Long-term Proposal Report
Spin-resolved Hard X-ray Photoelectron Spectroscopy
Spin-HAXPES

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Abstract

The spin-resolved electronic structure of buried magnetic layers is studied by hard X-ray photoelectron spectroscopy (HAXPES) using a spin polarimeter in combination with a high-energy hemispherical electron analyzer at the high-brilliance BL47XU beamline. Spin-resolved photoelectron spectra are analyzed in comparison with the results of magnetic linear and circular dichroism in photoelectron emission in the case of buried $Co_2FeAl_{0.5}Si_{0.5}$ layers. The relatively large inelastic mean free path (up to 20 nm) of fast photoelectrons enables us to extend the HAXPES technique with electron-spin polarimetry and to develop spin analysis techniques for buried magnetic multilayers and interfaces.

1. Introduction

The spin-resolved exploration of the electronic structure of buried ferromagnetic layers and interfaces is of great importance. It is needed for the selection of optimal materials for spintronic devices. For example, the efficiency of magnetic tunnel junctions (MTJs) is largely defined by the spin-dependent electronic properties of half-metallic electrode materials [1, 2] employed.

Hard X-ray photoelectron spectroscopy (HAXPES) was proved to be a bulk sensitive probe of the electronic band structure [3, 4]. The high bulk sensitivity of this technique results from the large inelastic mean free path (10-20 nm) of high-energy photoelectrons (6-10 keV). Such a high bulk sensitivity enables us to explore the electronic band structure of buried layers and interfaces. In this work, we present the results of the extension of a HAXPES experiment with a spin polarimeter implemented

at the BL47XU beamline [5]. This combination facilitates complete studies of the electronic band structure on buried layers resolving electron energy, momentum, and spin degrees of freedom.

Spin-resolved photoelectron emission studies performed in the Ultraviolet and soft X-ray modes of Photoelectron Spectroscopy (UPS/XPS) imply a high surface sensitivity due to the small inelastic mean free path of photoelectrons with kinetic energies in the range <2 keV. The implementation of spin detection in a bulk-sensitive spin-resolved HAXPES experiment implies rather strong requirements on the electron focusing system and conditions of high potential within a spin detecting system. This is crucial in the case of low-energy electron scattering in electron-scattering-type spin analyzers. Photoelectron spin polarization analysis is hampered by a strong reduction of intensity at the spin-

discriminating stage by 3-4 orders of magnitude. In combination with the low photoionization cross sections at high kinetic energies [3, 6, 7], this leads to low count rates.

Presently available spin detection techniques are based on the spin dependence in electron scattering and diffraction originating from spin-orbit interaction or exchange scattering. The error of spin-polarization measurements and their efficiency depend on the electron reflectivity at the spin-discriminating target surface and spin-resolving power S (Sherman function) defining the figure of merit of the employed electron spin detector. Widely used Mott detectors [8] suffer from a low figure of merit (FoM of 10^{-4} order), which is improved up to 10^{-3} order in the case of SPLEED-type detectors [9] based on the Spin-Polarized Low Energy (about 100 eV) Electron Diffraction. Rather efficient are the spin detectors based on the spin-dependent reflection (exchange scattering) of very low energy electrons (scattering energy of about 6-15 eV) from magnetized surfaces [10] with the reported FoM of 10^{-2} order [11]. Prospective breakthrough in the spin-resolved photoelectron spectroscopy is expected from the recently suggested multichannel spin-filtering technique [12] with the FoM of 2.1 achieved.

Related information on the majority and minority spin characters of the electronic states may also be obtained in magnetic linear and circular dichroisms in X-ray absorption [13] and photoelectron emission [14, 15]. Magnetic dichroism phenomena in photoelectron emission exemplify a preferential interaction of polarized X-rays with electrons of a particular spin direction defined by the experimental geometry. They enable us to elucidate spin splitting in core multiplet states [16] due to the exchange interaction of the core hole with the spin-polarized bands of valence electrons. The present studies involve a comparative analysis of spin-resolved photoelectron spectra together with data on magnetic circular and linear dichroisms in angular distribution (MCDAD, MLDAD) in photoelectron emission.

2. Experimental Procedure

The spin-resolved HAXPES experiment has been implemented by a combination of a Scienta R-4000-10 keV hemispherical analyzer with a spin detector based on Spin-Polarized Low-Energy Electron Diffraction (SPLEED) at a W(100) surface [17]. For the spin-resolved measurements with the SPLEED-type detector, the photon energy was set to 5.95 keV because of the higher photoelectron intensity expected from the increase of ionization cross section at lower energies. The photon flux at 5.95 keV was about 10^{11} photons/s with a 50 meV intrinsic bandwidth after a Si(333) channel cut post-monochromator [7]. The total energy resolution for spin-resolved measurements was set to about 1 eV with a fixed 2 mm entrance slit of the SPLEED detector and a 200 eV pass energy of the analyzer.

