a much more sophisticated tuning of the inherent optical, electronic and magnetic properties compared with single-phase NCs [1]–[7]. They represent robust and multifunctional entities with coexisting physical–chemical behaviour and can be produced in an onion-like core/shell arrangement as well as in noncentric geometries [8]–[13]. In both cases, the coexistence of two domains, which are different in their chemical nature, can be useful for a large variety of applications. They are useful for example because of the possible fine tuning of the overall physical properties as well as the introduction of new chemical surfaces for the anchoring of relevant biomolecules [14, 15]. A large variety of hybrid nanosystems can be produced, for example by variation of the relative volumes of the domains, and are expected to have an impact on a wide range of applications in, e.g., medicine, biology, nanotechnology, data storage and processing, and environmental remediation [3], [16]–[30]. In the field of NCs, and even more for HNCs, the chemistry and the final morphology depend strongly on the preparation technique and are governed by surface and interface phenomena. Their derived physical properties are strongly related to structural aspects, which can be sensitively tuned. Therefore, it becomes an indispensable task to correlate the local physical and chemical-structural properties. In addition, and especially in the case of magnetic NCs, physical studies usually describe averaged bulk and surface behaviours even if it is well known that the surface shows different properties to the bulk. Those surface effects therefore strongly influence the overall magnetic behaviour in particles with a high surface-to-volume ratio.

In terms of one component iron oxide based NCs, the total ferromagnetic moment is reduced due to the dilution and the ferrimagnetic arrangement. The magnetic moments in iron
oxides have rather low specific magnetization values, up to a maximum of about 300 emu cm\(^{-3}\). Combinations with nanomaterials of larger magnetization values could overcome this limit. Hereby the system FePt is of special interest for several reasons: it has a magnetic moment of 1125 emu cm\(^{-3}\), is relatively corrosion resistant and can be transformed thermally into the highly coercive L\(_{10}\)-phase at 650 °C. The latter, along with its strong magnetocrystalline anisotropy, is important to overcome the superparamagnetic limit even for very small particle sizes. For a long time iron oxide nanoparticles in particular have been studied in biology and medicine due to their easy dispersion in water, their biocompatibility and possibility of functionalization [30, 31]. In the case of very small magnetic iron oxide nanoparticles, the room temperature magnetization will be significantly reduced due to superparamagnetism [32]. In addition, from the centre to the outer surface, the chemical structure can be a complex composition of \(\gamma\)-Fe\(_2\)O\(_3\) (maghemite) and Fe\(_3\)O\(_4\) (magnetite) like materials, strongly depending on synthetic details [33, 34]. Maghemite and magnetite, which are isostructural, cannot be easily distinguished by transmission electron microscopy (TEM). In principle, electron energy loss spectroscopy (EELS), performed in a high-resolution TEM, is able to distinguish between them, providing the necessary spatial accuracy in combination with the required energy resolution [35, 36]. Nevertheless, the highly focused electron beams needed for this kind of analysis usually provide unknown heating and oxygen loss phenomena. In addition, only averaged spectra along the electron transmission column are observed. This usually gives convoluted spectral information even for very slightly tilted side surfaces and makes it very difficult to separate the bulk and surface properly. In principle, Mößbauer spectroscopy is also able to distinguish between different iron compounds, again without providing spatial information [37]. Therefore, Mößbauer spectroscopy cannot separate surface- and bulk-related properties either.

Recently, it has been shown that bi-magnetic FePt/iron oxide heterodimers of sizes between 3 and 20 nm can be obtained. Their magnetic properties, such as the blocking temperature and magnetocrystalline anisotropy, are tailored by controlling their chemical composition, total size and iron oxide/FePt volume ratio in the single particle [38]. For these systems in particular the compositional analysis of fractional \(\gamma\)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) contributions appears to be very complex and has not been performed yet.

As mentioned above, TEM and x-ray diffraction (XRD) techniques can hardly provide any structural separation of maghemite- and magnetite-like phases. In contrast, a combination of high-resolution x-ray absorption spectroscopy (XAS) and its magnetic counterpart, x-ray magnetic circular dichroism (XMCD), provides detailed insights from the O K-edge and Fe L\(_{2,3}\)-edges fine structures. These are strikingly different for intermetallic iron alloys and different iron oxide types [9], [39–42]. In particular, XMCD spectra are powerful tools for chemical and magnetic characterization and provide quantitative information about spin and orbital magnetic contributions per Fe-atom via the so-called sum rules [43–45].

