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XAFS Measurements on Co-K and Pt-L_{III} Edges in (111) CoPt₃ Films

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Abstract. XAFS measurements at the Co-K edge and Pt-L_{III} edge were performed in an (111) epitaxial CoPt₃ film with strong perpendicular magnetic anisotropy. The analysis of XAFS data obtained using in-plane and out-of-plane polarization show the existence of an anisotropic local order characterized by preferential heteroatomic pairs out of the film plane balanced with preferential homoatomic pairs in the (111) plane. The isotropic local order found in a magnetically isotropic CoPt₃ film from Pt-L_{III} edge data should be confirmed by XAFS measurements on Co-edge.

1 Introduction

Recently, the Co_xPt_{1-x} alloy films have received much attention as promising candidates for high density magneto-optic recording at short wavelengths, owing to strong perpendicular magnetic anisotropy and increased Kerr rotation at blue wavelength[1]. In molecular beam epitaxial (111) CoPt₃, magnetic anisotropy was found strongly dependent on the growth temperature with maximal perpendicular anisotropy in films grown around 690 K[2,3]. The microscopic origin of such anisotropy in (111) disordered fcc CoPt₃ films is still unclear, since in addition to the [111] growth direction, they are three other equivalent axis at 70.5° from [111]. In contrast, the disappearance of perpendicular anisotropy in films grown at temperatures higher than 780 K was clearly related with L1₂ long-range chemical ordering, favoured by an increase of bulk diffusion during preparation. Epitaxial (0001) hexagonal Co₈₂Pt₁₈[4,5] and (111) fcc Co₅₄Pt₄₆, also grown around 690 K and exhibiting increased perpendicular anisotropy, show long-range or medium-range chemical ordering along the growth direction. This suggests that similar chemically anisotropic structural order can exist in (111) CoPt₃ films but restricted on a local range since no diffuse halo or superlattice peaks was measured by X-ray diffraction for this composition. X-ray absorption fine structure (XAFS) is ideally suited for the study of such anisotropic effects since the polarization sensitivity of the XAFS signal allows us to sort out neighbor atoms that are located in the same (111) plane as the absorbing atom or out of this plane. Here, the purpose of the XAFS experiments in two CoPt₃ films of different magnetic behavior, using in-plane and out-of-plane polarization, is then to search a microscopic structural origin of perpendicular magnetic anisotropy.

2 Experimental technique

Co_xPt_{1-x} films (x~0.25,0.32) of 500 Å thickness were deposited at 690 K and 800 K from two Co and Pt electron gun sources in a 10⁻¹⁰ torr vacuum, onto a 150 Å (0001)Ru buffer grown at 900 K on (001) mica substrate. The films were covered by a 15 Å protective Pt layer. The deposition rates of Co and Pt were equal to 0.05 and 0.2 Å/s, respectively. X-ray diffraction measurements have shown that the film deposited at 690 K exhibits a fcc disordered structure, while the film grown at 800 K presents L1₂-type chemical ordering with a chemical order parameter of 0.2. An L1₂ CoPt₃ bulk alloy was also prepared to be used as reference sample. The order parameter obtained in the bulk alloy after successive annealing treatments is of 0.67, i.e. in average a Co atom is surrounded by 10.4±.2 Pt and 1.8±.2 Co atoms and a Pt by 8.6±.1 Pt and 3.4±.1 Co.

XAFS measurements were performed on the bending magnet CRG-IF beamline at ESRF on Pt-L_{III} and Co-K edges with a Si(311) double crystal monochromator. The spectra were collected using a total electron yield detector with He gas flow working at liquid nitrogen, designed by the CRG-IF team and described in detail in these proceedings[6]. The samples were stuck with Ag lake on a special 360 deg rotating sample holder in order to avoid Bragg peaks and making an inclination angle of 8 deg with the incident photon beam. The change from in-plane to out-of-plane polarization sample geometries was realized by rotating the sample holder by 90 deg.

