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Depth dependent local structures in CoPt thin films

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Abstract. X-ray absorption spectroscopy (XAS) has been used to clarify the thickness-dependent magnetic properties in nanometric CoPt films. We get benefit from the variation of the sampling depth with the grazing angle to investigate the variations of the local order within the film. In order to properly resconstruct the 3D information the experiments were performed either in the in-plane as in the out-of-plane geometries and supported by ab initio calculations. A depth dependence in the chemical order is revealed and the magnetic behavior is interpreted within this framework.

1. Introduction

Improvement of low-cost high-storage density magnetic media is an emerging technological challenge [1]. A clear understanding of the macroscopic magnetic properties requires a knowledge of its dependence with layer thicknesses and the complex microstructural effects frequently localized at the interface with the substrate or the surface of the films. Such effects can only be studied using experimental techniques able to peer selectively along the sample's depth. Analysis techniques based on X-ray diffraction (XRD) and giving the long range order as a function of the probed thickness have been successfully developped in the last past decades [2, 3]. The versatility in the geometries and detection schemes enables the association of X-ray Absorption Spectroscopy (XAS) to advanced experimental setups, providing renewed original insights to the material science. Grazing incidence (GI) XAS is already used worldwide [4] and its sensitivity in probing in-depth by tuning the grazing incidence is becoming an explored issue [5, 6].

Under specific growth conditions, the equiatomic CoPt nanometric films develop a chemical ordering along the c axis ($L1_0$ tetragonal phase) in a direction perpendicular to the film surface plane, giving rise to perpendicular magnetic anisotropy (PMA). Many structural parameters are determinant for the films quality. Fine characterization of the stoichiometry and the structural order is mandatory, as well as a proper determination of the surface states. Moreover, anisotropic chemical order at short range scale is sufficient to promote PMA [7, 8]. A crucial issue is then to fully recover the 3D-information, either at the short range as at the long range scale.

Here we focus on CoPt films grown by magnetron sputtering following an experimental procedure promoting the growth of the $L1_0$ chemically ordered phase normally to the film surface [9]. The magnetic properties of the CoPt studied films exhibit singular thickness dependence. The overall perpendicular magnetic anisotropy (PMA) is very large in thin samples (<10nm), partially lost in samples with intermediate thickness and almost recovered in the larges samples (>200nm). The scope of the study was to elucidate the origin of the drop in the PMA, and specially whether this drop was due to inhomogeneous disorder or to in- depth structural heterogeneity. As the

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sampling depth is strongly dependent on the incident angle, near the critical angle for total reflection [10], we used GIXAS with controlled incidence to get information about the local order depth profiles in samples with different thicknesses. XANES and XMCD measurements revealed a inhomogeneous disorder with the modification of the chemical order in the film plane [5]. This showed the capability of the method, that has been recently completed by the development of an approach based on the recursive Parrat method to quantitatively deconvolute the thickness dependencies of the XANES information [6]. Owing to the support of *ab initio* calculations, we will show, however, that in plane measurements are insufficient to provide an univocal reconstruction of the 3D chemical local order in CoPt films. The complete depth profile is attained by combining in plane and out of plane resolved GIXAS measurements.

2. Experimental and procedures

The studied 50nm thick CoPt film was grown by magnetron sputtering following an experimental procedure promoting the growth of the $L1_0$ chemically ordered phase normally to the film surface. Details on sample preparation and characterization of the films can be found elsewhere [9].

Grazing incidence x-ray absorption measurements were carried out using the linear polarization produced by the undulator beamline 4-ID-D of the Advanced Photon Source. The sample was placed in the center of rotation of a 8-circle diffractometer to facilitate measurements of XANES spectra as a function of the grazing angle in the geometries with the electric field aligned parallel (in-plane IP) or perpendicular (out-of-plane OP) to the surface of the film. In the series of measurements for both geometries the XANES data were collected with grazing incidence angles from 0.2 to 1 degrees with steps of 0.05 degrees. The accuracy of the grazing incidence alignment is better than 0.02 degrees, with angular motor resolution of 0.0001 degrees. The fluorescence photons from Co K edge were collected with a photodiode and double checked with a Si-drift one element SSD detector.

Ab initio simulations of XANES spectra are calculated using the code FDMNES [11] in the multiple scattering theory within the muffin tin approximation. CoPt clusters with 6 Å-radius have been considered. XANES spectra have been performed on the CoPt alloy in the chemically ordered $L1_0$ in two polarizations: with the electric field parallel to the $L1_0$ [001] direction (c-XANES) and with this field in the (100) plane (a-XANES). The XANES in the fcc structure has been calculated using the atomic positions obtained by Monte Carlo simulations [12] on a 2nm-large cluster (400 atoms). The calculated spectra have been further convoluted with a Lorentzian shape function to account for the core-hole and final state lifetime, and the experimental resolution.

