XMCD of Oxygen Adsorbates on Fe, Co, and Ni Monolayers

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Abstract. Oxygen is used as a surfactant to improve the layer-by-layer growth of ultrathin ferromagnetic Fe, Co, and Ni films. During this process 0.5 monolayers of oxygen ions are floating on top of the ferromagnetic film. XMCD enables us to study the magnetism of such films at their $L_{2,3}$ edges and in the same experiment the induced magnetic moment of the oxygen at the *K* edge. In addition, NEXAFS at the O *K* edge is used to investigate the bonding of the adsorbate to the 3*d* metal. The experimental findings are combined with DFT calculations to reveal the crystallographic and electronic structure as well as the magnetic properties of Fe, Co, and Ni monolayers grown with oxygen surfactant.

Keywords: oxygen, surfactant, induced magnetism, O *K* edge, XMCD, NEXAFS, magnetic films
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INTRODUCTION

Ultrathin ferromagnetic films of Fe, Co, and Ni of a few atomic monolayers (ML) are presently a main research topic in the field of nanomagnetism. However, the preparation of ultrathin films or nanostructures on a substrate surface may be very difficult and the magnetic properties largely depend on the details of the growth modes. For example, pseudomorphic growth of crystalline films, laser deposition growth, or etching techniques produce different crystallographic structures on the atomic scale. Changes in the crystallographic structure of ~ 0.05 Å may change the magnetic anisotropy by a factor of 100 to 1000 [1]. One way to manipulate the growth modes and consequently the crystallographic structure is to use adsorbed atoms or molecules as a surfactant. For instance, it has been shown that half a monolayer of O on a Cu surface modifies the growth of Fe, Co, and Ni films such that with O surfactant the layer-by-layer growth is much better than without [2, 3, 4, 5].

X-ray absorption spectroscopy (XAS) is a technique of choice to investigate such systems. Exploiting the element specificity of the method, we can investigate the O *K* edge of the surfactant as well as the $L_{2,3}$ edges of the 3*d* ferromagnet. Angular-dependent NEXAFS spectra give detailed information on the electronic band structure. Using circularly polarized synchrotron radiation and taking the difference between the absorption coefficients for left and right circular polarization, i.e. the X-ray magnetic circular dichroism (XMCD) $\Delta\mu = \mu^+ - \mu^-$, enables us to investigate the magnetism of each constituent element.

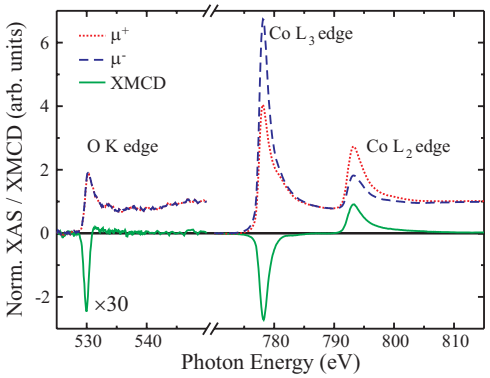

FIGURE 1. (Color online) X-ray absorption coefficient and XMCD at the O *K* edge and Co $L_{2,3}$ edges for a surfactant grown Co film of 4 ML. The XMCD at the O *K* edge has been scaled by a factor of 30 for better visibility.

EXPERIMENT

The measurements of the present work were carried out at the UE56/2-PGM2 and UE56/1-PGM undulator beamlines at BESSY in Berlin, Germany. Prior to evaporation of the FM films oxygen has been adsorbed onto the Cu single crystals which thereby undergo a surface reconstruction [2]. As an example, Fig. 1 shows the case of 4 ML Co grown on Cu(100) in presence of 0.5 ML oxygen [2]. Grazing incidence XAS (X-ray beam parallel to the magnetization) is shown for left and right circular polarization in the upper part. At the bottom, the XMCD spectra are given. The easy axis of magnetization is in-plane for this film. XAS and XMCD were recorded *both*

