Magnetic circular x-ray dichroism of submonolayer Mn on Fe(100)

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The magnetic behavior of monolayer and submonolayer quantities of Mn adsorbed on an Fe(100) surface is studied using the element-specific magnetic circular x-ray dichroism (MCXD) method in absorption. The shape of the Mn-MCXD spectrum for 0.02 monolayer coverage agrees well with a recent calculation for high-spin Mn if experimental broadening is taken into account. Also the size of the MCXD effect indicates a large net magnetic moment, with the asymmetry at the L_3 edge reaching 80% of the value predicted by the theoretical spectrum for the atomic d^5 configuration. The sign of the Mn moment is antiparallel to the Fe substrate. With increasing coverage the net Mn magnetic moment rapidly decreases and vanishes for a complete monolayer Mn/Fe(100). [S0163-1829(97)03033-6]

Magnetic transition-metal surfaces covered with another magnetic element represent composite materials with interesting magnetic and electronic properties.[1] Fe, Co, and Ni, elements which are in their bulk form ferromagnetic, were found to form ferromagnetic monolayers on top of ferromagnetic $3d$ metals, and their magnetic structure is not supposed to change dramatically for further reduced thicknesses. Such changes are, however, expected for manganese. Bulk α-Mn exhibits a complicated antiferromagnetic structure with only small magnetic moments of $0.65\mu_B$ on average, whereas the possible maximum $3d$ moment amounts to $5\mu_B$. For the two-dimensional case of a Mn monolayer on top of the (100) surfaces of Pd and Ag, an antiferromagnetic ground state with large magnetic moments (about $4\mu_B$) was predicted.[2]

Such a Mn monolayer represents a particularly interesting system when brought into contact with a ferromagnetic substrate because the resulting magnetic structure is uncertain: The tendency for antiferromagnetism in the overlayer has to compete against the exchange interaction with the ferromagnetic substrate, which tries to reach ferromagnetic alignment within the overlayer. In calculations of the Mn/Fe(100) interface in multilayers[3,4] and of 1 monolayer (ML) Mn/Fe(100) (Ref. 4) ferromagnetism with parallel coupling between Mn and Fe moments was found most favorable, however, with the antiparallel solution energetically close by. Very recently, some calculations predicted ferrimagnetism with very small net magnetic moment in the monolayer Mn/Fe(100).[5–7]

Two experiments have so far detected magnetism for Mn on Fe(100) around monolayer coverage: Spin-polarized electron energy loss spectroscopy[8] gives a large and positive exchange asymmetry for 1 ML Mn, meaning antiparallel coupling to the Fe. For low coverages (about 0.4 ML were studied[8]) the exchange asymmetry is negative. Although that experiment was spectroscopically optimized for detecting the Mn surface layer, the sign of a submonolayer Mn moment is difficult to extract since the Fe substrate signal might be dominatant. A most recent study of Mn/Fe(100) using spin-resolved core-level photoemission[9] obtains antiparallel coupling just below monolayer coverage but with very small Mn $3p$ integral spin polarization indicating a very small net Mn moment. For lower thicknesses (down to 0.25 ML) the spin polarization is found to be enhanced.[9]

The aim of this report is to reassess the magnetism of 0–1 ML Mn/Fe(100) experimentally using a third method of investigation. Applying magnetic circular x-ray dichroism (MCXD) in absorption we obtain element-specific information. By studying much smaller thicknesses than most recently achieved with spin-resolved photoemission,[9] one can explore the feasibility of the MCXD method towards very low coverages and might observe the effect of a reduced Mn-Mn coupling.

The measurements were conducted at the BESSY synchrotron light source using the Petersen/III monochromator for circularly polarized soft x rays. About 80% circular polarization is obtained when adjusting to 0.6 mrad off the orbital plane of the storage ring.[10] We prepared clean Fe(100) surfaces by epitaxial growth of 15 ML Fe on a Pd(100) single crystal held at room temperature.[11,12] The system Fe/Pd(100) has been thoroughly characterized previously by quantitative low-energy electron diffraction (LEED).[11] We observe a clear $p(1\times1)$ LEED pattern although the spots are somewhat less sharp than for Fe growth on, e.g., Ag(100). We know from our previous spin-resolved photoemission studies of surface states and interface states[12,13] that using the Pd as substrate generates a pure Fe surface which is not affected by surface segregation of the substrate material as is the case with Ag and Au substrates. Mn was subsequently evaporated typically at rates of 0.2 ML/min as checked with an oscillating quartz. We cross checked the evaporation rates *in situ* by deposition of 0.5 ML Mn onto a Cu(100) crystal monitoring the formation of an intense $c(2\times2)$ LEED pattern.[14] The smaller thicknesses were cross checked using the edge jumps of absorption spectra. The base pressure of the chamber was 7×10^{-11} mbar and rose to 7×10^{-10} mbar and 2×10^{-10} mbar during the evaporation of Fe and Mn, respectively.