3 Results and discussion

XAFS signals were extracted using standard techniques for atomic absorption removal and data normalization. The structural parameters describing the nearest neighbor environment around the central atom are obtained by fitting

the XAFS filtered signal using the formula[7]:

$$\lambda(k) = \sum_j \frac{N_j^*}{k R_j^2} F_j(k) \exp(-2k^2 \sigma_j^2) \exp(-\frac{2R_j}{\lambda(k)}) \sin(2k R_j + \phi_j(k)) \quad (1)$$

where R_j is the mean distance between the absorbing atom and the j -th shell, $F_j(k)$ the backscattering amplitude of the j -th neighbor atom, σ_j the rms deviation from the average distance R_j , $\lambda(k)$ the mean free path of photoelectron and $\phi_j(k)$ the total phase shift. For nonisotropic systems N_j^* is the polarization dependent effective coordination number[7]:

$$\begin{aligned} N_j^* &= 3 \sum_{i=1}^{N_j} \cos^2 \alpha_{ij} && \text{for Co - K edge} \\ N_j^* &= (0.5 + c) N_j + (1.5 - 3c) \sum_{i=1}^{N_j} \cos^2 \alpha_{ij} && \text{for Pt - L}_{III} \text{ edge} \end{aligned} \quad (2)$$

α_{ij} being the angle between the E vector and the bond between the absorbing and the j -th neighbor atom and $0 \leq c \leq 0.2$. For Pt-L_{III} edge the polarization sensitivity of XAFS is weakened by the isotropic term $0.5N_j$.

The XAFS spectra for the bulk alloy are independent on the polarization geometry. The analysis of the first-shell of the filtered data allows to test the transferability of the backscattering amplitudes and phase functions calculated by McKale et al[9]. The first-shell XAFS data are perfectly reproduced with a single shell at a distance of 2.724Å with the numbers of Co and Pt backscattering atoms given in table 1. The analysis of bulk sample allowed to extract the E_0 and the Γ parameters to be kept fixed in the film analysis to improve fit reliability.

Figure 1: Modulus of the Fourier transforms of $k\chi(k)$ for out-of-plane (—○—) and in-plane (—) polarizations.

Fig.1 shows the Fourier transforms (FT) of the $k\chi(k)$ curves measured in the two polarization geometries, on both edges for the film grown at 690 K and on Pt-edge only for the film grown at 800 K. Clear differences from the out-of-plane and in-plane polarizations appear on Co-edge, the splitting of the first peak is due to the Pt first shell. On Pt-L_{III} edge the polarization effects are smaller. In addition to the isotropic term in N_j^* (2), the contribution of the expected isotropic Pt protective layer, estimated at 7.5% of XAFS signal (relying on an escaping depth of electrons about 200 Å[8]), and the decreased sensitivity to the environment around the majority atoms can explain such result at least for the film grown at 690 K.

The fitted curves of the inverse Fourier transforms of the first coordination shell using the formula (1) are shown in Fig.2 and the structural parameters extracted from the fitting procedure are summarized in table 1. The Co edge analysis reveal an anisotropic local order characterized by a number of CoCo pairs higher in plane than out of the plane (inversely for the CoPt pairs): the out-of-plane signal could be fitted using only one shell of $N_{CoPt}^* = 10.5$ atoms at about 2.71 Å. The addition of a small amount of Co-Co pairs does not significantly improve the best fit. On the contrary the best fit of in-plane data require a double shell with $N_{CoPt}^* = 8.3$ at about 2.71 Å and $N_{CoCo}^* = 3.8$ at about 2.69 Å.

