ESRF	**Experiment title:** **Field induced Magnetic dichroism in Paramagnetic Solids**	**Experiment number**: **HE966**
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We report on two sets of ID12 experiments obtained on 4,5d nano particles and metals:

1- Low temperature XMCD experiments on Pt metal, Pt and Au particles

It is well known that the properties of metallic nano-particles, less than 1000 atoms, are different from those of metal in bulk and that the binding energies of these particles vary periodically, due to *quantum size effect* and that nano-particles are not just aggregates of metallic atoms. The development of preparative method of the mono dispersed metallic particles has permitted the synthesis of particles of Pd[1], Pt[2] or Au[3] in presence of linear polymer, ligand…etc. The dispersion of the distribution changes from 0.3 nm to 0.8 nm with a diameter range of 2-4 nm. The saturation moment estimated from the magnetisation curve is about $18\mu_B$/part for Pd particles and surprising more for the Au particles : 22 μ_B/part.

We have performed XMCD experiments on Pt metal, Pt and Au particles. The main results can be summarised by:

a) The limit of the sensibility of the XMCD method is given by the amplitude of the L_3 dichroic signal observed in the Pt metal (4K and 7T), indeed we were not able to detect any magnetic signal at the Pt-L_2 edge. This limit reaches 2.10^{-3} part of the edge.

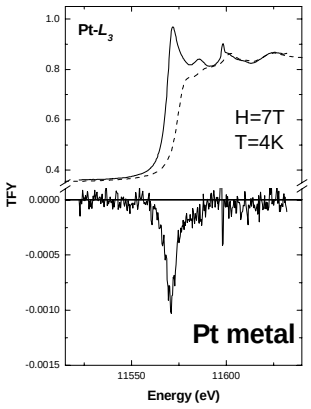

Figure 1. *L_3 edge and XMCD for Pt metal (1000Å Pt films), at T=4K and H=7T. the dashed line corresponds to the Au-L_3 edge*

The Thole sum rules[4] for the Pt-$L_{2,3}$ can be written as follows[5]:

$\langle L_z\rangle = 2(A_3+A_2)(n_{5d}/3\sigma_{iso})$ and $\langle S_z\rangle = 1.5(A_3-2A_2)(n_{5d}/3\sigma_{iso})$,

where $A_{2(3)}$ are the integrals over the dichroic signal at the $L_{2(3)}$ edges, n_{5d} is the hole number in the *5d* band and σ_{iso} the isotropic cross section corresponding to the $2p\rightarrow 5d$ transitions. In order to separate the transitions to unoccupied *5d* states from the other $2p\rightarrow nd$, *s* dipole transitions, we use the Au-$L_{2,3}$ absorption edges obtained on a Au foil. The energy scales of the Au and Pt spectra are aligned using the two XANES structures and the intensities normalised before and after the edge (see Figure 1). Follow Sham[6] we suppose that the difference between these two lines corresponds to the white line only due to the $2p\rightarrow 5d$ transitions and then,

$\sigma_{iso}/n_{5d} = [\sigma_{iso}(Pt) - \sigma_{iso}(Au)]/[n_{5d}(Pt) - n_{5d}(Au)]$.

At this stage we have two alternatives: either use the calculated hole number and determine the *5d* magnetic moment or start from the well known bulk susceptibility and then extract the *5d* holes number. Using the Pt metal susceptibility χ_{Pauli} (4K) =1.1 10^{-6} cm^3/g, *i.e.* $M(4K,7T)=2.710^{-3}\mu_B$, the XMCD analysis leads to $[n_{5d}(Pt) - n_{5d}(Au)] = 0.55\pm0.15$. The large error bars come essentially from the $\langle L_z\rangle=0$ hypothesis, this constraint being due to the ignorance of L_2 dichroism. The n_{5d}(Pt) number has to be compared to the calculations on the Pt metal[7].

From these Pt metal-$L_{2,3}$ experiments the most important conclusion to be drawn relates to the dichroic limit for spin measurements, namely $\approx 1.10^{-3}$ μ_B, which corresponds to the lowest spin values for the transition metals, in laboratory magnetic fields (7teslas).

b) The observation of a dichroic signal at the Pt-$L_{2,3}$ edges in metallic Pt particles (figure 2) demonstrates the polarisation of the *5d* orbitals in this system and the qualitative analysis shows the increase of the moment per atom compared to the metal.

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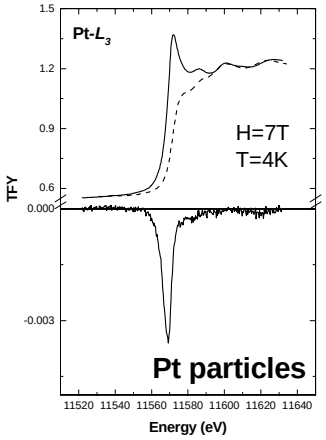

Figure 2. *L_3 edge and XMCD for Pt particles, at T=4K and H=7T, the dashed line corresponds to the Au-L_3 edge*

In a rough analysis we adopt a simple linearity relationship between the dichroic signal observed in the Pt metal and the Pt particles, that means that we suppose that the *5d* hole number remains the same in the two systems (!). From the normalised dichroic signal of the Pt particles, about 6.10^{-3}, we found a magnetisation M(4K,7T) ≈ $0.1\mu_B$/Pt atom (±15%). Contrary to the Pt metal case a L_2 signal was detected and evidences the existence of an orbital moment $\langle L_z \rangle \neq 0$. The fluorescence corrections, which are in progress, would permit a quantitative determination of this *5d* orbital contribution in the Pt particle clusters.

c) Despite the existence of a polarisation on the Au particles[3], larger than for the Pt ones as demonstrated by SQUID measurements, we were not able to detect any dichroic signal at the Au-$L_{2,3}$ edges at the lower temperature available (2K). We have any explanation for this negative result.