Here we report on XAS and XMCD studies of bi-magnetic FePt–iron oxide heterodimers of sizes between 16 and 20 nm. The spectra were recorded in the more surface sensitive total electron yield (TEY; detection of secondary electron emission) and in the bulk sensitive transmission mode. By deconvolution into reference spectra and a comparison of TEY and transmission results, we give a detailed analysis of the magnetic and nonmagnetic nanostructure which actually showed the presence of a very thin oxide shell surrounding the total surface of the HNCs.
2. Experimental aspects and results

Bi-magnetic FePt/iron oxide HNCs were produced by a ‘one-pot’ synthesis following a previously reported procedure [38]. In general terms, the synthesis took place in a unique surfactant environment by temperature-driven sequential reactions. The homogeneous nucleation of FePt seeds at low temperatures was followed by the heterogeneous nucleation and growth of iron oxide at higher temperatures.

For our study we chose NCs of larger sizes: the dimensions of the particles were determined by TEM (figure 1), and are in the range between 16 and 20 nm (semi-major axis). The size of the particles has been chosen in order to optimize the signal-to-noise ratio and to minimize possible artefacts like self-absorption in transmission mode [43, 46]. The composition of the FePt seeds and the FePt/iron oxide HNCs were determined with an inductively coupled plasma atomic emission spectrometer (ICP-AES) and was determined to be Fe\textsubscript{19}Pt\textsubscript{81} for the metallic domain. The FePt and iron oxide domains are easy to distinguish, due to the TEM contrast from the heavy metal Pt. Phase-contrast high-resolution TEM analysis exhibited a clear inverse spinel crystal structure for the iron oxide domain, matching the crystal structure of γ-Fe\textsubscript{2}O\textsubscript{3} or Fe\textsubscript{3}O\textsubscript{4}.

The investigated sample has been magnetically characterized with a superconducting quantum interference device (SQUID) magnetometer in an applied field of 5 mT. In figure 2(a) magnetization loops are shown at 15 and 300 K with a corresponding saturation magnetization of 0.31 ± 0.01 \(\mu\text{B}\) Fe\textsuperscript{-1} (0.21 ± 0.01 \(\mu\text{B}\) Fe\textsuperscript{-1}), respectively. This is about a factor of three times smaller than the XMCD results shown in the next paragraph. This difference could be explained by an organic surfactant layer all around the surface of the nanoparticles consisting of long chains of organic acids or amines. Due to their unknown mass contribution to the probed sample, all magnetization values measured with the SQUID show lower values per mass than expected [37].

The NCs show superparamagnetic behaviour at high temperatures (300 K) and ferromagnetic behaviour at low temperatures (15 K) with a coercive field of 47 mT. Figure 2(b) shows zero field cooled (zfc) and field cooled (fc) temperature-dependent magnetization curves, providing a blocking temperature of 140 ± 5 K. For comparison with the XMCD results (shown below) we determined the ratio between the low- and high-temperature saturation magnetizations to be

\[ \frac{M_{15\text{K}}^{\text{sat}}}{M_{300\text{K}}^{\text{sat}}} = 1.47. \]

The XMCD and XAS experiments were performed at the PM3 bending magnet beamline, BESSY II Berlin. All spectra were simultaneously recorded in TEY and the transmission mode with an energy resolution of \(E/\Delta E \approx 5000\). To allow transmission experiments, the solution of nanoparticles was dropped on a commercially available ‘Silson’ SiN-membrane with 100 nm thickness and 1 mm \(\times\) 1 mm width. All results have been corrected for the degree of circular polarization, which was 92 ± 4\%, and have been normalized by the incoming beam intensity \(I_0\), measured by an Au-coated Cu grid. All spectra were measured in an applied magnetic field of 2 T, which was flipped at each energy data point to ensure maximum sensitivity and to minimize synchrotron-related drift phenomena. Therefore, we used a superconducting magnet system, providing fast field switching in less than 6 s at ±2 T.
Figure 1. TEM images of the investigated FePt/FeO$_x$ HNCs. (a) and (b) Low-resolution TEM images, where the scale bar corresponds to 100 nm and (c) high-resolution TEM image. The scale bar in this case corresponds to 5 nm.
**Figure 2.** (a) SQUID magnetization curves $m$ (H) in Bohr-magnetons per Fe atom at 15 and 300 K for FePt/Fe$_x$O$_y$ heterodimers of 18 nm size and (b) magnetic measurements of the temperature dependence indicating a blocking temperature of 140 K.

