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XMCD at the $L_{2,3}$ -edges of Pt in ordered TPt_3 alloys ($T = \text{Cr, Mn, Co}$)

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We present x-ray magnetic circular dichroism (XMCD) experiments at the $L_{2,3}$ edges of Pt in ordered TPt_3 alloys ($T = \text{Cr, Mn and Co}$). The derived Pt $5d$ spin and orbital magnetic moments are found to be in good agreement with band structure calculations. The extraction of $5d$ magnetic moments from measured x-ray-absorption spectra is discussed in detail.

Keywords: Pt; XMCD; Binary Alloys.

1. Introduction

Among the alloys of the $3d$ ferromagnetic transition metal elements and the $5d$ non-magnetic elements, the ordered TPt_3 alloys ($T = \text{V, Cr, Mn, Fe and Co}$) crystallizing in the Cu_3Au structure have attracted much attention because of their interesting magnetic properties (*i.e.*, a large Kerr rotation at short wavelength or/and a strong magneto-crystalline anisotropy (Suzuki *et al.*, 1997; Weller *et al.*, 1993)). Also, these compounds are model systems for the study of the magnetic properties of $3d$ - $5d$ systems since one would expect to find systematic and linear trends with the filling of the $3d$ band. Therefore, several band structure calculations attempted to reproduce the magnetic properties of these compounds (*i.e.*, the magnetic ground state and the determination of the magnetic moments on both the Co- $3d$ and Pt- $5d$ electrons) (Hasegawa, 1985; Tohyama *et al.*, 1989; Iwashita *et al.*, 1996; Oguchi *et al.*, 1997; Suzuki *et al.*, 1997; Lu *et al.*, 1998). In particular, the recent calculations of Iwashita *et al.* and Suzuki *et al.*, which have investigated the orbital polarization of the Pt $5d$ electrons, have contributed to get a reliable information on the magneto-optical properties of the TPt_3 alloys. As compared to these numerous theoretical investigations, there have been only few experimental studies (namely, magnetization or neutron diffraction measurements (ref. 1)) on these compounds.

Here, we present XMCD experiments at the $L_{2,3}$ edges of Pt in ordered TPt_3 alloys ($T = \text{Cr, Mn and Co}$), which allows us to get a quantitative information on the $5d$ spin and orbital magnetic moment. The results obtained from dichroism experiments are found to be in good agreement with band structure calculations. We show, however, that the application of the Thole sum rules (Carra *et al.*, 1993) at the $L_{2,3}$ edges of Pt requires a thorough analysis.

2. Experimental results

The polycrystalline TPt_3 compounds ($T = \text{Cr, Mn and Co}$) were prepared by arc-melting stoichiometric amounts of the pure constituents in an Ar atmosphere. Standard annealing treatments ensured the formation of the ordered Cu_3Au -type crystal structure.

The MnPt_3 and CoPt_3 compounds are known to be ferromagnetic ($T_C = 370$ K and 290 K, respectively), whereas CrPt_3 is ferrimagnetic ($T_C = 450$ K). X-ray-absorption spectra (XAS) were measured at the European Synchrotron Facility (ESRF) in Grenoble (France) on the ID12A beamline. The straight section ID12 is equipped with the helical undulator Helios-II, that covers an energy range from 3 to 22 keV (Goulon *et al.*, 1995). For these experiments performed at the $L_{2,3}$ edges of Pt, the third harmonic of the undulator Helios-II was chosen and a double Si-(111)-crystal monochromator ensured the monochromatization of the beam. At the energy range requested for the present investigation (11–14 keV), the polarization transfer function given by the Si crystal is extremely high resulting in a circular polarization rate of about 0.9. The XAS spectra were monitored at 10 K in the total fluorescence detection mode. The XMCD signal was obtained by reversing the direction of the 3-T applied magnetic field, keeping the helicity of the incoming beam fixed.

