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Rapid Communications

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Influence of adsorbates on surface magnetism studied by spin-resolved photoemission spectroscopy

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The influence of adsorbates (O_2,CO) on the spin-resolved photoemission spectrum has been studied for two different systems: Ni(110) and an Fe-based ferromagnetic metallic glass. While the influence of oxygen on the amorphous Fe sample is only slight it causes a merging of the spin-split peaks of the Ni sample, suggesting the creation of magnetic dead layers. For CO on Ni no such effect is observed.

The interaction of adsorbates with ferromagnetic $3d$ transition metal surfaces and the influence on magnetism has been a subject of interest for several decades. Early work on finely dispersed supported metal catalysts showed that, in general, the magnetization is reduced by adsorption.[1] This was confirmed by more recent work on thin films using ferromagnetic resonance under ultrahigh vacuum (UHV) conditions.[2] There it was found that one H atom on Ni destroys one magnetic moment, whereas the effect of CO is twice as large. Spin-polarized field emission for H on Ni(100) showed a reduction of the spin polarization from 3% for the clean suface to zero for hydrogen-exposed surfaces.[3] Electron-capture spectroscopy also showed a dramatic decrease of the spin polarization (from -96% to -8%) for H on Ni(110).[4] Thus, it is generally agreed on that the magnetization decreases with coverage of adsorbates. In this Rapid Communication we apply spin-resolved photoemission spectroscopy (energy and angle resolved) to the adsorption of oxygen on Ni(110) and on an Fe-based metallic glass ($Fe_{82}B_{12}Si_6$) and of Co on Ni(110) to gain insight into the detailed nature of the influence of adsorbates on the ferromagnetic electronic structure.

Before discussing the results, we should recall how angle-resolved photoemission spectra can be understood, in general, and discuss which situation is best suited for studying adsorbates. For clean surfaces most of the spectral features normally can be attributed to bulk-band direct transitions. In special cases the spectrum may be dominated by surface-induced effects, such as emission from surface states or resonances or, if for a certain photon energy there are no bulk final states available, by direct emission into evanescent waves ("band-gap emission"). We should mention that present state-of-the-art photoemission calculations ("one-step models") are able to reproduce experimental spectra for clean surfaces quite well.[5,6] For adsorbates the situation is much more complex. Most of the angle-resolved photoemission work up to now has therefore concentrated on adsorbate-derived levels (like the molecular orbitals of CO), which are well separated from, e.g., the $3d$ bands of a transition metal substrate. The adsorption normally results in an attenuation of the $3d$ emission. It has been customary to display the difference spectrum, although the significance of this procedure is not clear, because the difference spectrum is certainly almost always a combination of initial- and final-state effects. The initial-state effect, i.e., redistribution of electronic states upon adsorption is, of course, the one of primary interest. One of the final-state effects is the varying escape depth of the photoelectrons. For studying adsorbates it is clearly desirable to have a small electron escape depth so that most of the signal originates from the first atomic layers. This situation can be realized, e.g., by using band-gap emission conditions.

It has been previously shown that a very fortunate situation exists for normal emission from Ni(110) using Ne I(16.85 eV) radiation. Under these conditions—if appropriately polarized light is used—only the spin-split states of S_4 symmetry at the X point of the Brillouin zone contribute to the photoemission spectrum.[7] Also in this situation, band-gap emission is realized so that the mean escape depth is only about 3.5 atomic layers.[6] Given this well-defined and well-understood situation for the clean surface, we studied the influence of O_2 and CO on the spin-resolved photoemission spectrum of Ni(110).

The experiments were performed in the same apparatus described previously.[8] The energy resolution was 100 meV. The Ni sample was a "picture frame" single crystal[7] and the amorphous Fe sample was ribbon with the one end clamped atop of the other to form a circular loop.[9] For intensity reasons we chose, in this exploratory study, not to use polarized light. Therefore the Ni single-crystal spectra are composed of contributions from band states with S_4 and S_3 symmetry, the S_3 component being smaller by about 50% (see Ref. 7). The main S_3 contribution shows up as a shoulder in the up-spin spectrum on the low binding-energy side (near 100 meV, see Fig. 1, lower left panel). The influence of adsorption of O_2 and CO is shown in Fig. 1 for 1 L (1 L$=10^{-6}$ Torr sec) exposure at room temperature. There is a quite dramatic decrease in intensity for both adsorbates (35% for O_2, 50% for CO). The effect on the spin-resolved energy distribution curves (EDC's) is shown in the lower panels of Fig. 1. For both adsorbates it is seen that the down-spin intensity is attenuated more strongly than the up-spin intensity (more pronounced for CO). For oxygen the spin-resolved EDC's approach each other, leaving a splitting of only 50 meV, whereas for CO the peak splitting is unchanged from the value of the clean surface (150 meV).

