Atom-specific surface magnetometry

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A powerful atom-specific surface magnetometry can be based on efficient measurements of magnetic dichroism in $l>0$ core level photoemission. The temperature dependence $M(T)$ of the Fe(100) surface magnetization was obtained from the photoemission magnetic asymmetry of $3p$ core levels, providing the measure of the surface exchange coupling via the spin-wave stiffness and of the surface critical exponent. Beyond the magnetic order $\langle M \rangle$ the photoemission dichroism allows us to derive the energy splitting of the magnetic sublevels of the photoexcited core hole. Fe $3p$ photoemission dichroism probes directly the magnetic moment changes of iron atoms at Fe(100) surfaces as a function of structural disorder or sulfur segregation. The appearance of dichroism in the $2p$ photoemission of segregated sulfur atoms in the $c(2\times2)$S/Fe(100) superstructure measures the magnetic-moment transfer and shows the possibility of investigating surface magnetochemistry in a very direct way.

Recent experiments have shown qualitatively that photoemission dichroism of core levels is a diagnostic of magnetic order at surfaces[1-6] and interfaces.[4,7] Magnetic dichroism occurs in photoemission of $l>0$ core levels when the core hole state of angular momentum j is split by the interactions with the spin-polarized valence band into sublevels with a given projection m_j on the magnetic quantization axis. The different components of the hole state with different projections m_j are readily distinguished in photoemission experiments using circularly polarized light, or by measuring the angular distributions arising from interference in the photoionization final states.[5,8-11] The most efficient way to measure the magnetic dichroism is to perform chiral photoemission experiments with linearly polarized light and to obtain the photoemission asymmetry between mirror experiments.[2,4] In this case the sensitivity to magnetism costs only a factor 2 more measurements than standard core-level photoemission spectroscopy for surface chemical analysis, and data can be collected very efficiently taking advantage of the intense sources of linearly polarized synchrotron radiation, or even of unpolarized laboratory sources.[6,7]

The fine structure of the Fe $3p$ photoemission magnetic sublevels in bcc, fcc, and random-close-packed iron could be derived by comparing the integral and dichroism spectra with calculated angular matrix elements for six m_j sublevels of a single atomic final state configuration.[5] More recently complete atomic calculations,[10] also including multiple scattering in the final state,[12] have reproduced the effect. The atomic description of Fe $3p$ photoemission dichroism appears well supported.

The central problem in surface magnetism is to establish a clear connection between magnetism-sensitive spectroscopies and the physical quantities that describe magnetism, i.e., the order parameter $\langle M \rangle$ and its temperature dependence, the surface magnetic moment, and its structural and chemical dependence. X-ray absorption magnetic dichroism has become a useful tool in magnetism since the validity of the sum rules was demonstrated.[13]

Here we show, with experiments on Fe(100), that photoemission dichroism can be practically used to measure accurately the physical quantities that describe the magnetism of surfaces: the surface to bulk exchange coupling and the changes of the surface magnetic moment as a function of surface structure and chemistry, in an atom-specific way.