3. Data analysis

Since fluorescence yield (FY) measures the decay of the core hole created in the absorption process, it gives an indirect measure of the absorption cross section. Assuming a proportionality between FY and the absorption coefficient requires therefore a thorough analysis. Some of the main difficulties encountered in the FY measurements consist of self-absorption effects, leading to a distortion of the absorption spectra (Eisebitt *et al.*, 1993). To get rid of these effects, we have therefore compared the isotropic spectrum absorption (*i.e.*, approximately the half sum of the spectra recorded for the two directions of the magnetic field) measured in FY to that obtained in Total Electron Yield at normal incidence. Assuming that saturation effects are not polarization dependent, we can correct

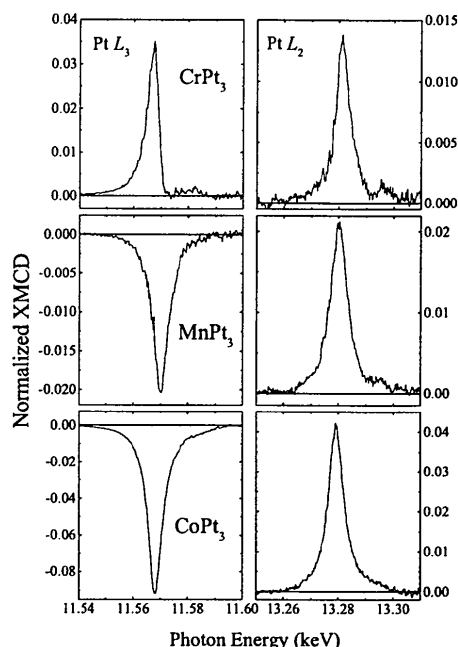


Figure 1

The XMCD signals measured at the Pt $L_{2,3}$ edges in the series of TPt_3 ($T = \text{Cr, Mn and Co}$) ordered alloys ($H = 3$ T, $T = 10$ K). The corresponding absorption spectra have been normalized by adjusting the step height ratio of the L_3 and L_2 edge jumps to 2.22. Units in % of the L_3 edge jump.

the spectra for self-absorption effects and get the proper dichroism (shown in Fig. 1). The obtained XMCD signals look quite similar to those measured recently by Maruyama *et al.* (Maruyama *et al.*, 1995) on the same compounds in the transmission method. However, the data analysis of Maruyama *et al.* seems to us quite controversial. Indeed, Maruyama *et al.* made crude approximations in the applications of the Thole sum rules (Carra *et al.*, 1993) that could lead to large errors in the determination of the spin and orbital magnetic moments. We will, however, return to this point later on.

We now discuss the renormalization of the experimental absorption spectra: An interesting feature of the $L_{2,3}$ absorption edges of Pt is that the ratio r_L of the L_3 and L_2 edge jumps deviates from the statistical ratio expected from the degeneracy of the core hole states. Mattheiss and Dietz (Matheiss and Dietz, 1980) found $r_L = 2.22$ in pure Pt and attributed this effect to a difference between the $R^{2p_{1/2}}$ and $R^{2p_{3/2}}$ radial functions, resulting from the large $2p$ spin-orbit coupling. To account for this effect, we have thus normalized the XAS spectra recorded in the TFY detection mode by adjusting the step height ratio to 2.22. We emphasize that this procedure is far from insignificant since an important assumption in the Thole sum rules is that the radial integrals should be independent of both the energy and spin direction (ref. 2).

The next step in the analysis consists in applying the Thole sum rules, that allow to get the ground state expectation value of the operators L_Z and S_Z acting on the shell l that receives the photoelectron. However, the determination of the spin and orbital contribution to the total magnetic moment may be a difficult task for experimentalists since there are some quantities (such as the number of holes and the isotropic absorption cross section corresponding to this specific l shell) that have to be precisely known. As outlined, the analysis of the XMCD response at the $L_{2,3}$ edges of Pt is not straightforward and there seem to us that the main controversial points in the analysis of Maruyama *et al.* are the following:

(i) To separate the transitions to unoccupied $5d$ states from the continuum, Maruyama *et al.* use a simple step-like function. This is certainly a good approximation for the determination of the $3d$ near edge resonance (Co and Fe $L_{2,3}$ edges), but this could lead to large errors in the case of Pt since the Pt $L_{2,3}$ edges do not exhibit a strong white line.

(ii) It is assumed that the initial electronic configuration is $5d^9$. This is, however, a totally unjustified assumption since band structure calculations find that the value of $5d$ holes is close to 1.8 (Stoeffler, 1997).

(iii) Finally, Maruyama *et al.* choose to fit both the XMCD spectrum and the $5d$ isotropic absorption cross section with a Lorentzian function. Such a simplistic notion of XMCD signals is quite unconvincing.