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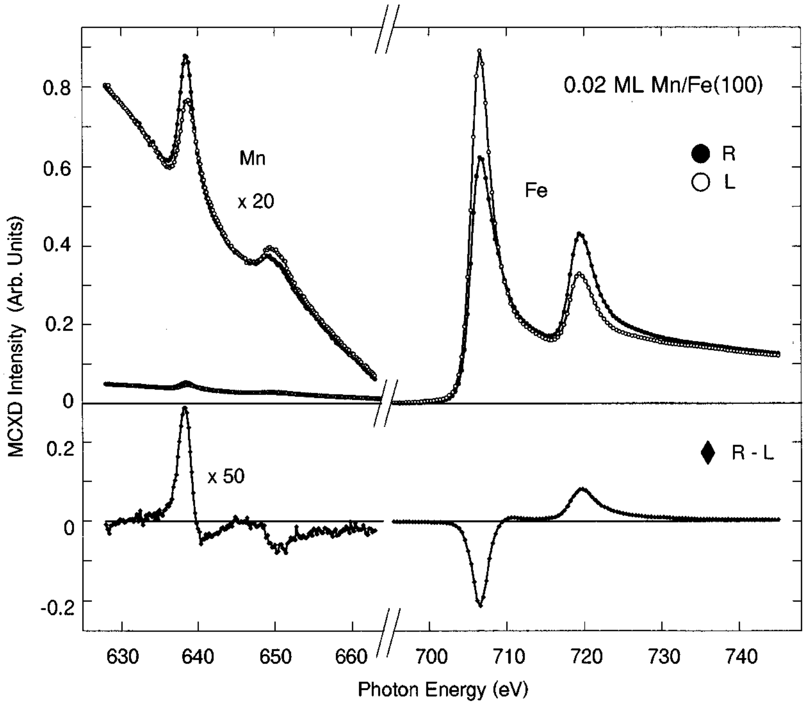

FIG. 1. MCXD spectra for 0.02 monolayer Mn on Fe(100). Spectra for magnetization and photon spin parallel (R) and antiparallel (L) as well as the difference between the two indicate a large Mn magnetic moment and antiparallel coupling to the Fe. The spectra are raw data (see text).

Magnetic circular x-ray dichroism in absorption has in the past few years been established as a tool to investigate the magnetic ordering in element specific manner.[15] We have chosen to obtain dichroism spectra measuring the total electron yield via the sample current in two consecutive runs reversing in between the magnetization direction of the sample. The sample was remanently magnetized by a magnetic pulse along the Fe [001] direction in the surface plane, forming an angle of 23° with the incident light, which reduces the measured dichroism by a factor of 0.92.

Figure 1 shows Fe and Mn $L_{2,3}$ absorption spectra from the smallest Mn coverage measured in this experiment, 0.02 ML Mn/Fe(100). The figure contains spectra taken with the magnetization parallel (R) and antiparallel (L) to the spin of the incident photons as well as the difference between the two, the MCXD spectrum (R−L). The Fe spectrum to the right is essentially identical to the ones measured prior to Mn deposition. We do not observe the strong reduction in MCXD asymmetry [(R−L)/(R+L)] reported in Ref. 16 for thick Fe films on Pd(100) as compared to pure Fe. Our asymmetry at the L_3 edge reaches 87% of the one measured for pure Fe in Ref. 17. It is presently not clear whether the remaining difference is due to domain formation of the Fe. In that case the measured Mn MCXD signal would have to be slightly corrected upwards, but this was not done here.