**Figure 3.** In the upper part, the XAS spectra of an FePt/FeO$_x$ HNCs sample are shown in TEY mode (a) and in transmission mode (b). The corresponding XMCD spectra at RT and 15 K are shown below (c) and (d). For a better description, the peaks are numbered as follows: I (708.85 eV), II (710.86 eV) and III (710.05 eV). The XAS spectra are edge normalized, while the XMCD signal shows the difference for parallel and antiparallel aligned magnetization with respect to the circular polarization.

The upper part of figure 3 shows the nonmagnetic XAS spectra (left TEY; right transmission), and in the lower part, the corresponding magnetic difference XMCD spectra at RT and 15 K.
Table 1. Sum rule determined spin and orbital moments given in $\mu_B$ per electron hole.

|        | Spin | Orbital |
|--------|------|---------|
|        | RT   | 15 K    | RT   | 15 K |
| TEY ($\mu_B$) | $0.12 \pm 0.02$ | $0.21 \pm 0.02$ | $<0.01 \pm 0.02$ | $<0.01 \pm 0.02$ |
| Trans ($\mu_B$) | $0.12 \pm 0.02$ | $0.17 \pm 0.02$ | $<0.01 \pm 0.02$ | $<0.01 \pm 0.02$ |

Switching from transmission to TEY measurements in the XAS spectra provides enhanced spectral weight for the central peak B at 710.5 eV indicating a higher oxidation state at the surface [9, 39, 42, 47, 48].

The XMCD spectra have a three-peak-like shape with two negative peaks (I and II) and a positive peak (III) at the centre, which is typical for iron oxides [9, 39, 40, 42]. The comparison between TEY and transmission mode XMCD spectra shows a clear intensity change in the ratio between peaks I and II, which is higher for the transmission mode spectra. Cooling down to about 15 K provides an enhanced XMCD signal which corresponds to the enlarged sample saturation magnetization.

3. Analysis and interpretation
3.1. Integral XMCD results

For a quantitative determination of the magnetic spin and orbital moments, sum rules have been applied [43]–[45]. The determined spin and orbital moments (in $\mu_B$ per electron hole), related to the different measurement modes and temperatures are shown in table 1.

Due to experimental reasons and the limited energy range of the available reference spectra, we used a reduced sum rule integration range, which results in slightly different values for the calculated spin and orbital moments [42, 47]. This limited energy range does not affect the quality of the fit significantly because the intensity of the XMCD signal in the extended energy range is very small. So the main issue of this contribution, the deconvolution of different iron species discussed below, is not influenced by this, because only the local spectral shapes are compared to the reference data. If the reference data provide a sufficient energy range and the measured spectra are in fact only a superposition, then the deconvolution is correct. Therefore we will only talk about ‘magnetite-like’ and ‘maghemite-like’ spectral contributions in this report, because the ‘real’ material could be something in between. The error bars given in the tables take this issue into account.

The cold/warm ratio from the SQUID measurements (1.47) is the same as observed for the transmission XMCD measurement (1.4). This clearly demonstrates the bulk sensitivity of the transmission mode XMCD experiment. This ratio is increased to 1.75 in the TEY mode, indicating a stronger temperature dependence of the magnetization at the surface.

To determine the absolute average iron magnetic moment using sum rules we have to estimate the average number of holes in the iron 3d shell. From the fit results shown in the next
section we can estimate a volume fraction related average number of holes in the Fe 3d shell of \( \langle n_h \rangle = 4.7 \). This estimate is used to calculate an average sum rule related spin moment of 0.8 \( \mu_B \) for the low-temperature transmission signal. This value is reduced by a factor of two compared to pure iron metal and slightly smaller compared to magnetite [42]. From the TEY signal we can conclude that the Fe magnetization in the FeO\(_x\) outer shell is about 1.0 \( \mu_B \) (with \( \langle n_h \rangle = 4.8 \))\(^6\), and therefore only slightly reduced compared to pure magnetite single-crystal results [42].

