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The early stages of growth of Mn deposited at room temperature on Ag(001) studied by Mn *K*-edge SEXAFS and Mn L_2,L_3-edges XAS

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The atomic structure of the $Ag_{0.5}Mn_{0.5}$ ordered surface alloy formed in the two topmost layers of the Ag substrate when 1 monolayer (ML) Mn is deposited at room temperature on Ag(001) is determined by using Mn K-edge surface extended X-ray absorption fine structure (SEXAFS). The results, which are in agreement with the c(2X2) low energy electron diffraction (LEED) pattern and X-ray photoelectron diffraction (XPD), establishes that Mn adopts here an unusally large atomic volume which is consistent with a large atomic-like moment. The Mn L_2L_3 edges soft X-ray absorption spectroscopy (XAS) study of 1ML Mn in-situ deposited confirms that Mn adopts a stable high spin state. For thicker deposits, the growth of a body-centered tetragonal lattice of pure Mn on this diffuse interface is confirmed.

Keywords: Metal-metal magnetic thin film structure, X-ray absorption spectroscopy

The epitaxial growth on Ag(001) was previously predicted by theory as a way to increase the Mn atomic volume with respect to bulk Mn-α room temperature (RT) stable phase and consequently its magnetic moment up to a value close to the atomic $^6S_{5/2}$ ground state (Blügel & Dederichs, 1989). The magnetic properties are therefore tightly correlated to the crystallographic structure of the thin films and to the interface formed with the substrate. Previous investigations showed that, when Mn is RT deposited, deviations from single layer by layer growth are observed, and a Mn-rich epitaxial alloy is formed (Schieffer & al., 1996a,b). Particularly, in the initial stages of growth, instability of this interface has been demonstrated, essentially due to an atomic place exchange of Mn atoms with substrate Ag atoms (Schieffer & al., 1997). In this work the atomic structure of the Mn/Ag interface formed when Mn is RT deposited on Ag (001) is completely determined by using Mn K-edge SEXAFS. The magnetic properties of Mn atoms located in this interface are investigated by Mn L-edge XAS and magnetic circular dichroism (XMCD).

The Mn K (5435eV) and L_2-L_3 edges (652 and 641 eV respectively) XAS data were recorded at LURE (Orsay, France), on the DW21 (DCI) and SU23 (Super ACO) beam lines respectively. Both sets of data were recorded at low temperature from in situ prepared and LEED controlled films, the former in fluorescence mode, the latter by monitoring the total yield sample current. The Mn was deposited at RT on clean Ag(001) substrate in ultrahigh vacuum. Details on the preparation and XPD measurements are given elsewhere (Schieffer & al., 1996a, 1997). The measurements were performed after a delay of two hours or more in order to get a stable surface structure. The Mn K-edge spectra were collected at two angles between the electric field of the x-rays and the normal to surface (Schieffer & al., 1998a). For the L_2-L_3 spectra, the incidence of X-rays on the surface was 45°, which was also the direction of the field (300 oersted) applied in XMCD experiments (Schieffer & al., 1998b).

For low coverages (≤2 ML), a c(2X2) LEED pattern is observed and the Mn $2p_{3/2}$ XPD spectrum presents a single maximum at 45°, which corresponds to the forward scattering by nearest neighbor (NN) along the [101] bond direction of fcc lattice (Schieffer & al., 1996a). The lack of the peak at 0° ([001] direction) attests the confinement of Mn in the two topmost layers of the Ag substrate. Combining these structural information to angle resolved ultra-violet spectroscopy (ARUPS) results, it was possible to conclude at this stage that the Mn/Ag interface is diffuse and a MnAg interfacial alloy is formed in the two topmost layers on the Ag (Schieffer & al., 1996a).

