A Comparison of EMCD with XMCD

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The CHIRALTEM project was established and funded by the European Union in order to prove whether it would be possible to detect circular magnetic dichroism by electron energy loss spectroscopy (EELS) in transmission electron microscopy (TEM). The only other method available to study the same phenomena requires the use of the spin polarized photons generated by a synchrotron storage ring and it is a well established technique called X-ray magnetic circular dichroism (XMCD). Since the early days in which the idea [1] behind the project was born, it was clear that XMCD would have been the term of comparison for the new technique, based on TEM and named, by analogy, electron Energy-loss Magnetic Chiral Dichroism (EMCD). This is why CHIRALTEM is inherently an interdisciplinary project and one of its work packages was dedicated to the comparison between XMCD and EMCD and to build a bridge between the relevant communities allowing to look at the same phenomena from different points of view. This aspect is of particular relevance as it paves the way to new scenarios for the understanding of the magnetic properties of matter at the highest spatial resolution. Looking at the XMCD world, it was possible to imagine for the EMCD technique a scenario that indeed has been, in many points, confirmed by the scientific results subsequently achieved in the project.

The comparisons between XMCD and EMCD required the design and the realization of specimens suitable for both kinds of experiments, without any further process that could introduce artefacts in the relevant spectra. It was decided to use as case study a magnetic layer of Fe deposited on a GaAs (001) substrate by molecular beam epitaxy (MBE). Ferromagnetism of Fe ultrathin films epitaxially grown on GaAs(001) with in-plane orientation, was already established and studied by XMCD also in our laboratory. GaAs has a relatively low lattice mismatch with Fe (~1.2%) and many procedures have been developed to achieve smooth and artefact-free TEM specimens. Furthermore the Fe XMCD signal at the L_2 and L_3 edges for Fe/GaAs(001) is relatively high. In order to allow both XMCD and EMCD experiments on the very same sample the GaAs substrate was pre-tinned to electron transparency, but only from one side, preserving the surface crystallinity of the side of the epitaxial growth, before growing the iron layer. This approach allowed for the first time to demonstrate the possibility to detect magnetic circular dichroism in a transmission electron microscope. The results were published in Nature [2] in 2006 and had a strong impact on the scientific community, but also on non-specialized audience as the news were reported on several newspapers and press agencies in Italy, Czech Republic and Austria.

In Trieste 20 specimens were prepared for the purposes of the project. The magnetic layer was deposited on a disk of GaAs (100) of 3 mm of diameter in order to fit inside a standard TEM specimen holder. Then a special specimen holder was designed and realized to handle the specimens in the MBE chamber where the Fe film (10 nm or 15 nm thick) was finally grown in UHV conditions and analysed in situ by different techniques. The purity of the GaAs (100) surface was measured with Auger electron spectroscopy (AES) at each step of the preparation, and its crystal structure was monitored with low energy electron diffraction (LEED). After Fe layer and Cu capping deposition, the magnetic properties were measured by Kerr effect and XMCD. The latter measurement was performed on different points of the sample's surface, with a beam spot size of about 200x150 μm.

Figure 1 shows a representative result of the XMCD and EMCD experiments performed on the same specimen.

