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Surface vs. bulk magnetic moments from photoemission dichroism

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Abstract

The value of the surface spin magnetic moment of Fe(100) is obtained by measuring the energy spread of the photoemission dichroism spectra of Fe3p core levels from bulk and surface. The bulk and surface signals have been resolved exploiting the photoemission diffraction effects in a linear magnetic dichroism of the angular distribution (LMDAD) experiment with soft X-rays. The LMDAD lineshape and energy width of the bulk contribution has been independently obtained from angular and from photon energy dependent experiments: it provides a gauge for determining the magnetic moment of the surface Fe3p atoms in the hypothesis of a linear dependance between energy width of dichroism and local spin magnetic moment. © 2000 Elsevier Science Ltd. All rights reserved.

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Magnetic moments at surfaces and interfaces can be very different from bulk [1–3]. Their theoretical understanding and estimation has advanced greatly in the early nineties, thanks to band structure calculations [4–6], but the experimental determination remains the most challenging task. Both element sensitivity and atomic-site sensitivity are necessary to resolve surface from bulk magnetometry. We present photoemission Fe3p spectra for *bulk bcc iron* and for (100) *surface iron* as resolved in linear magnetic dichroism of the angular distribution (LMDAD) experiment [7] with variable energy soft X-rays. From the Fe3p spectra the LMDAD asymmetry can be formed:

$$A_{s,b} = \left(\frac{I_{up} - I_{down}}{I_{up} + I_{down}}\right)_{s,b},$$

where $(I_{up\ (down)})_{s,b}$ are the photoelectron spectral intensities obtained with the magnetization in the upward (up) or downward (down) directions for the surface (s) and the bulk (b). The LMDAD asymmetry provides a diagnostics of long-range surface magnetic order as it was established with $M(H)$, $M(T)$ experiments [7] as well as with experiments on exchange coupled layers [8,9]. Within the atomic model approximation [10–12], the energy spread of the LMDAD signal measures the energy splitting of the 3p (or 2p) core hole interacting with the effective spin field determined by the spin polarized valence band at the core hole site, i.e. the LMDAD *energy width* (W_{LMDAD}) bears a proportionality to the *local spin magnetic moment*. A conversion factor between core hole splitting energy and local spin moment is nevertheless hard to establish even in the atomic model. Experimentally, the LMDAD magnetometry was insofar limited to the measure of *relative changes of* W_{LMDAD} observed for different iron surfaces [7] or for Co–Fe bcc alloys for various compositions [13], without the possibility of assigning to a single atomic site a given spectrum, i.e. without a calibration point.

Obtaining the experimental bulk Fe3p W_{LMDAD} provides an internal calibration of the LMDAD data, since the bulk spin magnetic moment ($\mu_{spin,b}$) of iron is known from gyromagnetic ratio measurements [14]. Consequently the surface Fe3p W_{LMDAD} can be interpreted quantitatively yielding the measure of the surface spin magnetic moment $\mu_{spin,s}$.

The Fe3p photoemission data were resolved by exploiting the differences in the bulk and surface photoemission

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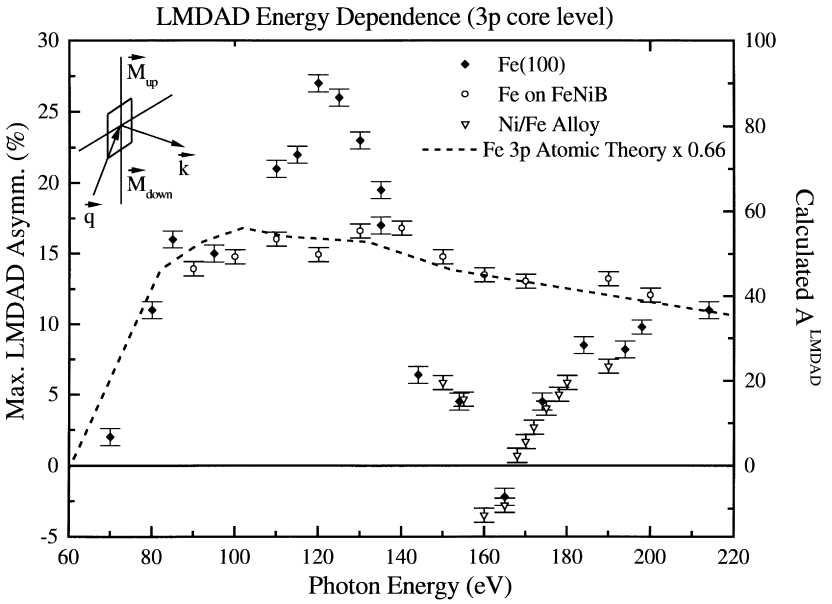

