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Magnetic coupling at the Mn/Fe(001) interface

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The magnetic coupling at the Mn/Fe(001) interface is experimentally investigated for Mn coverages ranging from 0.25–2 monolayers (ML) using spin-resolved core level photoelectron spectroscopy. In the submonolayer regime we observe in-plane ferromagnetic order in the Mn overlayer with antiparallel Mn-Fe coupling. At higher coverages our results are consistent with a transition to antiferromagnetic order at 1 ML coverage followed by a change to layered antiferromagnetism for a coverage of 2 ML, as recently predicted.

The magnetic properties of ultrathin overlayers on ferromagnetic materials currently receive much interest, especially in connection with the question for the role of the spacer layer in oscillatory exchange coupling of ferromagnet/nonferromagnet/ferromagnet sandwich systems. Cases of special interest are the Fe/Mn/Fe (Ref. 1) and the Fe/Cr/Fe (Ref. 2) systems, where the spacer layer, due to its antiferromagnetism in the bulk, may play an active role in mediating the exchange coupling.[3] Here the properties of the *interfaces* are of special importance. For the Cr/Fe system it has been shown by spin-resolved core level photoemission (SR-XPS) (Ref. 4) and by other methods,[5] that a Cr monolayer on Fe(001) is ferromagnetically ordered at room temperature, and that the magnetic moments of the Cr couple antiparallel to the moments of the underlying Fe substrate. This is in accord with theoretical results.[6] For thicker Cr films layer-by-layer oscillations in the sign of the coupling were found.[7,8] In Ref. 8 the sign of the exchange asymmetry, from which the sign of the coupling was determined, for a Cr thickness of approximately one monolayer (ML) was found to depend on preparation.

Mn is of special interest as a high magnetic-moment material. In the Hunds rule limit, Mn can have a moment of $5\mu_B$. From XPS measurements of the Mn $3s$ core level splitting[9] it was concluded, that Mn on Fe(001) may be partly in a high magnetic-moment state,[10] while this experiment gave no information about a possible long-range magnetic order. No indications of ferromagnetic order in the Mn overlayer were found by ferromagnetic resonance (FMR) measurements,[10] and it was concluded that Mn on Fe(001) may be either nonmagnetic or antiferromagnetic. Recently, an oscillatory behavior of the magnetization similar to that found for Cr/Fe was observed for Mn overlayers on Fe by spin-polarized electron-energy-loss spectroscopy (SPEELS).[11] At low overlayer thicknesses antiparallel Mn/Fe coupling was found. Calculations for Fe/Mn/Fe sandwich systems indicate that at the Mn/Fe interface both kinds of coupling, parallel and antiparallel, are possible, with the parallel coupling energetically favored.[1,3] In the monolayer regime, a strong sensitivity of the magnetic properties on the film thickness was predicted recently.[12] In this context, an experimental investigation of the Mn/Fe interface is highly desirable.

In this work, we concentrate on the Mn/Fe interface and investigate the magnetic coupling of ultrathin (<2 monolayers) Mn films to the Fe substrate. By employing spin-resolved core level photoemission (SR-XPS), we combine the chemical selectivity and surface sensitivity of XPS with the sensitivity for long-range magnetic order of spin-resolved photoemission. In this way the magnetic order of the Mn adlayer and the Fe atoms in the interface region can be investigated independently. In our experiment we use s-polarized light and detect photoelectrons under normal emission. In this geometry spin polarization due to spin-orbit interaction, as recently observed for different experimental conditions,[13] cannot occur. The observation of a nonzero spin polarization in a core line therefore unambigously indicates the presence of long-range magnetic order in the specific material across the probed sample area.

The sign of the observed spin polarization in the adlayer core line allows us to determine the sign of the coupling of the adlayer to the substrate. According to Hund's rules, due to intra-atomic exchange interaction the leading structure of the core spectrum should show a negative (minority) spin polarization. This is in fact experimentally observed for the $3p$ and $2p$ spectra of the $3d$ ferromagnets,[14,4] and also in calculations of core level spectra of ferromagnets.[15] Also, distinct differences in the line shapes are observed, and a negative overall spin polarization is found. These criteria allow us to identify the minority- and majority-spin channels of the overlayer, and thus to distinguish between parallel and antiparallel coupling of the substrate and adlayer moments.