Usual background subtractions and conversion to k-space were applied to the raw Mn K-edge SEXAFS data (Michalovicz, 1997).The Fourier transforms (FT) between 2.4 and 12.2 $Å^{-1}$ of k^1-weighted $\chi(k)$ experimental data of 1 ML Mn RT deposited are shown on the top of Fig. 1. The FT exhibit a split next-neighbor contribution stretching from 1.8 to 3.8 Å. The first and second components can be attributed to Mn-Mn and Mn-Ag pairs, in spite of complicated interference between the two (Schieffer & al., 1998a). Moreover, the curves present a very weak anisotropy versus the incidence of photons on the surface, which is not consistent with a single layer growth. Since previous investigations showed that RT deposited Mn atoms remain confined in the two topmost layers and substitutes Ag in fcc lattice, only few structural models have to be tested. However, the SEXAFS data should be a linear combination of both top and interfacial layer sites. The FEFF6 code (Zabinsky & al., 1995), which takes into account the polarization dependence, provided a facility in testing the possible interfacial models: the theoretical spectra are shown in Fig 1 (a to f) together with these structural models, drawn in Fig. 2 (a to f). First, a bilayer growth of Mn islands (1-a and 2-a) gives rise to an enhanced first component and a lack of the second, which is unconsistent with experimental data. Secondly, when the calculation is performed for a single layer of Mn atoms located either in the top (1-b and 2-b) or buried under an Ag monolayer (1-c and 2-c), the resulting spectra exhibit a strong anisotropy versus polarization, which does not account for the experimental data. At last, $Ag_{0.5}Mn_{0.5}$ Mn-rich alloys were built by using convenient linear combinations of several Mn sites, either statistically distributed (1-d and 2-d) or ordered (1-e and 2-e). The former gives rise to a nearly isotropic distribution, but the Mn component is still overestimated with respect to the Ag one. The latter is in better agreement with experimental data, the amplitude ratio beween the two components being satisfactory for normal incidence. However, the ratio of out-of plane Mn NN seems to be overestimated, since

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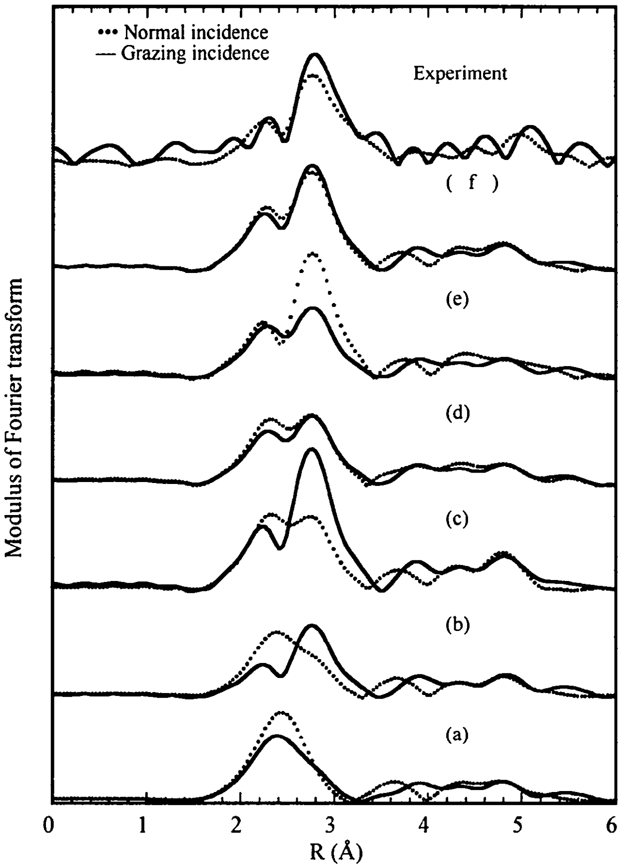

Figure 1
Comparison between FT of (top) polarization dependent SEXAFS spectra recorded from 1 ML deposited at RT on Ag(001) and calculated ones for the various structural models drawn in Fig. 2 : (a) 2 ML Mn islands; (b) 1 ML Mn; (c) burried 1 ML Mn; (d) statistically distributed 50% Mn-50% Ag alloy; (e) c(2x2) reconstructed 50% Mn-50% Ag alloy; (f) average of (d) and (e); (dots) normal; full line (grazing) incidence.