We have performed LMDAD (linear magnetic dichroism in the angular distribution) measurements of the Fe $3p$ core levels from a Fe(100) (3% Si stabilized) single crystal surface as a function of the temperature, from cryogenic temperatures up to the Curie temperature (T_C). The single crystal was Ar-ion sputter cleaned and showed only small traces of surface segregation of C at temperatures higher than 300 °C replaced by S for $T>500$ °C. The data were collected in a spectrometer with a residual pressure of 2×10^{-11} mbar using linearly polarized photons of $h\nu=120$ eV from the Swiss-French undulator beam line SU3 of the SuperAco storage ring at Orsay, and a hemispherical electron energy analyzer collecting photoelectrons with an angular acceptance of $\pm1°$, centered at 45° from the incoming beam direction. In these conditions about one-third of the photoemission signal arises from surface atoms, and about one-fourth from the subsurface atomic plane. Mirror experiments were obtained by aligning the in-plane magnetization of the Fe(100) surface up or down along the vertical direction, perpendicular to the scattering plane, as shown in Fig. 1. The magnetic asymmetry is defined as $A=(I_{up}-I_{down}/\ I_{up}+I_{down},)$ where $I_{up\ (down)}$ are the photoelectron spectral intensities obtained with the magnetization in the upward (up) or downward (down) directions. The maximum asymmetry measured at 140 K is 46% of the Fe $3p$ intensity (corresponding to a 22% variation of the total photoemission including background). The absolute value of the measured asymmetry is modified by photoelectron diffraction, in particular in forward scattering conditions;[15] the
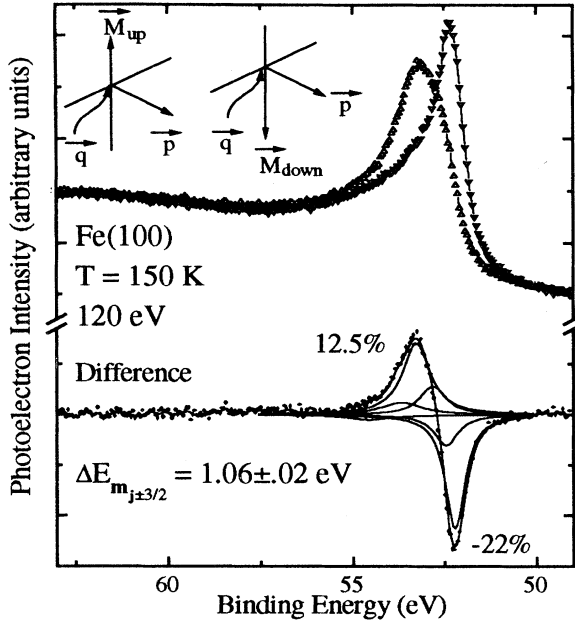
FIG. 1. Fe $3p$ photoemission mirror experiments obtained in the chiral geometries represented in the inset. The difference curve represents the LMDAD dichroism of Fe $3p$ from the Fe(100) clean surface, as measured at $T=150$ K with linearly polarized, monochromatic synchrotron radiation of 120 eV. The dichroism is fitted by a sextuplet of magnetic sublevels as in Ref. 5, which are weighted for the angular matrix elements. The fitted curves show that the extrema of the dichroism curves coincide with the $j=3/2$, $m_j=\pm 3/2$ sublevels.

sample position and photon energy must therefore be kept fixed throughout the experiment. In Figs. 2 and 3 we plot the temperature dependence of the Fe $3p$ LMDAD asymmetry along with bulk magnetization curves $M_B(T)$ obtained *in situ* by measuring the magneto-optic Kerr rotation. Figure 2 also shows the spin polarization (SP) of the secondary electron yield ejected from the iron surface as measured with a 100-kV Mott-scattering experiment.[16]

For $T \leq 0.4 T_C$, the thermal decrease of the relative surface magnetization $\Delta M_S(T)/M_S(0)$ of atomically clean Fe(100) is consistently measured by LMDAD and by SP. The results are described by the law $M(T)/M(0)=1-kCT^{3/2}$ of spin-wave theory.[17] The Kerr data measure the bulk thermal decrease of relative magnetization with $k=1$ which determines the bulk constant C. A surface enhancement factor $k \simeq 2.5$ is obtained by fitting the LMDAD and SP data to the $T^{3/2}$ law: it represents the reduced exchange interaction of the Fe(100) surface atoms along a path perpendicular to the surface.[18] Both LMDAD and SP actually measure an effective k due to the (nearly identical) finite probing depth. If we assume that the change of spin-wave stiffness is limited to the surface plane, then $k_{surf} \simeq 5.5$, which implies a reduction of the exchange perpendicular to the Fe(100) surface by a factor of 10 with respect to the bulk exchange.[17] This must be considered an upper limit for the reduction of the perpendicular exchange of Fe(100), since second layer softening could also exist. In the critical region (Fig. 3) the Kerr rota-
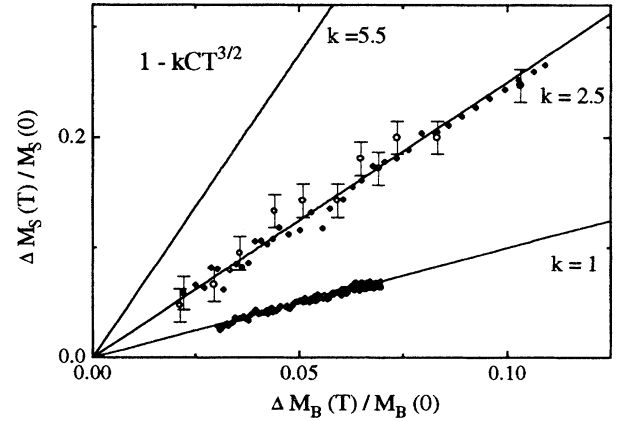