Fig. 1. Energy dependence of the measured Fe3p LMDAD asymmetry measured for polycrystalline iron film of ~2 nm thickness (open circles), bcc-Fe(100) (diamonds) and a ~0.5 nm thick ~Fe_3Ni_7 epitaxial alloy onto Fe(100) (open triangles). The dashed line is from the atomic-model calculation of Ref. [11].

intensities from single crystals, which are due to the photoelectron diffraction (PD) effects. The PD effects in normal emission experiments are generally weak for surface photoelectrons, which can only undergo backscattering but they can be very large for bulk photoelectrons, which are strongly focussed in the forward direction along rows of atoms on the way to the external analyzer [15]. PD effects in LMDAD spectra have been recently measured and interpreted within a single scattering formalism [16,17]. In the present experiment we have measured the Fe3p photoelectrons at *intermediate kinetic energies* (50–150 eV) corresponding to an average scattering length for the photoelectrons of the order of 5 Å, yielding a very high surface sensitivity. The measurements were performed at the SU3 undulator beamline of the SuperAco storage ring at Orsay in conditions as described previously [7].

In Fig. 1 we show the value of Fe3p LMDAD photoemission dichroism asymmetry measured in the normal emission geometry (sketched) as a function of the photon energy from three atomically clean surfaces of iron: a finely grained polycrystalline Fe film grown onto a random-close-packed (rcp) amorphous substrate (Vitrovac ribbon); a Fe(100) single crystal surface and a ultrathin epitaxial ~Fe_3Ni_7/Fe(100) alloy. The hν dependence of the LMDAD magnitude from polycrystalline Fe is well approximated by the atomic calculation of van der Laan [11] (dashed line rescaled to the experiment) showing that the data are described by the sole atomic ingredients of the LMDAD dichroism effect. The data from bcc-Fe(100) and from an epitaxial ~Fe_3Ni_7/Fe(100) interface instead deviate greatly from the atomic-like behavior showing a large positive peak at 125 eV followed by a crossing of the atomic curve at 140 eV and a large negative peak (with a reversal of the sign of LMDAD asymmetry: down-up instead of up-down) at 165 eV.

PD in the Fe(100) direction determines the large modulation of the LMDAD signal in the Fe(100) and ~Fe_3Ni_7/Fe(100) single crystal experiments: the positive peak at ~125 eV corresponds to scattering of photoelectrons of ~70 eV internal kinetic energy, i.e. of a de Broglie wavelength of $\lambda_e = 1.43$ Å, which matches exactly 1/2 of the lattice spacing of bcc Fe, i.e. the interplane distance in the (100) direction of photoemission. This signal has the same sign of LMDAD asymmetry as the atomic-like signal. The negative peak for the LMDAD asymmetry at h$\nu = 165$ eV corresponds to scattering of photoelectrons of ~105 eV internal kinetic energy, i.e. $\lambda_e = 1.17$ Å corresponding to the interplane spacing of (211) planes; this signal has opposite sign with respect to that of polycrystalline Fe. The large LMDAD positive peak at ~125 eV is then understood as the sum of surface and bulk LMDAD signals of same sign of asymmetry with a PD enhanced bulk contribution. Correspondingly, the negative LMDAD peak at hν = 165 eV is interpreted as the combination of bulk and surface signals of opposite sign. The one to one correspondence of the LMDAD asymmetry peaks and photoelectron wavelengths matching bulk interplanar distances is a strong evidence that the photoelectron diffraction effects are bulk effects, i.e. modify the bulk photoemission current relative to the surface photoemission. The sign reversal of the bulk

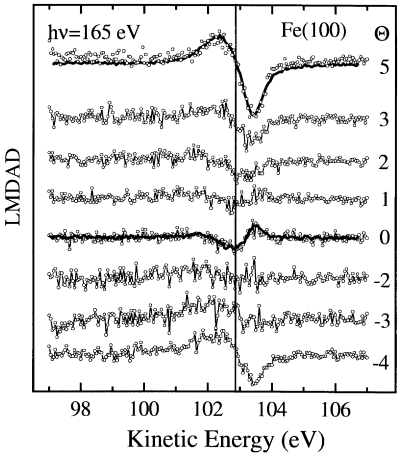

Fig. 2. LMDAD spectra of Fe(100) as a function of emission angle with respect to the surface normal with $h\nu = 165$ eV. The spectrum at $\Theta = 5°$ off-normal is compared to the spectrum of polycrystalline Fe (solid line). The spectrum at $\Theta = 0$ is compared to the LMDAD obtained from the solid curves of Fig. 3(d).

asymmetry for $\lambda_e = 1.17$ Å is a key observation since it allows a very accurate bulk vs. surface signal filtering.