This study will have advantageously to be supplemented by measurements as a function of magnetic field and temperature in order to confirm the superparamagnetic character of these nano particles.

2- Field-induced Magnetic Dichroism in Pd metal

Since the first experiments of circular magnetic dichroism on paramagnetic compounds[8], the interest for the field induced magnetic circular dichroism was reinforced, compared to those on spontaneously magnetized solid, thanks to new detection limits (*cf* before) of the dichroism signals due to the important improvements of the beam line set-up. Moreover, a recent theoretical, approach due to Ebert[9], will help us for magnetic studies in many systems characterised by multi source of magnetism, paramagnetic state or close to a ferromagnetic state.

The experimental difficulties for the dichroism study of *4d* metals are the same that for the *5d* metals, except that, in addition, the rate of polarisation becomes more an more weaker for energies ranging from $L_{2,3}$ of Pd to Rh.

The example of the Pd metal

Figure 3 illustrates the $L_{2,3}$-edges and XMCD for Pd metal, at T=4K and H=7T. The data are corrected for the incomplete rate of polarisation (P_C~12% at the L_3-edge and Pc~19% at the L_2-edge) and the branching L_3/L_2 ratio was set to 2.08. Since Pd was a thick single crystal, we have first corrected the raw data from the saturation effects, due to the use of the Total Fluorescence Yield (TFY) mode to record the absorption. After correction from saturation effects and then from the polarisation degree, the obtained XANES spectra were nearly identical to the Pd-*L* white lines measured in thins films of PdFe[10]. The amplitude of the measured dichroic signal is about 4.10^{-2} part of the L_3-edge. From the branching ratio of the XMCD at the L_2 and L_3 edges it is glaringly obvious that the orbital moment is different from zero.

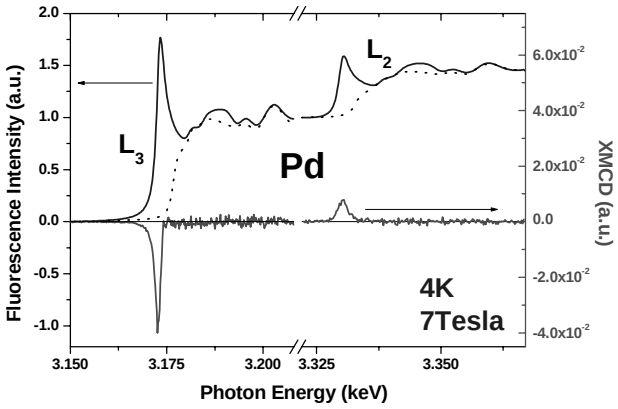

Figure 3. *XANES and XMCD for Pd metal recorded at the $L_{3,2}$-edges at T=4K and H=7T. The dashed lines represent the XAS of Ag metal. The data shown are corrected for incomplete polarisation rate and saturation effects.*

The quantitative analysis of the magnetic responses on Pd metal is the same to that proposed on the Pt systems: we have defined the Pd-$L_{2,3}$ white lines by comparison with the cross section of the Ag metal measured on a 1000Å Ag film (dashed line on figure 3). The sum rules application lies on the knowledge of the n_{4d} holes number. Taking the values proposed by Vogel[10] in the PdFe study, namely $[n_{4d}(\text{Pd})-n_{4d}(\text{Ag})]= 0.92$, the orbital and spin contributions for the *4d* band are:

$\langle L_z \rangle = -0.0035\mu_B$, $\langle 2S_z \rangle = -0.012\mu_B$ (±15%), supposing that $\langle T_z \rangle = 0$.

Note that the respective signs of $\langle L_z \rangle$ and $\langle S_z \rangle$ are in agreement with those expected for a heavy *d* transition metal and that the orbital-to-spin magnetic moment ratio is about 28%. This ratio is higher compared to Pd in a ferromagnetic environment that is about 10%[10]. These magnetic contributions lead to a susceptibility, $\chi_{4d}=1.18\ 10^{-5}$ cm^3/g, which can be advantageously compared with the macroscopic bulk susceptibility of the Pd metal, $7.5\ 10^{-6}$ cm^3/g measured by VSM.

To summarize, these magnetic studies on nano particles (Pt) and non-magnetic *d* metals (Pd and Pt) have evidenced the existence of XMCD signals induced by the sole external magnetic field. The sum rules leads to the spin and the orbital susceptibilities. The differences observed with the macroscopic bulk values suggest that some other contributions must be taken into account, like the diamagnetic contribution in the macroscopic measurements and /or the dipole magnetic term $\langle T_z \rangle$ contribution in the sum rules.

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