### 3.2. Deconvoluted XAS/XMCD results

In order to separate the FePt from the FeO\(_x\) magnetization and to examine the relative magnetite- and maghemite-like fractions, we fitted the measured XAS and XMCD spectra by a linear superposition of the reference data shown in figure 4 (\( \gamma \)-Fe\(_2\)O\(_3 \) [39], Fe\(_3\)O\(_4 \) [42, 47] and FePt [9, 48]).

We would like to mention that all reference spectra used here have been measured in the surface sensitive measurement mode. This could lead to variations if the reference data are not representative for the bulk magnetism of the corresponding sample.

\(^6\) The average number of holes is calculated with the number of holes of the single components weighted with the XAS deconvolution results shown in the next paragraph.

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With respect of the relative XMCD peak amplitudes (I and II) at the \(L_3\)-edge one can clearly see by direct (visual) comparison with the reference data that the transmission signal is more magnetite like, whereas the TEY-signal looks like an equal mixture of maghemite and magnetite.

Figure 5 shows the different contributions for the XAS and the XMCD spectra, which are the results of the fitted spectra. One has to keep in mind that the XAS fit parameters represent the ‘real’ chemical material contribution, while the XMCD fit parameters represent the magnetic contributions of each component of the material. Therefore, it is possible to identify a quite large chemical fraction of one component which is only slightly magnetized, as we will show for maghemite below.

The chemical analysis of the nanoparticles was deduced from the XAS fit results by determining the fractions of each component which are shown in percentage in table 2.

From the different diameters, derived from the TEM images, one could roughly estimate an average FePt volume fraction of about 40 \(\pm\) 10\%. This matches the XAS fit-related average FePt-based Fe fraction of 42\% (see table 2)\(^7\).

\(^7\) The volume per Fe ion varies only slightly from about 25 (\(\text{Fe}_3\text{O}_4\)) to 27 (FePt) \(\text{Å}^3\). Therefore the atom fraction for each component is a good approximation for the volume fraction.
Table 2. Nonmagnetic relative Fe contributions of each component of the HNCs given in percentage for TEY and transmission data at RT. The average error is estimated to be 10% of each value.

| Component       | Transmission (%) | TEY (%)  |
|-----------------|------------------|----------|
| $\gamma$-Fe$_2$O$_3$ | 13.2 ± 1.3       | 26.8 ± 2.7 |
| Fe$_3$O$_4$     | 44.9 ± 4.5       | 53.2 ± 5.3 |
| FePt            | 41.9 ± 4.2       | 19.7 ± 2.0 |

Figure 6. Magnetic contributions of the single components of the HNCs given in percentage for TEY and transmission data at 15 K and RT, respectively. The lines are only guides to the eye. Open symbols represent transmission data.

From the XMCD fit we determined the fractional magnetic contributions of each component to the overall magnetic moment using a combination of the sum rule values of the reference spectra and the relative spectral weight determined by the fit. The results are shown in figure 6. The upper part shows only the relative magnetic contributions, determined for each measurement mode and temperature separately. The sum for each measurement is normalized to 100%. The lower part shows the absolute magnetic contributions, where the 100% reference is related to the low-temperature TEY result. By comparing these single contributions for different temperatures, we see that the increase in the total magnetic moment is mainly provided by FePt and Fe$_3$O$_4$, but dominated by Fe$_3$O$_4$ (see TEY and transmission data, respectively).

In addition, the sum over all fit-related magnetic moments is in perfect agreement (within the error bars) to the sum rule related total magnetization, confirming the validity and quality of the fit (see table 3).

From the fitted XAS and XMCD results one can obtain a rough estimate for the magnetic moments of the three different contributions derived by the application of sum rules from the
Table 3. Comparison of the overall magnetic moment (spin and orbital contribution) derived from the experimental data and from the fit, respectively.

| Temperature | TEY          | Transmission | TEY          | Transmission |
|-------------|--------------|--------------|--------------|--------------|
| 300 K       | 0.13         | 0.12         | 0.11         | 0.10         |
| 15 K        | 0.20         | 0.21         | 0.17         | 0.15         |

relative spectral weight and the estimated number of 3d holes related to the nominal chemical Fe 3d configuration of each compound. The estimated projected Fe 3d spin moments for FePt, Fe$_2$O$_3$ and Fe$_3$O$_4$ are 1.6, 0.5 and 0.61$\mu_B$, respectively.

