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Spin-resolved iron surface density of states

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The spin polarization of photoemitted valence-band electrons from polycrystalline Fe films shows good qualitative agreement with the calculated spin-resolved density of states (SRDOS) of bcc Fe. The quantitative differences are accounted for by the surface contribution to the photoelectron intensity. Simple subtraction of calculated bulk Fe SRDOS from the photoemission spectra yield an experimental surface SRDOS that agrees well with the calculation for Fe(001) and Fe(110). The Fe surface spin polarization is enhanced by (12±8)% over the bulk, consistent with theoretical predictions.

Spin-polarized electron spectroscopies have had important impact on the current understanding of magnetic properties of solids and their surfaces as well as artificially structured layers and multilayers.[1–3] Angle-resolved spin-polarized photoemission spectroscopy (SPPES), in particular, has revealed the spin and wave-vector dependence of the electronic structure of magnetic materials,[4,5] which permits very detailed comparison with the calculated spin-resolved band structure. Angle-integrated SPPES, on the other hand, which can measure the spin-resolved total density of states (DOS), has not been performed to date even though the imbalance between majority- and minority-spin DOS is the most basic characteristic of any magnetic material.[6,7] The spin polarization of the occupied DOS of Fe has been probed recently by the technique of circular dichroism in x-ray emission (CDXES).[8] This technique, unlike SPPES, is a local probe that must rely on spin conservation in the radiative decay of the spin-polarized core holes. SPPES experiments, being surface sensitive, also provide the exciting possibility of directly testing one of the basic predictions of surface magnetism: do the surfaces of $3d$ transition metals exhibit enhanced magnetization?[9–12] Although there have been many magnetic studies of ultrathin $3d$ transition-metal layers,[3,13] to our knowledge, the only investigation to date of the enhanced magnetization of a free Fe surface is a spin-polarized low-energy electron diffraction study.[14] Theoretical modeling[15,16] of this experiment supports the idea of enhanced surface magnetization, but photoemission experiments provide a unique opportunity to directly probe the surface magnetization by measuring the spin-resolved surface DOS.

In this paper we present results of an angle-integrated spin-polarized valence-band photoemission from Fe. The full Brillouin-zone averaging in photoemission can be achieved either by summing over all photoelectron emission directions (using an angle-integrating analyzer or a polycrystalline sample) or by relying on phonon-assisted indirect transitions at higher photon energies [x-ray phonon spectroscopy (XPS)].[17] Due to the lack of angle-integrated spin-resolving analyzers and the low photoelectric cross section of valence levels at x-ray energies,[18] we performed soft x-ray experiments using well-characterized polycrystalline Fe films. Our SPPES data from these films show good qualitative agreement with calculated spin-resolved bulk DOS and recent CDXES experiments. Small quantitative differences exist, however, which cannot be reconciled by any photoemission effect or sample condition. They are, on the other hand, fully accounted for by the surface contribution to the measured photoemission spectra. The extraction of the spin-resolved surface DOS by subtracting the calculated bulk DOS from the measured photoemission spectra yields a surface spin polarization of (37±3)%, in qualitative agreement with predictions for both Fe(001) (Refs. 10 and 12) and Fe(110) (Refs. 11 and 12) surfaces.

The spin-polarized photoemission experiments reported here were carried out on a newly constructed electron energy and spin analyzer that will be described in detail elsewhere. Briefly, spin detection is achieved with a version of the NIST low-energy spin detector[19] mounted on the exit lens of a commercial (100-mm radius) hemispherical analyzer.[20] The angular acceptance cone of the analyzer was $\pm 6°$. Linearly polarized soft x-ray light was provided by the U13UA wiggler beamline[21] installed on the vacuum ultraviolet ring at the National Synchrotron Light Source. The overall energy resolution (photon plus electron) in the spectra presented here is 0.75 eV. The angles of the incident photons and emitted electrons with respect to the surface normal were 45° and 0°, respectively. The Fe sample was magnetized in the photoemission plane using a small pair of coils. All the measurements reported here were performed at room temperature. The Sherman function of the spin detector was calibrated by comparing measured secondary, core-level, and Auger-electron spin polarization from thick Fe(001) films with published data.[22–25]

The Fe sample was relatively thick Fe film (~50 Å) evaporated *in situ* onto a polished disk ($\frac{3}{8}$-in. diam) of polycrystalline Al (final polishing with 0.25-μm diamond paste). The Al substrate was cleaned by cycles of argon-ion bombardment and annealing until contamination levels were below 1% of a monolayer as measured as measured by Auger-electron spectroscopy. Fe evaporation was provided by a home-built e-beam evaporator with LN_2 cooling. The pressure during evaporation was $\leq 3 \times 10^{-10}$ torr. The contamination level after Fe film growth was below 3% of a monolayer. No Al $2p$ photoelectrons were visible in our spectra for the Fe overlayer thicknesses of 25 Å or greater.