On Pt-edge excellent fits of the first-shell XAFS data are obtained using two shells Pt-Pt and Pt-Co but the effects of anisotropy are less evident than for the Co edge data. Nevertheless the Pt-edge parameters for the film grown at 690 K are consistent with those determined on the Co-edge, since an increase of PtCo pairs together with a decrease of PtPt pairs is found when changing from in-plane to out-of-plane polarization. The Pt-Pt interatomic distance higher than the Pt-Co one and the in-plane favored homoatomic pairs could explain the compression of the fcc stacking along the growth direction observed by X-ray diffraction in CoPt₃ films exhibiting strong perpendicular magnetic anisotropy[3].

The differences we observed for Co-Pt and Pt-Co distances are mainly due to the not negligible phase of the interference term at the Pt-L_{III} edge, as discussed in [7,8], and the right value must be that obtained from data at the Co-edge, i.e. 2.71 Å.

The parameters obtained from the analysis of the film grown at 800 K with L₁₂ long-range ordering show a reduced anisotropy, this effect can be related to the isotropic magnetic behaviour of this sample[3]. The disorder

factors σ are also reduced in this film which is in agreement with the decrease of static disorder observed in L_{12} -type ordered bulk alloys[10].

In summary, the results of XAFS experiments in the film grown at 690 K agree with a local structure in which Pt rich and PtCo planes alternate in a staking A/B/A sequence along the growth direction, while chemical disorder prevails in the (111) plane. The anisotropic distribution of nearest neighbor atomic pairs in this film, characterized by preferential CoPt pairs along the growth direction, clearly observed from Co-edge data, must play a major role in the appearance of strong perpendicular magnetocrystalline anisotropy in fcc disordered CoPt_3 films. As discussed in [3], this effect restricted on a local scale is driven by both Pt surface segregation and associated dominant surface diffusion processes during co-deposition. For the film exhibiting no magnetic anisotropy, the isotropic local order deduced from Pt-edge data remains to be confirmed by new measurements on the Co-edge where the polarization sensitivity of XAFS is enhanced.

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Figure 2: Filtered XAFS signals of the first coordination shell (○) and best fit (—) for the in-plane (upper curves) and out-of-plane (lower curves) measurement geometries.

	Out-of-plane polarization			in-plane polarization			Sample
	$N_j^\perp$	$R_j^\perp(\text{\AA})$	$\sigma_j^\perp(\text{\AA}) \times 10^{-2}$	$N_j^\parallel$	$R_j^\parallel(\text{\AA})$	$\sigma_j^\parallel(\text{\AA}) \times 10^{-2}$	
Pt-edge							CoPt ₃ bulk
PtCo	3.4±.2	2.724*	5.2±.2	3.5±.2	2.724*	5.2±.2	
PtPt	8.5±.3	2.724*	5.0±.2	8.6±.3	2.724*	5.2±.2	
Co-edge							
CoPt	11.2±.5	2.724*	5.4±.3	11.4±.5	2.724*	5.3±.3	
CoCo	(≤.5)	-	-	(≤.5)	-	-	
Pt-edge							Co ₂₅ Pt ₇₅ T _g =690 K
PtCo	3.2±.3	2.68±.01	6.3±.2	2.8±.3	2.68±.01	7.0±.3	
PtPt	8.1±.4	2.73±.01	6.5±.2	8.9±.4	2.74±.01	6.5±.2	
Co-edge							
CoPt	10.5±.5	2.71±.01	6.8±.2	8.3±.5	2.71±.01	6.9±.2	
CoCo	(≤.6)	(~2.69)	(~6.3)	3.7±.3	2.68±.01	6.3±.3	Co ₃₂ Pt ₆₈ T _g =800 K
Pt-edge							
PtCo	3.8±.3	2.69±.01	6.8±.2	3.7±.3	2.68±.01	6.6±.2	
PtPt	7.6±.4	2.73±.01	6.1±.2	8.0±.4	2.72±.01	6.3±.3	

Table 1: Structural parameters deduced from modeling Pt and Co-edge filtered XAFS data. (*)The coordination distances on CoPt₃ bulk sample were fixed at the values obtained by X-Ray diffraction data[3]

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