The experiments were performed employing linearly s-polarized synchrotron radiation from the TGM 5 undulator beamline at BESSY in Berlin. A hemispherical energy analyzer combined with an efficient Fe(001) VLEED (very low energy electron diffraction) spin polarimeter[16] was employed for electron energy and spin analysis. The light was incident normally on the sample, and the normally emitted electrons were detected. The Fe(001) samples were 5–10 nm thick films epitaxially grown at room temperature by electron-beam evaporation on a Ag(001) substrate cleaned by sputtering and annealing as usual. The base pressure was $<3\times 10^{-10}$ hPa (5×10^{-10} hPa during evaporation). Surface order and cleanliness were checked by LEED and by photoemission. Mn adlayers were also produced by electron-beam evaporation at room temperature. Epitaxial layers of Mn on

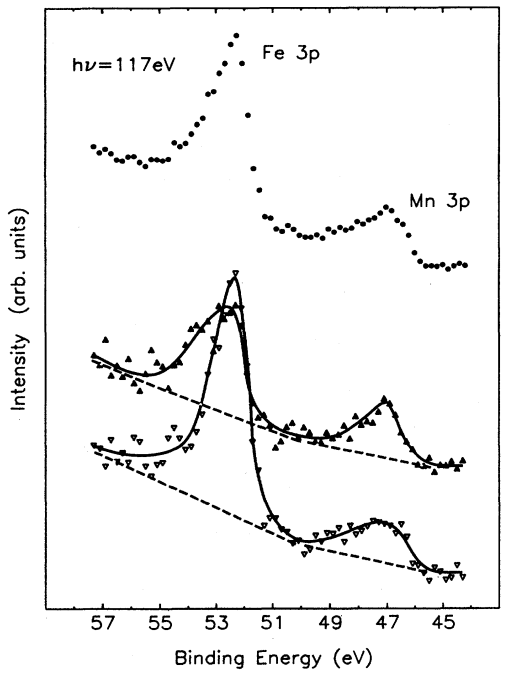

FIG. 1. Energy distribution curves (EDC's) of the Fe 3*p* and Mn 3*p* level for 0.75 ML Mn on remanently magnetized Fe(001), taken at $h\nu=117$ eV with *s*-polarized light. Dots: spin-integrated EDC; triangles: spin-resolved EDC. Full triangles: majority-spin channel; open triangles: minority-spin channel of Fe.

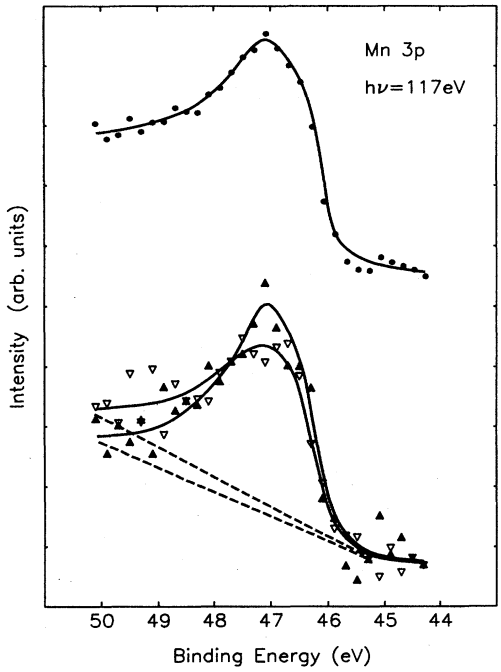

FIG. 2. Spin-integrated (dots) and spin-resolved (triangles) Mn 3*p* EDC's ($h\nu=117$ eV) for 0.75 ML Mn/Fe(001) with more data accumulated. Constant backgrounds are subtracted.

