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Magnetic dichroism in core-level photoemission from fcc Fe/Cu(001) films

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Circularly polarized x rays from a synchrotron light source were used in $2p$ core-level photoemission from thin (2–4 monolayer) fcc Fe films on a Cu(001) substrate. The exchange splitting of this level is resolved by varying the relative orientation of the photon helicity and sample magnetization from parallel to antiparallel. The intensity asymmetry and line-shape variations for parallel and antiparallel orientations are consistent with optical selection rules. Interestingly, the measured exchange splitting for the $3s$ and $2p$ levels in these films is reduced from that measured in bulk iron, reflecting differences in local bonding and d-band configurations for bulk and thin-film structures.

Recently, the availability of circularly polarized light from synchrotron sources has been exploited in the study of bulk ferromagnets using x-ray absorption[1,2] as well as core-level photoemission.[3] These measurements rely upon the helicity dependence of the interaction of the x rays with the magnetic material. The absorption experiments[1,2] are the x-ray counterparts of the magneto-optic Kerr effect. There the photoabsorption cross section at the K and L edges of ferromagnets depends on the relative orientation of the photon spin and sample magnetization, and the results can be interpreted in terms of the spin-split density of states above the Fermi level (E_F).[4–7] Dichroism observed in core-level studies can be described by spin-selective dipole transitions in the presence of spin-orbit coupling.[3,8,9] Due to the nature of these measurements, more specifically due to their surface sensitivity and elemental specificity, they are particularly attractive for the investigation of surface and thin-film magnetism. Very recently Tobin, Waddill, and Pappas[10] presented results demonstrating perpendicular magnetic dichroism in x-ray absorption measurements at the $L_{2,3}$ edge of Fe films [2–4 monolayers (ML)] on a Cu(001) substrate. There the $L_{2,3}$ branching ratio changes dramatically ($\sim 25\%$) between the extremes of photon spin and sample magnetization being parallel and antiparallel, and the results are consistent with a magnetic moment of $\sim 2\mu_B$/atom. In this paper we present results for Fe $2p$ core-level photoemission for the same Fe/Cu(001) system. Here, the excitation of the Fe $2p$ electrons is to free-electron states far above E_F. We will compare our results with analogous studies of bulk Fe concentrating on the differences between the two systems and their implications for the understanding of surface magnetism.

The measurements were made at the Stanford Synchrotron Radiation Laboratory (SSRL) using the spherical grating monochromator of beam line 8-2 that is part of the facilities of the University of California–National Laboratories Participating Research Team. The high degree of circular polarization for radiation just above or below the plane of the electron orbit in the storage ring is well documented[11] and was demonstrated on this beam line by Wu *et al.*[12] in their pioneering investigations of magnetic multilayer structures. The circularly polarized light is produced by translating the first collection mirror above and below the electron orbital plane to intercept predominantly left and right circularly polarized x rays, respectively. This has the unfortunate property of producing small, but nonnegligible, energy shifts for differently polarized photons. This effect can be overcome by reversing the sample magnetization *in situ* and thereby experimentally accessing the extremes of parallel and antiparallel photon helicity and sample magnetization without moving the first collection mirror. For the data presented here, the degree of photon polarization is estimated to be $\sim 90\%$.[13]

The Fe layers were grown on a Cu(001) substrate at ~ 150 K. The sample was cooled by coupling a liquid-nitrogen reservoir to the sample with a short Cu braid, and the temperature was monitored with a Chromel-Alumel thermocouple mounted on the sample plate. Details of sample cleaning and Fe evaporation may be found in Ref. 14. Following deposition, the Fe film was magnetized by applying current pulses to a coil oriented along the surface normal. The magnetization could be reversed simply by changing the polarity of the current pulse. The maximum applied field was ~ 3 kOe and all measurements were made in remanance.

For thin Fe films on Cu(001), the easy axis of magnetization is along the surface normal so that the requirement of parallel or antiparallel orientation of photon spin and sample magnetization dictated that these measurements be made at normal photon incidence. The spectra are angle resolved with the analyzer 60° from the surface normal in the plane containing the surface normal and the [110] direction. The photon energy was typically 900 eV, although variations from 800–950 eV produced no changes in the results. Spectra were normalized to the incident photon flux. The samples were periodically monitored for contaminants using core-level photoemission and photon stimulated Auger spectroscopy. Sample lifetimes were typically 4 h.