The angle between the electron analyzer and the direction of photon incidence was fixed at 90 deg. The photoelectrons were collected from the sample in near-normal emission geometry. Linearly polarized photons of P_p=0.99 polarization degree were obtained from the undulator without any polarizing optics. The electric **E** vector of photons in this case was oriented in the plane of beam incidence (p-polarization), i.e., near perpendicular to the sample surface in the near-normal emission geometry used.

Studies of magnetic dichroism were performed with 7.94 keV photons. An in-vacuum phase retarder employing a 600 μm thick diamond (220) crystal [18, 19] has been installed at the BL47XU beamline in order to vary the polarization of the 7.94 keV photon beam. Polarization degrees of P_c=0.95 and P_s=0.90 have been reached for circularly polarized and linearly s-polarized photons, respectively. The photon flux at 7.94 keV was $\approx 4 \times 10^{11}$ photons/s with a bandwidth of 38 meV achieved with a Si(111) double crystal monochromator and a Si(444) channel cut post-monochromator [7]. The total energy resolution for magnetic dichroism studies was set to 150 meV.

An experiment was performed on exchange-biased $Co_2FeAl_{0.5}Si_{0.5}$ (CFAS) thin films shown to be a half-metallic Heusler compound with a high spin polarization exhibiting the lowest temperature dependence among the known half-metals [20].

CoFe (10 nm)/$Ir_{22}Mn_{78}$ (10 nm)/CoFe (0.5 nm)/CFAS (15 nm)/MgO (2 nm)/AlO_x (1 nm) multilayers were deposited on a MgO(100) substrate. An exchange bias field of 12 kA m^{-1} was achieved for the in-plane magnetization after the in-vacuum annealing of a multilayer stack at 300 °C followed by cooling in a magnetic field of 400 kA m^{-1}.

The spin-polarized electronic states of buried magnetic layers were studied with special emphasis on the bulk sensitivity of HAXPES and the correlation of the spin-resolved photoelectron spectra with magnetic linear and circular dichroism in photoelectron emission from a CFAS layer buried under a 3 nm thick protective coating. The results are discussed in terms of a multiplet model, explaining the magnetic dichroism in photoelectron emission.

3. Results and Discussion

Figure 1 shows the spin-resolved photoelectron spectra of the Fe $2p_{3/2}$ state upon excitation with *p*-polarized 5.95 keV photons. A maximum polarization of about 50% is obtained after background subtraction according to the following equation:
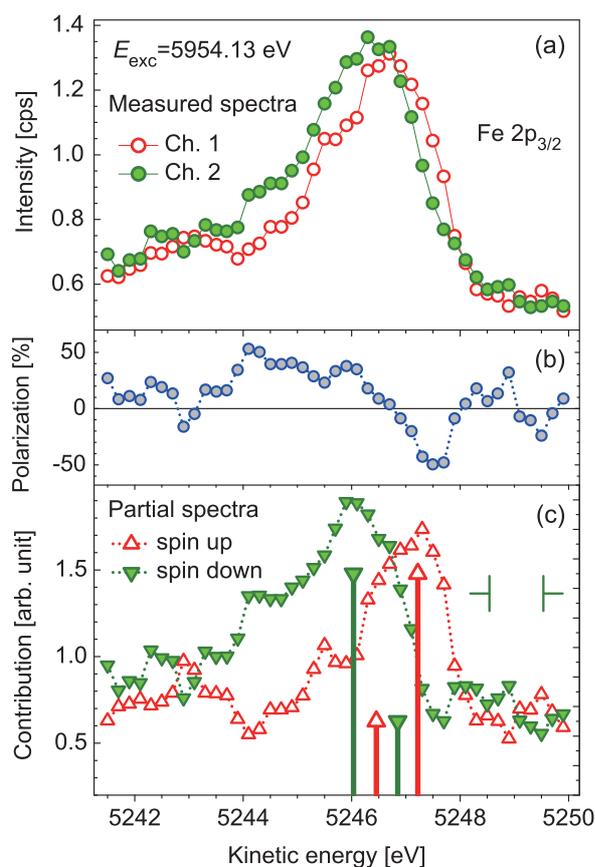