3. Results and discussion

The *ab initio* calculated c-XANES and a-XANES correspond respectively to OP and IP measurements in the ideal case of the film perfectly oriented with $L1_0$ chemical order normal to the film surface. The two spectra (the two upper curves, in figure 1) show significant differences. In the ordered structure $L1_0$ structure, Pt and Co planes alternate along the [001] axis. Pt neighbours to the central Co atom are only found in the [001] direction. Only c-XANES contain their contribution, while only Co neighbours contribute to the a-XANES signal. The difference between the two spectra are similar to those identified in a CoPt alloys with increasing Pt content [13, 14] and can be interpreted in the same way. In the c-XANES, the increase of the white line B accounts for the drop in occupied states associated to a small charge transfer from Co $3d$ to Pt $5f$ orbitals. The presence of a splitted structure (B - C) just above the edge is a known experimental signature of fcc structure and arises from band structure effect. The splitting is found in ab initio calculations for cluster size including the fifth neighbouring shell of the fcc structure, ie , in the case of CoPt, for cluster size above 6.1A. The C structure intensity is largely independent on the short range chemical order. The A shoulder is essentially due to Co $4p$ band.

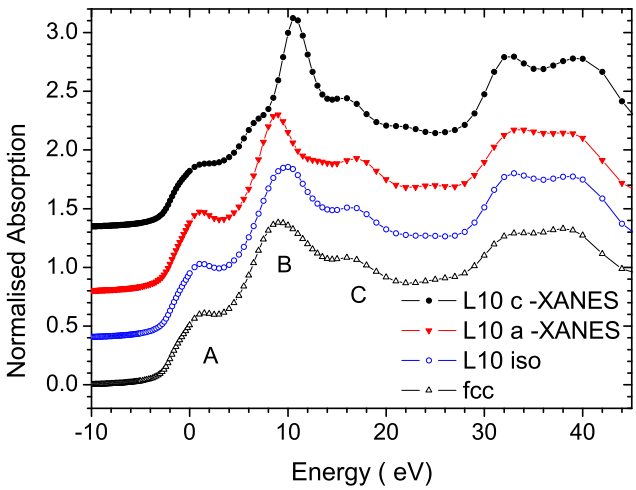

Figure 1. Calculated XANES spectra for CoPt chemically ordered and disordered structures.

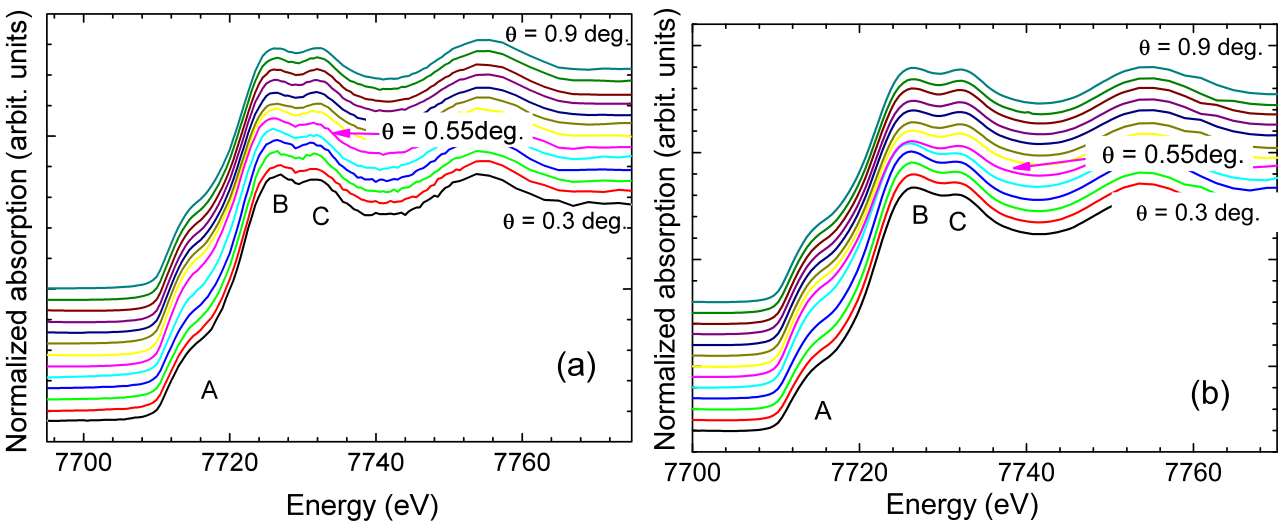

Figure 2. XANES experimental data at the Co K edge in the CoPt film, for grazing angles from 0.3 deg. to 0.9 deg. with steps of 0.05 deg steps. for in plane (a) and out of plane (b) geometries. For grazing angles above 0.50 deg, the structure B drops and the shoulder A increases. Both features are associated to an increase of the Pt content along the $L1_0$ [001] axis.