Fe(001) are known to grow in a body-centered-tetragonal (bct) structure,[1] with the overlayer having the same in-plane spacing $a=0.287$ nm as the substrate, while the out-of-plane spacing c is 0.327 nm. Sample thickness was controlled with a quartz monitor and checked by comparing the core level photoemission intensities of substrate and adlayer. The samples were remanently magnetized *in situ* by current pulses through magnetization coils.

Figure 1 shows spin-integrated and spin-resolved energy distribution curves (EDC's) of the Fe 3*p* and the Mn 3*p* levels for a Mn coverage of 0.12 nm, corresponding to 0.75 ML (equivalent monolayers), taken at a photon energy of 117 eV. The peaks are superimposed on a spin-polarized secondary electron background increasing towards the high-energy side of the spectrum. The energy separation of the Fe and Mn peaks is 5.2 eV. The Fe 3*p* line shows the well-known polarization features,[4,14] i.e., a sharp and intense peak in the minority-spin channel of the Fe valence band, and a broader and weaker peak in the majority-spin channel. The integral spin polarization[17] of the Fe 3*p* peak is of minority type and amounts to -37%. The Mn 3*p* peak also shows spin polarization. The general features are similar to those of the Fe 3*p* peak, but with opposite sign of polarization. This is more clearly seen in Fig. 2, where the Mn 3*p* peak is displayed with more data accumulated. Here constant backgrounds have been subtracted, so that the majority- and minority-spin EDC's match at the low-energy side of the spectrum. The EDC's are spin dependent, and in the spectral features the roles of majority- and minority-spin channels are interchanged with respect to the Fe 3*p*. This shows directly that a net in-plane magnetic moment exists in the Mn layer, and that the mutual orientation between the net overlayer moment and the moment of the Fe substrate is antiparallel. This analysis can be extended further into the submonolayer regime, as is shown in Fig. 3. Here spin-integrated and spin-resolved EDC's of the Mn 3*p* level for a Mn coverage of 0.04 nm (approximately 0.25 ML) are displayed. The comparatively small Mn 3*p* peak is superimposed on a steeply increasing secondary electron background. The spin-resolved EDC's displayed in the lower part of Fig. 3 show a strong spin polarization, again proving the existence of a net in-plane magnetic moment in the Mn adlayer coupled antiparalle to the Fe moment.

Figure 4 shows Mn 3*p* and Fe 3*p* integral spin polarization values[17] obtained in the Mn thickness range from $d=0.04$ to 0.33 nm (0.25–2 ML). The largest Mn 3*p* polarization (19.6%) is measured for the film with the lowest coverage. A rapid decrease of the Mn 3*p* polarization is observed with increasing overlayer thickness, with an apparent dip near 1 ML. At 2 ML coverage, the polarization is very small (2%). The quasisimultaneously measured Fe 3*p* polarization also shows a decrease with increasing Mn coverage, although the variation is much smaller.

Calculations for bct-Mn with the measured lattice spacings of Mn/Fe(001) result in a stable AF-I phase (layered antiferromagnetism) with a high moment of $2.49\mu_B$.[1] Focusing on the Fe/Mn *interface*, calculations for Fe/Mn/Fe multilayers show that in these sandwich systems both parallel and antiparallel coupling at the Fe/Mn interface is possible, with the *parallel* coupling energetically favored as compared to the antiparallel one.[1,3] Here the energy of the whole sandwich system for a given magnetic configuration is calculated,