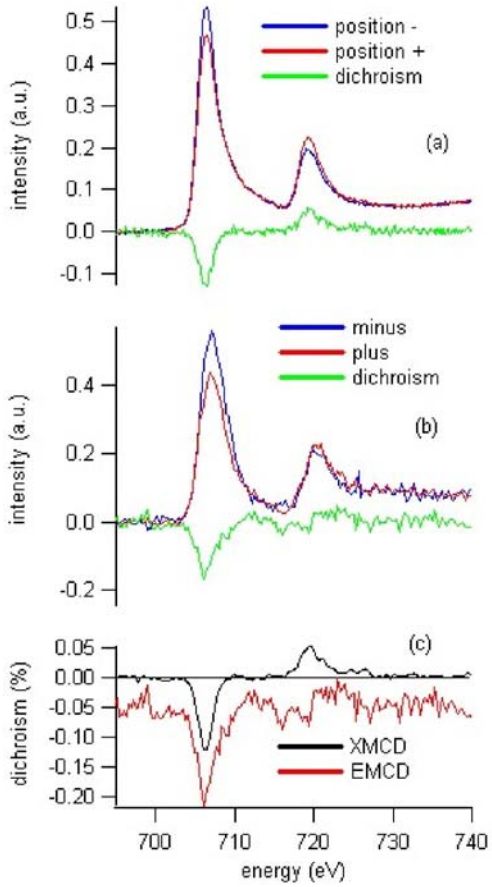

Figure 1:

(a) *In situ* XAS spectra and XMCD signal measured on 15nm Fe film
(b) EELS and EMCD spectra collected on the same film
(c) Direct comparison between EMCD and XMCD signal

The XMCD spectra were acquired *in situ*, on the APE-INFM beam line at the ELETTRA storage ring in Trieste, in Total Electron Yield (TEY) mode, at the Fe ionization edge in remnant magnetization and by reversing the sample magnetization with current pulses in an electromagnet producing ~400 Oe field pulses; the XMCD signal is the difference of X-ray absorption spectra (XAS) renormalized for photon beam circular polarization (75%) and incident angle (45°) The dichroic signal, as measured by XMCD, is -13%±2% at L_3 edge and 10%±2% at L_2 edge (fig. 1a). EMCD were performed on the same specimen at the TEM laboratory of the Vienna University of Technology. The EMCD signal in figure 1b is the difference between two EELS spectra collected shifting the energy loss spectrometer entrance aperture from position "+" to position "–" (which is equivalent to a change in helicity), following the procedure reported in details in reference [1]. All specimens were studied by using the so-called "intrinsic mode", described in details in the CHIRALTEM project, in which the specimen itself acts as an interferometer. Under carefully chosen scattering conditions the sample forms two diffracted beams with the proper geometry and dephasing to reveal the dichroic signal. EMCD signal at L_3 edge is about -16%±4%, while at L_2 is hardly detectable over the noise level (fig. 1b). This latter effect could be ascribed to the high noise content of the measurement. Indeed, one of the challenges of the new technique consists in obtaining a good signal to noise ratio (S/N). A new method for performing EMCD measurements with better S/N has been recently suggested by Schattschneider and co-workers [3]. It is also worth to remark that this new approach so far reached routinely a resolution of 10 nm and it could, in principle, achieve a spatial resolution of the order of 1 nm. XMCD and EMCD signals are directly compared in fig. 1c. This kind of experiments has evidenced that the two techniques produce comparable results, within the experimental errors, as far as the intensity of the dichroic signal is concerned. The measure of the dichroic signal in XMCD and the use of the optical sum rules can be used to evaluate the orbital and spin moment of the specimen [4]. Recent results, presented for the

first time at the 3rd CHIRALTEM workshop in Trieste, have shown that, in analogy with XMCD, sum rules to quantify the magnetic moments can be derived also for EMCD [5,6]. The capability to obtain EMCD spectra with improved S/N and the establishment of sum rules indicate that EMCD could be used to measure the magnetic moment of a bulk specimen with a spatial resolution not achievable by XMCD.

To explore the sensitivity of the two approaches to the specimen surfaces, one sample was exposed to the air allowing the formation of a few nanometres of iron oxide on the Fe film. XMCD, measured with Total Electron Yield (TEY), is a surface sensitive technique, with a probing depth of about 2-3 nm. It was expected that EMCD could be a technique more sensitive to the bulk, because the experiment is executed in transmission mode. In fact, the experiments performed by EMCD after the oxidation were not influenced by the presence of the oxide layer giving the results in figure 1b whereas the XMCD signal was strongly reduced as shown in figure 2.