The drop of the A shoulder reflects the lowering of this band at Co sites, with the increase of Pt neighbours.

The isotropic spectra is the weighted average of c-XANES and a-XANES contributions and corresponds to polycrystalline samples with $L1_0$ structure but no preferential orientation. The XANES spectra has also been calculated on the isotropic CoPt fcc phase. We note that the isotropic XANES in the ordered and disordered phase are very similar (figure 1, the two lower curves), and have the same dominant features as in a-XANES. Consequently a perfectly ordered phase $L1_0$ structure will only be differenciated by XAS from the fcc structure if the direction of the electric field is near the 001 direction. For polycrystals this differenciation is possible only if a dominant number of crystals has its [001] axis close to the direction of the electric field. It is then clear that XAS measurements performed along a single polarization are insufficient to

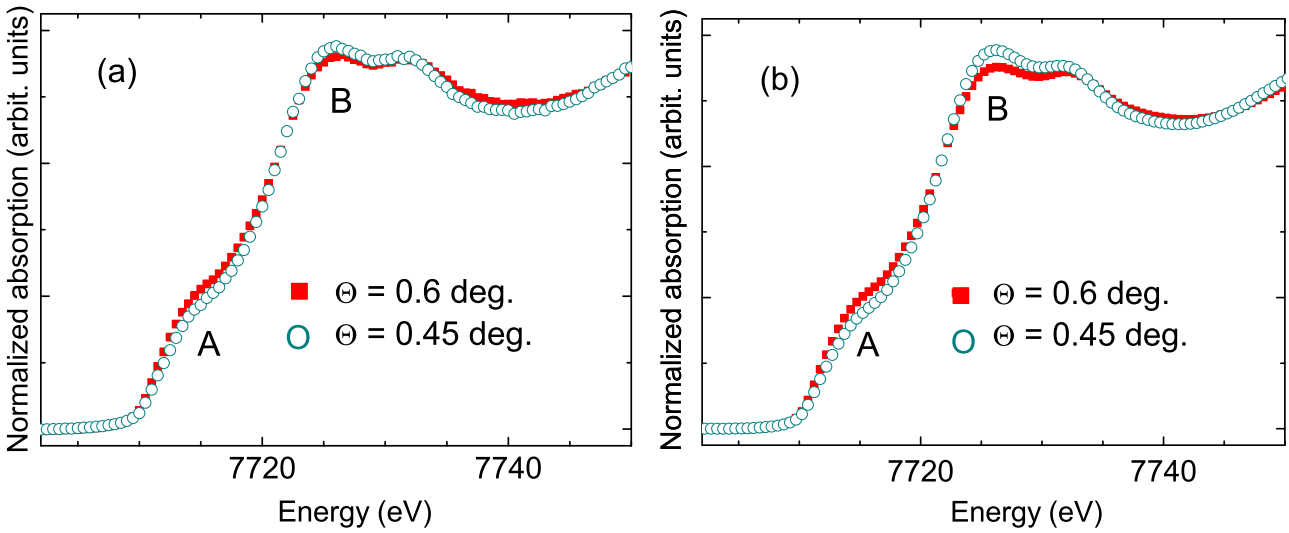

Figure 3. XANES above and below the critical angle $\theta_c \simeq$ 0.50 deg for measurements IP (a) and OP(b) .

give a unambigous information about the chemical order and our previous study [5] should be completed.

