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Layer-dependent spin-polarized 3*p* core-level photoemission from ultrathin Fe films

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We present the results of a spin-polarized photoemission experiment that yields unambiguous evidence of layer-dependent core-level magnetic exchange splitting in ultrathin films. Analysis of the layer dependence of 3*p*-level spin polarization also establishes the existence of bulklike local magnetic order at 1.5 monolayer thickness.

Recent experimental[1] and theoretical[2] studies have addressed the origin of and opportunities for exploiting spin-polarized photoemission from core levels in magnetic materials and from chemisorbed atoms at magnetic surfaces. Core-level photoemission offers a well-established probe of atomic-specific local environments[3] (both structural and chemical) based on core-level shifts resulting from chemical effects (charge transfer) and/or differences in local coordination (surface core-level shifts). The spin polarization of core levels is generally believed to result from interatomic (or intra-atomic in the case of adsorbate polarization) exchange.[2] In addition to the attractive features of non-spin-polarized core-level photoemission, spin-polarized core-level photoemission also offers the opportunity to probe atom-specific local electronic and magnetic structures.

Ab initio[4] calculations of the ground-state electronic properties of surfaces and thin films suggest that in most cases, bulklike local atomic environments are established very near the surface, typically in the second or third layer from the surface. In magnetic materials, the calculations also predict significant layer dependences in the magnetic moment per atom near the surface, and near interfaces in epitaxial film structures. Several competing effects account for these effects: strong film-substrate hybridization effects[5] apparently suppress ferromagnetism in the single monolayer (ML) films of Fe on W(100), but the lower coordination and expanded lattice constant for thicker films leads to strong ferromagnetic behavior. Surface atoms of bulk ferromagnetic materials have been predicted to have significantly enhanced magnetic moments[6] compared to atoms in the bulk material. There have been several experiments[7] that suggest the predictions are accurate.

Issues pertaining to layer-dependent magnetic behavior near the surface of a magnetic material or in ultrathin epitaxial magnetic films are excellent candidates for study using spin-polarized core-level photoemission. The few existing spin-polarized core-level photoemission studies of magnetic systems have already demonstrated important advantages of the technique. For example, the element specific feature was essential in probing exchange splitting of the (core) Auger lines in chemisorbed O on bulk[8] magnetic surfaces, and the layer sensitivity (surface core-level shift) was essential in observing antiferromagnetic coupling[9] between the surface layer and the bulk at the Gd(0001) surface. In both of these cases, the intrinsic linewidth of the spin integrated peaks was comparable to or greater than the magnetic splitting, and useful information was only obtained after the separate contributions from majority and minority spin states had been resolved by spin detection.

In this paper, we report layer-dependent spin-polarized 3*p* core-level photoemission studies of ultrathin epitaxial thin Fe films grown on W(110). Our experimental results and analysis of core-level spectra reveal layer-dependent magnetic effects that we interpret as resulting from layer-dependent core-level exchange splitting. Our studies therefore support the existence of significant layer-dependent magnetic properties at the surface, and demonstrate the very rapid evolution toward bulklike behavior of magnetic properties near the surface.

The spin-polarized photoemission experiments described herein were conducted on the U5 undulator beam line at the National Synchrotron Light Source, Brookhaven National Laboratory. Electrons photoemitted from the 3*p* core levels of 1.5- and 3.0-ML Fe films on W(110) were energy and spin analyzed using instrumentation described previously.[10] Energy and angular resolution of spectra presented here are 0.3 and $\pm 1.5°$, respectively. The data were acquired using normal emission geometry and *p*-polarized light. An electron beam cell was used to grow iron overlayers at a rate of ~ 0.2 ML/min on a spark cut W(110) surface aligned to $\pm 1°$ accuracy by x-ray Laue photography. The first ML was grown at 1000 K with subsequent growth at $T \sim 300$ K. It has been shown that these conditions produce well-ordered pseudomorphic overlayers.[11] Our low-energy electron diffraction studies confirmed the pseudomorphic nature of the growth. The films were pulse magnetized along the $[1\bar{1}0]$ direction by a nearby set of coils. Data were acquired by reversing the magnetization between sweeps; in this way spin-orbit effects were suppressed.

