Spin-resolved appearance potential spectroscopy investigations on Fe/Cu(001) overlayers

V. Popescu and H. Ebert

Institut für Physikalische Chemie, Universität München, Butenandtstraße 5-13, D-81377 Munich, Germany

L. Szunyogh

Center of Computational Materials Science, TU Vienna, Austria
and Department of Theoretical Physics, TU Budapest, Hungary

P. Weinberger

Institut für Technische Elektrochemie, TU Vienna, Austria
and Center of Computational Materials Science, TU Vienna, Austria

M. Donath

Physikalisches Institut, Universität Münster, Wilhelm-Klemm-Straße 10, D-48149 Münster, Germany

The theoretical description of spin-resolved appearance potential spectroscopy (SR-APS) developed recently to deal with bulk transition-metal systems has been extended to free surfaces of $Fe_n/Cu(001)$. Results of previous experimental work on fcc-Fe on top of a Cu(001) substrate were interpreted to indicate the coexistence of a few ferromagnetically coupled Fe layers on top of nonferromagnetic Fe layers for $T = 110$ K. Recent theoretical work, on the other hand, found for $n > 2$ that the ground-state of this system corresponds to antiferromagnetically coupled Fe layers. In order to clarify this situation the SR-APS spectra of $Fe_n/Cu(001)$ have been calculated assuming the metastable ferromagnetic (FM) as well as antiferromagnetic (AFM) configuration. While for the FM configuration pronounced deviations from experiment were found, a nearly perfect agreement was obtained for the AFM ground-state configuration. This means that the experimental SR-APS spectra are not in conflict with the theoretical prediction but, on the contrary, they strongly support it.

I. INTRODUCTION

Ultrathin films of iron grown epitaxially on a substrate with a fcc-like structure represent a unique and attractive way to study the magnetism of the γ (fcc) phase of Fe. Due to the small epitaxial misfit, a good layer-by-layer growth of Fe on Cu(001) has been expected and—for room-temperature grown samples—indeed found experimentally by various authors. This way the fcc phase of Fe could be stabilized for up to about 10 monolayers while for thicker Fe films a martensiticlike transition into a bcc related phase occurs.[1,2] The rich magnetic properties of the corresponding samples[3–5] depend strongly on the preparation conditions because of the competition of three different magnetic phases that are close in energy: a high-moment ferromagnetic (FM), a low-moment ferromagnetic and a low-moment antiferromagnetic (AFM) phase. For this reason the properties documented in the literature for the system Fe/Cu(001) seem to be partly contradictory. In spite of this situation there is a general consensus that the onset of magnetic ordering takes place at a 2 monolayers (ML's) coverage. Below this thickness, where the growth is dominated by island formation and atomic interdiffusion, no long-range magnetic ordering could be detected.[1,2] As determined by spin-resolved appearance potential spectroscopy[1] (SR-APS) and also by magneto-optical Kerr effect investigations,[4] the total magnetization is strongly reduced for very thick Fe films. The orientation is found to be along the surface normal up to about 10–12

ML's. For an increasing number of Fe layers it rotates into the plane of the film, accompanied by the structural phase transition. Temperature-dependent SR-APS measurements[3] could establish that the critical temperatures T_c for which the magnetization of the samples vanishes is strongly reduced as compared to the bulk. Furthermore, after a maximum of 330 K, for 2.5 ML's, the transition temperature T_c decreases with increasing film thickness and remains constant, at around 270 K, for coverages thicker than 5 ML's.

These findings have been discussed in the literature in a rather controversial way. While thinner films of 2–3 ML's behave like typical two-dimensional anisotropic Heisenberg ferromagnets,[3] for thicker ones different magnetic configurations have been proposed. In particular, it has been suggested that the SR-APS results mentioned above indicate the presence of an active ferromagnetic surface, of about 2 ML's thickness, on top of a paramagnetic or antiferromagnetic fcc-related Fe.

As for the experimental side, a lot of theoretical investigations have been devoted to the magnetic properties of fcc-like Fe.[6,7] In particular, the system Fe/Cu(001) has been extensively studied.[8,9] Using the so-called screened Korringa-Kohn-Rostoker (KKR) method, Ujfalussy *et al.*[8] investigated the ferromagnetically ordered phase of Fe/Cu(001) in a fully relativistic way for up to 6 Fe ML's on top of a Cu-(100) substrate. This study was completed later by Szunyogh *et al.*[9] who dealt with the antiferromagnetic configurations that were found to be energetically more favorable than the

ferromagnetic ones. For this reason it seemed to be interesting to calculate SR-APS spectra starting from a given magnetic configuration and to compare these with the corresponding experimental data. The theoretical framework for this type of calculation will be sketched briefly in the next section, followed by a presentation and discussion of results obtained for a varying number of Fe ML's and different magnetic configurations.

