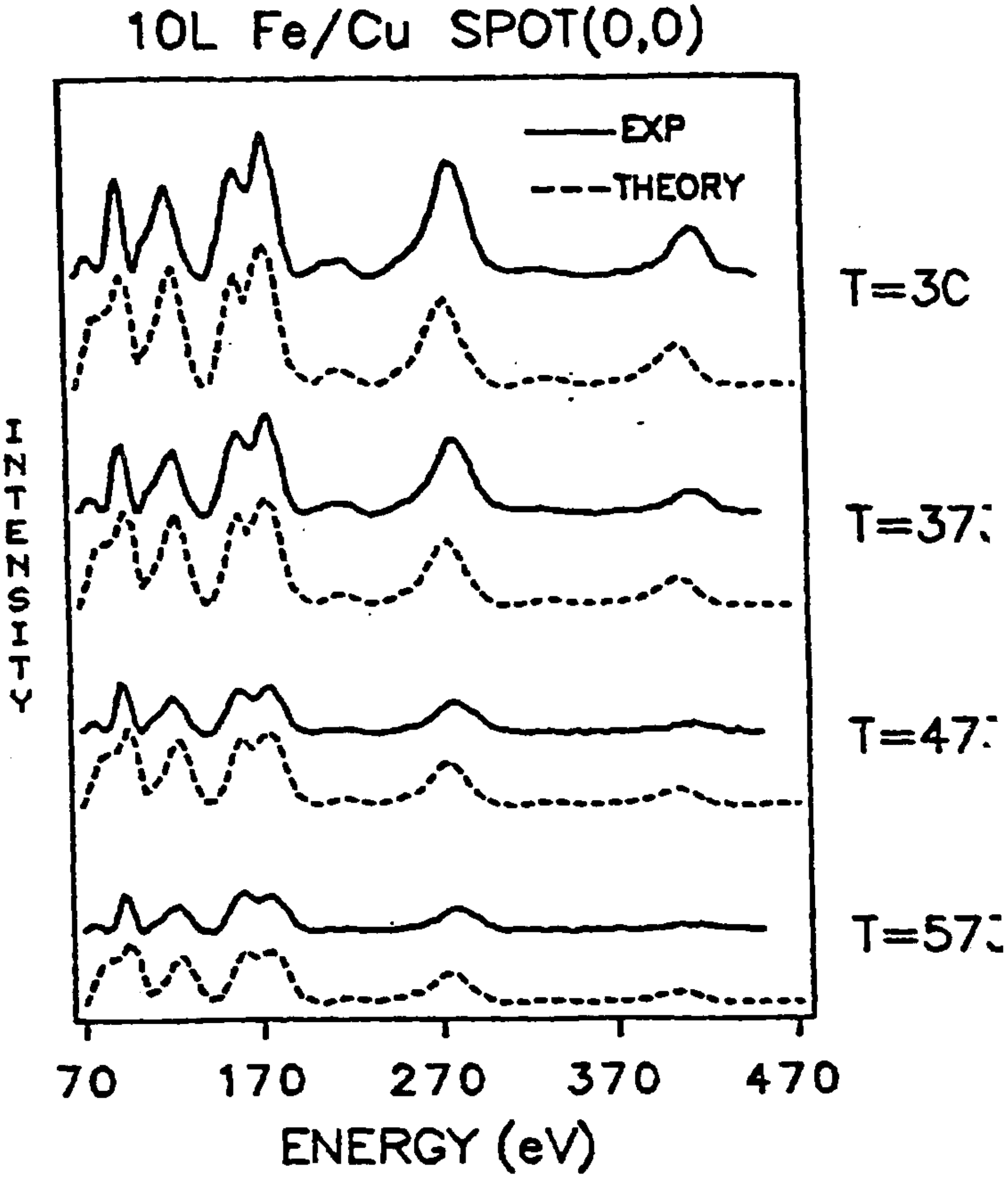
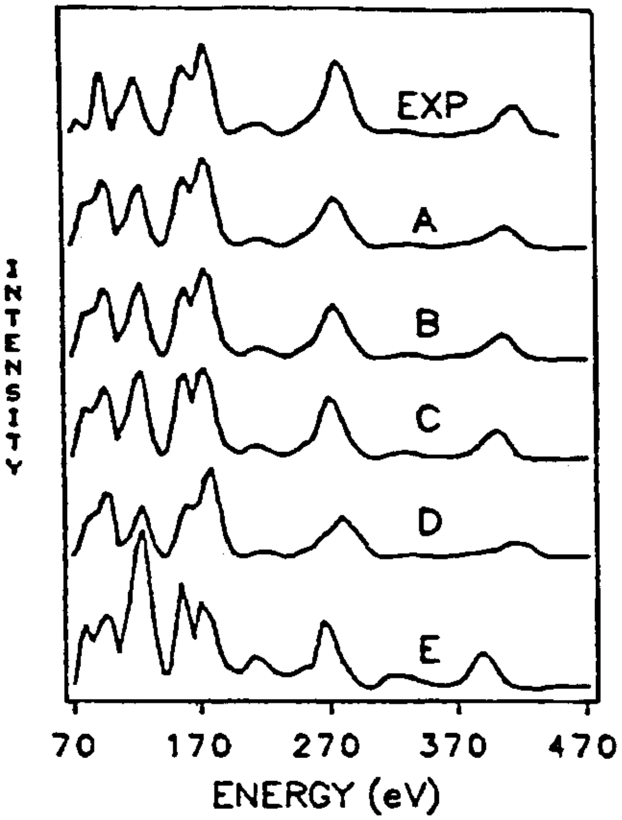