Figure 2 shows the effect of various exposures of O_2 on the spin-resolved photoemission spectrum of $Fe_{82}B_{12}Si_6$. For a discussion of the clean spectrum see Ref. 10. For increasing oxygen exposures mainly two effects are seen as follows. The growth of a peak near 5.5 eV due to O $2p$ states and a decrease of the metallic Fe $3d$ intensity. While the peak at 5.5 eV causes a decrease in spin polarization at that energy, the spin polarization of the Fe $3d$ states is only slightly affected by oxygen. We also note that the decrease in $3d$ intensity is also only slight (25% for 16 L O_2) compared to the Ni(110) case. Therefore the $O_2/Fe_{82}B_{12}Si_6$ system can probably be understood in simple terms. The oxygen adsorption quenches the ferromagnetism of the top Fe layer (or layers for heavily exposed surfaces). The oxidized Fe layer(s) attenuate the emission from the metallic $3d$ states underneath. The fact that the spin polarization in the regime of the metallic $3d$ emission is only slightly affected then proves two things.

(1) The Fe atoms below the surface which are not in direct contact with oxygen retain their ferromagnetism; i.e., there are no oxygen-induced magnetic "dead layers" beyond the oxidized layers themselves.

(2) Spin depolarization scattering in the oxidized layer is not important.

The single-crystalline Ni(110)/O_2 system is much more complicated because of the importance of band-structure effects. It is known that an exposure of 1 L O_2 leads to a coverage of 0.3–0.35 monolayers in a (2×1) structure. Unfortunately the situation is complicated by an oxygen-induced reconstruction, the most probable model being the so-called "saw-tooth reconstruction."[11,12] Because of this rather heavy reconstruction, and taking into account the short escape depth, a strong influence on the photoemission spectrum might be expected, as is actually observed. The main question is as follows: Where does most of the observed intensity originate from, i.e., is it coming mainly from the topmost reconstructed layers or is it sill coming from deeper unreconstructed Ni layers? We cannot unambiguously answer this crucial question at present. One-step photoemission model calculations are presently underway to study this question.[13] We believe, however, that still an appreciable amount of the signal originates from bulk Ni layers as evidenced by the rather similar positions and width of the spin-resolved peaks. Then we have to interpret the merging of the spin-split peaks as an indication of loss of magnetization, i.e., there are oxygen-induced dead layers, beyond the topmost layer in direct contact with the oxygen. This interpretation is supported by the very high sensitivity of the spin polarizations of secondary electrons upon oxygen adsorption in the low exposure (<0.5 L) range.[14] The role played by the surface reconstruction is not clear at present.[15]

For CO on Ni(110) the situation is simpler than for oxygen. CO adsorbs molecularly forming a $(2\times1)p1g1$ structure for saturation (1 monolayer). There is no reconstruction; on the contrary, CO is believed to lift a 4% surface layer contraction.[16] Therefore, a less drastic effect on the photoemission might be expected. The observed large intensity attenuation might mainly be due to final-state effects. We recall that the actual adsorbate coverage for CO (number of atoms per surface area) is about *six* times that for the oxygen case (two atoms per molecule and about three times the coverage). A very surprising effect is that the splitting of the peaks remains unchanged, despite the

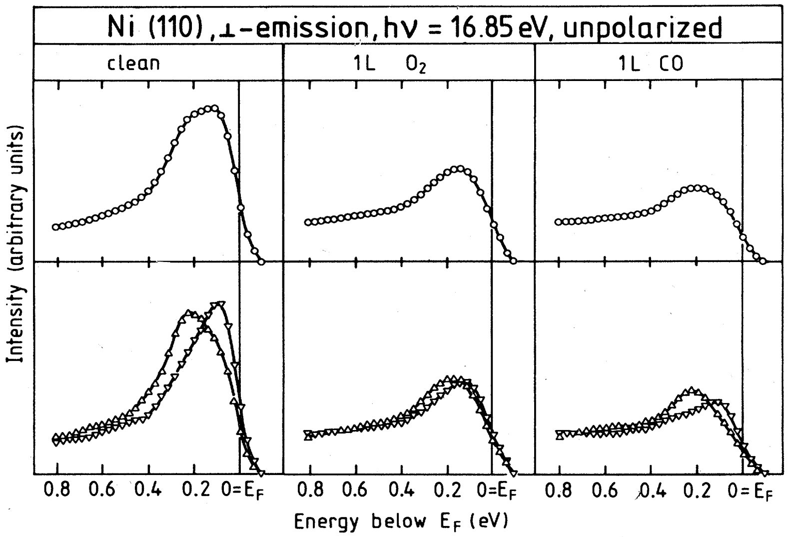

FIG. 1. Energy-distribution curves (EDC) for Ni(110) in normal emission (upper panels). Left column for the clean surface, second and third columns for the surface exposed to 1 L O_2 and 1 L CO, respectively. The lower panels show the spin-resolved EDC's (majority spins Δ, minority spins ∇).