Intensity and spin-polarization data for 1.5- and 3.0-ML thick films appears in Fig. 1. The spin-polarization is defined as $P=(N^{\uparrow}-N^{\downarrow})/(N^{\uparrow}+N^{\downarrow})$ where $N^{\uparrow}$ and $N^{\downarrow}$ are the number of electrons with spins aligned parallel to the conduction band majority and minority spin directions, respectively. The 3*p* core-level intensity-to-background ratio was 0.35. Counting rates were typically

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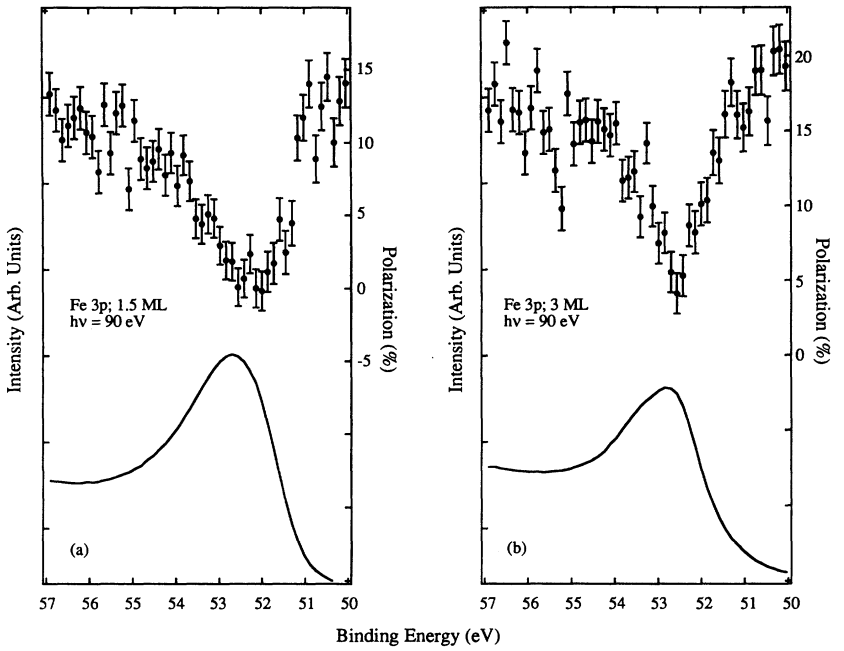

FIG. 1. Fe 3p polarizations and energy distribution curves for (a) 1.5-ML and (b) 3-ML films.

6 kHz at the peak position. The 3p peak is characteristically wide; it has an apparent width of ~2 eV full width half maximum in both cases. Furthermore, the spin polarizations are of comparable magnitude which suggests that the local magnetic environments of atoms contributing to the peaks are similar. Closer scrutiny reveals that the intensity and polarization data possess subtle differences. The 1.5-ML polarization data have a significantly more rounded dip and reaches a value 5% lower than that of the 3-ML film. These effects will be shown to be manifestations of interface emission in the 1.5-ML film data. The centroid of both peaks lies at the bulk Fe 3p position of 52.7 eV.

Spin-resolved intensities were obtained using the relations $I^{\uparrow}=I_0/2(1+P)$ and $I^{\downarrow}=I_0/2(1-P)$. As can be seen in Fig. 2, the 3-ML data appear to be composed of a single line, while two lines are required to fit the 1.5-ML data. The energetic ordering of the splitting is what one would expect from simple multiplet theory. When the remaining unpaired 3p spin is of the same orientation as the majority-spin conduction electrons, the exchange interaction acts to lower the final-state energy such that the minority-spin photoemission peak appears at a lower binding energy than the corresponding majority-spin peak. The effects of the magnetic structure are elucidated by curve fitting the spin-resolved intensities based on a Doniach-Sunjić[12] lineshape convolved with the known Gaussian instrumental response. The background was assumed to be flat for the fits shown in Fig. 2. Little difference in the character of the fits resulted from assuming a more complex background shape. The background polarizations, as recalculated from the fits, were flat and of similar size for the two films. The resulting binding energies and exchange splittings appear in Table I.

