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LETTER TO THE EDITOR

Local magnetic properties and magnetic ordering of the two-dimensional surface alloy $c(2 \times 2)$ Mn/Cu(001)

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Abstract. At a coverage of $\frac{1}{2}$ monolayer, Mn forms an ordered $c(2 \times 2)$ structure on Cu(100). This two-dimensional surface alloy exhibits a large outward relaxation of the Mn atoms, which cannot be explained simply by atomic-radius arguments. A recent total-energy calculation by Wuttig and Gauthier finds that this unusual two-dimensional alloy, for which there is no bulk analogue, is stabilized by magnetism of the Mn atoms. We investigate the magnetism of this surface alloy by soft x-ray absorption, photoemission and magnetic circular dichroism. Our soft x-ray absorption results conclusively show that the Mn atoms are in a high-spin ground state, which accounts for the large apparent atomic radius in the $c(2 \times 2)$ phase. Large binding-energy shifts, 0.8 eV, are found in the Mn 3p, 3s and 2p photoemission peaks, which we attribute to the change in screening that accompanies the large outward relaxation of the Mn atoms. Magnetic circular dichroism shows that the $c(2 \times 2)$ phase is stable above the Curie temperature for long-range ordering of the surface alloy. If the surface-alloy formation is stabilized by magnetic properties it is driven by the local high-spin character of the Mn atoms and not by long-range ferromagnetic coupling.

A number of unusual magnetic phenomena are expected in two-dimensional structures, including high-temperature perpendicular magnetization and enhanced magnetic moments. It has proven problematic, in many cases, to grow suitable ideally two-dimensional magnetic films because of experimental difficulties. A recent low-energy electron-diffraction (LEED) investigation by Wuttig and Gauthier [1] has identified a potential new class of magnetic systems, the two-dimensional ordered alloy of $c(2 \times 2)$ Mn/Cu(100). Their structural LEED analysis showed a highly corrugated surface with an Mn atom replacing every other Cu atom in the surface layer. The Mn atoms were found to be relaxed outward by 0.3 Å. Although no magnetic experiments were reported, *ab initio* total-energy calculations, assuming ferromagnetic long-range order, showed that the magnetic ground state was favoured over a paramagnetic layer. It was concluded that the surprising stability of the CuMn ordered monolayer, for which there is no analogous bulk compound, was due to the large gain in magnetic energy, which is accompanied by an outward buckling of the Mn atoms.

In this letter we report results of experiments to measure both the local and long-range magnetic properties of Mn atoms in the Cu(001) $c(2 \times 2)$ Mn surface alloy. The techniques used included soft x-ray absorption (SXA) spectroscopy, with both linearly and circularly polarized light, and synchrotron-radiation x-ray photoemission spectroscopy, at the Wisconsin Synchrotron Radiation Center. To unambiguously separate out surface from bulk

magnetic effects, we prepared two types of sample: the Cu(001) c(2×2) Mn surface alloy and five monolayer (ML) films of Mn on Cu(001). Each sample was prepared by evaporating Mn from an Al₂O₃ crucible onto a clean Cu(001) crystal at room temperature. The Cu(001) was cleaned by Ar ion bombardment and annealing to 700 °C. Sample cleanliness was monitored by core-level photoemission, which showed no O or C contamination. The Mn evaporation rate was 1 ML in 5 min. At $\frac{1}{2}$ ML coverage a sharp c(2×2) pattern, as viewed by LEED, was formed. The base pressure of the vacuum chamber was 5×10^{-11} Torr and the pressure during evaporation was 2×10^{-10} Torr.

We have found that there is a large change in the local magnetic moment of Mn in the ordered monolayer alloy phase, as compared to a bulk-like epitaxial film of Mn. The local magnetic moment of Mn atoms was inferred from SXA spectra with linearly polarized light. In figure 1 we show the Mn L_{2,3} SXA spectra for the Cu(001) c(2×2) Mn surface alloy and a 5 ML film of Mn on Cu(001). For comparison, the two spectra have been normalized to give the same intensity in the L₂ line at 652 eV. The relative intensities of the L₃ and L₂ peaks for the 5 ML sample are nearly identical to measurements we have made on 30 Å films of Mn grown on Cu(001) substrates, so we interpret the 5 ML spectrum as representing bulk (non-magnetic) Mn. The intensity ratio of the spin-orbit split lines, L₃/L₂, is only 3.0 for the bulk-like sample, but dramatically increases by a factor of 1.4 to L₃/L₂ = 4.3 in the monolayer alloy.