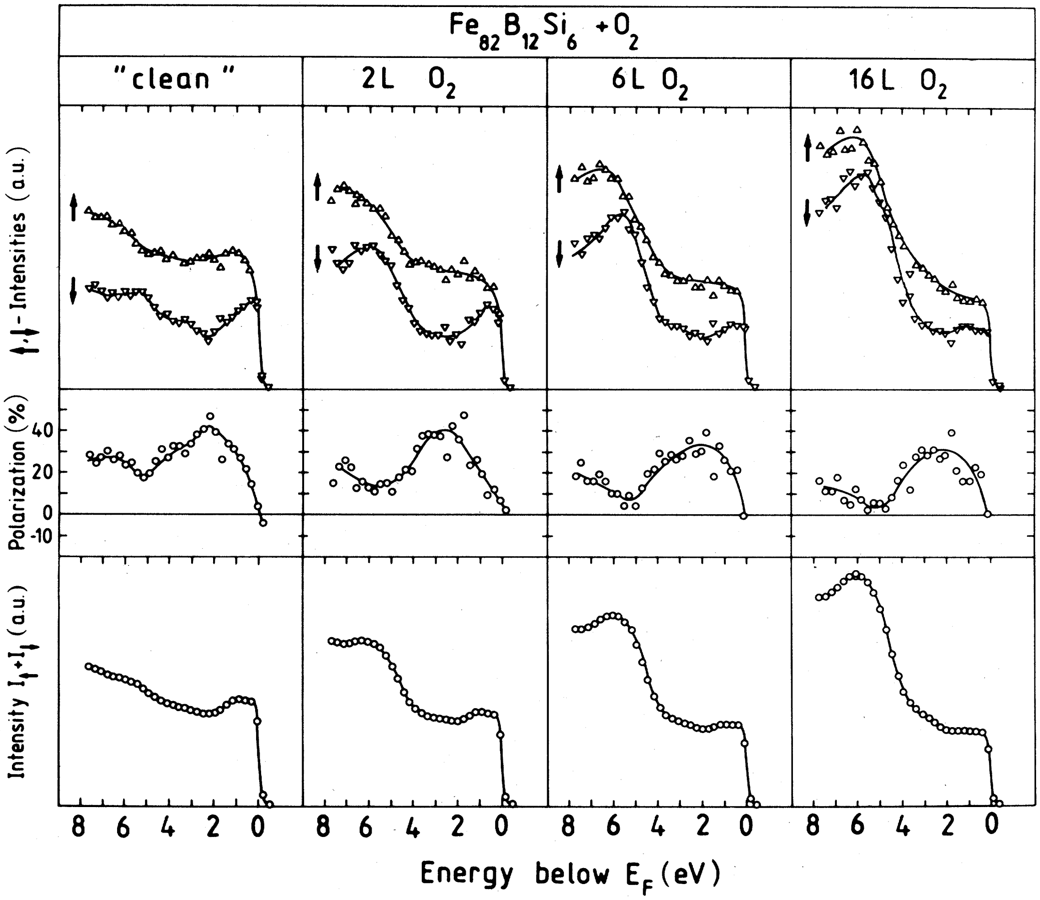

FIG. 2. Energy-distribution curves (EDC) for $Fe_{82}B_{12}Si_6$ exposed to different amounts of O_2 (lower panel). Upper panel: spin-resolved EDC's [majority spins (↑), minority spins (↓)]; middle panel: spin polarization for each case.

known decrease in net surface magnetization.[1,2] We have no explanation for this at present, but can only speculate about the possible causes for this. One possibility could be that the behavior of spin-split states upon adsorption is wave vector and/or symmetry dependent. We point out that we observe just one special k point (X) for one special symmetry (mainly S_4). This interpretation is in line with findings of DiDio, Zehner, and Plummer[17] for angle-resolved photoemission on the O_2/Cu(110) systems, where different Cu $3d$ bands are differently affected by oxygen due to the directional bonding. This k- and symmetry-dependent effect might also explain that in spin-resolved inverse photoemission spectroscopy for Ni(110) the empty state was not found to move upon oxygen adsorption,[18] in contrast to our photoemission peaks. Therefore, a complete understanding of the electronic structure of ferromagnetic surfaces upon adsorption needs more detailed experimental work, e.g., angle-dependent and photon-energy-dependent spin-polarized photoemission and inverse photoemission, as well as detailed k-dependent calculations of the electronic structure.

To summarize, we have shown in this paper that there are drastic effects on the spin-resolved photoemission spectrum of Ni(110) upon oxygen adsorption, but only relatively minor effects for oxygen on an Fe-based ferromagnetic metallic glass. Our tentative interpretation is that oxygen induces dead layers on Ni(110), whereas on the amorphous Fe sample it does not. For CO on Ni(110) the separation of the spin-split peaks is surprisingly unaffected by adsorption, despite the presumable decrease in magnetization.

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