

Large orbital moment in α -Fe phthalocyanine thin films: an XMCD study

J. Bartolomé¹, L.M. García¹, F. Bartolomé¹, G. Filoti², T. Gredig³, J.C. Cezar⁴.

¹Instituto de Ciencia de Materiales de Aragón. Departamento de Materia Condensada. CSIC-University of Zaragoza, 50009 Zaragoza, Spain

²National Institute of Research and Development, Magurele, Bucharest, Romania.

³Dept. of Physics. University of California at San Diego. 92093-0319, U.S.A.

⁴ESRF. F-38043, Grenoble, France.

barto@unizar.es

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 [1]. In MPc the M atom has square-planar coordination with four pyrrolic N atoms (Fig. 1). In previous work it was shown that the α -FePc phase is ferromagnetic below 10 K, differently to the β -FePc which remains paramagnetic at all temperatures [2].

These molecules may be deposited on a substrate forming a well defined film, by means of Organic Molecular Beam Epitaxy. In case of depositing on sapphire the MPc molecules stack in a herringbone structure forming long needles parallel to the substrate Fig. 2a. In contrast, when deposited on Au substrate the molecule plane is parallel to the substrate Fig. 2b. From Mössbauer experiments it was found to have the record highest hyperfine field ever measured on an Fe(II) ($B_{\text{hf}} = 66.2$ T). It was conjectured that could be related to the electronic configuration $d_{xy}^2(d_{xz}, d_{yz})^3d_{z^2}$, which has an orbitally degenerate ground state, and as a consequence, an expectation value of $\langle L_z \rangle = 1$ [3].

An X-ray Magnetic Circular Dichroism (XMCD) spectroscopic study has been performed on α -FePc thin films, deposited on sapphire and Au substrates. From the angular dependence of the XMCD spectra at the Fe L_3 and L_2 edges were measured as a function of incident angle, θ (Fig. 3a, and b) From the sum rule analysis the values for the $m_L(\theta)$ and $m_{S,\text{eff}}(\theta)$ moments were obtained (Fig. 4), concluding that the Fe magnetic anisotropy is nearly planar, in good agreement with previous SQUID magnetization data. From the analysis of the data in Fig. 4 with the relation $m_{L,\text{Seff}} = m_{L,\text{Seff}}^z \cos^2 \theta + m_{L,\text{Seff}}^{xy} \sin^2 \theta$, the orbital moment $m_L = 1 \mu_B$ is obtained, therefore, the conjecture is proven to be correct. The $m_{S,\text{eff}}$ moment is analyzed with the expression $m_{s,\text{eff}}(\theta) = m_s [1 + (7/2)(Q_{zz}^* \cos^2 \theta + Q_{xx}^* \sin^2 \theta)]$, which yields the values for the isotropic spin component $m_S = 1.2 \mu_B$, a strong dipolar component with components $Q_{zz} = 0.15$ and $Q_{xx} = Q_{yy} = -0.07$, which comply with the rule that $Q_{xx} + Q_{yy} + Q_{zz} = 0$.

The main conclusion of this work is that this compound has the highest orbital moment known for an Fe(II) atom, namely, $m_L = 1 \mu_B$. Such a large value of m_L is originated by the orbital degeneracy of the d_{xz} , d_{yz} level occupied just by three electrons, thus proving the conjecture proposed from previous Mössbauer spectroscopy.

References:

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- [3] G. Filoti, M.D. Kuz'min and J. Bartolomé. Phys. Rev. B **74**, (2006) 134420

Figures:

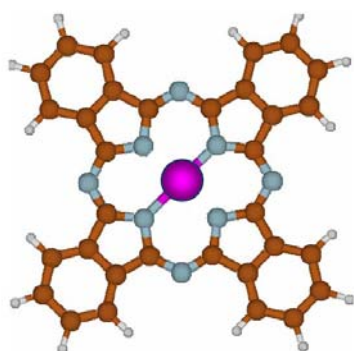


Fig 1. Fe Phthalocyanine molecule. The central Fe(II) has square-planar coordination with four pyrrolic N atoms.

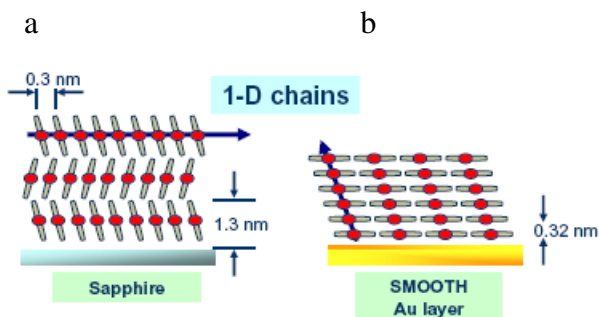


Fig 2. a) FePc molecules deposited on sapphire: molecules stack in a herringbone structure forming long needles parallel to the substrate. b) Deposited on Au: the molecules self-order parallel to the substrate.

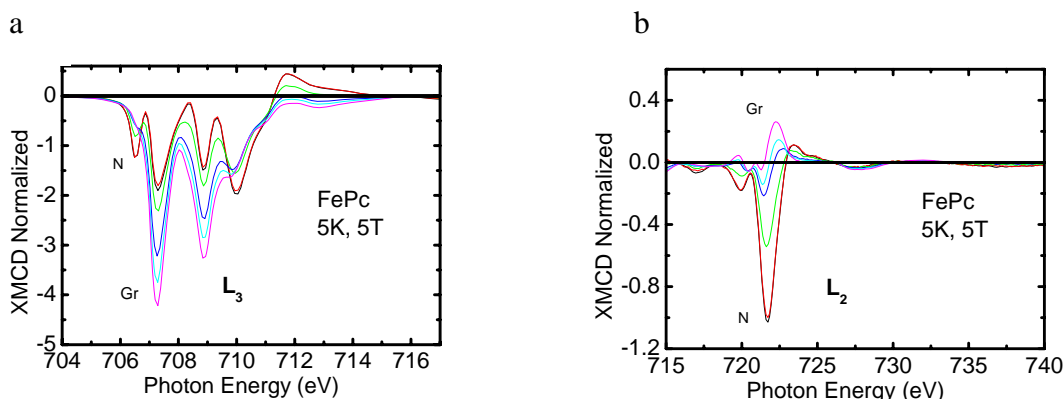


Fig 3. Angular dependence of the XMCD spectra: a) at the Fe L_3 edge, b) at the L_2 edge. (Gr: Grazing angle; N: Normal incidence)

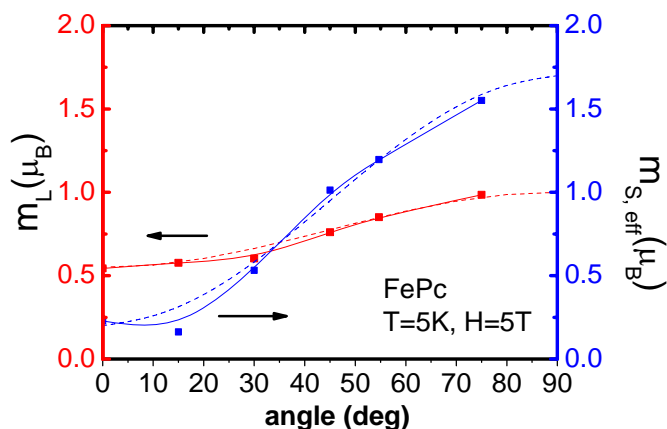


Fig 4. Angular dependence of the orbital moment m_L and effective spin moment $m_{S,eff}$ derived with the sum rules from the data in Fig. 3. The angle of incidence is given in degrees.