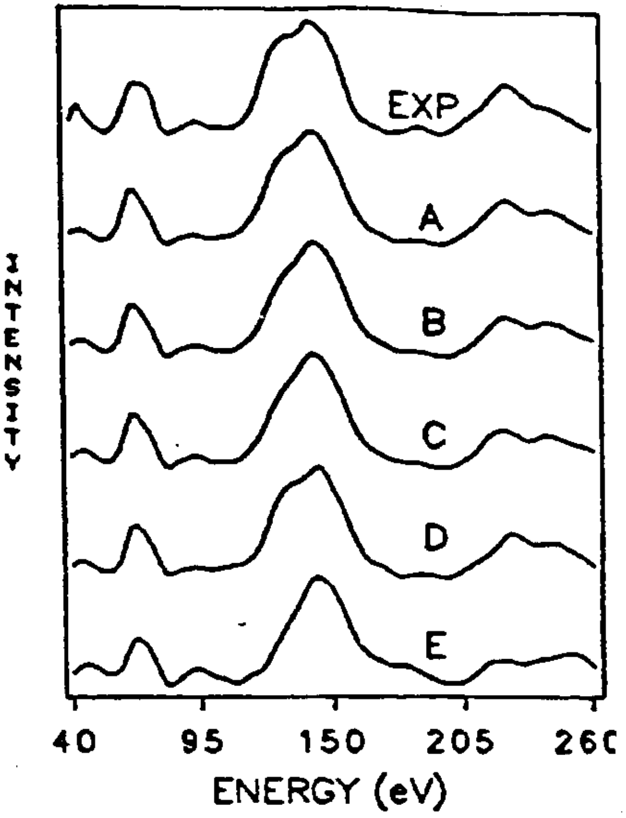
Fig 7