Figure 1(a) shows typical Fe $2p$ spectra from a 4-ML

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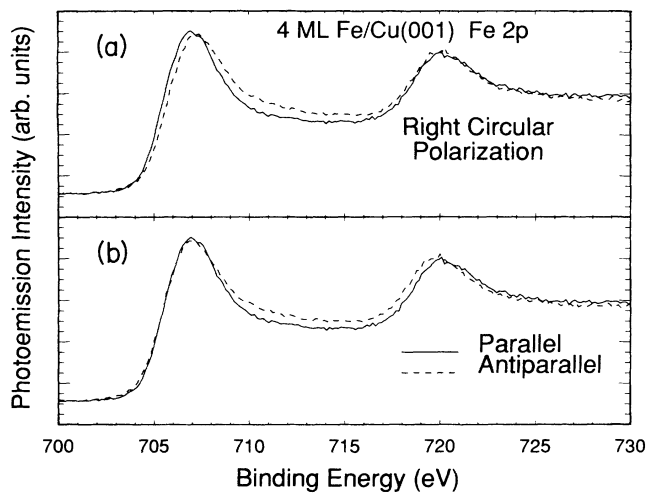

FIG. 1. Fe $2p$ spectra taken with $h\nu = 900$ eV and positive photon helicity. The solid lines are for parallel orientation of photon spin and sample magnetization and the dashed lines are for an antiparallel orientation. The two orientations were achieved by fixing the photon helicity and reversing the magnetization of the sample. (a) The spectra are as collected and show the differences in binding energy for the $2p_{3/2}$ and $2p_{1/2}$ levels for the two helicity and magnetization orientations. (b) The spectra are identical but have been shifted in energy to align the leading edge of the $2p_{3/2}$ level in order to emphasize line-shape differences between the two orientation extremes.

Fe film for photon spin and sample magnetization parallel, I_P (solid line), and antiparallel, I_A (dashed line). In Fig. 1(b), we show the same spectra that have been shifted to align the low-energy edge of the $2p_{3/2}$ peak to emphasize line-shape differences between the two orientation extremes. We will return to this point shortly. It should be emphasized that these spectra were obtained without moving the first collection mirror or the grating of the monochromator so that all energy shifts must be attributed to changes made at the sample. Upon reversing the magnetization of the sample, one sees a shift of the Fe $2p_{3/2}$ peak to higher binding energy and a smaller shift of the Fe $2p_{1/2}$ peak to lower binding energy for the antiparallel orientation. This leads to an apparent decrease in the spin-orbit splitting of these levels upon going from parallel photon spin and magnetization to an antiparallel orientation. The origin of this difference lies in the exchange interaction with the $3d$ valence electrons that shifts the majority spin electrons in both the $2p_{1/2}$ and $2p_{3/2}$ levels to higher binding energy relative to the minority spin levels. It is known that light of positive helicity preferentially excites majority electrons from the $2p_{1/2}$ level and minority electrons from the $2p_{3/2}$ level. Thus, by reversing the magnetization we can change the energy distribution of the majority and minority electrons, and this will manifest itself in energy shifts or asymmetry in the $2p$ spectra. The same is also true if the magnetization is held fixed and the photon spin is reversed.

From nonlinear least-square fits to several sets of data like that in Fig. 1 we obtain values for the exchange splitting of 0.22 ± 0.10 eV for the $2p_{3/2}$ level and 0.10 ± 0.10 eV for the $2p_{1/2}$ level. We note that these shifts are in opposite directions and so cannot be attributed to any systematic change in energy calibration of the monochromator or analyzer. In addition, the shifts are reproducible for both photon helicity extremes. Finally, although absolute binding-energy differences obtained for spectra taken with different photon polarizations cannot easily be compared, the binding-energy difference between the $2p_{3/2}$ and $2p_{1/2}$ levels can be compared for spectra with fixed sample magnetization and opposite photon polarization. In this case, the binding-energy difference represents the sum of the exchange splitting of the two $2p$ levels. In each case (magnetization into and out of the surface) the binding-energy difference between these two levels is found to decrease by 0.33 ± 0.14 eV on going from parallel to antiparallel photon and electron-spin orientation. This is consistent with the results above for the individual level exchange splittings obtained for fixed photon polarization.