To overcome the difficulties encountered in the determination of both the number of holes and the $5d$ isotropic absorption cross section, we present now an alternative analysis: The isotropic absorption cross section R per $5d$ holes can be written as:

$$\frac{R}{(10 - n_{5d})} = \int_{L_{2,3}} \frac{d\omega}{\omega} \left(\frac{\sigma_{tot}^{Pt}(\omega) - \sigma_{tot}^{Au}(\omega)}{n_{5d}^{Au} - n_{5d}^{Pt}} \right),$$

where $\int_{L_{2,3}} \frac{d\omega}{\omega} (\sigma_{tot}^{Pt}(\omega) - \sigma_{tot}^{Au}(\omega))$ is the integrated intensity of the difference between the isotropic Pt and Au normalized absorption cross section (*i.e.*, the usual cross section divided by the photon energy) over the L_3 and L_2 edges and $(n_{5d}^{Au} - n_{5d}^{Pt})$ is the electron number difference estimated to be 1.06 (Stoeffler, 1997). Note that the energy scale of the Au spectra has to be expanded to

account for the difference in the lattice parameter and aligned in energy with the Pt spectra on the fine structure.

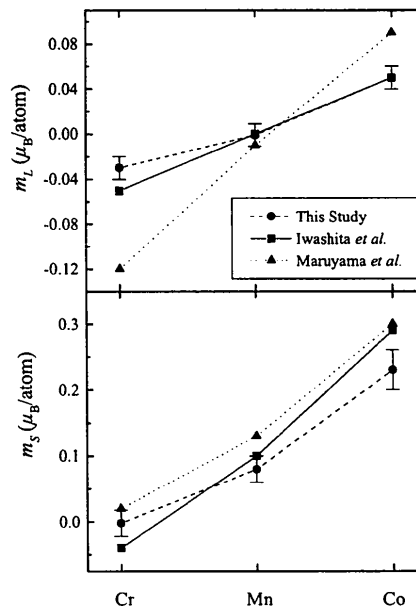


Figure 2

The Pt $5d$ spin and orbital magnetic moments (in units of μ_B per atom) measured in the series of TPt_3 ($T = Cr, Mn$ and Co) ordered alloys (circles). Triangles and squares denote respectively the values reported by Maruyama *et al.* (Maruyama *et al.*, 1995) and Iwashita *et al.* (Iwashita *et al.*, 1996). We have assumed that the contribution of the magnetic dipole term to the effective spin magnetic moment (*i.e.*, the quantity directly determined from the application of the Thole sum rules) is negligible due to the important $5d$ band broadening.

Figure 2 shows the values of the Pt $5d$ spin and orbital magnetic moments derived from the application of the Thole sum rules for the three ordered TPt_3 alloys under study. Also, the magnetic moments determined from band structure calculations (squares) and from the previous XMCD experiments of Maruyama *et al.* are presented (triangles). As expected, there are some discrepancies between our measurements and those of Maruyama *et al.*. In particular, Maruyama *et al.* overestimate the magnitude of both the Cr and Co $5d$ orbital magnetic moment (Lu *et al.*, 1998). As outlined by Iwashita *et al.*, there are systematic trends in the magnetic behavior of the TPt_3 compounds, that can be easily explained in terms of the strength of the $3d/5d$ hybridization: For instance, the fact that the $5d$ magnetic moment is smaller in $MnPt_3$ than in $CoPt_3$ is attributed to the decrease of the $3d/5d$ hybridization in $MnPt_3$, which results from the larger Mn $3d$ exchange splitting.

Finally, in the series of TPt_3 alloys, $CrPt_3$ present some interesting properties. In particular, the XMCD signal is found to be positive at both the L_2 and L_3 edge of Pt (this results from (i) the anti-parallel alignment of the Cr $3d$ and Pt $5d$ spin magnetic moments (ii) the existence of a $5d$ orbital magnetic moment larger than its spin counterpart (ref. 3)) and the L_3 edge shows a remarkable asymmetry.

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- Ref. 1. Note that neutron diffraction measurements cannot separate the spin and orbital contribution for polycrystalline samples. For single crystal, the separation is far from trivial and requires a deconvolution of the experimental data.
- Ref. 2. In a proper analysis, one should correct the sum rules for this effect by substitute $(\Delta L_3 - 1.11\Delta L_2)$ for $(\Delta L_3 - \Delta L_2)$ in the orbital sum rule and $(\Delta L_3 - 2.22\Delta L_2)$ for $(\Delta L_3 - 2\Delta L_2)$ in the spin sum rule, where $\Delta L_{3(2)}$ denote the integrated dichroism signal over the $L_{3(2)}$ edges, respectively. For these experiments, the discrepancy is lower than 10%, which is comparable to the precision of our measurements.
- Ref. 3. It is obvious that the L_3 edges has to be at least 2 (2.22) times larger than the L_3 edge to fulfill the third Hund's rule.

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