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Electronic structure and properties of epitaxial Fe on Cu(100): Theory and experiment

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Results of a combined experimental-theoretical study of the electronic structures and properties of epitaxial Fe on Cu(100) are reported. Angle-resolved photoelectron spectroscopy is used to determine the electronic structure of one, two, and four layers of epitaxial Fe on Cu(100). The experimentally determined two-dimensional energy bands of $p(1\times1)$Fe monolayers and bilayers verify predictions of local spin-density full-potential linearized augmented plane-wave calculations. Changes in electronic properties with coverage and the evolution of the bulk electronic structure of the substrate-stabilized fcc iron are described.

Advances in (i) novel sample preparation techniques, in particular epitaxial growth of layered structures, and (ii) in local spin-density electronic-structure theory of surfaces and interfaces are stimulating new interest and excitement in the field of thin-film magnetism. Taken together, they offer unique opportunities for developing new magnetic materials[1] as well as advancing our understanding of fundamental magnetic interactions in solids.[2] The opportunities for advancing our fundamental understanding of magnetic phenomena are particularly attractive in the subfield of solid-state physics in which carefully characterized materials of known structure are experimentally studied and the results coordinated with first-principles calculations.

In a recent publication[3] we reported experimental results for epitaxial $p(1\times1)$Ni films on Cu(100). This study presented some of the first detailed experimental evidence showing that high-quality epitaxial magnetic films could be grown on metallic single-crystal surfaces,[4] and that the two-dimensional electronic structure and magnetic exchange splitting of these films could be determined with sufficient accuracy to provide meaningful tests of the predictions of first-principles calculations.[5]

The present Rapid Communication continues to explore the prospects of advancing our understanding of two-dimensional magnetic structures based on the interplay between *ab initio* first-principles calculations and photoemission studies of novel thin-film structures fabricated by molecular-beam epitaxy. Our experimental results confirm the predictions of the computational studies,[5] and indicate that the $p(1\times1)$Fe on Cu(100) system is a *second* suitable candidate for detailed experiments in which electronic and magnetic properties can be probed by the rapidly increasing number of surface and spin sensitive spectroscopic techniques.[6]

Our experiments were performed at the Synchrotron Radiation Facility in Stoughton, Wisconsin. The 1-m stainless-steel Seya-Namioka monochrometer was used to dispense radiation from the Tantalus storage ring, and an angle-resolving photoelectron spectrometer, described previously,[3,7] was used to prepare the epitaxial crystals and to obtain the photoelectron spectra. Our sample preparation techniques and surface characterization methods were also identical to those described previously.[3]

The theoretical electronic structures were determined from local spin-density functional theory by means of the highly precise all-electron full-potential linearized augmented plane-wave (FLAPW) method.[8] The surfaces are modeled by a single-slab geometry with Fe layer(s) atop a five-layer Cu(001) substrate: The stacking has atoms in the fourfold hollow site of adjacent atomic planes. The Fe-Cu interlayer spacing was determined from total energy calculations. We find that Fe forms an ordered overlayer on Cu(001) with an Fe-Cu interlayer spacing which is very close (within 0.05 Å) to that of the substrate. This result is confirmed by low-energy electron-diffraction (LEED) studies described later. For the case of two monolayers $p(1\times1)$Fe/Cu(001), the problem is complicated by the magnetic coupling between the Fe layers. The magnetic ground state was therefore determined from a comparison of spin-polarization energy between various magnetic states. The ferromagnetic coupled bilayers are found to have the lowest total energy, whereas the antiferromagnetic coupling between the Fe layers exists as a metastable state with a total energy 0.2 eV above the ferromagnetic state.

Despite the presence of the nonmagnetic Cu substrate, strongly enhanced magnetic moments localized at the Fe site are found from these calculations: (1) $2.85\mu_B$ for 1 Fe/Cu(001); and (2) $2.83\mu_B$ and $2.58\mu_B$ for the surface and interface Fe layers, respectively, for the two monolayer coverage. The Fe-derived localized interface states and the narrowing of the d band appears to be the mechanism driving the enhancement of the magnetic moments over the value ($2.12\mu_B$) in bulk Fe.