4. Resulting structural and magnetic model for the hybrid NCs

In the XAS data the relative spectral intensity of Fe$_2$O$_3$ with respect to Fe$_3$O$_4$ is enhanced in TEY mode. This indicates a more maghemite-like surface, whereas the inner iron oxide part is more magnetite like.

Comparing TEY and transmission XMCD data, the Fe$_2$O$_3$ intensity is nearly constant, while the Fe$_3$O$_4$ fraction decreases for transmission. This suggests that the inner magnetite fraction is less magnetic for example close to the FePt domain.

The contribution of FePt in the HNCs is more visible in the XAS (figures 5(a) and (b)) and XMCD (figures 5(c)–(f)) transmission data, clearly indicating the internal character of the domain. This suggests a core–shell-like configuration of the two materials, and not a strictly dimeric structure as previously deduced from TEM analysis [35].

The strongest temperature dependence is present in the TEY-related Fe$_3$O$_4$ and FePt signal. This indicates a less saturated magnetic moment at room temperature which could be explained by a reduced Curie–Weiss temperature in the near-surface regions. The inner part reveals a less strong temperature dependence similar to bulk magnetite [42].

The following structural and magnetic model for the HNCs can be deduced from these results (shown in figure 7):

The FePt domain is located close to one side of the HNC. The schematic cube volumes correspond to the XAS fit results, while the size of the magnetization (indicated by the arrows) corresponds to the XMCD fit results.

One possible reason for the non-vanishing FePt signal in the TEY measurements is the side-by-side position of the FePt and the iron oxide (see TEM pictures in figures 1 and 7). So on the right side of the HNC in figure 7, FePt is close to the surface and therefore partially probed by the TEY measurement. Nevertheless, the spectral Fe contribution from the FePt (see figure 5) is much smaller as observed by Dmitrieva et al [48] for pure FePt-particles, which are slightly oxidized. A rough estimate suggests a thin iron oxide layer of about 1–1.5 nm on top of the FePt side.
5. Conclusion

For FePt/FeO$_x$ HNCs, prepared by a one-pot procedure, we have successfully demonstrated the deconvolution of XAS and XMCD spectra by a fitted superposition of FePt, magnetite and maghemite reference spectra. The chemical and magnetic relative volume and surface fractions have been determined and analysed by the comparison of TEY (surface) and transmission (bulk) spectra. The relative transmission and TEY signals obtained either by XAS or XMCD for the FePt domain seem to elucidate its internal character in the NC. Hence, a core–shell-like structure would be a more accurate term to describe this type of HNCs, instead of a dimer-like one as previously thought. A consistent picture of the relative magnetizations and their temperature dependence has been derived, showing that the dominant sample magnetization and its temperature dependence is due to the inner magnetite layer, while the outer more maghemite-like layer has a strongly reduced magnetization. The FePt domain itself has a magnetic moment close to the bulk material, and its fractional magnetization compared to the full magnetization of the whole nanoparticle is small, as expected from the small volume fraction and its Pt-rich composition.

Colloidal nanoparticles prepared and engineered with the aid of a precise mixture of surfactant molecules in organic solvents like the ones studied here, can easily be transferred into water by several methods [49]–[51], enlarging in this way the range of applications, especially in the biomedical field. There they could be used in hyperthermia treatments or as contrast agents for magnetic resonance imaging techniques as already proved in our previous publication [38].

This work demonstrates the potential of XAS/XMCD techniques for a precise structural and magnetic characterization with a high spatial resolution at the nanoscale. This is of enormous importance to understand the composition and physical behaviour of systems which are gaining more importance in several technological fields. This method could be generally used for many other types of HNCs [52, 53], allowing detailed investigations of preparation-related changes of structural and magnetic properties, in order to improve the construction of HNCs with specially tailored properties.
Similar studies with nanoparticles of other morphologies and sizes are on the way, to spread the use of the technique shown.

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