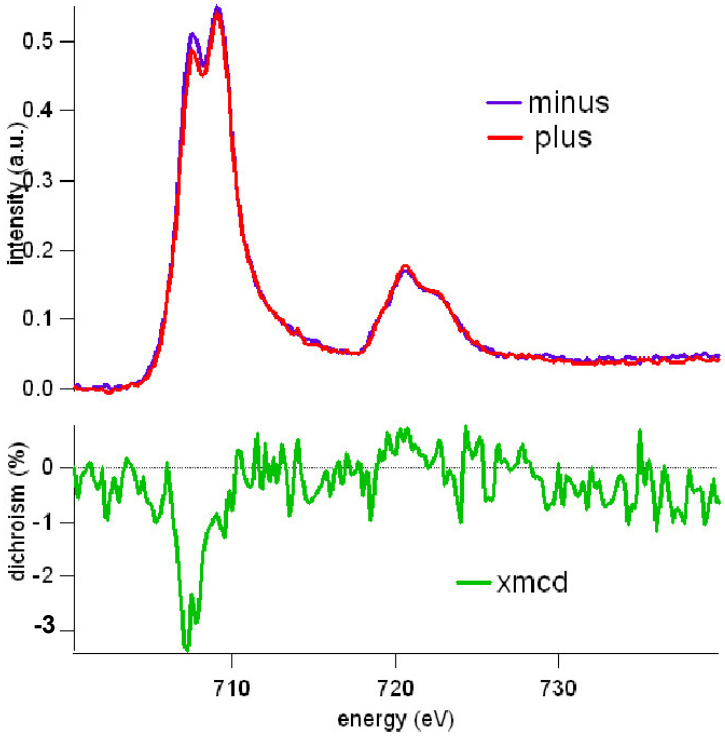

Figure 2: XMCD experiments performed on the specimen after the formation of few atomic layers of iron oxide on the Fe film.

It is worth noting that the XMCD signal on L_3 edge in figure 2 is decreased to 3%±2% and the dichroism at L_2 is no longer detectable. This result is related to the probing depth of about 2-3 nm of the XMCD recorded in TEY mode and hence most of the XAS signal comes from the oxidised layer. This kind of experiment demonstrate that EMCD and XMCD could give complementary information on the same material, XMCD being more sensitive to the surface, while EMCD is mostly sensitive to the bulk of the specimen.

Another sensitive point emerged from the study of the EMCD in the "intrinsic mode" is its dependence on the specimen thickness [7]. Figure 3 shows the expected dichroic signal as calculated theoretically:

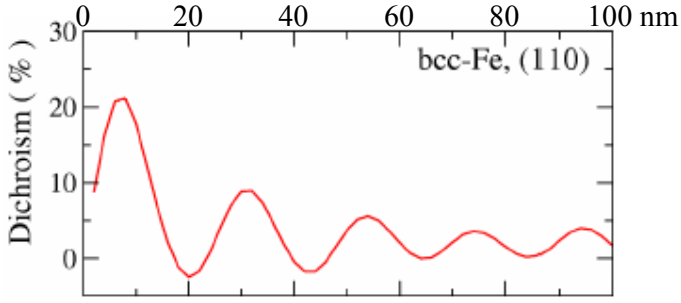

Figure 3: Theoretical calculation of the EMCD signal as a function of the specimen thickness for Iron oriented along the [001] zone axis, with the 110 spot in two-beam case.