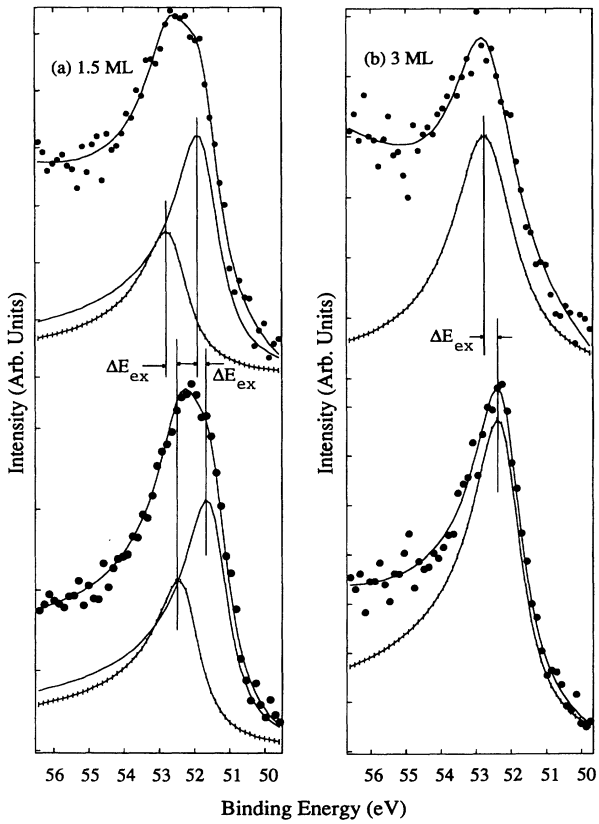

FIG. 2. Spin resolved intensities (●), fitted curves (—), and individual lineshapes (—) for (a) 1.5-ML and (b) 3-ML films. Upper curves are majority, lower are minority. The background curves are not shown. The peaks with bulk binding energies are hatched.

TABLE I. Spin-dependent binding energies and exchange splitting of Fe 3*p* levels as a function of thickness. Up and down arrows indicate majority and minority peaks, respectively.

Fe thickness (ML)	Binding energy (eV)	Exchange splitting (eV)
3.0	52.80(↑) 52.30(↓)	0.50
1.5	52.85(↑) 52.50(↓)	0.35
1.5	51.95(↑) 51.68(↓)	0.27

The 3-ML data was fit using a single line for each spin-resolved spectrum. We cannot rule out the existence of a small peak at slightly lower binding energies (see below), however, our discussion is independent of the existence of such a peak. The 3-ML data displayed in Fig. 2 exhibit a remarkable similarity to Fe(100) surface 3*p* core-level data.[13] The ratio of the majority and minority spin linewidths is 1.5, which is very close to the value of 1.6 reported for the Fe(100) surface. This ratio can be explained by a simple statistical argument. If the hole lifetime is proportional to the number of available electrons to fill a hole, then the larger width corresponds to shorter lifetimes and hence larger number densities. The ratio of majority to minority spin electrons in the conduction bands of bulk Fe is ~ 1.7. This is sufficiently close to the Fe(100) surface value of 1.6 and the 3-ML film value of 1.5 that the difference in linewidth can be attributed to lifetime broadening governed by the different number densities. The binding energies of the spin-split peaks are centered about the spin-integrated value of 52.7 eV. A core-level exchange splitting of 0.5 eV is evident in the 3-ML film. This compares favorably with more recent measurements of the Fe 3*p* core-level exchange splitting.[14] From these observations, we conclude that the 3-ML film may be regarded as bulklike. If the 3-ML film is truly bulklike, one might expect to detect a surface core level shifted from the bulk value. However, this is not the case for the Fe surface. Experiments on the Fe(100) surface show no evidence for any surface-related peak;[13] Citrin and Wertheim have calculated a surface shift of less than 25 meV for the Fe(110) surface.[15]