In order to check this result we have performed an independent experiment (data are shown in Fig. 2) where the angular dependence of the Fe(100) LMDAD spectra was measured with $h\nu = 165$ eV at emission angles spanning from -5 to $+5°$ with respect to the normal emission direction, i.e. going slightly 'off' the large diffraction conditions observed for $\lambda_e = 1.17$ Å. The scattering plane and chirality are fixed in all the experiments so that the atomic effect is fully cancelled when comparing spectra obtained at different emission angles. The LMDAD lineshape measured at 5° off-normal results in a standard up-down feature basically identical to the LMDAD spectrum (thick curve) of polycrystalline iron at the same energy; the lineshape measured at normal emission shows a 'derivative-like' LMDAD spectrum. By combining the information from Figs. 1 and 2 it is observed that: (a) the angle and energy values that produce the 'derivative-like' LMDAD spectra are very well defined; (b) the variation of the LMDAD asymmetry is connected with two distinct contributions, the surface and the bulk one, which undergoes large PD effects.

The bulk LMDAD contribution can be extracted from the raw photoemission spectra: Fig. 3 presents the magnetization dependent photoemission spectra from Fe(100) as measured with the magnetization up (curves a) and down (curves b) with $h\nu = 165$ eV ($\lambda_e = 1.17$ Å) at normal emission, and those measured at 5° off-normal emission. Even for the same field direction, the lineshape and the intensity of the photoemission spectra change dramatically with the emission angle. The spectra off-normal emission (dashed curves) have a similar lineshape to the spectra measured for polycrystalline Fe, but the spectra measured at normal emission (continuous curves) show an increase of the

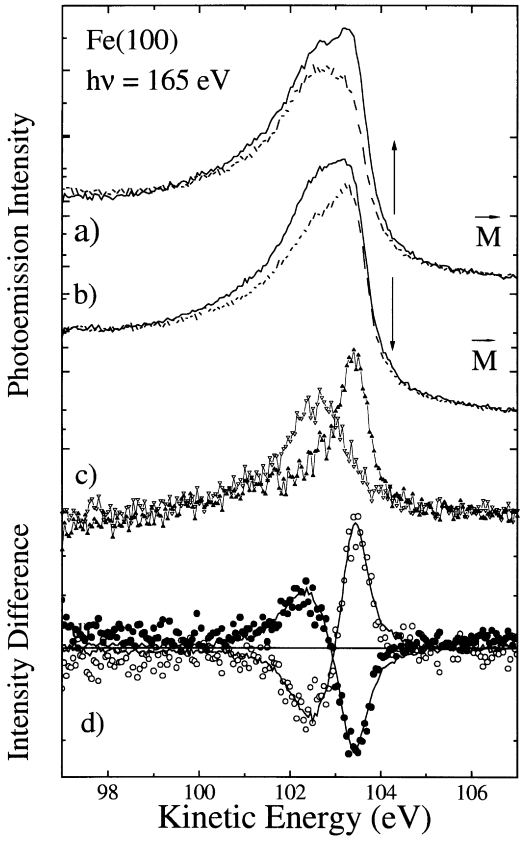

Fig. 3. Comparison of photoemission spectra as measured with $h\nu = 165$ eV for $\Theta = 5$ (dashed) and $\Theta = 0$ (solid): (a) spectra measured in the geometry shown in the inset of Fig. 1 with *M*-up; (b) same with *M*-down; (c) difference spectra $(\Theta = 0) - (\Theta = 5)$*M*-up (solid triangles) and $(\Theta = 0) - (\Theta = 5)$*M*-down (open triangles); (d) experimental LMDAD (solid dots) and the LMDAD formed by curves c (open circles). The continuous line through the data is a LMDAD spectrum of polycrystalline iron modified in binding energy and energy width to fit to the data.

primary 3p photoemission intensity without any change of the secondary background; this extra-intensity is the signature of the PD effects. The *extra intensity* appearing at normal emission is filtered by spectral difference in curves c. The LMDAD spectrum obtained from curves c is shown in Fig. 3(d) (open circles) and it is compared to the atomic-like LMDAD spectrum measured at 5° off-normal (filled circles). The *extra* LMDAD contribution appearing at normal emission has opposite sign, its energy width is reduced by 10%, and it is shifted by 80 meV towards higher kinetic energies with respect to the 5° off-normal LMDAD raw spectrum.