Previous experimental work[9] has established that the excellent bulk lattice constant match permits pseudomorphic growth of fcc Fe on Cu(001). Evidence for pseudomorphic

growth is based on transmission electron microscopy studies of 1000 Å Fe films grown on Cu(100) films in high vacuum (10^{-7} torr). Unlike the Ni on Cu(100) system, which we previously studied,[3] apparently, no structure studies of 1–5-monolayer films grown on well-characterized substrate surfaces in 10^{-10}-torr vacuum are currently available for the Fe on Cu(100) system. Therefore, we have conducted an extensive investigation of the growth properties and structure of thin Fe layers on Cu(100) surfaces. Our LEED and Auger analysis of this system are reported elsewhere.[10] The important results of this work relevant to the present paper are (1) $p(1\times1)$Fe grows on Cu(100) as an extension of the substrate with identical (±0.1 Å) lattice constant, (2) thicker films (up to 4 layers) appear to form excellent epitaxial layers of fcc iron stabilized by the Cu(100) substrate and having a lattice constant equal to the substrate, (3) interdiffusion on Fe and Cu at the interface is not apparent for substrate temperatures below 250 °C, and (4) the epitaxial growth appears to be dominated by a layer-by-layer mechanism at substrate temperatures of 150 °C.

Figure 1 displays representative angle-resolved photoemission spectra for one and two monolayers of $p(1\times1)$Fe on Cu(100) along the $\bar{\Gamma}$-$\bar{X}$ direction of the two-dimensional Brillouin zone. All of our energy distribution curves (EDC's) for epitaxial layers were taken using s-polarized light with the A vector along a symmetry axis of the crystal and with the emitted electrons detected either in that mirror plane (even symmetry) or perpendicular to it (odd symmetry). All spectra were taken at room temperature (300 K) at an energy resolution (monochromator plus analyzer) of approximately 100 meV. Approximately 200 spectra for one- and two-monolayer Fe films on Cu(100) were taken in even and odd geometry for $k_{\parallel}$ along $\bar{\Gamma}$-$\bar{X}$ and $\bar{\Gamma}$-$\bar{M}$ directions of the two-dimensional Brillouin zone. Several photon energies were used. Except for some minor variations of binding energies with film thickness (discussed below), spectra corresponding to a given symmetry and $k_{\parallel}$ value were consistent.

Figure 2 presents the two-dimensional electronic structure of one- and two-layer films obtained from our photoemission data. Solid lines and dashed lines in Fig. 2 represent calculated[5] majority spin and minority spin bands for a $p(1\times1)$Fe film on a five-layer Cu(100) slab which have over 50% of their wave function derived from Fe basis functions. These are the specific two-dimensional energy bands to which our experiments should be most sensitive.

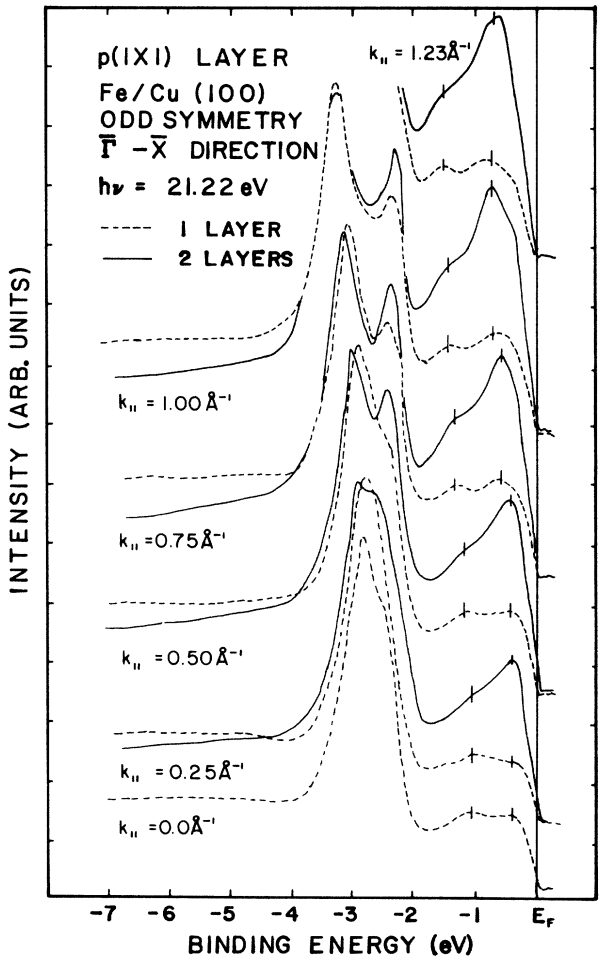

FIG. 1. Angle-resolved photoemission spectra for one- and two-layer $p(1\times1)$Fe films on Cu(100). Values of $k_{\parallel}$ correspond to the Γ-X direction of the two-dimensional Brillouin zone.