Spin-integrated valence-band photoemission spectra recorded from our polycrystalline Fe film using linearly polarized 260-eV photons closely resemble XPS spectra from polycrystalline Fe films and Fe(001) surfaces reported previously,[26–28] the only difference being a less pronounced 3-eV shoulder at 260 eV. No changes in spectral line shape were observed as a function of photon energy (200–300 eV), electron emission angle (0°–40°), and Fe film thickness (40–100 Å), indicating that our photoemission spectra represent a true angle-averaged emission from the Fe valence band and thus can be compared to Fe DOS.[29]

We have established that the magnetic properties of our polycrystalline Fe films are consistent with those of ferromagnetic bcc Fe by measuring the spin polarization of photoemitted core electrons (Fe $3p$), Auger electrons (Fe LMM), and secondary electrons. All of the measurements are in agreement (line shape and spin polarization) with the previously reported spectra from bcc Fe(001) surfaces.[22–25] The secondary electron spectra showed the well-known enhancement of spin polarization of very-low-energy ($E<6$ eV) secondary electrons[24,25,30] and a small polarization maximum at ~12 eV. Such a maximum has also been observed, albeit with greater strength, from Fe(001) (Ref. 25) and is attributed to the spin-resolved band structure of bcc Fe.[31] This observation strongly suggests that we have grown bcc Fe and thus makes valid our comparison to the DOS of bcc Fe.

In Fig. 1(a) we show spin-resolved valence-band photoemission spectra of a polycrystalline Fe film taken at 260-eV photon energy. As expected, the majority-spin spectrum exhibits larger spectral weight than the minority-spin spectrum. The majority-spin spectrum, which contains a main peak at ~1 eV binding energy (E_b) and a shoulder at ~3 eV, is considerably wider than the minority spectrum, which consists of a single peak at ~1 eV. The energy shift between the bottoms of the majority and minority spectra indicates an average exchange splitting of ~2.0 eV, in agreement with previous experiments.[32] Since the sum of the two spectra shown in Fig. 1(a) is consistent with spin-integrated Fe valence-band XPS spectra, our measurement reveals the spin polarization of these well-known XPS spectra. We note that SPPES measurements at lower photon energy (200 eV) and also from polycrystalline Fe films prepared on a sapphire substrate[33] have produced identical spectra. To what extent these spin-resolved spectra represent the spin-resolved density of states (SRDOS) can be estimated by comparison to the calculated SRDOS of ferromagnetic bcc Fe.[34] Due to the very low Fe $4s$ photoionization cross section relative to Fe $3d$ at 260 eV [σ(Fe $4s$)/σ(Fe $3d$)=0.02],[18] we show only the $3d$ component of the Fe SRDOS (Ref. 35) in Fig. 1(a). It is observed that all the main photoemission spectral features (peak positions, heights, and widths) are well predicted by the calculations, indicating that angle-integrated photoemission experiments are capable of measuring the true SRDOS.

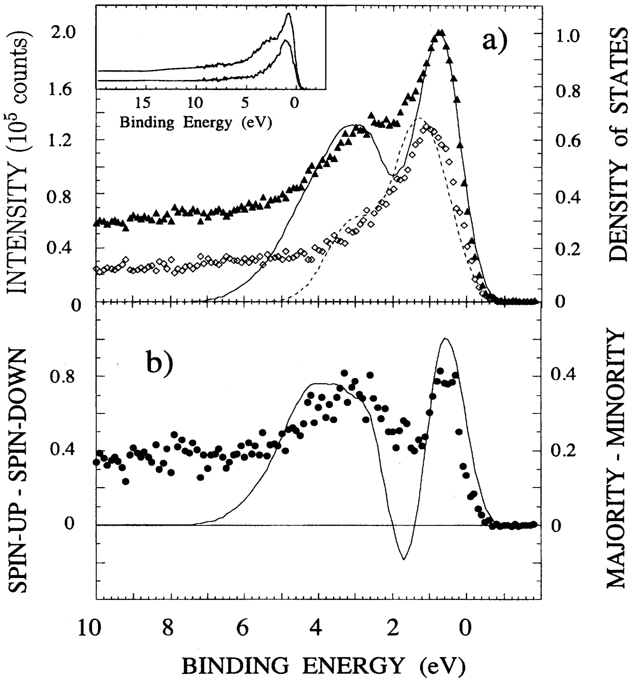

FIG. 1. (a) Majority-spin (▲) and minority-spin (◇) Fe valence-band photoemission spectra ($h\nu$=260 eV) from a polycrystalline Fe film, and calculated majority-spin (—) and minority spin (- - -) densities of states of ferromagnetic bcc Fe (Ref. 34). The densities of states have been convoluted with a 1.0-eV full width at half maximum Gaussian representing experimental resolution, and are scaled so that the majority-spin DOS matches the majority-spin photoemission intensity at ~1 eV binding energy. Inset: wide-range spectra. (b) Spin difference of the photoemitted Fe valence-band electrons (●) and of the calculated DOS of bcc Fe (—).