II. THEORETICAL APPROACH

The starting point of our investigations are the self-consistent (effective) potentials for the fcc-related system $Fe_n/Cu(001)$ ($n=1,\ldots,6$) assuming a ferromagnetic[8] as well as several antiferromagnetic configurations.[9] These calculations have been performed within the framework of spin-density-functional theory using the spin-polarized version of the screened KKR method of band-structure calculation. While this approach supplies a very reliable description of the electronic structure of layered systems and their magnetic properties, it has to be emphasized here that the influence of any possible lattice relaxation and imperfections at the interface have been ignored in our calculations.

Appearance potential spectroscopy (APS) is essentially an inverse Auger electron spectroscopy. This means in particular that a sample is bombarded with electrons of well-defined energy. At high enough energy, parts of these incoming electrons will excite core electrons into unoccupied band states above the Fermi level in a radiationless process mediated by the Coulomb interaction. This APS process can be observed only indirectly by monitoring the fluorescence radiation or the Auger electrons, respectively, of the subsequent relaxation step. In practice, the use of fluorescence radiation is seen to supply a more reliable mapping of the APS spectrum. Within an APS process, only the energies of the incoming and of the core electrons are fixed, while the energies of the two final states are restricted only by the energy conservation. For this reason, the APS signal $P(E)$ for a given energy E of the incoming electron is essentially given by a self-convolution of the density of states $n(E)$ of the unoccupied states above the Fermi level (see below). Additional information on the magnetic properties of the investigated system can be obtained using a spin-polarized incoming electron beam (SR-APS). A corresponding theoretical description derived recently was successfully applied to pure transition metals[10] and also to compounds.[11] An extension of this approach to deal with surface layers systems can be done in a straightforward way. Accordingly, the layer-resolved cross section $P_\sigma^i(E)$ is calculated in a first step using the expression

$$P_\sigma^i(E) = \int_{E_F}^{E+E_c-E_F} dE' \sum_{l',l''\sigma''} n_{l'\sigma}^i(E') n_{l''\sigma''}^i(E'')$$

$$\times W_{l'\sigma,l''\sigma''}^i(E',E''), \qquad (1)$$

with E being the energy of the incoming electron.

In Eq. (1) $n_{l\sigma}^i(E')$ is the layer (i), angular momentum (l) and spin (σ) resolved density of states (DOS), and $W_{l\sigma,l'\sigma'}^i(E,E')$ is the effective cross section connecting bandlike states of character ($l\sigma$) at energy E with those of

character ($l'\sigma'$) at energy E'. This means that the APS signal is a cross-section-weighted self-convolution of the DOS for the (unoccupied) states above the Fermi energy E_F. The energy integration range in Eq. (1) is determined by the Fermi energy and by the binding energies E_c of the involved core states. For the present calculations the later ones are the Fe $2p$ states. Because their chemical shifts for the individual Fe layers i are very small (in the order of ± 0.4 eV) it is not possible to resolve layerwise the spectra within a SR-APS experiment. For this reason a superposition of the individual layer signals $P_\sigma^i(E)$ is recorded. Due to the finite mean free path of the incoming electron the various layers contribute with different weights to the total experimental signal. Furthermore, the attenuation of the electron beam has to be accounted for when dealing with the theoretical total spectra. This leads to the expression

$$P_\sigma^{\text{total}}(E) = \sum_{i=1}^{n} e^{-(i-1)d/\lambda} P_\sigma^i(E). \qquad (2)$$

Here the layer index i starts at the topmost Fe layer, and d gives the thickness of the Fe layers. The electron mean free path length λ depends on the energy E of the incoming electron that in turn is closely related to the binding energy E_c of the core states (at the onset of the spectra one has the condition $E-E_F=E_F-E_c$). For the $2p$–core states of Fe to be considered here one has $\lambda(E)\approx 12$ Å.[12] This leads in Eq. (2) to the weights of 1.00, 0.86, 0.74, 0.64, 0.55, 0.47 for $i=1,\ldots,6$, respectively. Finally, it should be noted that Eq. (1) has been derived originally by averaging the so-called site-diagonal scattering path operator $\tau_{LL'}^\sigma(E)$ with respect to its m_l dependency (for further details see Ref. 10). Using the same approximation to calculate the CVV-Auger spectra it was found recently that, indeed, this leads for cubic systems to negligible deviations from the results obtained by full calculations.[13] This should essentially also hold for the systems investigated here, among others, because they have been treated by making use of the atomic-sphere approximation for the potential.

