Spin-dependent surface transmission in 3*d* metals: Implications for magnetic-dichroism measurements of the valence bands

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The interpretation of measurements of magnetic dichroism in angle-resolved photoemission from the valence bands of 3*d* ferromagnetic metals is complicated by the simultaneous presence of spin-dependent surface transmission of the spin-polarized photoelectrons into the vacuum. As a result, two separate mechanisms contribute to the change in the photoemission intensity spectra when the sample magnetization is reversed. The magnitude of the surface transmission effect in the "light" 3*d* metals has been measured using Cu(001) as a sample, and an intensity asymmetry of ±3% has been found. This is smaller than, but approximately the same size as, the magnetic dichroism measured for iron and cobalt, and demonstrates experimentally that neither mechanism can be generally neglected in favor of the other.

Since its report five years ago,[1] magnetic dichroism in angle-resolved photoemission has proven to be a versatile method to study ferromagnetic materials, which complements more time-consuming spin-resolved experiments. The technique was initially applied to relatively deep (2*p*) core levels to address the question of an intrinsic exchange splitting of these levels,[2] to study the magnetic properties of thin films,[3] and to understand the important role of the angle-resolved nature of these experiments.[4] Later, shallower (3*p*) core levels were studied and the internal structure of these states was greatly clarified.[5] Theoretical work allowed a qualitative,[6,7] and quantitative,[8,9] interpretation of these results. There is now great interest in applying magnetic dichroism in angle-resolved photoemission to studies of the valence bands of ferromagnetic films and surfaces, since it is these states that ultimately determine the magnetic properties of itinerant electron ferromagnets. The first experimental studies have already appeared.[10]

It is not yet clear whether or not measurements of magnetic dichroism of valence bands using ultraviolet light will be straightforward to interpret. Because the photon energy in ultraviolet photoemission is relatively small, the initial and final electronic states are qualitatively similar. Since both the magnetic exchange interaction and the spin-orbit interaction must be present to produce magnetic dichroism in photoemission, this implies that both interactions must be included in the treatment of the initial and the final electronic states. In addition, there can be no doubt that the effects of multiple scattering are important for photoelectrons in this energy range. These observations invalidate the simplifying assumptions, which resulted in a relatively simple interpretation of experimental results from core levels, that is, the neglect of spin-orbit coupling in the final electronic state[6,7] or the use of an "oriented atom"[9] as a model for a solid. The inclusion of both multiple-scattering and spin-orbit coupling in the final states yields two mechanisms (which have been traditionally thought of as distinct), each of which can lead to a kind of magnetic dichroism in its broadest sense—a change in the angle-resolved photoemission intensity spectrum upon reversal of the magnetization of the sample. These two mechanisms are magnetic dichroism in angular distribution (MDAD) of photoelectrons, and spin-dependent "surface transmission effects.[11]" The general theories which describe this more complicated system[8,12] are sophisticated one-step photoemission calculations, which are not usually immediately available to experimentalists and do not provide a simple qualitative guide to interpretation of the measurements.

The purpose of the present paper is to help clarify experimentally the relative importance of these two mechanism in valence-band photoemission from 3*d* ferromagnets. As an illustrative example, consider the photoelectron spectra for 6-monolayer (ML) Co/Cu(001) presented in Fig. 1(a). The cobalt film forms a fct structure at room temperature, with remanent magnetization in the [110] direction in the surface plane.[10] The angle-resolved photoemission was collected in the (110) mirror symmetry plane normal to the magnetization, with the electron wave vector **k** making an angle of 14° to the surface normal. The light was circularly polarized, with positive helicity, with an incident wave vector **q** antiparallel to **k**. Part (a) shows the separate intensity spectra for remanent magnetization along [110] ($\mathbf{M}=+$) and reversed magnetization ($\mathbf{M}=-$). The normalized difference between the two spectra is shown as the intensity asymmetry in part (b). Significant asymmetry values of $-3-+5$° are associated with the photoemission from the Co *d* bands within 2.5 eV of the Fermi level. The peak at −3 eV is due to the Cu substrate and does not exhibit a significant asymmetry.