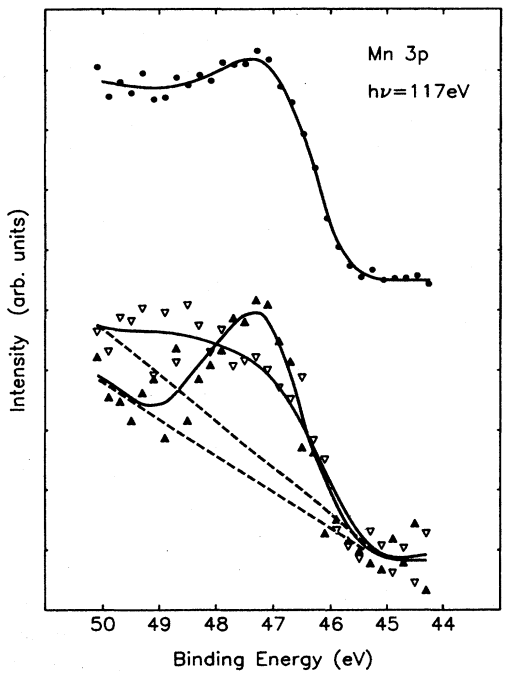

FIG. 3. Spin-integrated (dots) and spin-resolved (traingles) Mn 3*p* EDC's for 0.25 ML Mn/Fe(001) at $h\nu=117$ eV.

and this is a situation different from that of a thin Mn overlayer on Fe as investigated in this work. Theoretical work[18] for a free-standing Mn monolayer, as well as for Mn on Ag(001) and Pd(001), results in antiferromagnetic Mn. In the case of Ag(001), this has also been concluded from experiment.[19]

Recently, magnetic properties of an ultrathin Mn overlayer on Fe(001) have been calculated in a Mn(1–2 ML)/Fe(5–7 ML)/Mn(1–2 ML) slab geometry by Wu and Freeman.[12] In the submonolayer region the formation of *ferromagnetic* order in the Mn overlayer is expected, with opposite orientation of the moments with respect to the moments of the substrate. This is confirmed by our experimental result for 0.04 nm (0.25 ML) coverage, as can be seen from Fig. 4. For a qualitative comparison, we have also included in Fig. 4 theoretical polarization values deduced from the calculated moments under the assumption that the Mn polarization measured at the lowest coverage corresponds to the moment calculated for a ferromagnetically ordered layer ($3.2\mu_B$). For a coverage of ≈ 1 ML (0.16 nm) our measurements show a dip in the polarization curve (Fig. 4) with a strong decrease of the Mn 3*p* spin polarization (which to first order is proportional to the net Mn moment[4]), indicating a loss of in-plane ferromagnetic order. Here, the calculation interestingly yields *antiferromagnetic* order *within* the monolayer due to increased Mn-Mn interaction, accompanied by a $c(2\times2)$ reconstruction. The calculated absolute values of the Mn moments oriented opposite to each other are almost equal (3.10 and $3.26\mu_B$), so that they almost compensate to yield a net moment near zero ($\approx 0.08\mu_B$ per Mn atom) still antiparallel to the Fe moment. While we cannot make definite statements about the absolute magnitude of the moment, the thickness dependence we observe experimentally (Fig. 4), i.e., a substantial diminishment of the polarization as the coverage approaches the monolayer, is consistent with this prediction, since our measurement is sensitive to the net in-plane moment, which should approach zero. Increasing the coverage further to $d=0.22$ nm (≈ 1.4 ML), we observe a slight enhancement of the polarization. At $d=0.33$ nm (2 ML) finally the polarization reaches a very small, but still positive value (+2%). The calculation[12] for the bilayer predicts a *layered antiferromagnetic* ordering of the Mn moments, with the first layer adjacent to the Fe surface coupling parallel (with a reduced moment of $1.54\mu_B$) and the top layer coupling *antiparallel* ($2.51\mu_B$) to the moments of the Fe surface. In experiment the two Mn layers are probed with relative weights determined by the escape depth of the photoelectrons. Assuming an escape depth of 0.5 nm, this would yield a spin polarization of about +5%. This agrees with our measured value in sign, but is significantly higher in magnitude. This finding could be explained by the assumption that the absolute values of the moments of the two Mn layers differ less then calculated. A further contributing factor to this discrepancy might be the sample imperfection as compared to the theoretical model of two perfect monolayers.