The branching ratio (BR), defined as $I(L_3)/[I(L_2)+I(L_3)]$, is 0.81 for the surface alloy and 0.75 for the 5 ML film. It has been shown, both theoretically [2] and by experiment on Fe compounds [3], that the BR in SXA is larger for high-spin ground states. The reason for this can be seen by considering the excited state ($2p^5 3d^{n+1}$) of an atom in the absence of an L₂-L₃ spin-orbit interaction, i.e. in the LS coupling limit. If Hund's rule is obeyed, then the low-energy terms of the excited state will have high-spin character while the higher-energy terms will have low-spin character. When the spin-orbit interaction is turned on these terms are mixed and eventually, when the spin-orbit interaction is large, the *jj* coupling limit is reached. The BR will then have the statistical value of $\frac{2}{3}$. In the intermediate-coupling regime the high-spin LS terms evolve predominantly into the lower-energy L₃ state while the low-spin LS terms evolve predominantly into the higher-energy L₂ state. This, together with the $\Delta S = 0$ dipole selection rule, results in high-spin ground states being preferentially excited into the L₃ final state and low-spin ground states being preferentially excited into the L₂ state [2]. We see from figure 1 that Mn in the surface alloy has a higher-spin ground state than Mn in the 5 ML film.

The BR results for low-spin (bulk-like) Mn, and high-spin c(2×2) Mn/Cu(100) agree quantitatively with calculations performed by van der Laan and Kirkman [4] for a d⁵ Mn atom in a cubic crystal field. For zero crystal field, which corresponds to the high-spin ground state, the theoretical spectrum closely resembles our results for the monolayer alloy, both in terms of the BR and in other spectroscopic details, such as the 1.45 eV splitting in the L₂ line, and the presence of a shoulder on the L₃ line separated from the main peak by 3.95 eV. The low-spin absorption spectrum from 5 ML films also resembles the low-spin atomic calculation for an atom in a large crystal field ($10Dq = 3$ eV). The low-spin SXA spectrum is broader, and of course has a much smaller BR.

An alternative way to measure the local magnetic moment on the Mn atoms is by 3s photoemission. The Mn 3s photoemission, taken with 200 eV photon energy, is shown in figure 2 for the surface alloy and the 5 ML sample. Each of the spectra consists of an exchange-split doublet; however the surface alloy peak is broader and is shifted by 0.8 eV toward higher binding energy. Veal and Paulikas [5] have interpreted the size of the core-level splitting in transition elements as being due to the exchange energy of the 3s hole and

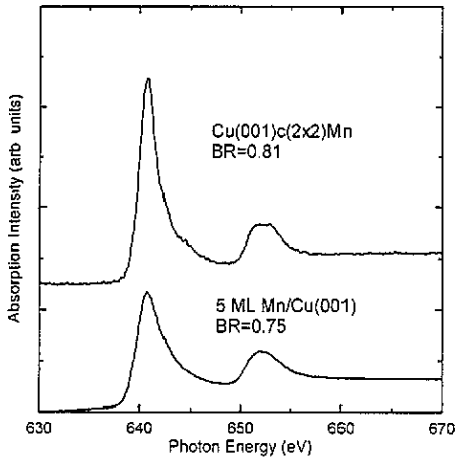


Figure 1. Mn $L_{2,3}$ SXA of Cu(001) $c(2 \times 2)$ Mn surface alloy (top) and 5 ML of Mn on Cu(001) (bottom). The L_3/L_2 line intensity ratio increases from 2.4 in the multilayer to 4.0 in the ordered alloy monolayer. The larger branching ratio $I(L_3)/[I(L_2)+I(L_3)]$ for the surface alloy indicates a ground state with higher spin.