We now turn to the 1.5-ML film data. Curve fits with low χ^2 could only be achieved if we included a second line for each fit. Addition of a third line resulted in nonphysical fitting parameters. Therefore the possibility of a third line has been excluded. The exchange splitting of the two sets of lines is similar, 0.35 and 0.27 eV for the high and low binding energy sets, respectively. The overall lower values of exchange splitting may be attributed to a smaller ground-state local magnetic moment. However, it is also possible that the W conduction electrons, which may be weakly polarized,[16] participate in the Fe deexcition channels, thereby diminishing the splitting. The fixed lines and summed intensities are shown in Fig. 2(b). The high binding energy peak in both the majority and minority spin spectra is located at exactly the 3 ML (bulk) position, while a second, more intense line lies at 0.8-eV lower binding energy. *This peak, which is not present in the 3-ML film, we attribute to emission from the first ML.* On average, the 1.5-ML film consists of equal areas of 2- and 1-ML Fe patches. If a substrate induced core-level binding energy shift exists (see below), emission from the second ML (Fe on Fe) and from the uncovered 1 ML (FE on W) areas should result in equal intensities of two distinct lines. To the total photocurrent must be added the intensity from the attenuated (covered) 1 ML patches. Provided the second ML does not appreciably alter the core-level binding energy of the covered ML areas, it is reasonable to expect a higher intensity in the low binding energy peak over that of the deeper line. The existence of the larger, more bulklike exchange splitting in the high binding energy peak is evidence that films even as thin as 1.5 ML possess some three-dimensional Fe magnetic character on a local scale. Curiously, this evolution toward a bulklike Fe magnetic moment is in the opposite sense of what is to be expected for a ferromagnetic film on a noble metal substrate. In such systems, because of the low Fe-substrate hybridization,[4] one should detect the largest moments at the interface. Apparently hybridization between the Fe 3*d* and the W 5*d* electrons is sufficiently strong to overcome the effects of an expanded lattice constant and drive the interface Fe atoms toward paramagnetism.

The existence of the core-level binding energy shift between the 1- and 2-ML patches may be easily understood by using the equivalent-cores approximation.[3] With this assumption, a Born-Haber cycle can be invoked to relate the core-level energy shifts to various known quantities, e.g., the adsorption enthalpy, $E_{\text{ads}}^{x/y}$, of material x upon material y. In this case, the shift is given by

$$\Delta E = (E_{\text{ads}}^{\text{Fe/W}} - E_{\text{ads}}^{\text{Fe/Fe}}) - (E_{\text{ads}}^{\text{Co/W}} - E_{\text{ads}}^{\text{Co/Fe}}) .$$

Unfortunately, experimental values for ΔE_{ads} do not exist for all the necessary systems and calculated values tend to err inconsistently for transition metal adsorbates.[17] However, a rough estimate from the calculated values suggests that the 0.8-eV shift is a reasonable expectation for the difference in the 2- and 1-ML Fe 3*p* binding energies.

In conclusion, we have presented the first application of spin-resolved core-level photoemission to the study of the evolution of the local magnetic structure in ultrathin ferromagnetic films. The locality of core-level photoemission has enabled us to see the onset of three-dimensional behavior in the magnetic structure of Fe/W(110). While similar conclusions have been reached with respect to Fe/W(110) (Ref. 18) and Ni/W(110) (Ref. 19) films using spin-resolved conduction-band photoemission, we have shown that it is also feasible to unambiguously measure the layer-dependent core-level exchange of splitting of ultrathin ferromagnetic films without recourse to assumed values of the electronic mean free path. It is not easy to relate the measured core-level exchange splittings to the local magnetic moment since there is not a one-to-one correspondence. However, inasmuch as the exchange splitting may be related to the local magnetic moment by calculation, we hope that these results and those to follow will spur theoretical interest in this area. A future refinement of this technique

will be to incorporate azimuthal and polar angle scans so as to determine the angular response of the polarization-dependent screening process. With a suitable choice of photon energy and a sufficiently bright light source, the previously unused power of spin-resolved core-level photoemission shows promise as a powerful tool for exploring the realm of low-dimensional magnetism.

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