Figure 2a shows XANES spectra collected in the in-plane geometry. The critical angle for total reflection in the sample is about 0.51 deg at 7750 eV. At this energy the penetration depth – taken as the depth where the incident beam intensity is attenuated by a factor 1/e, - is 2 to 5nm for grazing angle below 0.5 degree and higher than 20nm for angles above 0.6 degree. The XANES spectra collected at the lowest angle are only related to the upper layer of the film, while essentially the deeper layers are probed for the largest anglesFor the lowest values of the grazing angles the relative intensity of the first main resonance(B) is higher than for the second one (C). This intensity drops for an incident angle θ comprised between 0.5 and 0.55 degrees, i.e. close to θ_C. The two intensities become equivalent. This angular evolution is similar to that previously obtained. Equivalent intensities of the B and C structures are a known experimental signature of the fcc structure. In the fcc structure the B and C peaks are of almost equal intensities. Ab initio calculations show that similar relative intensities should be expected in L10 with electric field oriented along the normal to the (100) plane (figure 1a, a-XANES and fcc). Higher B resonance is only observed for electric field oriented parallel to the $L1_0$ [001] axis (c-XANES). The higher B resonance at low angle should be associated to the a presence of a $L1_0$ phase with the [001] axis in the film plane, in the upper layers of the sample. This feature drops at higher angles, indicating that for the buried atoms - i.e. close to the substrate- this order is not kept.

At this stage, various interpretations of the results are still possible. The layer close to the substrate may be mainly chemically disordered (fcc). However it can also have the chemically ordered $L1_0$ structure with the [001] axis normal to the surface plane. In order to check this later possibility, a series of measurement has been performed in the OP geometry (figure 2b). It shows the same angular evolution, and a drop at the same angular value as for the IP geometry. The XANES spectra obtained for angles above 0.55 degree are identical in the two orientations. There is no anisotropy in the XANES spectra. We shown that a perfect $L1_0$ structure - or well textured one - would yield to anisotropy in the XANES spectra, the lack of anisotropy in the XANES spectra allows to withdraw such structural anisotropy in the buried layer. The structure of this layer is then either chemically disordered (fcc) or formed by $L1_0$ grains with essentially random orientation, the technique being not able to discriminate among these two cases.

Moreover we observe that the changes in the A and B features are more marked for OP measurements (figure 3). It appears that the XANES taken in the OP geometry show a larger c-XANES character: higher B structure and lower A shoulder. So we can conclude that the upper layers of the films contain ordered grains, but more grains are oriented with the c axis normal to the film plane.

The presence of a layer without structural anisotropy close to the substrate explains the lowering the PMA performance in the 50nm thick sample. The growth conditions have been optimized to promote the growth of the L10 phase oriented with c perpendicular to the film plane,- and it is indeed for thin samples (below 10nm). The growth, on the substrate of a layer without structural anisotropy, acting as a "dead layer" for the PMA, is then surprising and must probably be related to dynamic processes in the growth by magneton sputtering. However the presence of the upper L10 layer partially texturized with c perpendicular to the film plane, explains the remaining PMA in the sample. It also explains the recovering of the PMA for larger samples, when the active upper layer becomes large when compared to the "dead" buried layer.

Acknowledgements
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[1] Weller D and Doener M F 2000 *Annu. Rev. Mat. Sci.* **30** 611–644
[2] Noakes T C Q, Bailey P, Hucknall P K, Donovan K and Howson M A 1998 *Phys. Rev. B* **58** 4934
[3] Santis M D, Baudoing-Savois R, Dolle P and Saint-Lager M C 2002 *Phys. Rev. B* **66** 085412
[4] Keil P, Lutzenkirchen-Hecht D and Frahm R 2005 *Europhys. Lett.* **71** 77–83
[5] Souza-Neto N M, Ramos A Y, Tolentino H C N, Martins A and Santos A D 2006 *Appl. Phys. Lett.* **89** 111910
[6] Souza-Neto N M, Ramos A Y, Tolentino H C N, Martins A and Santos A D 2009 *J. Appl. Cryst.* **submitted**
[7] Tyson T A, Conradson S D, Farrow R F C and Jones B A 1996 *Phys. Rev. B* **54** R3702–R3705
[8] Maret M, Cadeville C, Poinsot R, Herr A, Beaurepaire E and Monier C 1997 *J. Magn. Magn. Mat.* **166** 45
[9] Martins A, Fantini M C A and Santos A D 2003 *J. Magn. Magn. Mat.* **265** 13–23
[10] Als-Nielsen J and McMorrow D 2001 *Elements of Modern X-ray Physics* (John Wiley and Sons)
[11] Joly Y 2001 *Phys. Rev. B* **63** 125120–125129
[12] Mottet C, Tréglia G and Legrand B 2002 *Phys. Rev. B* **66** 045413
[13] Lee Y S, Rhee J Y, Whang C N and Lee Y P 2003 *Phys. Rev. B* **68** 235111
[14] Hlil E, Baudoing-Savois R, Moraveck B and Renouprez A 1996 *J. Phys. Chem.* **100** 3102–3107