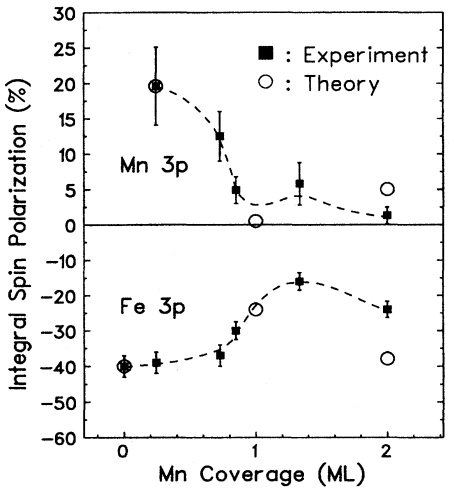

FIG. 4. Dependence of the Fe 3*p* and Mn 3*p* integral spin polarization (Ref. 17) on the Mn coverage (equivalent monolayers). Squares: experiment (lines are guides to the eye); circles theory; theoretical polarization is obtained from the calculated moments in Ref. 12 and normalized to the experimental polarization at the lowest coverage.

Turning our attention to the Fe, the Fe 3*p* polarization measured in our experiment drops from −39% for clean Fe to $\approx -25\%$ for 1 ML Mn coverage. The calculations also yield a reduced Fe moment at the interface of $1.35\mu_B$, with the Mn in the antiferromagnetic state, due to strong overlayer-substrate exchange interactions. This means a reduction of 40% as compared to the bulk value ($2.22\mu_B$). Again, while it is difficult to derive the absolute magnitude of the Fe moment, the observed reduction of the polarization (Fig. 4) lies well in line with the predicted decrease of the moment. In the intermediate region between 1 and 2 ML coverage, where the magnetic order of the overlayer is assumed to switch between antiferromagnetic and layered antiferromagnetism,[12] a slightly lower value is observed. For

2 ML coverage an Fe $3p$ polarization of $\approx -25\%$ is measured. This still means a substantial reduction of the moment at the interface as compared to the clean surface value, while in Ref. 12 a value close to the bulk value is predicted for this configuration.

A comparison of our results for the Mn/Fe coupling in the Mn submonolayer range to the results of the SPEELS experiment[11] is difficult, since the data shown in Ref. 11 in the submonolayer regime contain contributions not only from the Mn, but also from the Fe substrate, and thus hardly allow to draw conclusions about the Mn moment independently. In our SR-XPS experiment, in contrast, the adlayer and substrate signals are clearly separated (cf. Fig. 1). For a MN coverage of 2 ML the results seem to be compatible. Earlier ferromagnetic resonance (FMR) measurements[10] gave no indications of ferromagnetic order in a Mn overlayer. This does not mean a contradiction to our results since the Mn films investigated there were thicker. Also, an earlier spin-resolved photoemission experiment[20] did not find spin polarization in Mn on Fe(001). This can be understood by comparison to our results since the thickness of the Mn film in that experiment was about 2–3 ML, and the spin polarization to be expected for such large coverages is rather small. An additional problem might be the data aquisition time. Our measurements evaluated for the determination of the spin polarization have been stopped before any signs of contamination became visible. When the measurements were carried on for longer periods of time, a shift of the Mn $3p$ peak combined with a shape change and an increase in intensity became apparent, as also observed in Ref. 20. This finding might be explained by a small degree of initial alloying of the Mn with the Fe and a following resegregation to the surface, induced by interaction with contamination from the residual gas accumulated on the surface. The data presented here were all taken before any changes in the spectra were visible.

In summary, our results unambiguously show by element-specific spectroscopy the formation of ferromagnetic order in the Mn atoms at the Mn/Fe(001) interface in the submonolayer range, evidencing antiparallel orientation of the net in-plane moments of substrate and overlayer. We further observe a loss of in-plane ferromagnetic order consistent with a transition to antiferromagnetism within the overlayer at a Mn coverage of 1 ML, as predicted in a recent theoretical work by Wu and Freeman.[12] At a Mn coverage of 2 ML, our data can be explained by layered antiferromagnetism with parallel Mn/Fe coupling at the interface in qualitative agreement with Ref. 12, while quantitatively deviations in the magnitudes of the moments are observed.

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[1] S. T. Purcell, M. T. Johnson, N. W. McGee, R. Coehoorn, and W. Hoving, Phys. Rev. B **45**, 13 064 (1992).