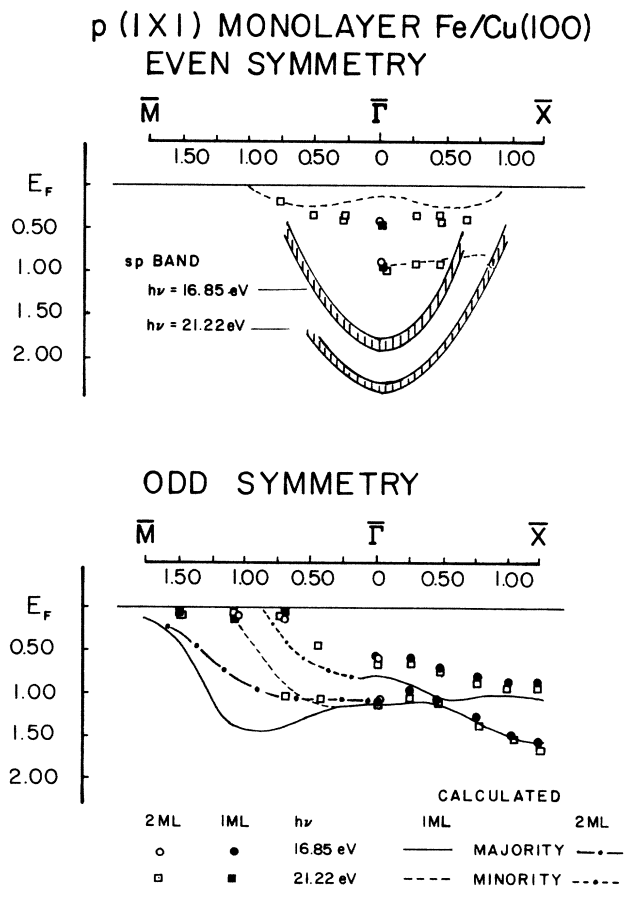

FIG. 2. Two-dimensional electronic structure of $p(1\times1)$Fe on Cu(100). The two broad curves indicate the regions of binding energy and $k_{\parallel}$ where a prominent structure resulting from the Cu sp band is observed. Light solid and dashed curves represent calculated (Ref. 5) surface Fe bands having over 50% surface character. Data are represented by empty (two-monolayer films) and solid (one-monolayer films) circles ($h\nu=16.85$ eV) and rectangles ($h\nu=21.11$ eV).

The broad shaded areas in the even symmetry bands represent regions of $k_{\parallel}$ where prominent features associated with the Cu *sp* band sweep through the angle-resolved energy-distribution curves (EDC's) near E_F. These structures were identified by $k_{\parallel}$ scans on clean Cu(100) surfaces; their presence precludes the study of even symmetry Fe bands in several regions of the two-dimensional Brillouin zone at specific photon energies. Interference of the *sp* band in studies of $p(1\times1)$Ni on Cu(100) (Ref. 3) and on Ag(100) (Ref. 11) is less of a problem because the overlayer Ni *d*-band features are much narrower than corresponding Fe features, and are therefore more easily distinguished from the *sp*-band features.