FIG. 2. Thermal decrease of the relative surface magnetization $\Delta M_S(T)/M_S(0)$ as measured by Fe 3p LMDAD asymmetry [$\Delta A(T)/A(0)$, circles] and by the SP [$\Delta SP(T)/SP(0)$, open diamonds] of the secondary electron yield versus the thermal decrease of the relative bulk magnetization $\Delta M_B(T)/M_B(0)$ measured *in situ* by the magneto-optic Kerr rotation (filled diamonds). The solid lines are the theoretical curves for $k=1$, $k=2.5$, and $k=5.5$.

tion and LMDAD signals vanish with, respectively, bulk and surface critical exponents according to $M_B \propto (1-T/T_{CB})^{\beta_B}$ and $M_S \propto (1-T/T_{CB})^{\beta_S}$, where T_{CB} is the bulk Curie temperature of iron.[19] The Fe $3p$ LMDAD results for Fe(100) are described by a critical exponent $\beta_{LMDAD}=0.81\pm 0.01$, to be compared with $\beta_B=0.38\pm 0.01$ from Kerr rotation. The results for temperatures near the Curie point are average values of quick heating runs, where S segregation starts while collecting the data, and slow cooling runs on surfaces saturated with 0.5 ML of S. Each individual run gave the same critical exponent. The value of β_{LMDAD} for Fe(100) is iden-
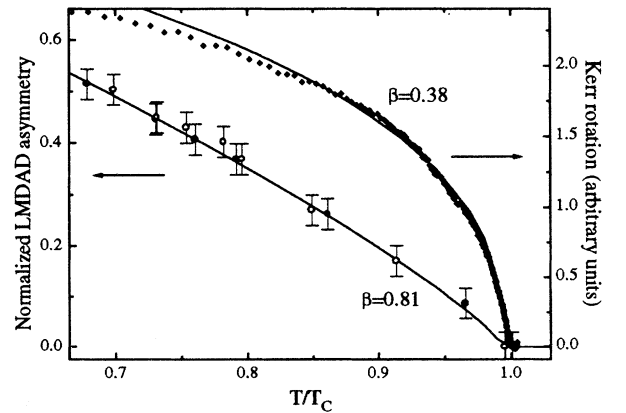

FIG. 3. LMDAD (filled symbols) and Kerr rotation (open symbols) as a function of reduced temperature in the near critical region. The critical exponents were obtained by maximizing the linearity of ln[LMDAD] vs $\ln[1-T/T_c]$ and of ln[Kerr rotation] vs $\ln[1-T/T_c]$. The solid lines are the theoretical curves fitted to the data.
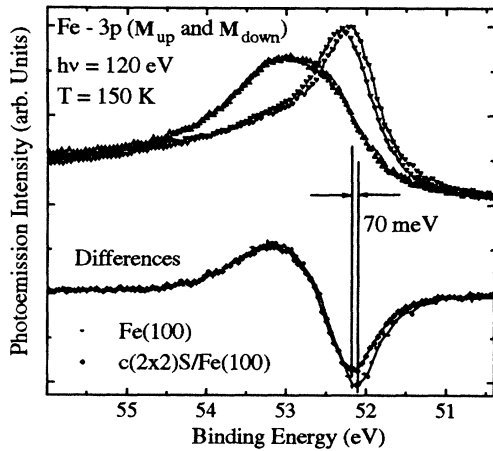
FIG. 4. Fe $3p$ LMDAD spectra for the clean Fe(100) surface (filled symbols) and the sulfur-segregated $c(2\times2)$S/Fe(100) surface (open symbols). All the spectra were measured at $T=150$ K. The reduced width of the dichroism spectrum reflects the reduced splitting of the $j=3/2$, $\mathbf{m}_j=\pm3/2$ sublevels.