To the left in Fig. 1 we show the Mn $L_{2,3}$ spectra on the same scale as the Fe ones and, in addition, enlarged by a factor of 20. The spectra in Fig. 1 are raw data. This means that, apart from the subtraction of a constant background, identical for both magnetization directions, no shifts were applied nor were corrections for the incomplete light polarization and its incidence angle made in the spectra. The Mn spectra show a large asymmetry indicating a large Mn magnetic moment. Large magnetic moments were predicted for the antiferromagnetic (or, more precisely, ferrimagnetic) Mn monolayer on Fe (for the two Mn sites $3.10\mu_B$ and $-3.26\mu_B$ in Ref. 5, $2.96\mu_B$ and $-3.28\mu_B$ in Ref. 6 and $3.37\mu_B$ and $-3.41\mu_B$ in Ref. 7), and for the ferromagnetic antiparallel monolayer on Fe ($-2.99\mu_B$ in Ref. 6; $-3.35\mu_B$ in Ref. 7), which is slightly higher in total energy.[6,7] Large moments were also found for the related surface-alloy system[18] 0.5 ML $c(2\times2)$ Mn/Ni(100) in Refs. 19–21. Interestingly, for single Mn impurities on magnetic surfaces, which have only most recently be studied theoretically, first-principles calculations do not predict a substantial further increase of the moment, and values of $3.41\mu_B$ [for a Mn atom adsorbed on Fe(100)] and $-3.36\mu_B$ [for a Mn atom incorporated into the Fe(100) surface atom layer] were calculated.[22]

Comparison of the MCXD difference spectra for Mn and Fe shows clearly that Mn moments couple antiparallel to those of the Fe substrate. This is in agreement with the finding in Ref. 9 for 0.25 and 0.75 ML and, interestingly, opposite to the coupling found for 0.5 ML $c(2\times2)$ Mn/Ni(100) (Refs. 19 and 21) and for Mn impurities in bulk Fe.[23,24] It is also opposite to the *ab initio* result of Ref. 22, which predicts that parallel coupling is favored by a Mn adatom and antiparallel coupling by Mn in the Fe surface layer. However, there are uncertainties in both theory and experiment: First, total-energy differences between magnetic configurations are very small;[22] this has also been found for the complete Mn monolayer on Fe.[5–7] Second, it cannot experimentally be excluded that Mn might be incorporated into the surface layer, although layer-by-layer growth has been reported.[8] Surface-alloy formation as for Mn on Ni(100) has been predicted,[6] but unlike on Ni we do not observe any ordering for 0.5 ML into a $c(2\times2)$ superstructure by LEED. Further efforts to characterize the initial growth are therefore required.

In Fig. 2 we compare the Mn MCXD difference spectrum (c) from Fig. 1 to the atomic calculation for a Mn^{2+} ion without crystal field from Ref. 25 before (a) and after (b) convolution with a Gaussian of 2-eV FWHM. We find that the shapes of this broadened theoretical spectrum and our

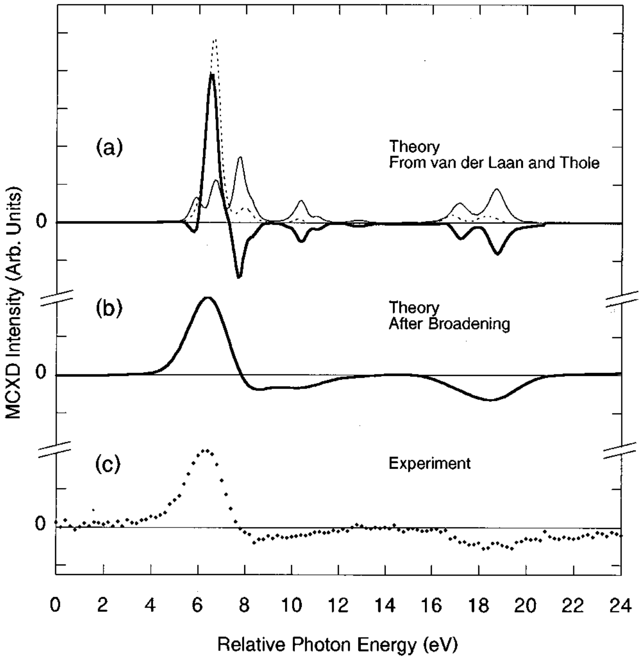

FIG. 2. (a): Calculated MCXD spectra of Mn^{2+} for left (dashed line) and right (thin solid line) circular polarization and the MCXD difference (solid line) taken from Ref. 25. (b): Calculated MCXD difference after broadening. (c): Experimental MCXD difference from Fig. 1.