Some results of the theoretical studies are shown in Fig. 2. It is clear from the comparison that the calculations are in reasonably good agreement with the results shown in Fig. 2 in the regions of the two-dimensional Brillouin zone effectively probed by our experiments. Based on the calculations, the most prominent features observed in even symmetry geometry in the vicinity of E_F should be minority spin bands. Clearly, spin-polarized photoemission studies of this system will be informative. Our experimental results around $\bar{\Gamma}$, where Fe-derived features are not masked by the Cu *sp* band, support the number of bands and their binding energies predicted by the calculations. Odd symmetry bands observed along $\bar{\Gamma}$-$\bar{X}$ also appear to agree rather well with the calculated results, although there are significant differences (0.25 eV) between measured and calculated binding energies. In general, we find that the measured bands lie closer to the Fermi energy than the calculations predict for the majority and minority spin bands. This result could imply that the magnetic exchange splitting is actually smaller than predicted theoretically, or could be a manifestation of the importance of many-body effects (i.e., core-hole relaxation and correlation). Our previous experimental studies of the bulk[7] and surface[12] electronic properties of ferromagnetic Fe have shown, however, that correlation effects appear to be small; we therefore assume that these effects are also of minor importance in the Fe overlayer system.

One source of the discrepancy between the experiments and the theoretical results could be due to the fact that our measurements were conducted at 300 K, and our calculations correspond to $T=0$ K. We have not yet attempted any low-temperature experiments or experiments above $T=300$ K to detect possible temperature dependences in the results. A second possible source of disagreement between our experimental results and the calculations are some subtle layer dependencies we have observed in electronic properties of the Fe layers. Our LEED studies revealed two domain (2×1) LEED patterns in the coverage range between 0.5 and 1.0 monolayers.[10] These structures were not observed above full monolayer coverage, but their presence at low coverage suggests a competition between the substrate stabilized fcc structure and the possible tendency for Fe to form some other structure, in particular the normal bcc structure of bulk Fe. Displacement of iron atoms too small to detect by our LEED measurements is not inconceivable, and such displacements would cause significant changes in the electronic properties, particularly in the $\bar{\Gamma}$-$\bar{M}$ portion of the two-dimensional Brillouin zone. As noted in detail elsewhere,[10] while we have eliminated film growth models that assume the second layer begins before the first layer is more than 85% complete, we cannot discriminate between film growth in which islands of the second layer begin to nucleate when there is less than 15% of the first layer remaining to be completed.

The calculated bands for two layers of Fe and Cu(001) are modified from those of the monolayer coverage. The overall Fe surface layer derived features and dispersions remain similar to those shown plotted in Fig. 1. However, the localization of the surface state wave functions on the surface Fe layer becomes less pronounced due to the hybridization between surface and subsurface Fe layers. This change of bonding also manifests itself in a reduced upward dispersion of odd symmetry bands (dominated by d_{xz} and d_{yz} character) along the $\bar{\Gamma}$-$\bar{M}$ direction (cf. Fig. 2). Furthermore, the calculation predicts the existence of additional majority spin bands having a strong admixture of wave functions localized on the subsurface Fe layer, in particular, odd symmetry bands with binding energy ≈ 2 eV along $\bar{\Gamma}$-$\bar{X}$, and an upward dispersion band along $\bar{\Gamma}$-$\bar{M}$ (not shown in Fig. 2). Interference from the Cu *sp* band precludes observing the new even symmetry band for two monolayers, and the broad peak widths associated with the Fe overlayers renders it very difficult to differentiate small differences in spectra for one- or two-monolayers. Since the size of the