The agreement between SPPES and SRDOS can be assessed in more detail by comparing the spin difference ($I_\uparrow - I_\downarrow$) of the photoemission intensity and of the calculated DOS, shown in Fig. 1(b). The two curves show similar line shape, with a pronounced dip just below 2-eV binding energy. The discrepancies between the two curves are mostly in magnitudes. In particular, the minimum in the DOS just below 2 eV becomes negative, whereas the corresponding feature in the photoemission data does not cross zero. The nonzero spin difference above 6.5 eV in the measured spectra is due to the spin polarization of the inelastic background. We note that the CDXES of Fe agrees well with the calculated Fe SRDOS, including the negative value of spin difference just below 2 eV (see Fig. 2 in Ref. 8). However, CDXES does not detect the DOS features (e.g., the 3-eV shoulder) which are observed in the photoemission measurement.

We will now discuss the quantitative differences between our SPPES data and the calculated SRDOS, the most important of which occur in the middle of the band ($1<E_b<3$ eV). In particular, the majority-spin SPPES spectrum does not show the pronounced minimum at ~2 eV as predicted by SRDOS [see Fig. 1(b)]. This discrepancy cannot be explained by instrumental spin sensitivity, poor energy resolution, or by any other photoemission process, as we show here. Reduction of the spin detector's Sherman function would reduce the magnitude, but not sign, of the spin-difference spectra. Additional energy broadening is also not able to account for the noted differences: convolution of the

SRDOS with a 2-eV Gaussian yields a small positive spin difference at $E_b \approx 2$ eV, but distorts the overall shape of the DOS (especially the overall bandwidth) such that overall agreement with the measured spectra degrades considerably. We have also modeled the effects of lifetime broadening[36] on the SRDOS. Although it is possible to raise the spin difference of the DOS at ~2 eV to a positive value, this requires a large lifetime broadening, which again results in much too large bandwidths. This is especially noticeable in the minority DOS, which becomes ~1.5 eV broader than the photoemission spectrum. Interaction of the photohole with the conduction electrons would have a similar effect on the DOS as lifetime broadening. A monotonic change in matrix elements with binding energy[24] also cannot bring the middle of the spectrum into better agreement with the calculated SRDOS without distorting the overall spectral line shape (widths and relative peak heights). Finally, the differences between SPPES and SRDOS also cannot be attributed to sample condition or impurities. In particular, small amounts of nonmagnetic or antiferromagnetic phases (like fcc Fe) would contribute equally to majority and minority spectra.

We will now show that the quantitative differences between the SPPES spectra and the calculated bcc Fe SRDOS can be fully accounted for by the contribution of surface DOS to the measured photoemission spectra. The surface contribution to the overall photoelectron flux is determined by the electron mean free path (λ). For the relatively-low-energy photoelectrons (260 eV) we use λ of 5.5±1.0 Å, which covers twice the range of published λ values.[37–39] This suggests that ~25% of the photoelectrons emerge from the surface (first atomic layer).

The surface "SPPES spectra" are extracted by subtracting the calculated bulk SRDOS from our measured SPPES data. Such difference spectra (using λ = 5.5 Å) for both the majority- and minority-spin components are shown in Fig. 2. The high binding-energy side ($E_b \geqslant 4$ eV) of these spectra is dominated by the photoemission inelastic losses. The lower binding-energy part ($E_b \leqslant 4$ eV) shows spectral weight, which we attribute to Fe majority and minority *surface* DOS. These extracted surface SRDOS's clearly exhibit two main characteristics predicted for all $3d$ transition-metal surfaces. First, both the majority and minority surface DOS's are narrower (by ~1 eV) than their bulk counterparts, which is expected due to reduced coordination of the surface atoms. Second, the maximum of the majority (minority) surface DOS is shifted to higher (lower) binding energy relative to the corresponding bulk SRDOS, which yields enhanced magnetization at the surface. In order to have a better sense of how these observations agree with the predictions, we include in Fig. 2 the calculated surface DOS, for which we use equal contributions of Fe(001) (Ref. 10) and Fe(110) (Ref. 35) surface DOS to represent our polycrystalline samples. The (001) surface was used because secondary electron spectra provide clear evidence of (001) crystallites in our films. The (110) surface is also included because this is the most close-packed surface of bcc Fe. There is remarkable agreement in peak position and intensity for both spin components between the calculated and extracted surface DOS.[40] It is interesting to note that the extracted surface SRDOS shows negative spin polarization close to the Fermi energy, a characteristic common to the calculated SRDOS of both Fe (001) and (110) surfaces, and opposite to that of the bulk Fe. Such information is important in spin-dependent transport properties as, for example, giant magnetoresistance.[3]