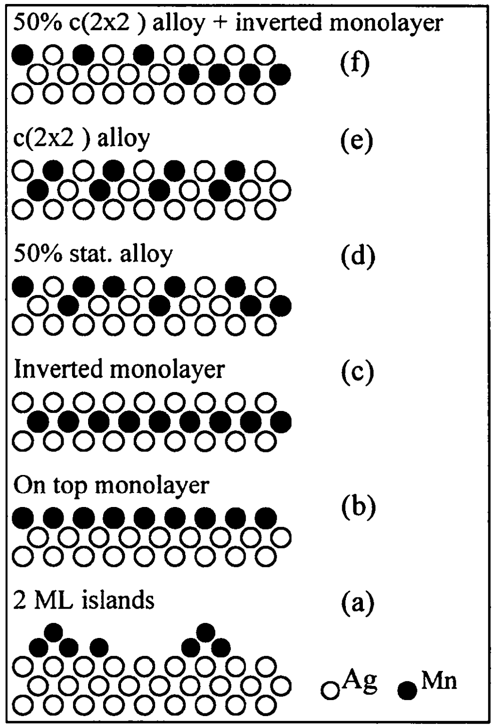

Figure 2
Various structural models tested in FEFF modeling in one to one correspondance with the relevant theoretical spectra shown in Fig.1.

the FT of calculated spectrum for grazing incidence (1-e, full line) shows two peaks of nearly equal amplitude. At this stage, we can conclude that, several hours after the RT deposition of a Mn ML, the interface formed between Mn and Ag consists mainly in a stable Ag$_{0.5}$Mn$_{0.5}$ interfacial alloy. This atomic arrangement is consistent with the c(2X2) LEED pattern. However, a part of Mn atoms have more Ag out of plane NN than expected for this alloy. If we compare the FT calculated for the inverted ML (1-c) and the Ag$_{0.5}$Mn$_{0.5}$ alloy (1-e), we remark that their relative amplitudes are inverted. By averaging the two spectra and calculating the FT, we obtain the curves of Fig 1-f, where the anisotropy versus polarization is quite suppressed. The best agreement with the experimental data is given by an interfacial structure (Fig 2-f) which is shared in domains of approximatively the same area : a part of Mn atoms is buried underneath a plane of Ag atoms, another part forms an ordered Ag$_{0.5}$Mn$_{0.5}$ alloy, which has no bulk equivalent and gives rise to the c(2X2) LEED superstructure. Further investigation showed that a fully inverted Mn ML can be stabilized by adjusting tne temperature of deposit (Schieffer & al., 1998d).

By using the effective coordination numbers corresponding to this interfacial model as fixed parameters of a conventional fit, we obtained accurate values for the other structural parameters : $R_{Mn-Mn} = 2.88 \pm 0.02$ Å and $R_{Mn-Ag} = 2.86 \pm 0.02$ and σ^2 of about 0.01 Å^2. The atomic volume of Mn in this unusual environment is close to 17 Å^3/atom, therefore considerabily increased as compared to 11.6 Å^3/atom in Mn-α bulk phase. A possible ferromagnetic behavior of Mn atoms was investigated for thin fims deposited on Ag . To this purpose, the XMCD signal was measured at Mn L_2 L_3 edges. No change in the intensity ratio of the spin-orbit splitted L_2 and L_3 lines was observed either under magnetization or in remanence, as in the case of the deposit of submonolayer films on Fe (001) (Dresselhaus & al., 1997). The deposit of Mn on a non-magnetic substrate does not lead to a ferromagnetic spin alignment similar to the one caused by antiferromagnetic coupling of Mn to Fe (001). Neverthless, the change in the shape and branching ratio of the Mn L absorption spectrum with respect to thicker coverage clearly indicates that Mn is in high spin state.