tical to the critical exponent measured by spin-dependent elastic electron scattering on Ni(100) and Ni(110) surfaces,[20] which suggests that the critical behavior of surface magnetism may have a universal character, irrespective of the bulk structure and surface orientation, consistent with statistical two-dimensional models. The above results provide firm experimental proofs that the measurement of photoemission magnetic dichroism is directly proportional to the order parameter of magnetization for the Fe surface atoms $\langle\mathbf{M}_S\rangle$. Albeit atom-specific magnetic-sensitive spectra have been obtained previously by spin-polarized Auger[21] and core photoemission spectroscopies,[22] they were penalized by the low efficiency (of the order of 10^{-3}) of spin detection. Previous measurements of the surface exchange were obtained by SP on FeNiB$_{0.5}$, permalloy,[18] and Fe(110),[14] and by Mössbauer spectroscopy on Fe(110) interfaces.[23] LMDAD allows us to perform a complete atom-specific surface magnetometry study.

When a $3p$ core hole is created in ferromagnetic iron the sixfold degeneracy of the atomic $3p$ subshell is lifted: the details of the energy splitting of the magnetic sublevels are determined by the combination of the electrostatic and exchange interactions between the core hole and the spin-polarized valence electrons and of the core level spin-orbit interaction.[10] The spin-orbit interaction for Fe $3p$ can be derived from photoemission spectra of nonmagnetic semiconducting βFeSi$_2$, and it is 1.05 ± 0.05 eV.[24] Within the atomic picture the magnitude of the interaction between the core hole and the spin-polarized valence electrons can be directly obtained from the energy width of the $j=3/2$ multiplet for effective magnetic interactions well below the Paschen-Back limit.[25]

A simultaneous fit of the Fe $3p$ unmagnetized (M averaged) and dichroism spectra with a sextuplet of Gaussian-Lorenzian peaks identifies the energy distribution of the $\mathbf{m}_j$ sublevels.[5] The energy order of the sublevel indicates that the splitting is driven by spin-spin interaction, which inverts the
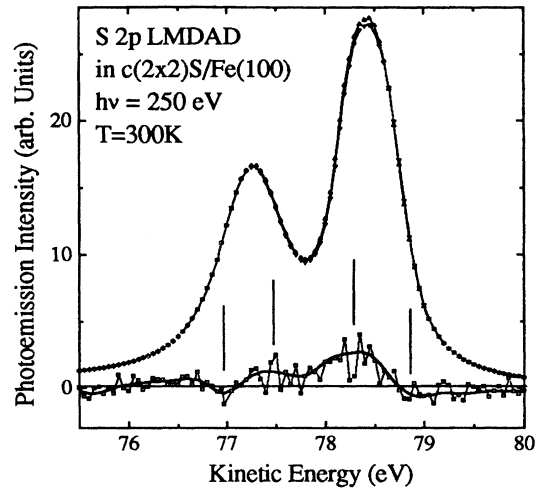

FIG. 5. S $2p$ LMDAD spectra measured at $T=300$ K. The continuous line through the difference curve is a Fourier smoothing of the data. The down-up-up-down shape of the dichroism clearly indicates that the effect is due to spin-spin interaction, i.e., that a magnetic moment is present on the S atoms of the $c(2\times2)$S/Fe(100) superstructure.