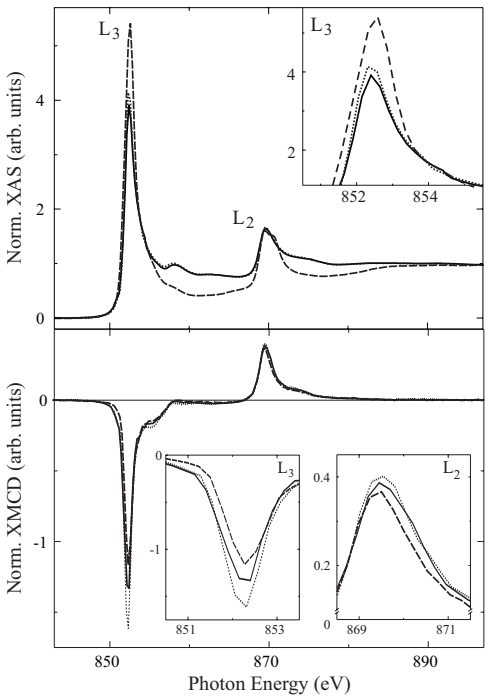

FIGURE 2. Top: XAS at the Ni $L_{2,3}$ edges of clean bulk-like Ni (solid), 6.5 ML Ni on O/Cu(110) (dotted) and NiO (dashed). Bottom: XMCD at $T = 30$ K at the Ni $L_{2,3}$ edges of bulk-like Ni (solid), 6.5 ML Ni on O/Cu(110) (dotted) and 5.5 ML on O/Cu(100) (dashed).

at the Co $L_{2,3}$ edges (right part of the figure) *and* the O *K* edge (left part of the figure) in the same experiment. Clearly, an XMCD spectrum is detected at the O *K* edge together with the XAS. Note the scaling factor of 30 for the XMCD. Despite the smallness of the XMCD signal at the O *K* edge, all spectra have an excellent signal to noise ratio by virtue of the undulator beamlines.

RESULTS

We investigated ultrathin Ni films on two substrate surfaces Cu(100) and Cu(110) in a thickness range where the easy axis of magnetization is perpendicular to the surface. Consequently, the XAS and XMCD spectra were taken at normal incidence of the X-rays. In the upper part of Fig. 2 the XAS spectrum of 6.5 ML Ni grown with O surfactant (dotted line) is shown. It is compared on the one hand with the XAS of metallic bulk-like Ni (solid line) and on the other hand with bulk-like NiO (dashed line). Clear differences are monitored for the oxide spectrum with respect to the spectra of the metallic Ni and the Ni film grown with oxygen surfactant. The white line at the L_3 edge is much higher for the oxide. However, in the regime between the L_3 and the L_2 edge and the one above

TABLE 1. Calculated spin and orbital magnetic moments induced in the oxygen of surfactant grown 3*d* FM films together with the total magnetic moment of the bulk FM (in μ_B/atom).

FM	m_S(O)	m_L(O)	$m_{\rm tot}$(FM)
Fe	0.053	0.0024	2.1
Co	0.132	0.0047	1.6
Ni	0.053	0.0021	0.6

the L_2 edge (around 880 eV) it is smaller. The intensity of the white line depends on the number of unoccupied final states which here are the 3*d* states. This intensity is much larger for the oxide ($3d^8$) than for the metal. In contrast, the finite absorption cross-section above the L_3 and L_2 edges is determineded by the number of unoccupied final states in the conduction band. This is larger for the metallic film. The XAS spectra reveal that the surfactant grown Ni films are metallic and do not form a bulk-like oxide. A small enhancement of XAS directly at the edges results from a charge transfer from Ni 3*d* to O 2*p* states [6]. The lower part of Fig. 2 shows the corresponding XMCD spectra. A thick 18 ML Ni film (solid line) is compared with thin surfactant-grown Ni films on Cu(110) (dotted line) and Cu(100) (dashed line). For the thin film on Cu(110), the XMCD at both the L_3 and the L_2 edge is larger than the bulk spectrum. In contrast, for the thin film on Cu(100), both intensities are smaller. This is interpreted as an increase of the magnetic moment of Ni on the (110) surface and small reduction of the Ni magnetic moment on the (100) surface. We attribute this effect to the different surface roughnesses that occur on the two surfaces. For details see Refs. [6, 7].

A systematic study of the O *K* edge has been performed for the three elements of Fe, Co, and Ni. The results are summarized in Fig. 3 and compared to *ab initio* calculations in density functional theory (DFT) using the "thin-film full potential linearized augmented plane wave" (FLAPW) method [2]. Within this method the local density approximation (LDA) yields a distance between the oxygen atom and its nearest FM neighbor which agrees well with the experimentally determined $R_{nn} = (1.85 \pm 0.03)$ Å from SEXAFS data [2].