For a direct comparison with the experimental SR-APS data mentioned above Eqs. (1) and (2) have to be used in their differential form to get $(d/dE)P_\sigma(E)$ because the experimental spectra have been recorded using a modulation technique. In addition, the influence of various intrinsic and apparative broadening mechanisms have to be accounted for. Comparison with experiment led to broadening parameters that are more or less identical to those found appropriate for Fe in $FeNi_3$.[11]

III. RESULTS AND DISCUSSION

The properties of the FM phase of Fe layers on top of Cu(001) have been investigated and discussed in great detail among others by Ùjfalussy *et al.*[8] The most prominent feature of the corresponding magnetization profile is that the spin-only magnetic moment of the topmost layer ($i=1$) is enhanced as compared to those below ($2 \le i \le n-1$ for $n > 2$). This enhancement, accompanied by a strong charge depletion[8] is a common property of many ferromagnetic surfaces and is attributed to band narrowing at the surface. The same feature, although somehow reduced, can be noticed for
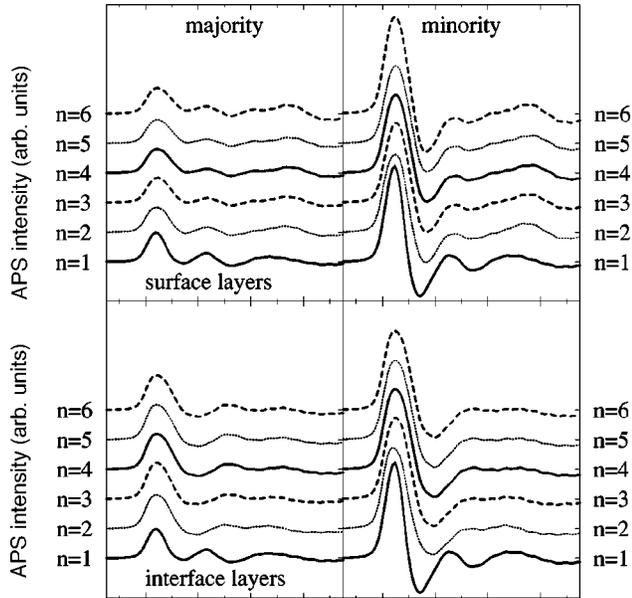
FIG. 1. Spin-resolved APS spectra for Fe in the FM ordered systems Fe$_n$/Cu(001). The top panels give the spin-resolved spectra for the topmost Fe layer, while the bottom panels give the corresponding spectra for the Fe interface layer for $n=1,\ldots,6$.

FIG. 2. Spin-resolved APS spectra for Fe in the FM ordered systems Fe$_n$/Cu(001). The top panels give the total spectra for $n=1,\ldots,6$ for the majority (left) and minority (right) channels. In addition to the theoretical spectra based on Eq. (1) corresponding experimental data are given by open circles (Refs. 3,14). The lower panels of the figure give a layer by layer decomposition of the spectrum for $n=6$ with the weighting factors omitted [see Eq. (2)].

the interface Fe layer ($i=n$) as well, probably due to the weak hybridization between Fe and the Cu substrate.

The APS spectra related to the FM ordered Fe surface layer systems are presented in Fig. 1. Due to the electron mean free path the signal stemming from the Fe topmost layer is, of course, dominating in the total spectrum. The upper panel of Fig. 1 shows the APS signal of this layer (majority channel on the left, the minority one on the right) for different numbers of Fe layers n on top of the surface. The corresponding spectra for the Fe interface layer are given in the lower panel. It should be noted that for $n=1$ the interface and topmost layers are of course identical. For all the other calculated systems ($n=2,\ldots,6$) the topmost layer related spectra have a narrower shape than those of the other layers. Also the spin asymmetry A, defined as the difference of the minority- and majority-spin spectra, is higher for the topmost layer spectra, as a direct consequence of the corresponding stronger spin polarization. Here it seems appropriate to point out that the terms majority- and minority-spin spectra only specify the spin orientation of the incoming electron with respect to the magnetization of the sample. Since the cross section $W^{i}_{l\sigma,l'\sigma'}$ in Eq. (1) allows spin cross terms to occur, these spectra are not exclusively linked to the electronic structure of the majority- and minority-spin systems. For a more detailed discussion of this point see for example Ref. 10.