The origin of this dependence on thickness and specimen orientation can be traced back to the dephasing between the incident and diffracted beam that determines (together with the condition that $\mathbf{q} \perp \mathbf{q'}$) the helicity of the virtual photon absorbed. This dephasing is defined by the difference in the optical path of the two electron beams before the ionisation process occurs (or after, for the outgoing wave) and depends on the *z* position of the target atom. The result of this dependence is that the polarization of the virtual photon changes with the specimen thickness and the expected EMCD signal can be, at most, equal to XMCD with fully polarized photons.
This finding poses a problem related to quantitative measurement of the dichroic signal in EMCD even provided that simulations can indicate the optimal experimental conditions to maximize the dichroic signal. The preparation of magnetic layers with different thickness is still in progress to study experimentally this aspect of the EMCD and confirm the theoretical predictions.
There is another aspect that should be underlined: the specimens studied by XMCD and EMCD were also studied by high resolution TEM and high spatial resolution energy dispersive x-ray spectroscopy to better understand, in a direct way, the relationship between the GaAs substrate, the Fe film and the capping layer. For example, it was possible to directly evidence how the capping layer of Cu on Fe grows forming islands and hence leaving the surface of the magnetic layer unprotected allowing the formation of the oxide if exposed to the atmosphere, whereas the growth of the Fe film over GaAs (001) was below the critical thickness and hence no structural defects were observed. This is an important point to be marked: EMCD allows the study of the chiral properties of the materials but at the same time on the same specimen it is possible to study also the crystal structure, the chemistry, the morphology and the electronic structure with atomic resolution.

The possible synergies between XMCD and EMCD were one of the main points discussed in the third CHIRALTEM workshop held in Trieste on May 31st – June 1st where more than 50 scientists involved in XMCD and EMCD participated. In fact, the main aim of the workshop was to put together the community of those who use the synchrotron to study the chiral properties of the matter with the community, formed very recently thanks to the CHIRALTEM project, of those who use the transmission electron microscope to study the same phenomena. It has been immediately clear that despite the few contacts between the two communities in the past, several new collaborations could be useful also with respect to, for example, the realisation of a TEM integrated in a beam line.

Finally, it could be helpful also to compare the timetable of the development of XMCD and EMCD up to now. The theoretical prediction that circular magnetic dichroism could be observed by using circularly polarized x-ray photons was made by Erskine and Stern in 1975 [8]. The first experimental observation of the predicted effect was reported twelve years later by G. Schütz [9] studying the XMCD effect on K edge of Fe. The sum rules, necessary to extract the information about the magnetic moment of the specimen, were derived about five years later [10,11]. The experimental confirmation of the validity of the sum rules followed shortly thereafter [4].
In the case of the EMCD the theoretical prediction was published in 2003 [1] and the experimental confirmation of the effect was obtained less than three years later [2]. The sum rules for EMCD [5,6] were first presented in 2007 at the 3rd CHIRALTEM workshop and are already available to the

public. The next logical step is to achieve the first quantitative measurement of the magnetic moment by EMCD, which is likely to be obtained in the near future. Concluding, the results achieved by the CHIRALTEM project and the comparison between EMCD and XMCD (summarized in Table 1) indicate that a new approach to the study of the magnetic properties of the bulk material is available based on an unexpected physics effect. The comparison between XMCD and EMCD has been, so far, of great help and guidance to achieve these important results and contacts between the two communities should be increased in the future, opening new scenarios in the understanding of the chiral properties of the matter but also possible development of new equipment designed to this aim.

Table 1: comparison between the various EMCD and XMCD techniques.

	Spatial resolution	Intensity (S/N)	Energy resolution	Collection time
EMCD (phase lock)	100 nm	low	1-2 eV	1-5 min
EMCD (det. shift)	100 nm	acceptable	1-2 eV	1-5 min
EMCD (OA shift)	50 nm	low	1-2 eV	1-5 min
EMCD (E-q diagram)	5-10 nm	good	0.7 eV	10 sec
EMCD LACDIF	5-10 nm	good	0.7 eV	10 sec
EMCD ESI*	50 nm	low	1 eV	30 min
EMCD ESD*	50 nm	low	1 eV	30 min
XMCD PEEM	50 nm [12]	high	0.1 eV	15 min
XMCD Absorption	15 nm [13]	high	0.1 eV	30 min

*obtained by the CEMES group in Toulouse.

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