order of the $j=1/2$ sublevels[8] and the total $j=3/2$ splitting is 1.06 ± 0.02 eV for the clean Fe(100) surface. The comparable magnitude of spin-spin interactions between core hole and valence electrons and of core spin-orbit interactions defines the intermediate coupling regime.[25] The energy splitting is considered here to be linearly dependent on the atomic exchange interaction within the physical range of variations: although this approximation is better suited for deeper core levels with large spin-orbit splitting, like Fe $2p$, the calculations of Ref. 10 show that, for small variations of the exchange, it is justified even for Fe $3p$ levels. The sharp extrema of the dichroism spectrum correspond to the energy positions of the $\mathbf{m}_j=\pm3/2$ sublevels, which are pure spin-orbit states and display the largest magnetic asymmetry. The "width" of the dichroism spectrum is therefore proportional to the atomic exchange interaction for the $3p$ core hole which reflects the local magnetic moment of the excited atom.

The atomic exchange depends upon the details of the spin-polarized electron states of the valence band which are determined by crystal structure and chemistry at the surface. We compare in Fig. 4 the $3p$ dichroism spectra of clean Fe(100) and S-segregated Fe(100). Sulfur segregation occurs at temperatures higher than 500 °C and saturates when an ordered $c(2\times2)$ superstructure is completed (clearly observed in low-energy electron diffraction) for annealing above 600 °C.[26] The $3p$ LMDAD dichroism spectra of Fe(100) and $c(2\times2)$S/Fe(100) at 300 K are shown in Fig. 4. The narrowing of the Fe $3p$ dichroism spectrum for the sulfurated surface shows that the $\mathbf{m}_j=\pm3/2$ splitting is reduced to 0.99 ± 0.02 eV. If we assume that the reduction of the splitting is entirely due to the surface Fe atoms directly bonded to S (representing $\approx30\%$ of the Fe $3p$ photoemission intensity), this would imply a reduction of magnetic

moment of 20%. From the inspection of the magnetization-dependent spectra one observes a clear "magnetochemical shift" of the peak dominated by the (minority spin) $\mathbf{m}_j = +3/2$ sublevel when sulfur is present at the surface, i.e., a reduction of the final state energy of the photoemission peaks reflecting the modified electrostatic *and* exchange interactions in the new environment.

The reduced magnetic moment of the Fe(100) surface atoms when S atoms occupy the fourfold surface sites corresponding to the $c(2 \times 2)$ superstructure can be attributed to hybridization of the Fe $3d$ bands with the S sp valence electrons.[27] This fact has implications for the valence configuration of the $c(2 \times 2)$ S atoms. In Fig. 5 we show the LMDAD spectra for the S $2p$ core level for the segregated $c(2 \times 2)$S surface of Fe(100): the presence of dichroism shows that bonding with Fe implies a transfer of magnetic moment on the sulfur, in agreement with spin-resolved valence band spectroscopy results[28] and theoretical predictions.[27] The $\mathbf{m}_j = \pm 3/2$ splitting of the S $2p$ $3/2$ peak is ≈ 0.45 eV.

It is clear that photoemission magnetic dichroism provides a powerful magnetometer, both as a measure of the order parameter $\langle \mathbf{M} \rangle$ from the asymmetry, and from the measure of the effective spin interaction on $l > 0$ core levels. All the advantages of surface sensitivity and chemical sensitivity of the photoemission technique are transferred to the dichroism magnetometry. This allows us to address both of the key problems of surface magnetism, the changes of the surface magnetic moment and the changes of surface to bulk exchange, with an atom-specific probe. Photoemission spectroscopy can be extended to bulk atoms by using suitable monochromatic sources of x rays in the 1–3-keV energy range for excitation of photoelectrons at high final state energies corresponding to large mean-free paths. Although the LMDAD asymmetry is a matrix element effect and depends on photon energy, the core level splitting reflects fundamental interactions in the ferromagnets. Bulk sensitive photoemission dichroism will allow us to measure the core level splitting for bulk atoms and therefore to put on an absolute scale the surface magnetic measures reported in the present study.

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