The Mn 2p absorption spectra are drawn in Fig. 3 for 0.9 and 10 ML for deposition at RT. The spectra are normalized to give the same intensity at the the maximum of the L_3 line. The spectrum obtained for the thicker coverage presents a broad metallic shape without any fine structure and the branching ratio $I(L_3)/I(L_2)+I(L_3)$ is 0.69, i.e. close to the statistical value of 2/3. This line shape reflects a low spin configuration with itinerant Mn 3d electrons. The full analysis of the SEXAFS data

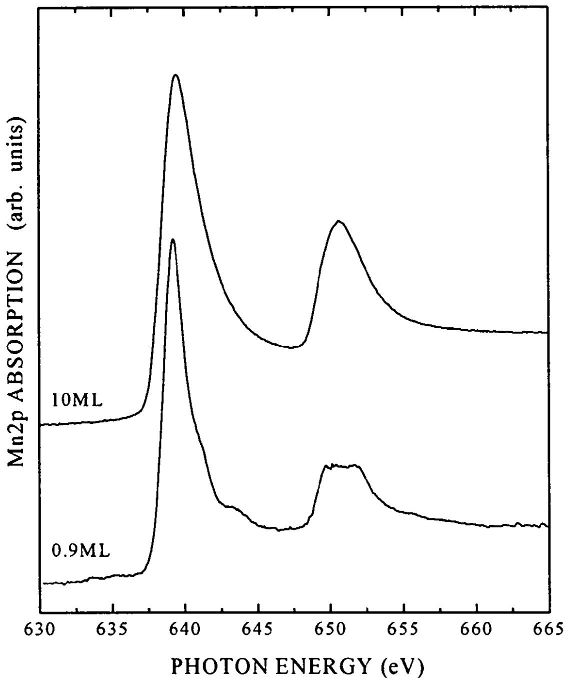

Figure 3
Mn L absorption spectra for 0.9 and 10ML of Mn deposited at RT .

demonstrate that the short range order around Mn is consistent up to 6 Å with a pseudomorphic bct lattice of pure Mn which is contracted along surface normal with respect to Ag (fcc). The shortest out of plane Mn-Mn distance is found to be to 2.60 ± 0.05 Å, whereas the NN in plane Mn-Mn remains equal to that of Ag fcc, i.e. 2.88 ± 0.02 Å (Schieffer & al, 1998c). In this lattice, Mn occupies an atomic volume of 13.3 Å^3/atom instead of 17 Å^3/atom in the interfacial alloy. This results in major changes in the spectral shape in the monolayer range. For a coverage of 0.9 ML, an increase of the branching ratio is observed. The lines become narrower and present detailed features. This kind of spectrum, which was previously observed in c(2x2) MnCu/Cu(001) and MnNi/Ni(001) surface alloys (O'Brien & Tonner, 1995) dilute Mn alloy (Thole & al., 1985) and submonolayer amounts of Mn/Fe(001) is well described by atomic calculations based mainly on the high spin Hund's rule $3d^5$ ($^6S_{1/2}$) ground state (Dresselhaus & al., 1997). This ground state is characterized by a large spin local moment (4 μB) close to the free atom.

In conclusion, the Mn K-edge SEXAFS study of Mn RT deposited on Ag(001) added accurate information on the interfacial structure of Mn RT deposited on Ag(001) to the previous XPD-LEED study. The data are consistent with a linear combination of theoretical spectra calculated for two atomic environments around Mn : a Mn-rich surface alloy and an inverted monolayer which is formed after atomic place exchange of Mn with Ag. In both, the Mn occupies an unusual atomic volume, which is found to be close to 17 Å^3/atom. The Mn L_2-L_3 XAS study confirms that Mn is in a high spin state. However, the XMCD signal is found to be zero, showing that when Mn is grown on the Ag non-magnetic substrate, no ferromagnetic long range order is observed above 80K. The thicker deposit consists in a bct lattice of pure Mn, where the atomic volume shrinks to 13.3 Å^3/atom. The resulting XAS spectrum has a broadened metallic shape. In conclusion, though XAS and XMCD are powerful tools in the investigation of the local magnetic properties of thin films of transition metals, the complete structural study by now conventional methods like XPD, LEED, SEXAFS has to be carried out in order to understand the relation between these.properties and the crystallographic structure of the deposits.

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