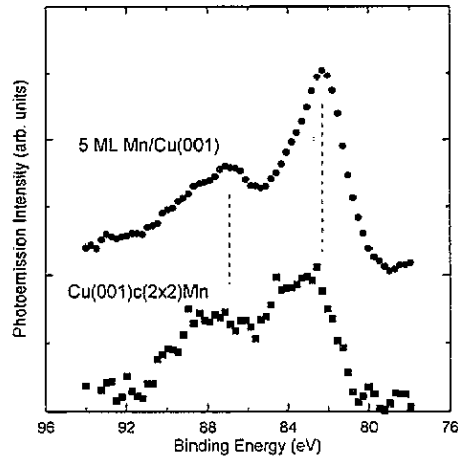


Figure 2. Mn 3s photoemission of Cu(001) $c(2 \times 2)$ Mn surface alloy (bottom) and 5 ML of Mn on Cu(001) (top). The relative intensity ratio for the high-binding-energy peak is greater for the surface alloy. We interpret this as being due to the higher local moment of Mn for the surface alloy. The binding energy of the doublet is shifted to 0.8 eV higher binding energy in the alloy.

the 3d electrons, which in some cases may be used as a measure of the local moment on the transition-metal atom. Also, recent photoemission studies on Fe 3s in FeV alloys [6] suggest that the relative intensity ratio of the two peaks is also a measure of the local moment, with the intensity of the high-binding-energy peak increasing with increasing magnetic moment. The splitting in each is approximately the same for the two samples studied, 4.5 eV, but the relative intensity of the high-binding-energy Mn 3s peak is much larger for the surface alloy. Since we know from the SXA results that Mn in the surface alloy has higher spin character than Mn in the thin film we believe that this change in intensity ratio is also related to the local spin density of the Mn atoms.

The relative energy shift between the Mn 3s peak in the surface alloy and that in bulk Mn is very large. Additional insight into the origin of the 0.8 eV shift can be found in the 3p and 2p photoemission. The Mn 3p photoemission spectra (figure 3) show a similar binding-energy shift to that found for the 3s line. The surface-alloy peak is shifted toward higher binding energy by 0.8 eV, and it is considerably broadened with respect to the 5 ML bulk-like peak. This 0.8 eV shift can be explained by the large outward relaxation of the Mn atoms on the Cu(001) $c(2 \times 2)$ Mn surface alloy, which results in a reduction in core-hole screening and an increase in the apparent binding energy. We make no attempt to explain the additional broadening of the surface-alloy photoemission peaks; however, similar results were found for the Mn 2p photoemission (not shown).

Having established that the CuMn surface alloy has an unusual, high-spin ground state, we turn to an examination of the long-range magnetic ordering. As a probe of surface magnetism, we use the circularly polarized light now available on the 10 m toroidal grating monochromator located at the Synchrotron Radiation Center [7]. The degree of polarization is estimated to be 90% for the results presented here. It has been shown [8,9] that the BR of an SXA spectrum taken with circularly polarized light depends on the relative orientation between the x-ray helicity vector and the sample magnetization. This effect, known as

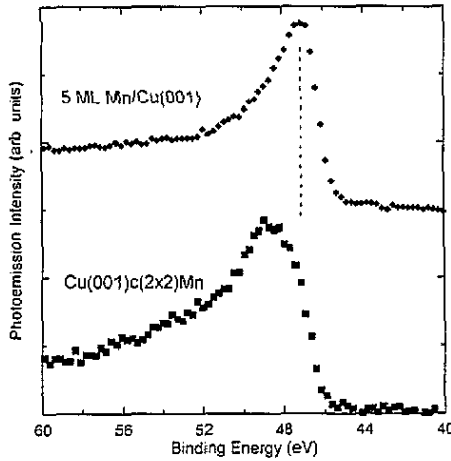


Figure 3. Mn 3p photoemission of Cu(001) $c(2 \times 2)$ Mn surface alloy (bottom) and 5 ML of Mn on Cu(001) (top). The binding energy is 0.8 eV higher for the surface alloy, in agreement with the Mn 3s photoemission results (figure 2). We interpret this shift in binding energies as due to the large outward relaxation of Mn in the surface alloy.

x-ray magnetic circular dichroism (XMCD), is an element-specific technique for measuring magnetic ordering at surfaces [10]. In our present experimental arrangement the x-ray helicity vector is held constant and the sample magnetization is changed. The samples can be magnetized in the ultra-high-vacuum system, either in plane (parallel to the surface) along any particular direction as determined by LEED, or perpendicular to the surface. All measurements were made on the remnant magnetization created by the applied field.