10L Fe/Cu SPOT(0,0)
EXP
THEORY
INTENSITY
T=30
T=37
T=47
T=57
70
170
270
370
470
ENERGY (eV)

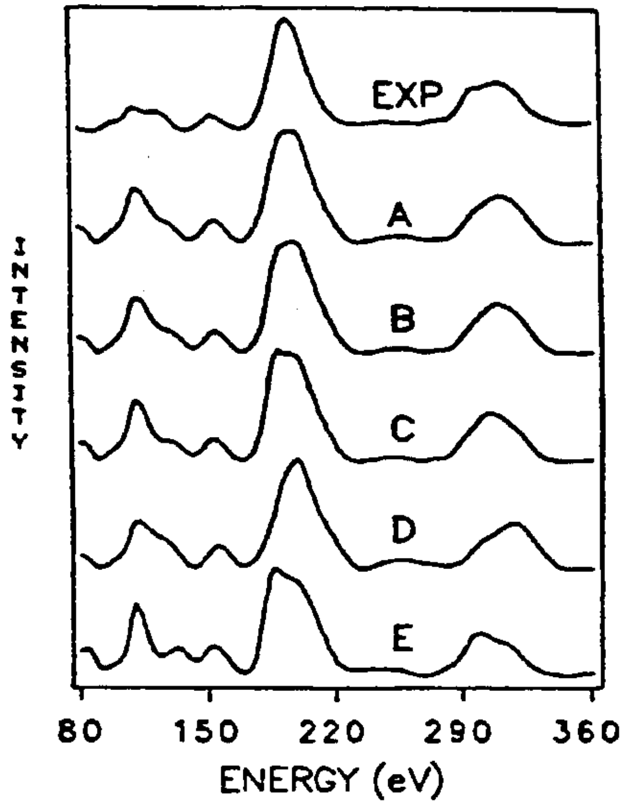
10L Fe/Cu SPOT(0,0)



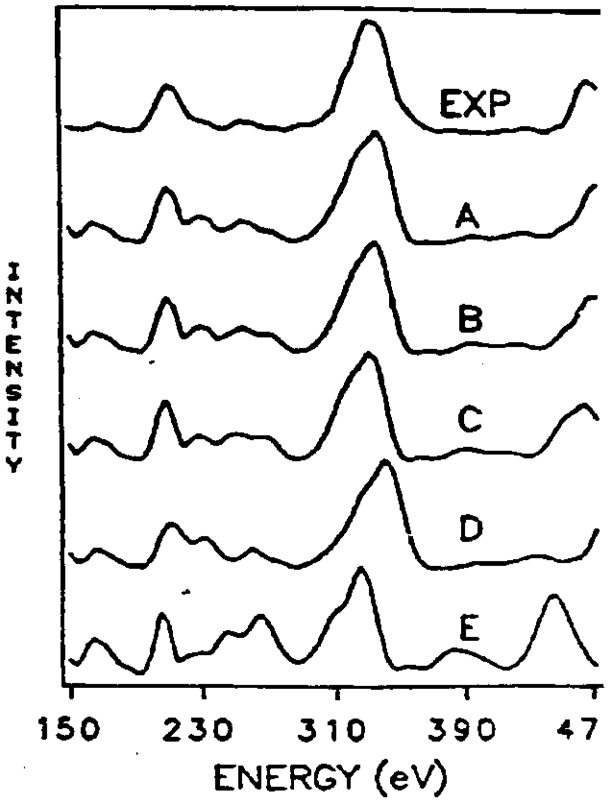
10L Fe/Cu SPOT(1,0)