The observed asymmetry could arise from either MDAD, surface transmission, or a combination of both. MDAD is magnetic dichroism in angle-resolved photoemission, which occurs upon reversing the magnetiza-

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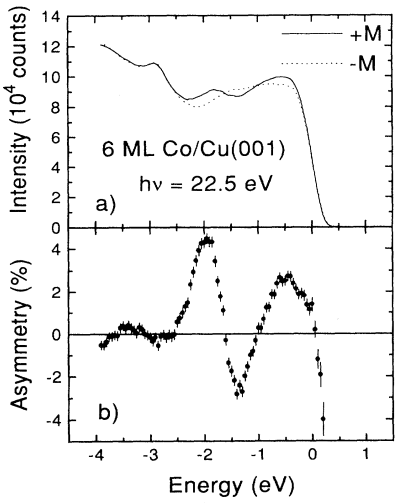

FIG. 1. (a) Angle-resolved photoemission intensity spectra from a 6-ML Co film on a Cu(001) substrate for remanent magnetization in the surface plane along [110] (+**M**) and [−1 −1 0] (−**M**). The experimental geometry is given in the text. (b) The intensity asymmetry for the spectra in (a).

tion.[13] The existence of MDAD requires the presence of both the exchange interaction, to give rise to a spontaneous magnetization, and the spin-orbit interaction in the ground state, to tie the magnetization in spin space to the lattice. The spin-orbit coupling must be strong enough to remove the energetic degeneracy of electronic states of a given orbital angular momentum. In the 3*d* ferromagnetic metals, the remanent magnetization vector **M** lies in a spatial mirror plane of the solid. Since magnetization is an axial vector, the experimental operation of reversing the direction of magnetization is equivalent to reflection in this spatial mirror plane. In angle-resolved photoemission, however, the photoelectron wave vector **k** and the electric field vector **E** of the light are altered by the reflection. The even parts of these vectors maintain their sign; the odd parts reverse sign. Thus, MDAD compares photoemission intensity spectra from two inequivalent experimental geometries, which are related by a mirror operation—there is chirality. It can be shown that the difference in the intensity spectra (the magnetic dichroism) depends only on the interference terms in the photoexcitation matrix element. Thus, MDAD is an interference term between even and odd parts of the dipole operator,[6] or the photoelectron wave function,[7] or, in a complicated geometry (such as that in Fig. 1) a combination of the two. For instance, consider the peak at −1.9 eV for **M**=+ and the shoulder at −1.7 eV for **M**=−, which lead to a strong asymmetry in Fig. 1. These could represent exchange-split initial majority or minority spin states, which have been perturbed in energy in opposite senses by the spin-orbit interaction. The asymmetry would then be because of MDAD.

Surface transmission effects, on the other hand, require only spin-orbit coupling in the photoemission states. Electronic eigenstates of a semi-infinite solid are pure spin-up and spin-down states in the vacuum, and a mixture of the two spin states in the solid (because of the presence of spin-orbit coupling). At the interface there is a matching condition, which conserves spin but, in general, gives different reflection probabilities for spin-up and spin-down electrons. These relations can be formally summarized in a surface-scattering matrix,[14] which is at the basis of spin-polarized low-energy electron diffraction. If photoexcitation in a solid leads to spin-polarized photoelectrons, the photoelectron intensity distribution measured in vacuum will depend on the sign of the spin polarization through the spin-dependent surface scattering. Reversing the spin polarization will therefore result in a change in the measured intensities. In a magnetic sample, reversing the magnetization will reverse the spin polarization of the valence electrons, and thus the photoelectrons, resulting in photoemission intensity changes due to surface transmission. Returning again to Fig. 1, the same two peaks near −1.8 eV could represent separate allowed transitions of opposite spin, with the observed intensity of each being modulated by spin-dependent transmission. The fact that the Cu peak does not have an asymmetry associated with it does not rule out the surface transmission mechanism. This is because Cu is nonmagnetic and the photoelectrons may be spin polarized only through photoexcitation involving the circularly polarized light. Since **k** is in a mirror plane, the resulting spin-polarization vector of the photoelectrons from Cu must also lie in this mirror plane.[11] But, since this plane is normal to **M**, reversing the magnetization does not alter the spin polarization in the Cu peak, and the transmission effect will not be observed.