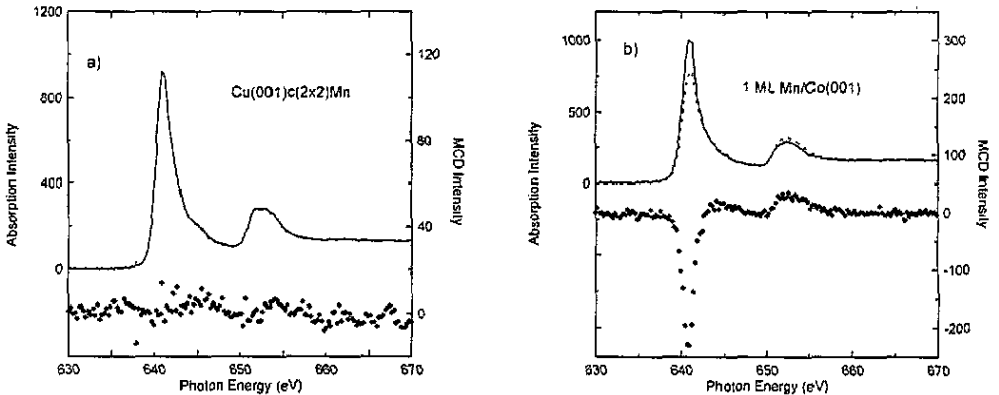


Figure 4. (a) Top, Mn $L_{2,3}$ SXA spectra of the Cu(001) $c(2 \times 2)$ Mn surface alloy obtained with sample magnetization parallel and antiparallel to the x-ray helicity vector for in-plane magnetization; bottom, these two spectra are identical to within the experimental noise as shown by their difference, the MCD intensity. (b) Top, Mn $L_{2,3}$ SXA spectra of the 1 ML of Mn on Co(001) obtained with sample magnetization parallel (full curve) and antiparallel (broken curve) to the x-ray helicity vector for in-plane magnetization. The MCD spectrum is also shown (bottom).

Shown in figure 4(a) are the XMCD spectra for the surface alloy using circularly polarized x-rays, with the sample magnetized in plane along the (110) direction. The two spectra,

which appear to be identical, were taken by measuring the total electron yield. The photon angle of incidence was 65° and the magnetization vector was either nearly parallel or antiparallel to the x-ray helicity vector. The difference between these two spectra, the magnetic circular dichroism (MCD), is practically zero, suggesting either no long-range magnetic order or in-plane antiferromagnetic coupling for the surface alloy. We have made similar measurements for in-plane magnetization along the $\langle 100 \rangle$ direction and for magnetization perpendicular to the sample surface. In each case we find no long-range magnetic ordering. The surface alloy is either magnetically disordered or antiferromagnetic. In either case it is clear that ferromagnetic ordering does not drive the formation of the surface alloy. Similar measurements on the 5 ML Mn film showed no measurable MCD signal.

To further investigate the long-range magnetic ordering of the surface alloy we have measured the MCD of monolayer films of Mn on Co(001), where the Co substrate was grown epitaxially on the clean Cu(001) surface. We have found that Mn is ferromagnetically coupled to the FCC Co(001) substrate. The circularly polarized SXA spectra and the MCD spectrum obtained for 1 ML of Mn on Co(001) are shown in figure 4(b). The BR for the Mn on Co(001) is 0.8 (high-spin ground state). Observation of ferromagnetic coupling of the high-spin Mn/Co(001) monolayer supports the idea that the Cu(001) $c(2 \times 2)$ Mn surface alloy is also ferromagnetic, but that the Curie temperature is below room temperature in the CuMn case.

In conclusion, the BR in SXA shows an enhanced local moment on the Mn atoms in the surface alloy. The Mn 3s photoemission spectra for both surface alloy and the 5 ML film consist of an exchange-split doublet, with an enhanced high-binding-energy peak in the surface alloy. We believe that this increased relative intensity is due to the higher local moment. Photoemission results on Mn 2p, 3p and 3s show a 0.8 eV shift toward higher binding energy compared to the 5 ML film. This large shift is attributed to the large outward relaxation, 0.3 Å, of the Mn atoms in the Cu(001) $c(2 \times 2)$ Mn surface alloy. MCD measurements show that the CuMn surface alloy does not have long-range magnetic order at room temperature. The combination of spectroscopic evidence shows that high-spin Mn is produced in the CuMn surface alloy, but long-range magnetic order is not required to stabilize the formation of the ordered surface alloy. By comparison to atomic calculations [9], it is the reduced coordination at the surface that drives the Mn atoms into a high-spin configuration, which can be interpreted as an example of Hund's rules. The high-spin atom in turn has a larger atomic radius due to the more localized d-state electron density, which creates a pressure that pushes the Mn atoms out of the Cu(100) surface plane.

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