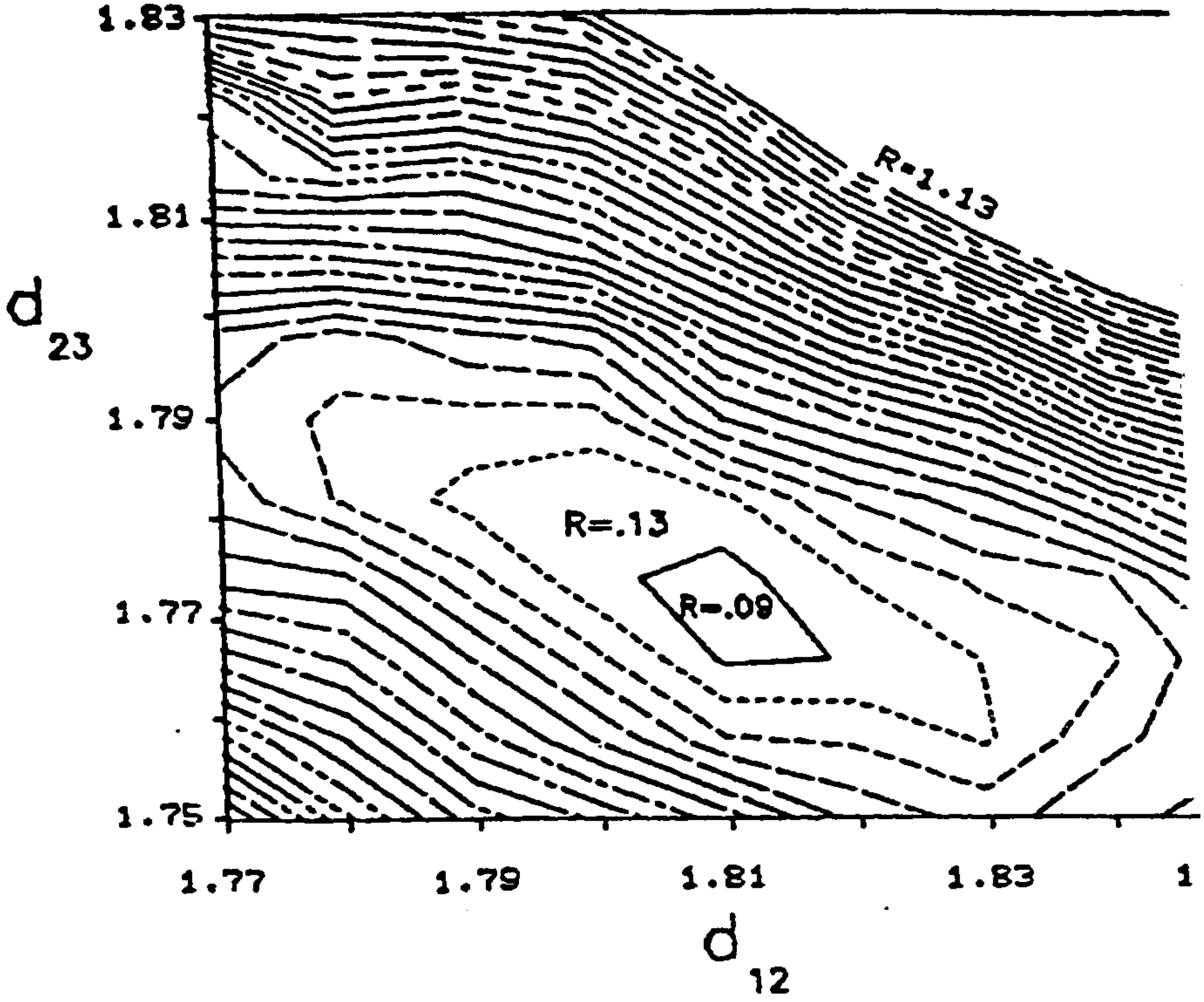
10L Fe/Cu SPOT(1,1)



10L Fe/Cu SPOT(2,0)



Reliability Factor



# 4. SURFACE ELECTRONIC BEHAVIOR OF Fcc IRON ON COPPER

(Quarterly Report July 16, 1986 - October 15, 1986)

## ABSTRACT

We have studied the electronic structure of fcc iron grown epitaxially on (100) copper with ultraviolet photoemission (UPS), surface magneto-optic Kerr effect (SMOKE), low energy electron diffraction (LEED) and self-consistent film linearized muffin-tin-orbital (FLMTO) calculations. This study identifies and explains novel characteristic UPS features of fcc iron and a substantial change in the work function compared to bcc iron. The SMOKE measurements show that fcc iron grown on copper has two metastable states lying close in energy. One of these is not ferromagnetic and occurs in growth at room temperature, while the other is ferromagnetic and occurs in growth at 190C. As shown by LEED, the ferromagnetic state has an (about 3%) expanded lattice constant; and UPS shows exchange splitting in that state.

## 1. Introduction

Understanding the mechanisms that select the crystal structures of the elements is one of the fundamental questions of solid state physics.[1] This is an especially interesting question for iron, since the structure (at atmospheric pressure) is bcc up to 910C, then undergoes a transition to fcc, before returning to a bcc structure at 1390C prior to melting. Since this indicates a small energy difference between the bcc and fcc structures, the intriguing possibility suggests itself of studying the energetics of formation of fcc iron by growing it epitaxially, essentially as a thick interface before reverting to bcc, on an appropriate fcc substrate.

