ESRF	Experiment title: **Quadrupole transitions in alfa-Fe Phthalocyanine thin film (Fe-K edge)**	Experiment number: HE-3009
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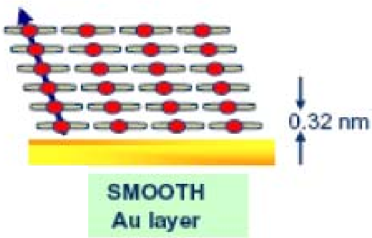
Names and affiliations of applicants (* indicates experimentalists):

Dr. Juan BARTOLOME *
Dr. Luis-Miguel GARCIA VINUESA*
Dr. Fernando BARTOLOME *
Lcda. Adriana Figueroa*
ICMA y Departamento de Física de la Materia Condensada
CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain
Dr. George FILOTI
National Institute for Research and Development, Magurele, Atomistilor 105BIS, ROMANIA
Dr. Thomas GREDIG
Dept of Physics & Astronomy, California State University, Long Beach CA 90840, USA



The metal phthalocyanines (MPc) form a family of compounds with a very wide range of commercial applications such as catalysts or dyes, and more recently in thin film technology. In MPc the M atom has square-planar coordination with four pyrrolic N atoms. These molecules may be deposited on a substrate forming a well defined film. In case of depositing on Au substrate the molecule plane is parallel to the substrate Fig. 1 (Denoted FePc/Au). These structures are similar in stacking angle with respect to the chain axis to the α phase, which orders ferromagnetically at approximatelly 10 K [1].

Fig.1. Sketch of the FePc/Au thin film.

From Mössbauer experiments it was conjectured that the record highest hyperfine field ever measured on an Fe(II) (B_{hf}=66.2 T) could be related to the electronic configuration $d_{xy}^2(d_{xz},d_{yz})^3d_{z^2}$, which has an **orbitally degenerate** ground state [2]. Indeed, in the experiment HE2486 we found evidence of the existence of a large orbital moment (L_{xy}=0.52 μ_B) from the analysis of the XMCD at the Fe $L_{2,3}$-edge performed at T=7 K, H=6 T, as a function of incident angle [3].

Because of the large orbital moment obtained in the previous experiment it was deemed of interest to explore the K-edge excitation, whose XMCD reflects only the orbital moment of the p states. In the present experiment we have performed angle dependent measurements of the Fe K edge XMCD since it allows us to determine the L_z^{4p} moment of the 4p states, uncontaminated of any spin contribution. L_z^{4p} may contribute to the total orbital anisotropy, and thus, to the exceptional orbital moment present in this compound. Besides, an important contribution to the XMCD from **quadrupole transitions (1s → 3d) Δm=2,** was expected because of the high orbital moment and of 4p-3d hybridization of the final states.

The XMCD at the Fe K edge of the same sample as in experiment HE2486; namely, an FePc film of 80 nm thickness, has been measured at the ID12 experimental beam. The experimental conditions were T=7 K and applied field H=6 T. An APPLE 2 undulator, and a double-Si(111)-crystal monochromator were employed, with a polarization rate of 90%. The detection technique used was fluorescence in backscattering geometry. The field was parallel to the incident beam and the incident angle was varied between zero (normal incidence) and 75^o (grazing angle). The XMCD signal was obtained by a direct difference of the XAS spectra recorded with opposite helicities at the fixed magnetic field for both orientations of the field. At each incident angle a XAS scan in a broad energy region was measured to establish the 1 atom normalization, and a second XMCD scan in the photon energy region of interest (Fig. 2a)

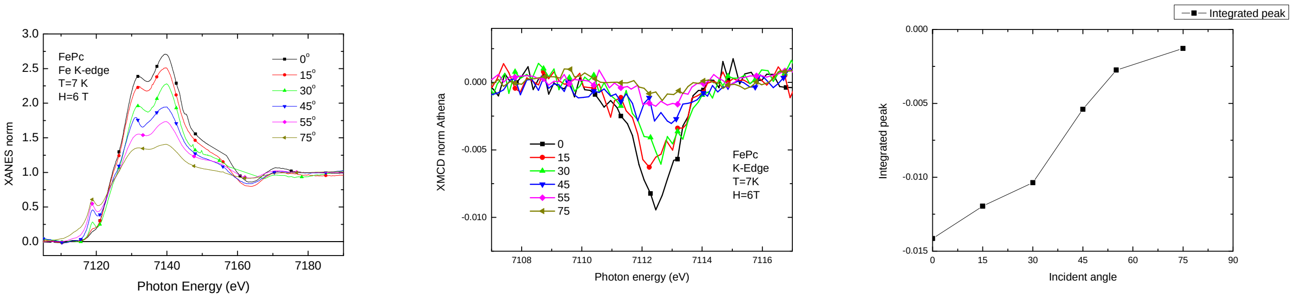


Fig. 2. a) XANES of Fe Pc at the K-edge as a function of incident angle, b) XMCD from the quadrupolar transition, c) integrated area of the peaks in b), as a function of incident angle.

To achieve a correct normalization of the spectra the wide energy scans were treated with the ATHENA interface part of the IFEFFIT program for XAFS analysis to subtract the pre- and post-edge lines. From the step at the Fermi energy the scaling factor was determined, allowing thus to normalize the XANES and XMCD per Fe atom.

The XANES spectra show several features: A pre-peak below the Fermi energy that increases strongly with increasing incident angle. This is due to Fe 4p-states hybridized with other orbitals of the same symmetry in the molecule.

The white line shows two peaks which decrease in intensity with increasing incident angle, and the first ondulation due to EXAFS at 7164 eV.

Around 7112.5 eV, a very small bump appears in the XANES, which gives rise to the XMCD peak caused by the quadrupole transitions ($\Delta m=\pm 2$) (Fig. 2b). The intensity of this peak decreases with increasing incident angle. After subtraction of the XMCD signal not originating from the quadrupolar contribution, the integrated peak areas have been determined and the results are collected in Fig. 2c. as a function of incident angle. This transition (1s – 3d) depends exclusively on the orbital moment of the empty Fe 3d states.

The quantitative interpretation of these experimental results are underway.

References

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