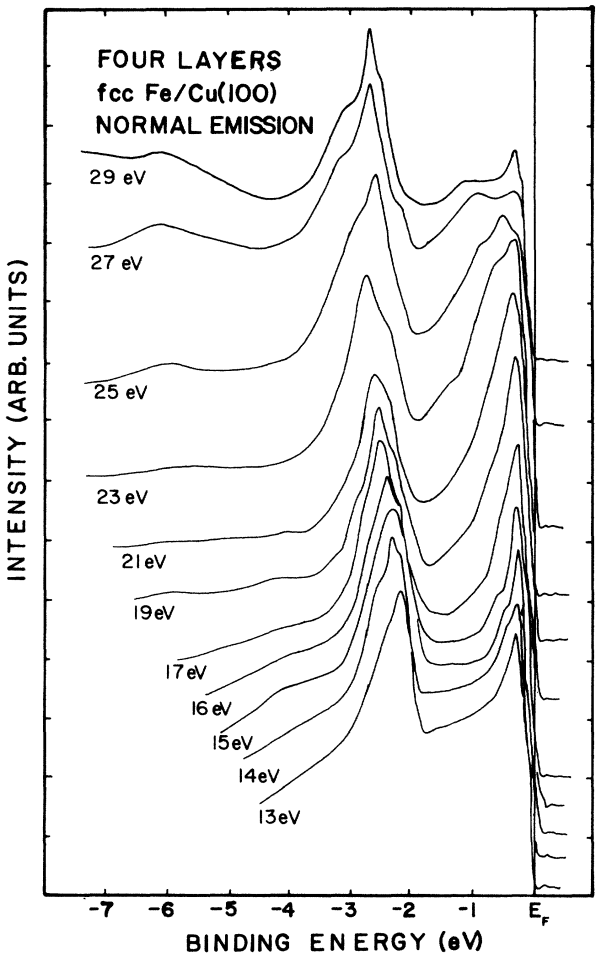

FIG. 3. Normal emission photoemission spectra for four-layer fcc Fe films stabilized on the Cu(100) surface. Peaks near E_F result from the Fe film and exhibit clear evidence of direct bulk interband transitions.

magnetic moments for the surface Fe layers remains almost identical for one- or two-monolayer coverage, the exchange splitting (ΔE_{ex}) is expected to be the same for both cases ($\Delta E_{ex} \approx 2.65 \pm 0.05$ eV).

Figure 3 displays normal emission spectra for four layers of Fe on Cu(100). Our LEED analysis[10] has shown that high-quality fcc films of epitaxial Fe form at this coverage. Features in the spectra near E_F are definitely due to emission from the Fe overlayer. This assignment was checked by obtaining corresponding spectra for clean Cu(100). Peaks near E_F exhibit clear dispersion with photon energy ($k_\perp$), indicating strong influence of direct bulk transitions. Dipole selection rules limit the symmetry of initial states probed in normal emission to Δ_1 and Δ_2 symmetry. The dispersion of the peaks near E_F with $k_\perp$ is consistent with the calculated bulk bands[13] of fcc Fe along the Γ-X direction of the three-dimensional Brillouin zone. It is therefore possible to carry out detailed energy band measurements of the bulk band structure of the fcc phase of ferromagnetic iron stabilized on Cu(100).[14]

In summary, our results have identified a second thin-film magnetic system in which considerable success has been achieved in the synthesis of the film, in its characterization, and in obtaining accurate electronic structure information. The $p(1\times1)$ Fe on Cu(100) appears to represent an additional excellent model system in which to explore the relationship between magnetism and electronic structure from the point of view of thin-film magnetism (two-dimensional magnetism), and the magnetism of a new artificially stabilized bulk phase (fcc Fe).

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[1]R. M. White, Science **229**, 11 (1985).

[2]U. Gradmann, Appl. Phys. Lett. **3**, 161 (1974), and references therein.

[3]M. Thompson and J. L. Erskine, Phys. Rev. B **31**, 6832 (1985).

[4]Epitaxy of metals is not new; see, for example, the review article by E. Bauer, Appl. Surf. Sci. **11/12**, 479 (1982). Our experiments are among the first to explore the electronic properties and magnetic exchange splitting of epitaxial magnetic films using photoemission. One previous study of a similar nature has been reported by R. Miranda, F. Yndurain, D. Chandesris, D. Lecante, and Y. Petroff, Phys. Rev. B **25**, 527 (1982).

[5]C. L. Fu, A. J. Freeman, and T. Ogucht, Phys. Rev. Lett. **54**, 2700 (1985).

[6]J. M. Kirschner, *Springer Tracts in Modern Physics* (Springer, New York, 1985), Vol. 108.

[7]A. M. Turner, A. W. Donoho, and J. L. Erskine, Phys. Rev. B **29**, 2986 (1984), and references therein.

[8]E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981), and references therein.

[9]K. W. A. Jesser and J. W. Matthews, Philos. Mag. **15**, 1097 (1967).

[10]M. F. Onellion, M. A. Thompson, J. L. Erskine, C. B. Duke, and A. Paton (unpublished).

[11]M. A. Thompson, M. F. Onellion, and J. L. Erskine (unpublished).

[12]A. M. Turner and J. L. Erskine, Phys. Rev. B **30**, 6675 (1984); **28**, 5628 (1983).

[13]D. Bagayoko and J. Calaway, Phys. Rev. B **28**, 5419 (1983).

[14]M. A. Thompson and J. L. Erskine (unpublished).