The total Fe-APS spectra computed according to Eq. (2) for an increasing number of Fe layers are plotted in the upper panel of Fig. 2. For both spin channels the main peak tends to become broader and the second positive peak moves towards higher energies and gets smoother. (The connection of the prominent peaks with the underlying electronic structure is discussed for example in Ref. 10). However, for $n\geq4$ the changes are rather small, indicating a kind of saturation. The spin asymmetry decreases as the number of Fe layers in-

creases. For example, for $n=6$ one finds $A=45\%$. This seems to be much too high when compared with the corresponding experimental spectrum that gives about 30%.[1,14] The various experimental spectra shown in Fig. 2 have been recorded at the L_3 edge of Fe using the fluorescence detection mode. For this reason they can be seen to give a rather direct and reliable representation of the APS intensity. In order to investigate the pronounced difference between the experimental and theoretical asymmetry that can be seen in the top panel of Fig. 2, layer-resolved APS spectra for $n=6$ are presented in the lower panel of this figure. For a better comparison of their relative magnitude, the individual layer spectra are plotted without any weighting factor. The main peak of the total signal near the energy zero is strongly broadened because of the different position of this peak in each individual layer spectrum. One sees that the spectra for the inner layers ($i=2,\ldots,5$) exhibit essentially the same features and clearly differ from those for the outer layers ($i=1,6$), i.e., at the interface and at the surface. Compared to the latter ones, the bandwidths of the inner layers are larger and their spin polarization—reflected in the spin asymmetry of the spectra—is smaller. However, due to the slowly decreasing attenuation factor in Eq. (2), their contribution to the shape of the total signal is still important. In particular, it should be noted that the partial spectra are very similar to those of a fcc system (see, for example, Ref. 11) and modulate the total signal.

The theoretical spectra in Fig. 2 were scaled relative to the main peak in the minority channel of their experimental counterparts. Although the theoretical spectra reproduce correctly the bandwidth and the relative peak positions of the experimental ones, it is obvious that the spin asymmetry A is
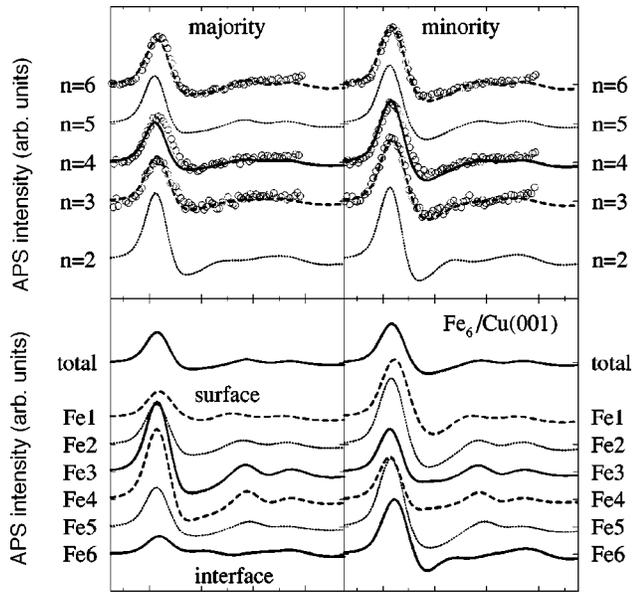
FIG. 3. Same as Fig. 2, but for the (stable) AFM configurations.

FIG. 4. Comparison between the theoretical SR-APS spectra of the stable (upper panel) and metastable (lower panel) AFM configurations of $Fe_6/Cu(001)$.

overestimated by the calculations. Inspection of the layer-resolved spectra in the lower panel of Fig. 2 clearly indicates that the main reason of this discrepancy is the assumed FM configuration. At first sight this seems to support the suggestion of the existence of a few active Fe layers on top of nonmagnetic Fe layers (see above). However, this suggestion is in conflict with the results of various theoretical investigations.[7,8] In particular it has been found by Szunyogh *et al.*[9] that only the ground state of $Fe_2/Cu(001)$ refers to a FM spin configuration while the other multilayer systems ($n > 2$) have antiferromagnetically (AFM) ordered configurations. Completely in line with experiment a perpendicular orientation of the easy axis has been found for these spin configurations, while the corresponding FM spin configurations yielded an in-plane orientation of the easy axis.