In order to disentangle these two mechanisms, conditions must be found where one or the other is rigorously absent. Spin-dependent surface transmission is absent for normal emission from solid surfaces with at least two spatial mirror symmetry planes.[14] This fact has been used to demonstrate that MDAD from cobalt and iron has a normalized size of 4–10 % in ultraviolet photoemission.[10] It is not possible to similarly isolate the transmission effect in a magnetic sample. However, since it scales with the spin-orbit interaction, it should be possible to determine its size by using a nonmagnetic metal. Previous studies found a ±5% peak-to-peak effect on W(001) (Ref. 11) and a ±10% and ±40% peak-to-peak effect on Pt (111) (Ref. 15). Scaling these results by the square of the atomic number suggests a ±0.5–±4 % peak-to-peak effect for 3*d* metals. Since these estimates span the range where surface transmission may or may not be significant compared to MDAD, an experimental determination for the 3*d* metals is necessary.

The photoemission experiments we conducted at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY) synchrotron ring, using a 6.5 meter normal incidence monochromator,[16] which provides light of ≈90% circular polarization. Light with a photon energy of 12 eV was normally incident on a clean Cu(100) single crystal, and photoelectrons were collected at a polar angle of $\theta=32°$ from the surface normal, at a series of azimuthal angles ϕ about the surface normal [$\phi=0$ corresponds to emission within

the (010) mirror symmetry plane]. The electron spectrometer[17] had an acceptance angle of approximately $\pm 3°$ and an energy resolution of about 0.25 eV. In order to remove experimental artifacts due to movement of the light spot on the sample, the light passed through an aperture 2 mm in diameter, which was placed directly in front of the sample but not obscuring the path of the photoelectrons. Each time the light helicity was changed, the light spot was positioned by adjusting the monochromator exit mirror to maximize the photoelectron count rate.

Figure 2(a) presents representative intensity spectra for $\phi = -11°$. The two spectra for positive and negative light helicity have had a background (determined before the Fermi level) removed, and have been scaled uniformly to compensate for a change in photon flux as the synchrotron current decayed during the measurements. No attempt has been made to account for the secondary electron background, or for the incomplete polarization of the light. The intensity spectra show two clear peaks from the Cu d bands 2–3 eV below the Fermi energy, as is expected for this low-symmetry direction of electron emission. The wider peak at lower energy is, in fact, due to optical transitions from two bands, which have been split by the spin-orbit interaction by an energy too small to be resolved by the experiment. Previous spin-resolved studies at normal photoelectron emission,[18] have shown that this spin-orbit splitting is approximately 100 meV and that the spin-polarization of the photoelectrons excited from each band by circularly polarized light is opposite in sign, with magnitudes of $P = +45\%$ and -25%. The sign of these spin-polarizations reverse when the helicity of the light is reversed, resulting in the observed change in the intensity spectra in Fig. 2(a) because of surface transmission effects.[19]

The intensity asymmetry due to surface transmission is illustrated in Fig. 2(b). There is a clear $\pm$ feature about 2.5 eV below the Fermi energy, which is associated with the broad peak at higher binding energy. Since the measured asymmetries are small, it is important to discriminate between those caused by surface transmission and those caused by small geometrical and instrumental artifacts. This can be done by measuring the asymmetry on either side of the mirror plane at $\phi = 0$. Surface transmission effects should change sign,[14] whereas experimental artifacts will not. In Fig. 2(c), the intensity asymmetry for $\phi = +23°$ is presented. Indeed, the only feature that reverses is the strong $\pm$ derived from the intensity peak at higher binding energy. It is clear that the peak-to-peak size of this feature represents the size of the surface transmission effect.

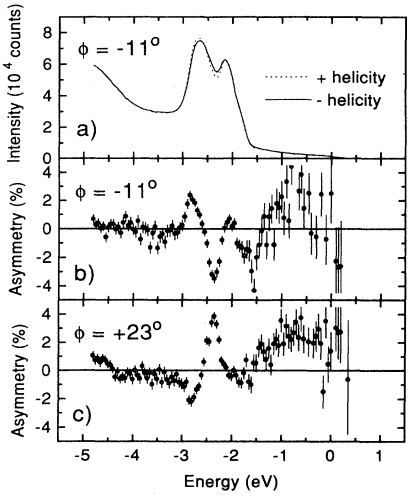

FIG. 2. (a) The angle-resolved photoemission intensity spectra from Cu(001) using a photon energy of 12 eV and emission angles of $\theta = 23°$ and $\phi = -11°$ plotted against the initial-state energy. Light of positive (dotted line) and negative (solid line) helicity was used. (b) The intensity asymmetry for the spectra in part (a). (c) The intensity asymmetry for a different emission angle $\phi = +23°$.