The ability to prepare fcc iron films by epitaxial growth on a copper substrate has, in fact, been successfully demonstrated[2,3] in recent years. We report here UPS and work function measurements in coordination with self-consistent electronic structure calculations, and we report SMOKE measurements that unambiguously show[4] whether or not a sample is ferromagnetic. The electron emission spectroscopy (UPS) information, measured as a function of fcc iron thickness, can be related to the change in electronic structure and associated properties from that of bcc iron. To do this we have performed FLMTO calculations[5] for paramagnetic fcc iron and for a monolayer of fcc iron on copper, and these calculations are in excellent agreement with the UPS and work function measurements on the fcc iron on copper samples deposited at room temperature. Remarkable differences are observed between the electron distribution curves (EDC's) for fcc and bcc iron. A large difference in work function is measured between fcc iron and copper, in close agreement with the results of the self-consistent FLMTO calculations. Such strong differences in the surface properties should have important implications for the catalytic properties of fcc iron as compared to those for the standard bcc structure. The role of magnetic behavior in helping to stabilize one or another of the competing crystallographic structures is a central question.[6-9] The SMOKE measurements, supplemented by LEED and UPS, reveal a remarkable competition between two closely lying in energy metastable states of fcc iron on copper. SMOKE measurements on samples deposited at room temperature show that fcc iron thus deposited is not ferromagnetic at thicknesses from 1 to 17 layers. However, iron deposited at 190C shows ferromagnetism in coincidence with a substantial (3%) expansion. This is a transient phenomenon that disappears on cooling to room temperature.

## 2. UPS Measurements and Electronic Structure Calculations

To perform our measurements, we have grown fcc iron epitaxially on a Cu(100) crystal. The samples were characterized by Auger spectroscopy and low energy electron diffraction (LEED). For one monolayer of iron deposited at room temperature, a small relaxation was observed of the (iron-to-copper) interplanar distance, from 1.81Å (as occurs between Cu(100) planes) to 1.78Å. The substrate relaxation is negligible. Such a small interplanar relaxation is not surprising since the lattice parameters of fcc iron and copper are very close.[1,2] The results of the UPS measurements at room temperature are shown in Figure 1 as a function of iron coverage. The spectra were collected using a retarding field spectrometer (angular integrated measurements) and HeI (21.2 eV) radiation as a source. The work functions were determined from the width of the EDC.

We have carried out fully-warped all-electron self-consistent FLMTO electronic structure calculations[5] for: (1) five layers of fcc Cu(100), (2) five layers of fcc Fe(100), (3) a monolayer of Fe(100) on each side of a five layer slab of fcc Cu(100). Initially the Fe was taken to have the same lattice constant as fcc Cu (3.61Å), and the Fe overlayer sites were chosen as a continuation of the fcc Cu lattice. These nonmagnetic FLMTO calculations require only about 12 basis functions per atom to produce quality results.[5]

The experimental EDC's of iron grown epitaxially on the Cu(100) surface (see Figure 1) show markedly different features from those of bcc iron. The EDC's of Figure 1 show two peaks, at -1.3 and -3.4 eV (with respect to the Fermi energy, $E_F$) for iron coverages of 3 to 10 layers on Cu(100). The feature at 1.3 eV below $E_F$ is seen to grow sharply with higher Fe coverages. We believe this newly observed peak is characteristic of fcc iron having the same lattice constant as fcc Cu. In fact, our calculated fcc Fe sphere-projected density of states (DOS) curves in Figure 2 show a sharp peak located exactly at the same energy, and this DOS peak is sharpest in the center layer. Thus the experimental observations can be explained as follows. In the UPS experiment the electrons that are detected have a mean free path of about 5-8 Å, i.e., they are emitted from the first 4 or 5 layers below the surface. The experimental EDC is a measure of the combined (convoluted) sphere-projected DOS curves that are shown in Figure 2. Experimentally (Figure 1), at 1 overlayer coverage of Fe on Cu(100) the feature at 1.3 eV below $E_F$ is starting to appear. At 3-10 overlayer coverages of Fe, this feature is quite sharp, i.e., growth of more iron strengthens this peak. We were initially concerned that the peak at -1.3 eV was due to surface states and consequently performed measurements after exposure to small amounts of $O_2$ and CO. We did not observe any significant changes in peak intensity or position after such exposures, ruling out the possibility of surface states. Hence it cannot be a true surface iron feature, but should be present in the inner fcc Fe layers. This is exactly what is seen in the calculated fcc Fe DOS (Figure 2). The calculated peak at 1.3 eV below $E_F$ is sharpest in the center layer Fe atom and is present in all layers in excellent agreement with experiment. The experimental[10] EDC's and calculated[5] DOS of bcc iron do not show any sharp features around 1.3 eV below $E_F$, and hence this feature is definitely characteristic of fcc iron epitaxially grown on Cu(100).