In Fig. 2 we show the asymmetry, $A = (I_P - I_A)/(I_P + I_A)$, of the spectra in Fig. 1. The asymmetry is greater and sharper for the $2p_{3/2}$ peak. Reversing the photon helicity leads to identical results. Note that the maximum asymmetry is $\sim 9\%$ at ~ 714 eV. This is substantially larger than the value of $\sim 2\%$ observed for bulk Fe for reasons to be discussed shortly.

In Fig. 1(b), we show the spectra in Fig. 1(a) shifted in energy to emphasize line-shape differences. For the antiparallel arrangement of photon and electron spin the $2p_{3/2}$ peak has a much broader tail on the high binding-energy side of the peak. This is true for all arrangements of photon spin and magnetization with antiparallel orientation. Qualitatively, such an effect is calculated by van der Laan[8] based on spin-selective dipole-allowed transitions between the initial- and final-state m_j levels. The spin selectivity, $\Delta m_j = -1$ for positive helicity and $\Delta m_j = +1$ for negative helicity, gives rise to asymmetry similar to that of Fig. 2, while the transition probabilities deter-

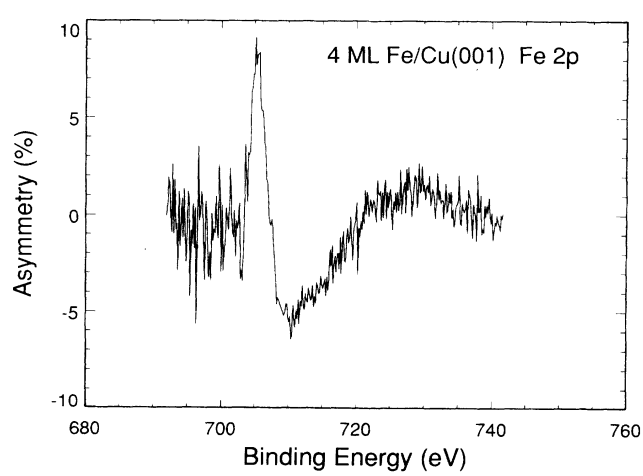

FIG. 2. Asymmetry of the photoemission intensity observed for parallel (I_P) and antiparallel (I_A) orientation of photon spin and sample magnetization, $A = (I_P - I_A)/(I_P + I_A)$. This curve is obtained for fixed photon helicity and two different sample magnetizations.

mined by the Wigner-Eckart theorem dictate the overall line-shape differences which are consistent with our measurements.

Finally, it is interesting to compare our results to those obtained from an analogous experiment on a bulk Fe crystal.[3] As previously mentioned, the asymmetry in the Fe $2p$ spectra measured here for the fcc Fe overlayer is ~ 4 times greater than that measured for bulk iron. It is important to remember that for thin Fe layers like those studied here, the easy axis of magnetization is perpendicular to the sample surface while for bulk Fe(110) it is parallel to the surface. This dictated a glancing incidence experiment for the bulk sample[3] and could explain the observed asymmetry difference. This is because perfect alignment of photon and electron spin is more problematic for glancing incidence than for the normal incidence required for studying Fe thin films. Recently, Schneider, Venus, and Kirschner[15] have demonstrated that the measured asymmetry is dependent upon the precise experimental configuration, and that it surprisingly does not vanish when x-ray helicity and sample magnetization are perpendicular. Other sources of discrepancy could be differences in photon polarization and/or sample magnetization, and possibly to differences in d-band width and interactions with the core hole in the two systems.[8]

Another systematic difference between the thin film and bulk system is the magnitude of the $2p$ exchange splittings. For both the $2p_{3/2}$ and $2p_{1/2}$ levels the splitting measured here for the 4-ML film is about half of the value measured for Fe(110) (0.3 ± 0.2 and 0.5 ± 0.2 eV for the $2p_{1/2}$ and $2p_{3/2}$ levels, respectively). This trend is consistent with earlier measurements for the Fe $3s$ level. An exchange splitting of 4.4 eV for the $3s$ level was first reported by Fadley and Shirley[16] for bulk Fe. Spin-polarized photoemission studies have established that these two levels are spin up and spin down in magnetized samples.[17,18] In Fig. 3 we show the Fe $3s$ spectra for 1.6-ML Fe/Cu(001) where the exchange splitting is measured to be only 3.8 eV.[14] When first observed, the $3s$ exchange splitting in a number of materials was significantly less than predicted by free-ion calculations. This discrepancy was satisfactorily removed if the effects of covalency in chemical bonding were included.[16] More recently, Kakehashi, Becker, and Fulde[19] have demonstrated that the magnitude of the exchange splitting in these systems depends critically on a number of parameters including the exchange and Coulomb interaction between the core hole and the valence electrons, the Coulomb interaction among the valence electrons, and the band width of the valence electrons. The differences observed between thin Fe films and bulk Fe then suggest variations in the above quantities for the two systems and demonstrate the importance of such measurements in developing a more complete understanding of surface magnetism.