The upper part of Fig. 3 shows the NEXAFS at the O *K* edge for normal (solid line) and grazing (dashed line) incidence. Clearly, the difference in the angular-dependent NEXAFS is monitored corresponding to the density of unoccupied $2p_z3d$ and $2p_{xy}4sp$ hybridized states. The three films show similar features: (i) a larger intensity of the white line at 530 eV at grazing incidence indicating the out-of-plane orientation of the O $2p_z$ final states and (ii) a stronger resonance at $535-540$ eV for normal incidence, i.e. for in-plane unoccupied final states. These experimental findings agree qualitively very well

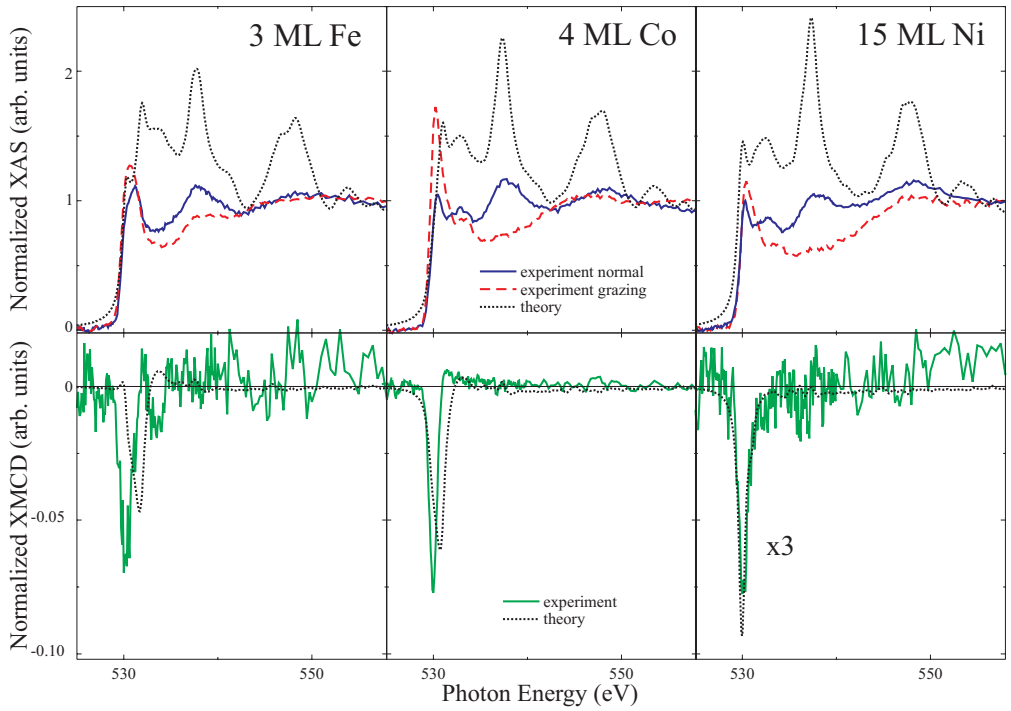

FIGURE 3. (Color online) Comparison of measured and calculated XAS and XMCD at the O *K* edge of the 3*d* ferromagnets grown on Cu(100) with oxygen as a surfacant.

with the *ab initio* calculations (dotted line) except that the intensities of the individual peaks in theory are more pronounced. In the lower part of Fig. 3, the XMCD at the O *K* edge is shown. In all three cases, we detect an induced magnetic moment at O 2*p* levels parallel to the one of the FM (in-plane for Co, out-of-plane for Fe and Ni). Considering that at *K* edges no spin-orbit splitting for the initial states occurs, our experimental XMCD data prove directly only the orbital moment of the final O *p* states [8, 9]. In addition to the NEXAFS and XMCD spectra the values of spin and orbital moments $m_L(O)$ and $m_S(O)$ of the O result from the calculations. They are given in Table 1 in comparison to the total magnetic moment $m_{\mathrm{tot}}(\mathrm{FM})$ of the corresponding ferromagnet.

SUMMARY

We have grown ultrathin ferromagnetic films of Fe, Co, and Ni with oxygen as a surfactant and investigated their NEXAFS and XMCD both at the $L_{2,3}$ edges of the FM and the O *K* edge. We find that the films show metallic behavior and do not form bulk-like oxides. Exploiting the element-specificity and sensitivity of the measuring technique at modern undulator beamlines we determine not only the influence of the O on the ferromagnetic films themselves but also an induced magnetic moment which occurs at the O site. The experimental results are completed by DFT calculation of the XAS and XMCD spectra. Furthermore, the calculations yield the values of the induced magnetic moments of the oxygen.

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