In the calculated band structure of fcc Fe(100) we find portions of flat bands (predominantly $d_{x^2-y^2}, d_{z^2}$ in orbital character) along $\bar{\Gamma}\bar{X}$ in the vicinity of 1.3 eV below the Fermi level. These are the source of the observed density of states peak at this energy, and more than four-fifths of the calculated states along these carry over a 50% bulk (center + subsurface) weight, and none of those states contained a surface weight above 70%. Thus we conclude that the observed peak in DOS is not due to surface states. A combination of theory and experiment strongly suggests that the above peak in DOS of fcc iron is a bulk feature and it can be used to identify fcc iron from bcc iron. Kübler's[11] calculated bulk fcc Fe DOS also has a peak at a slightly lower energy than our result but we believe it is the same feature. This is the first report of experimental confirmation of this characteristic fcc iron feature.

The weak feature at 6 eV below $E_F$ in Figure 1, observed for thicker films, is probably associated with traces of oxygen on the surface; while the feature in the EDC's seen at around 3.4 eV below $E_F$ is mainly due to the Cu substrate, and corresponds to the sharp peak seen at about 3.2 eV below $E_F$ in all the sphere-projected DOS for Cu atoms in our calculation for a monolayer of fcc Fe on Cu(100) shown in Figure 3. Growth of fcc iron on copper diminishes and broadens this peak in the EDC's as seen in

Figure . This is in agreement with our expectations from the calculated DOS of Figures 2 and 3. As seen in Figure 3, for low Fe coverage, the features characteristic of fcc Fe DOS curves are not as sharp or as strong as the features of the Cu DOS around 3.2 eV below $E_F$; and hence the broadening and diminishing of the feature at 3.4 eV below $E_F$ in the EDC's is expected to occur with the growth of more fcc iron on Cu, where the EDC's reflect the convolution of the DOS of pure fcc Fe in Fig. 2.

As seen in Figure 3, for the monolayer of Fe-on-Cu system our calculated DOS shows that although the Cu substrate atoms near the surface undergo significant changes compared to the surface atoms in clean Cu (clean Cu DOS are shown as dashed curves in Figure 3), the surface Fe atoms do not undergo significant changes compared to surface atoms in clean fcc Fe. The narrowing of the surface Cu DOS seen in clean Cu disappears when a monolayer of fcc Fe is deposited on Cu(100). Center layer Cu DOS features in Fe-on-Cu (Figure 3) closely resemble those of the center layer pure Cu DOS, indicating the adequacy of the 5-layer substrate thickness. In fact, even one layer below the surface one can see the bulk features beginning to appear in the Cu DOS in Fe-on-Cu. Most of the changes seen in the substrate Cu atoms are quite similar to those seen in a FLAPW calculation[12] for Ni-on-Cu(100). Both Fe in Fe-on-Cu and Ni in Ni-in-Cu have a fairly strongly diminishing effect on the neighboring layer Cu atom DOS peak at 2 eV below $E_F$. This is likely to be associated with the onset of bonding between surface Fe (or Ni) and subsurface Cu atoms, thereby pushing the energy bands in this region to higher bonding energies. The peaks in both surface Fe and subsurface Cu in the range 3.2-4.0 eV below $E_F$ in Fe-on-Cu correspond to these bonding states that have dropped to higher bonding energies.