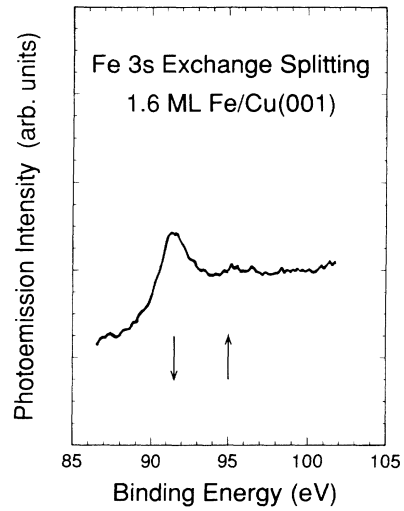

FIG. 3. Angle-resolved photoemission spectra with $h\nu = 190$ eV of the Fe $3s$ exchange splitting for 1.6-ML Fe/Cu(001). The splitting is ~ 3.8 eV.

In conclusion, we have presented results for magnetic x-ray dichroism in core-level photoemission from monolayer films. This effect is understood in terms of spin-dependent excitation by circularly polarized light and in splitting of the core levels due to the exchange interaction with the d electrons. Systematic differences are observed between monolayer Fe films and bulk Fe samples that demonstrate the importance of these measurements in obtaining a better understanding of mechanisms involved in surface and thin-film magnetism.

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[1]G. Schütz, M. Knülle, R. Wienke, W. Wilhelm, W. Wagner, P. Kienle, and R. Frahm, Z. Phys. B **73**, 67 (1988).

[2]C. T. Chen, F. Sette, Y. Ma, and S. Modesti, Phys. Rev. B **42**, 726 (1990).

[3]L. Baumgarten, C. M. Schneider, M. Petersen, F. Schäfers, and J. Kirschner, Phys. Rev. Lett. **65**, 492 (1990).

[4]J. B. Goedkoop, B. T. Thole, G. van der Laan, G. A. Sawatzky, F. M. F. de Groot, and J. C. Fuggle, Phys. Rev. B **37**, 2086 (1988).

[5]G. van der Laan and B. T. Thole, Phys. Rev. B **42**, 6670 (1990).

[6]P. Carra, B. N. Harmon, B. T. Thole, M. Altarelli, and G. A. Sawatzky, Phys. Rev. Lett. **66**, 2495 (1991).

[7]P. Carra and M. Altarelli, Phys. Rev. Lett. **64**, 1286 (1990).

[8]G. van der Laan, Phys. Rev. Lett. **66**, 2527 (1991); J. Phys. Condens. Matter **3**, 1015 (1991).

[9]B. T. Thole and G. van der Laan, Phys. Rev. Lett. **67**, 3306 (1991).

[10]J. G. Tobin, G. D. Waddill, and D. P. Pappas (unpublished).

[11]See, for example, J. D. Jackson, *Classical Electrodynamics*,

2nd ed. (Wiley, New York, 1975), Chap. 14; or C. Kunz, in *Photoemission and the Electronic Properties of Surfaces*, edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, New York, 1978).

[12]Y. Wu, J. Stöhr, B. Hermsmeier, M. Samant, and D. Weller (private communication).

[13]M. Rowen (private communication).

[14]J. G. Tobin, M. K. Wagner, X.-Q. Guo, and S. Y. Tong, Mater. Res. Soc. Symp. Proc. **208**, 283 (1991), and references therein.

[15]C. M. Schneider, D. Venus, and J. Kirschner, Phys. Rev. B **45**, 5041 (1992).

[16]C. S. Fadley and D. A. Shirley, Phys. Rev. A **2**, 1109 (1970).

[17]C. Carbone, T. Kachel, R. Rochow, and W. Gudat, Z. Phys. B **79**, 325 (1990).

[18]F. U. Hillebrecht, R. Jungblut, and E. Kisker, Phys. Rev. Lett. **65**, 2450 (1990).

[19]Y. Kakehashi, K. Becker, and P. Fulde, Phys. Rev. B **29**, 16 (1984).