Figure 1
Count rates in spin detector channels (a), spin polarization (b) and spin-resolved spectra of Fe $2p_{3/2}$ photoelectrons (c) from buried CFAS layer. The energy resolution interval (1 eV) is shown with a vertical slit mark.

$$P = \frac{1}{S}\frac{(N_1 - N_2)}{(N_1 + N_2)} \qquad (1)$$

with $N_{1,2}$ denoting the countrates in the spin detector channels and with the Sherman function S being set to 0.25 [17]. The majority and minority spin partial spectra were determined as

$$I_{\uparrow,\downarrow} = I_{total}(1 \pm P)/2. \qquad (2)$$

For details on the spin polarization detection see [21, 22].

The structure of the Fe $2p_{3/2}$ m_j multiplet (shown as bars in Fig. 1c) was taken from the band structure calculation of $Co_2FeAl_{0.5}Si_{0.5}$ performed by the Spin-Polarized fully Relativistic method of Korringa-Kohn-Rostoker (KKR) Green's function (SPR-KKR) [23]. The bars topped with filled and hollow triangles depict the states with negative and positive spin projection m_s values; the larger and smaller bars correspond to the $|m_j|$=3/2 and $|m_j|$=1/2 states, respectively. The sub-states of the $2p_{3/2}$ core electrons with well-defined spin up (m_j=+3/2; m_s=+1/2) and spin down (m_j=-3/2; m_s=-1/2) are clearly reproduced by maxima in the spin-resolved photoelectron spectra (Fig. 1c). The electron spin (m_s) is not well defined for $2p_{3/2}$ states with m_j=± 1/2 since the respective m_j values (m_j=m_l+m_s) may be obtained with different m_l and m_s combinations. The $2p_{3/2}$ state with m_j=-1/2 is, however, revealed as a shoulder in the spin down component. Thus, the features of Fe $2p_{3/2}$ core states are well reproduced in the measured spin-resolved phototelectron spectra showing a good agreement with the one-step model of photoelectron emission.

One should note the broadening of the measured spin-resolved photoelectron spectra. This broadening may originate from a relatively poor resolution of the spin-resolved measurements, but this is not the only reason. After electron escape from the Fe 2p orbital, the coupling of the $2p^5$ ($^2P_{3/2}$) core hole with $3d^5$ ($^6S_{5/2}$) valence electrons results in a variety of ionic $^{7,5}P_{|L+S| \approx J \approx |L-S|}$ configurations (see [24] for details). The difference in the energy levels of the ionic states implies a broad kinetic energy distribution for the emitted electrons and the broadening of the photoemission spectra, particularly at the side of higher binding energies [25].

The observed spin polarization of photoelectrons from a core state may be considered as an indirect

evidence for the spin-polarized valence states. It arises due to the presence of a strong exchange field (Weiss field) in the material. The spin polarization at the Fermi level can only be elucidated from a spin-resolved measurement of the valence states. However, the density of valence states is reduced by about one order of magnitude as compared with that of the core states. Therefore, the spin-HAXPES experiment on the valence states has been planned as a further step forward after commissioning the modified SPLEED-type spin detector with an improved transmission efficiency of its electron focusing system and we are going to implement also the novel multichannel concept of electron spin detection [26] in HAXPES mode.

Figure 2 shows the correlation between spin-resolved photoelectron spectra and magnetic circular dichroism (MCDAD) as well as magnetic linear
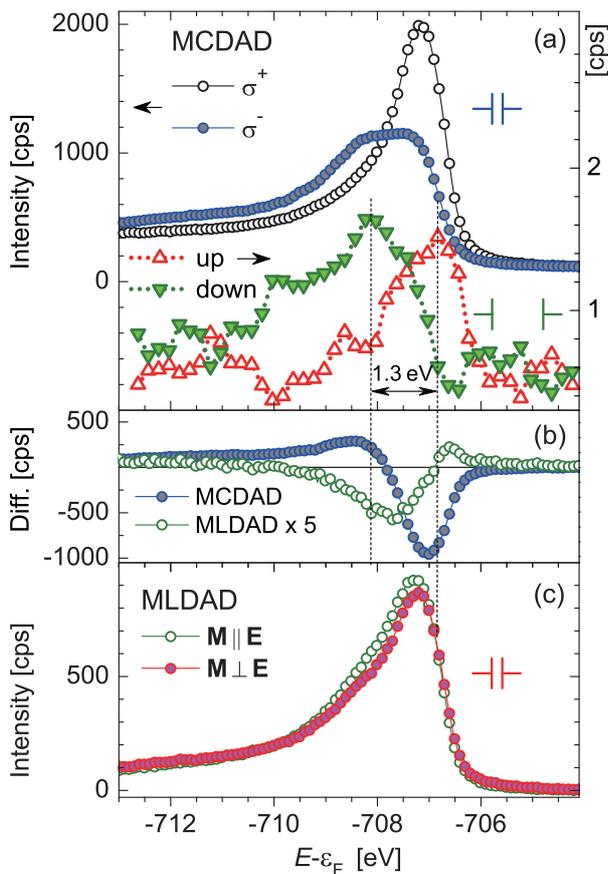
dichroisms. MCDAD in photoelectron emission (acceptance angle of ±7 deg. tilted by 2 deg. with respect to the sample surface normal was measured with the helicity vector σ of circularly polarized 7.94 keV photons directed nearly parallel (σ^+) and antiparallel (σ^-) to the magnetization vector **M** of the in-plane magnetized sample. A maximal MCDAD value of 45% was reached for the Fe $2p_{3/2}$ photoelectrons from the CFAS layer.