The resulting spin and orbital magnetic moments for the AFM configuration can be found in Ref. 9. Here it is interesting to recall that as for the FM phase and due to the same reasons, the topmost and the interface layer carry enhanced magnetic moments. Concerning the buried layers, reduced absolute values compared to those with FM coupling were found. An extremely interesting feature, common to all AFM stable films, is that the $i=1$ and $i=2$ layers always couple ferromagnetically, as it was anticipated by experimental investigations.[1,5,15]

Calculating the SR-APS spectra for the AFM configurations one finds that the general features of these do not differ much from those for the FM configuration. As can be seen in the lower panel of Fig. 3, where the total and layer-resolved spectra for the AFM ground state of $Fe_6/Cu(001)$ are shown, the layer-related signals maintain their structure as compared to the corresponding spectra in Fig. 2. The major difference is that, as expected, the majority channel is now dominating for layers $i=3$ and $i=4$. Similar changes were found also for the other systems ($n < 6$) with an AFM configuration.

To compare the resulting theoretical spectra for the AFM configurations with experiment the same scaling procedure
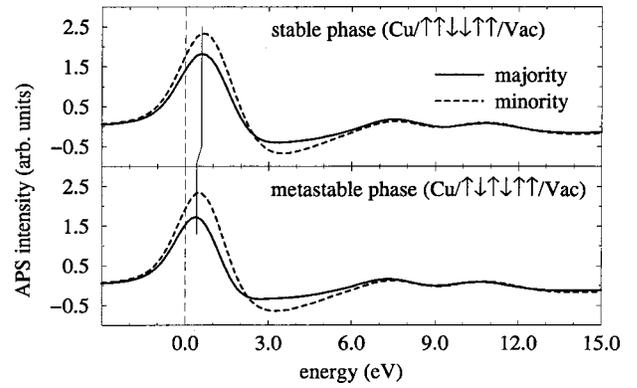
has been applied as for the FM case; i.e., the amplitude has been adjusted to the same height in the most prominent peaks of the minority-spin channel. As one can see in Fig. 3, nearly perfect agreement is found now with experiment also for the majority channel. In particular the asymmetry ratio A is found in full accordance with experiment. Consequently, one has to conclude that the ground state of the $Fe_n/Cu(001)$ systems investigated here has indeed an AFM configuration as predicted theoretically[7,9] and confirmed by means of SR-APS.

It is obvious from the results shown in Figs. 2 and 3 that the differences of the SR-APS spectra for the FM and AFM configurations are pronounced enough to rule out unambiguously the FM configuration to correspond to the experimental situation. Because there are several other, slightly different, AFM configurations that compete with the ground state AFM configuration it seems interesting to investigate whether those can be clearly distinguished by means of corresponding SR-APS spectra. For $Fe_6/Cu(001)$ Fig. 4 shows the spectra for the AFM ground-state configuration ($\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow$) and the metastable configuration ($\uparrow\downarrow\uparrow\downarrow\uparrow\uparrow$). As one can see, there is only a small energy shift of about 0.2 eV for the main peaks. Apart from this difference, there are hardly any other shifts noticeable. For this reason one has to conclude that SR-APS is not able to distinguish between these very similar and energetically close AFM configurations.

IV. SUMMARY

The theoretical description of SR-APS in bulk materials developed recently has been extended to allow a treatment of layered systems. In the latter case the major modifications are the requirement that one has to calculate the partial spectrum for each layer individually. In setting up the total spectrum the mean free path length of the incoming electron has to be accounted for.

Application to Fe in the system $Fe_n/Cu(001)$ with ferro- as well as antiferromagnetically ordered configurations revealed that the various partial spectra are quite different, reflecting thus the local electronic structure in a spin-resolved way. Comparison with corresponding experimental data clearly shows that there are pronounced deviations from ex-

periment if a FM configuration is assumed. Using instead an AFM configuration nearly perfect agreement is achieved. Comparing the theoretical spectra of two slightly different AFM configurations one had to conclude that the difference between these presumably is too small to be clearly distinguished in the experiment. Nevertheless, the present investigation clearly demonstrates that a FM configuration for Fe_n/Cu(001) can be ruled out for $n>2$. In addition, it is also obvious that there is no conflict between the experimental SR-APS data for Fe_n/Cu(001) and the AFM ground-state configuration predicted by theory.

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