Figure 3 shows a compilation of data for a number of values of azimuthal angle. Part (a) shows the relative heights of the two peaks in the intensity spectra, once the spectra for positive and negative helicity have been summed. This quantity is independent of spin polarization and should be even about the mirror plane. It has been used to calibrate the position $\phi = 0$ used in all the figures. Part (b) plots the peak-to-peak value of the intensity asymmetry measured in the $\pm$ feature. The intensity asymmetry shows obvious odd symmetry about an angle close to $\phi = 0$. In fact, the zero crossing is probably a more sensitive indicator of the position of the mirror plane than the intensity ratio in part (a), but the aim is to demonstrate rather than assume a transmission effect. Evidently, a spin-dependent surface transmission effect of $\pm 3\%$ must be expected for photoemission experiments in the $3d$ metals. This should be close to an upper bound, since it was measured under ideal conditions: highly spin-polarized photoelectrons, well-resolved photoemission intensity peaks on a small background, and low excitation energy such that spin-orbit effects in the photoemission state are not removed by lifetime broadening.

The experimental results for Cu indicate that spin-

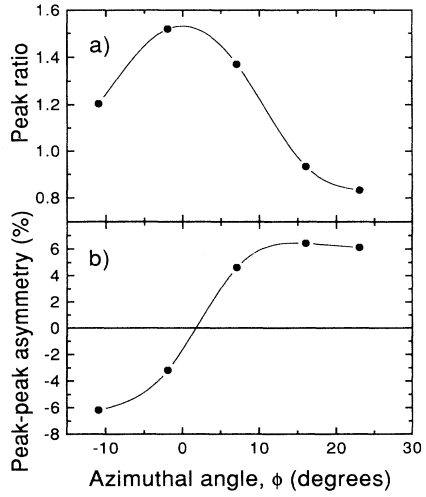

FIG. 3. (a) The ratio of the heights of the two peaks seen in the photoemission spectra in Fig. 2(a) as a function of the azimuthal angle of emission, ϕ. (b) The peak-to-peak size of the $\pm$ feature in the intensity asymmetry as a function of ϕ.

dependent transmission and MDAD are the same magnetic in 3*d* metals, and that it is not generally possible to neglect one in favor of the other. This precludes a straightforward interpretation of the experimental results except in specific emission geometries. In normal emission from a surface with at least two mirror planes and **M** lying in the surface plane, only MDAD is nonzero. For emission in a mirror plane containing **M**, the surface transmission effect is nonzero but should be greatly reduced. This is because the surface-scattering matrix is sensitive only to spin polarization normal to the mirror plane, and reversing the magnetization in the mirror plane will have little effect on this polarization component. Thus unambiguous MDAD experiments in the valence bands of 3*d* metals will be restricted to a single line in the surface Brillouin zone. In general, one-step photoemission calculations will be required to interpret measurements performed in other experimental geometries.

However, there may be experimental signatures that allow the separation of the two effects. Surface transmission affects the intensity of highly spin-polarized photoemission peaks, but not their position in energy. In 3*d* ferromagnets, where the exchange splitting of the majority and minority bands is large, two peaks that are closely spaced in energy will most often derive from the same spin system and have nearly the same spin polarizations. Then the observed asymmetry should be a single + or − lobe, rather than the ± feature seen in Cu. MDAD, on the other hand, shows up as an apparent shift in peaks position when the sign of the exchange interaction is reversed. This should result in a characteristic ± feature in the asymmetry even in ferromagnetic systems. Another distinguishing characteristic may be the sensitivity of the observed asymmetry to the electronic structure. Transmission effects should be primarily sensitive to the surface electronic structure at the final-state energy and would therefore depend strongly on the kinetic energy of the photoelectrons. MDAD should be primarily sensitive to the electronic structure at the initial-state energy. Finally, it may be necessary to move to greater photon energies, so that spin-orbit coupling is less important in the photoemission state. This, however, will lead to a degradation of the momentum resolution, which could compromise the usefulness of the technique.

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