The 1.3 eV gap between the maxima of the spin-resolved photoelectron spectra is in good agreement with the exchange splitting revealed by MCDAD measurements. Such a relatively large exchange splitting proves the magnetic moment to be localized at Fe sites in CFAS. The extrema of the MCDAD signal show a slight shift to higher binding energies as compared with the maxima of the spin-resolved peaks.

Having the photoelectron spin-resolved spectrum and magnetic circular dichroism measured for a core state, one can estimate the spin and orbital moments using the sum-rules-type procedure suggested by Thole and van der Laan [27]. However, this procedure implies the calculations of the spin-resolved core level photoelectron spectra measured for both spin-orbit components upon excitation with isotropic light (spherically polarized photons). Such experiment can be implemented upon the excitation with an incoherent superposition of two normally oriented beams of unpolarized and linearly polarized photons.

Magnetic linear dichroism (MLDAD) was measured with s-polarized photons (7.94 keV) and the sample magnetization along or perpendicular to the **E** vector of the X-rays. The MLDAD signal changes its sign at approximately 706.8 eV (Fig.2b) where the "minority" signal in the spin-resolved photoelectron spectra starts to increase. The MLDAD shows a well pronounced negative asymmetry with a 12% amplitude in the range of the Fe $2p_{3/2}$ state with the spin of the minority sign. The higher probability for the emission of the Fe 2p electron with a minority spin (as it is recognized for **M** ‖ **E**, Fig. 2c) is caused by the higher probability for the coupling of the Fe $2p^5$ hole with Fe $3d^5$ electrons resulting in the state with a maximal majority spin. Thus, the magnetic dichroism in photoelectron emission elucidates the spin-polarized electronic states and

Figure 2

Comparison of spin-resolved Fe $2p_{3/2}$ spectra with MCDAD and MLDAD for photoelectron from buried CFAS layer. The corresponding energy resolution intervals are shown by vertical slit marks.

enables us to recognize the spin sign relatively to the majority *d* states of the valence band. MLDAD measurements show a higher intensity for the electrons with a minority spin when the magnetization vector **M** is aligned parallel to the **E** vector of the photons.

Conclusions

In summary, a spin-resolved HAXPES experiment was successfully performed on a buried magnetic layer. The implemented Spin-HAXPES technique facilitates the direct observation of the spin polarization of emitted electrons. The measurements prove that a spin polarization of about 50% is retained during the transmission of photoelectrons emitted from the Fe $2p_{3/2}$ state through a 3 nm thick oxide capping layer. The reported spin-resolved photoelectron spectra agree well with the magnetic circular and linear dichroisms. The informations from spin polarization and magnetic dichroism are different and their combination provides a detailed insight into the dynamics of photoemission from a ferromagnetic material. The reported experiment paves the way to the realization of the spin-resolved spectroscopy of buried layers and buried interfaces, one of the issues inaccessible by the classical low-energy approach.

The magnetic states can be elucidated from magnetic dichroism measurements providing much higher detection efficiency [24] than that achieved in spin-resolved measurements with a spin detector. However, this does not exclude the necessity in direct spin-resolved measurements with spin detectors since the technique of spin-polarized state restoration from MCDAD and MLDAD is not well established yet.

Thus, spin-resolution in the HAXPES of valence states is highly desirable because it will provide the true electronic band structure of a bulk material. In particular, it avoids the various problems caused by surface states, surface reconstruction, and its termination or contamination.

Acknowledgments

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