In summary, the LMDAD measured off-normal at $h\nu = 165$ eV checks well with the reference polycrystalline LMDAD. The derivative-like LMDAD measured at normal emission for $h\nu = 165$ eV can be decomposed, through spectral filtering of raw data, in two contributions: one

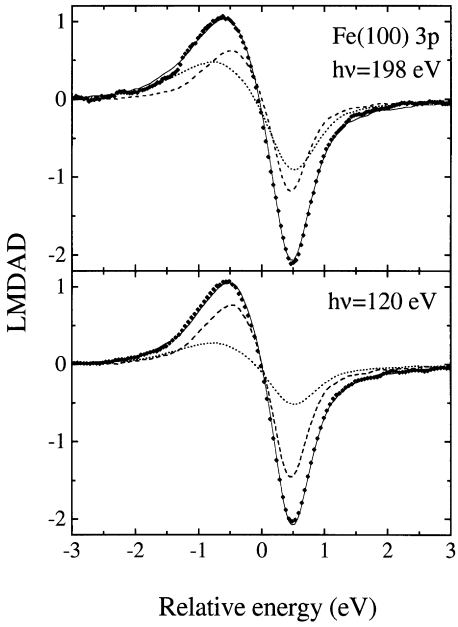

Fig. 4. LMDAD spectra of Fe(100) as measured with $h\nu = 198$ eV and $h\nu = 120$ eV. The curves are fitted (continuous line) with two components: the bulk-iron LMDAD spectrum (long dash) and the Fe(100) surface component (short dash).

LMDAD spectrum of same sign as the reference, and an extra LMDAD contribution arising from PD effects. The first contribution is attributed to the surface, and the second, sign reversed and energy shifted LMDAD to the bulk. Consequently, curves c of Fig. 3 represent the 3p photoemission spectra of bulk iron atoms. From their LMDAD asymmetry *d* (Fig. 3) one obtains the 3p *photoemission binding energy* of bulk iron: 52.57(2) eV below the Fermi level, as measured at the zero asymmetry point of the bulk LMDAD spectrum, which in the atomic model, is the center of the $J = 3/2$ multiplet [10,18]. The width of the bulk Fe 3p LMDAD signal is $W_{\mathrm{LMDAD}} = 0.95(2)$ eV.

The bulk 3p LMDAD lineshape can be fit to all of the Fe 3p dichroic spectra as measured at various photon energies and angles: the difference between the as-measured spectra and the bulk lineshape represents the signal originating from the surface. In most data the sign of bulk and surface LMDAD asymmetries are the same, but the binding energies are consistently different and the relative intensities of bulk vs. surface contribution varies. The variation is of course connected with the change of the escape depth (which is nevertheless small in this energy range) and to the large changes of the photoelectron diffraction of the bulk signal.

In Fig. 4, we compare the 3p LMDAD spectra of Fe(100) obtained with $h\nu = 198$ eV (atomic-like value) and $h\nu = 120$ eV (strong scattering of bulk signal on (100) planes at $2\lambda_e \cong 2.866$ Å). The lineshape of the surface 3p LMDAD results to be shifted in energy by 115(5) meV towards higher binding energies with respect to the bulk LMDAD; the LMDAD width is 1.29(5) eV. The ratio of surface vs. bulk signal is ~0.3 for the spectrum obtained with $h\nu = 198$ eV and ~0.2 for the spectrum obtained with $h\nu = 120$ eV. All the 3p photoemission raw spectra, at any energy and angle, are explained by identical bulk and surface components, in different proportions according to the weight and sign of the diffracted bulk signal, which also determines the overall sign of LMDAD asymmetry. This explains the results of Fig. 1 for bcc single crystal iron. The data for the ~Fe_3Ni_7 ultrathin epitaxial alloy on Fe(100) (to be discussed in detail elsewhere) can be analyzed in the same way, yielding the same Fe3p bulk lineshape originating from the single crystal iron substrate and a surface-alloy Fe3p component shifted to 340(10) meV higher binding energy and with a LMDAD with 20% larger than the bulk one.