experimental one are very similar. In particular, the negative MCXD intensity at the higher photon energy side of the L_3 peak appears in both spectra but not in the calculated MCXD spectrum of Ref. 5 for 1 ML Mn/Fe(100), which is derived from a band-structure calculation. It was very recently pointed out that, due to the relatively small spin-orbit splitting in Mn, L_3 and L_2 contributions are not well separated, which yields errors as large as 30% in a sum-rule determination of the magnetic moment.[26] Instead, we determine the size of the MCXD effect considering the asymmetry. The Mn MCXD asymmetry at the L_3 maximum from Fig. 2(a) amounts to about 0.60. The 2-eV broadening reduces it to 0.34 due to the negative MCXD intensity mentioned above. On the other hand, the experiment, Fig. 2(c), gives an asymmetry of 0.20 before and of 0.27 after correcting for polarization degree and angle of the synchrotron light.

In view of the similarity of the MCXD difference spectrum with the atomic calculation after broadening, it seems that the expected strong hybridization between Mn and Fe 3d states does not alter the shape of the spectrum significantly. Thus, the only indication our spectrum gives for a reduction of the magnetic moment with respect to the atomic value of 5 μ_B is the size of the MCXD effect. As we measure about 80% of the predicted asymmetry, we may estimate the net magnetic moment to be around 80% of the atomic value, or 4μ_B. This value might still be smaller than the absolute moment due to the possibility of clustering of Mn atoms with nonferromagnetic coupling and of domain formation on the Fe. However, our estimate requires proportionality between the asymmetry and the net magnetic moment, which is not established yet. An MCXD calculation performed for such a reduced magnetic moment would be helpful in this situation, however, the band calculation[5] for a monolayer Mn/Fe(100) fails to describe the measured spectral shape.

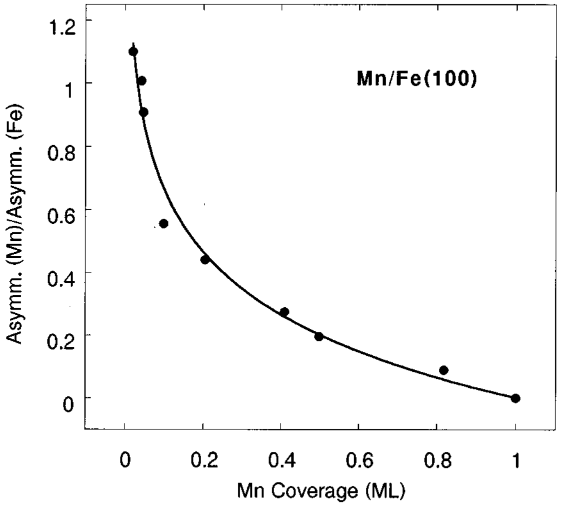

FIG. 3. Normalized Mn asymmetry as function of Mn coverage. The solid line is a logarithmic fit to the data. The rapid decrease of the net moment down to zero for one monolayer is consistent with antiferromagnetic Mn-Mn coupling.

We also compared our experimental spectrum to the recent calculation for Mn^{2+} in an O_h symmetry crystal field.[26] We again find good agreement of the MCXD spectral shape after broadenng, but here the size of the MCXD effect is much smaller than in Ref. 25, possibly due to the strong octahedral crystal field ($10Dq = 1.5$ eV were used), which is less likely to describe a metallic adsorbate system well.

Figure 3 shows the behavior of the net Mn magnetic moment with increasing coverage between 0.02 and 1 ML. The asymmetry at the L_3 maximum of Mn normalized by that of the Fe is plotted. The net Mn moment drops more rapidly with increasing coverage than could be expected from the decay of the Mn-3p spin polarization.[9] We assume the main cause for the rapid decrease to be antiparallel coupling of Mn next neighbors as the coverage increases rather than a strong decrease of the Mn moment itself. The Mn asymmetry and net moment approach zero for 1 ML coverage, which is consistent with antiferromagnetic order[2] (or ferrimagnetic order with very small net moment) within the Mn monolayer on Fe(100) as predicted very recently[5–7] for this system.

In conclusion, we find using MCXD that Mn moments couple antiparallel to the Fe moments for small coverages of Mn on Fe(100). Mn is initially in a high-spin state as revealed from comparison of shape and asymmetry of the MCXD spectrum to an atomic calculation. The size of the MCXD effect indicates that the Mn moment might be very large; a rough estimate gives 4μ_B as lower limit. However, it needs to be explored further how the asymmetry varies with the magnetic moment for moments away from 5μ_B. The coverage dependence is consistent with recent predictions of antiferromagnetic coupling within the Mn monolayer.

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