[2] C. Carbone and S. F. Alvarado, Phys. Rev. B **36**, 2433 (1987); J. Unguris, R. J. Celotta, and D. T. Pierce, Phys. Rev. Lett. **67**, 140 (1991); S. T. Purcell *et al.*, *ibid.* **67**, 903 (1991); S. Demokritov, J. A. Wolf, and P. Grünberg, Europhys. Lett. **15**, 881 (1991).

[3] D. Stoeffler and F. Gautier, J. Magn. Magn. Mater. **121**, 259 (1993).

[4] F. U. Hillebrecht, Ch. Roth, R. Jungblut, E. Kisker, and A. Bringer, Europhys. Lett. **19**, 711 (1992).

[5] Y. U. Idzerda *et al.*, Phys. Rev. B **48**, 4144 (1993); H. B. Rose, Ch. Roth, F. U. Hillebrecht, and E. Kisker (unpublished); G. Turtur and G. Bayreuther, Phys. Rev. Lett. **72**, 1557 (1994).

[6] R. H. Victora and L. M. Falicov, Phys. Rev. B **31**, 7335 (1985).

[7] J. Unguris, R. J. Celotta, and D. T. Pierce, Phys. Rev. Lett. **69**, 1125 (1992).

[8] T. G. Walker, A. W. Pang, H. Hopster, and S. F. Alvarado, Phys. Rev. Lett. **69**, 1121 (1992).

[9] F. R. McFeely, S. P. Kowalczyk, L. Ley, and D. A. Shirley, Solid State Commun. **15**, 1051 (1974).

[10] B. Heinrich, A. S. Arrot, C. Liu, and S. T. Purcell, J. Vac. Sci. Technol. A **4**, 1376 (1986).

[11] T. G. Walker and H. Hopster, Phys. Rev. B **48**, 3563 (1993).

[12] Ruqian Wu and A. J. Freeman, Phys. Rev. B **51**, 17 131 (1995); J. Magn. Magn. Mater. (to be published).

[13] Ch. Roth, F. U. Hillebrecht, H. B. Rose, and E. Kisker, Phys. Rev. Lett. **70**, 3479 (1993); Ch. Roth, F. U. Hillebrecht, W. G. Park, H. B. Rose, and E. Kisker, *ibid.* **73**, 1963 (1994).

[14] C. Carbone and E. Kisker, Solid State Commun. **65**, 1107 (1988); B. Sinkovic, P. D. Johnson, N. B. Brookes, A. Clarke, and N. V. Smith, Phys. Rev. Lett. **65**, 1647 (1990); G. A. Mulhollan, A. B. Andrews, and J. L. Erskine, Phys. Rev. B **46**, 11 212 (1992); T. Kachel, C. Carbone, and W. Gudat, *ibid.* **47**, 15 391 (1993); Ch. Roth, H. B. Rose, W. G. Park, F. U. Hillebrecht, and E. Kisker (unpublished); L. E. Klebanoff, D. G. Van Campen, and R. J. Pouliot, Phys. Rev. B **49**, 2047 (1994); M. Finazzi *et al.*, *ibid.* **50**, 14 671 (1994).

[15] B. T. Thole and G. van der Laan, Phys. Rev. Lett. **67**, 3306 (1991); Phys. Rev. B **44**, 12 424 (1991).

[16] F. U. Hillebrecht, R. Jungblut, and E. Kisker, Phys. Rev. Lett. **65**, 2450 (1990); R. Jungblut, Ch. Roth, F. U. Hillebrecht, and E. Kisker, Surf. Sci. **269-270**, 615 (1992).

[17] The spin polarization is determined by integrating over the apparent base width of a peak after subtraction of the secondary electron background (assumed to be linear).

[18] S. Blügel, M. Weinert, and P. H. Dederichs, Phys. Rev. Lett. **60**, 1077 (1988); S. Blügel, B. Drittler, R. Zeller, and P. H. Dederichs, Appl. Phys. A **49**, 547 (1989).

[19] B. T. Jonker, J. J. Krebs, and G. A. Prinz, Phys. Rev. B **39**, 1399 (1989).

[20] T. Kachel, Ph.D. Thesis, Universität Köln, 1991.