The Fe3p W_{LMDAD} is connected to the energy splitting of the $J = 3/2$ hole multiplet [12] interacting with the spin-polarized valence band: a change of the local value of the spin magnetic moment is reflected in a stronger or weaker spin-field acting on the photoexcited core hole and consequently in a broader or narrower energy splitting of the $J = 3/2$ hole multiplet. Previous experiments showed that the Fe3p LMDAD width coincide within experimental error to that of Fe $2p_{3/2}$ LMDAD [19], confirming its direct relation to the energy splitting of the $J = 3/2$ hole multiplet with no relevant effects related to the spin–orbit splitting. The first-order dependence of the LMDAD width with respect to the magnetic moment is *linear* [19].

The bulk Fe3p LMDAD width provides the gauge for interpreting the relative enhancement of the surface LMDAD width in terms of enhanced surface magnetic spin moment. The spin magnetic moment of Fe is $2.09\mu_B$ from gyromagnetic ratio measurements [14]: from the present experiment this corresponds to a Fe3p W_{LMDAD} of 0.95(2) eV. The 36% larger W_{LMDAD} measured for the Fe(100) surface corresponds to a surface enhanced spin moment of $2.84(11)\mu_B$. The LMDAD of Fe in the ultrathin Fe–Ni alloy (approximately Fe_3Ni_7) is 20% larger than bulk, i.e. the alloyed iron spin moment is $2.54(11)\mu_B$.

Several theoretical calculations of the surface magnetic moments have appeared in the last decade [4–6]; all indicate that the surface magnetic moment of Fe should be enhanced. The largest enhancement is predicted for the Fe(100) surface with a 32–34% increase of the *spin moment* with respect to the bulk and a 140% increase of the orbital magnetic moment, which sum to a total surface magnetic moment approaching $3\mu_B$ [4–6]. Some calculations predict an oscillation of spin moments in the under-layers converging to the bulk at the fourth layer [6], others predict a faster convergence [4,5]. The 115 meV energy shift of Fe3p surface photoemission signal of Fe(100) was neither measured nor explicitly predicted before. The large surface iron magnetic moment corresponds to the narrowed density of states and strong ferromagnetic character of Fe(100) (fully occupied majority d-band unlike in bulk bcc iron)

[20]. The narrowing of the surface d-band is also reflected in the screening of the 3p core hole and therefore in the final state energy of the surface 3p photoelectrons.

The results for the Ni–Fe alloy are consistent with the known changes of Fe magnetic moment in bulk alloys [21]. We stress that our present analysis relates the *energy width* of LMDAD to the *spin-moment* in Fe and is different from the analysis of circularly polarized photoemission dichroism of Ni3p by van der Laan and others [22] who related the experimental *magnitude of dichroism* to the surface change of *orbital magnetic moment*.

In conclusion, we have measured the surface spin magnetic moment of Fe(100), which is $2.84(11)\mu_B$ and the spin moment of Fe in an ultrathin $\sim Fe_3Ni_7$ alloy, which is $2.54(11)\mu_B$, by resolving the surface and the bulk LMDAD spectra in experiments where the relative *intensity and sign* of the two signals are strongly modulated by photoelectron diffraction. We have shown that when the raw LMDAD asymmetry spectra changes sign the LMDAD spectrum has a derivative-like lineshape, which is due to the sum of a surface LMDAD spectrum and of a bulk LMDAD spectrum with reversed sign as a consequence of PD. The derivative-like lineshape of LMDAD spectra measured in those circumstances allows for a very accurate determination of the surface and bulk lineshapes, of the relative binding energy shift and of the Fe3p W_{LMDAD} of each component. The quantitative interpretation of the Fe3p W_{LMDAD} relies on the assumption of linear dependence of the $J = 3/2$ hole multiplet splitting to the local spin moment of the atom. These results provide experimental data for the surface spin magnetic moment of Fe(100), which check well with the previously untested theoretical values [4–6]. The atom specificity and site specificity of the method allows to distinguish surface iron from bulk as well as to measure the iron spin magnetic moment in the $\sim Fe_3Ni_7$ ultrathin surface alloy epitaxially grown onto iron.

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