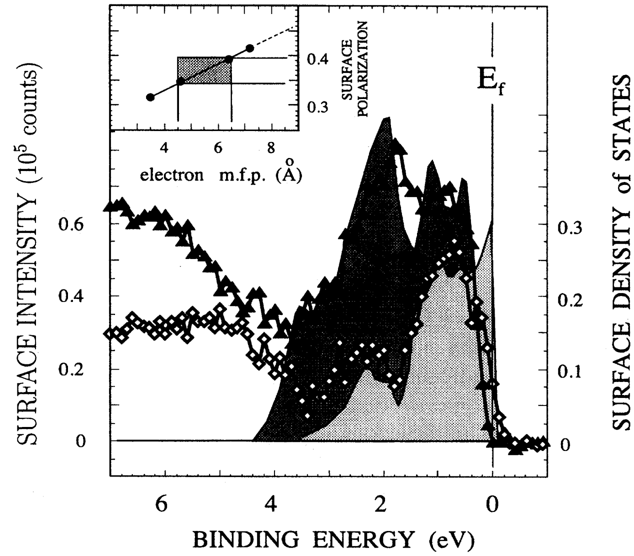

FIG. 2. Majority-spin (▲) and minority-spin (◇) difference spectra obtained by subtracting the calculated Fe bulk DOS from the measured photoelectron spectra [Fig. 1(a)]. Calculated Fe-surface majority (dark-shaded area) and minority (light-shaded area) DOS [equal sum of Fe(001) (Ref. 10) and Fe(110) (Ref. 35)]. Inset: deduced surface spin polarization as a function of electron mean free path.

We estimate the surface spin polarization by integrating over the extracted majority and minority surface DOS ($E_b \leqslant 4$ eV). The extrinsic (inelastic) background in this energy range is taken to be negligible.[41] As expected, different values of λ lead to different values for the surface magnetization, as shown in the inset of Fig. 2. Including a large uncertainty in the value of λ (5.5±1.0 Å), we find a surface polarization of (37±3)%, which is (12±8)% greater than the Fe bulk value ($3d$ contribution only)[35] at room temperature. Correction for the temperature dependence of the surface magnetization[42] brings the value of surface enhancement of spin polarization to (24±10)% for $T = 0$ K. This is in good agreement with the theoretical predictions for both the Fe (001) [~30% (Refs. 10 and 12)] and Fe(110) [~15% (Refs. 11 and 12)] surfaces. Some fraction of the surface magnetization enhancement may be due to surface roughness, which has been demonstrated to further enhance the surface magnetization.[43] It is interesting to note that we obtain essentially the same degree of surface spin polarization (37% at room temperature) integrating the spin-resolved intensities (spin polarization =34% for $0 < E_B < 15$ eV and beyond, up to 30 eV) and using λ=5.5 Å, a result that does not depend on theoretical DOS.

It is important to realize that the contribution of the surface layer is also significant at XPS photon energies, even though XPS is ~3 times less surface sensitive than the present measurement. This is because the surface DOS peaks where the bulk DOS has a pronounced minimum (at $E_b \sim 2$ eV). This explains the overall resemblance of the 260-eV and

XPS spectra and the slightly more pronounced 3-eV shoulder in the XPS spectrum, as noted earlier.

In summary, we have presented an angle-integrated valence-band spin-polarized photoemission measurement from Fe, which has shown good qualitative agreement with calculated bulk SRDOS of bcc Fe. The quantitative differences between the calculated bulk SRDOS and the SPPES data are well accounted for by the contribution of surface DOS to the photoemission spectra. Simple subtraction of bulk SRDOS from the SPPES spectra yields surface SPPES "spectra" that are consistent with the main features of the calculated surface SRDOS of Fe(001) and Fe(110). The deduced surface spin polarization exhibits (12±8)% enhancement compared to bulk values at room temperature, which is in qualitative agreement with predictions for both Fe(001) and Fe(110) surfaces. Spin analysis of the valence-band photoemission spectra also resolves the quantitative differences between well-known spin-integrated Fe valence-band XPS spectra and calculated bulk DOS by invoking the surface contribution to measured photoelectron flux. We emphasize that such conclusions could not be unequivocally derived from spin-integrated data. Thus, this work demonstrates how spin analysis of photoemitted electrons provides new and independent insight into the photoemission process.

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