We have also calculated the sphere-projected density of states for a monolayer of fcc iron on (100) copper with the iron-to-copper interplanar distance decreased (relaxed) by 2% compared to the system shown in Figure . There is essentially no change in the DOS from that of Figure 3. The calculated work function for the unrelaxed system is 5.58 eV, while that for the relaxed system is 5.48 eV. This latter value is virtually identical to the work function for the (100) 5-layer fcc iron slab of Figure 2, 5.45 eV. Our earlier calculated results$^5$ for (100) bcc iron and for (100) fcc copper were 4.77 and 4.93 eV respectively.

Experimentally, a remarkable increase in the work function of fcc iron deposited at room temperature is observed as compared to Cu(100) in close agreement with the predictions of the calculations as given above. We measure a work function of 5.5±0.1 eV for one monolayer of iron. The value for the Cu(100) face work function oscillates between 4.6 and 4.7 eV. The value for 0.5 monolayer of iron on Cu(100) is 5.3±0.1 eV; while for more than a monolayer the value remains around 5.4 eV. A word of caution is necessary concerning the work function measurements. We observed a decrease in work function as a function of time. After one hour, a smaller value of 4.5 eV is measured for fcc iron. We attribute the phenomenon to a reaction with residual gases in the vacuum system, due in great part to the high reactivity of the iron surface.

Our calculated electron density maps help explain the significant work function change seen theoretically and experimentally. When an Fe monolayer is deposited on the Cu substrate as here, the electron density in the surface region is clearly seen to increase, which strengthens the surface dipole barrier giving rise to an increase in the work function. The Fe orbitals which are less spatially localized compared to Cu, and the stretched, near surface Cu orbitals are responsible for the above change.

## 3. Magnetic State and SMOKE Results

The question of whether the fcc iron on copper is ferromagnetic was first investigated for the samples discussed above deposited at room temperature, and then for samples deposited at 190C. First, SMOKE was employed to detect the presence or absence of ferromagnetism at room temperature. The SMOKE results show the absence of ferromagnetism up to about 17 layers of iron, i.e., no hysteresis loop is detected. At 19 layers of iron on Cu(100) the SMOKE scans clearly showed the presence of ferromagnetism. This coincides with the appearance of bcc iron as observed by LEED measurements. From the SMOKE measurements we conclude that throughout the thicknesses observed (1 to 17 layers), fcc iron deposited on copper at room temperature does not show ferromagnetism. However, when iron is deposited on the substrate at 190C, measurements of the EDC at this temperature show evidence of a splitting of the d-bands (about 0.5 eV, see Figure 4). It is observed that the EDC changes when the sample is cooled down to room temperature and does not return to its original spectrum when heated back to 190C. SMOKE measurements, as shown in Fig. 5, performed on such samples deposited at 190C show the same behavior for various coverages of iron, i.e., the presence of ferromagnetism at 190C and its disappearance at room temperature. It is noted that the ferromagnetism disappears also as a function of time at 190C. (In about one hour the SMOKE signal disappears; a similar result is obtained in the UPS measurements.)

We believe that the appearance of ferromagnetism is related to changes in the volume due to lattice expansion on deposition at 190C (3% expansion in lattice constant), but that eventually the elastic strains force the fcc iron to relax to its nonferromagnetic ground state. For bulk fcc iron, theory has predicted[6-8] a low moment to high moment transition with increasing volume; and recent theoretical work of Moruzzi et al[8] suggests the possibility of having two metastable states lying close in energy, but with different (high and low) magnetic moments. The present experimental results, with contrasting behavior for deposition at room temperature and at 190C, support a similar picture. However, more experimental and theoretical work on the magnetic state of fcc grown on Cu(100) is necessary to understanding this interesting behavior.

## 4. Summary

In summary, we have shown that fcc iron can be epitaxially grown to a many-layer thickness on a copper (100) substrate, and that spectroscopic features characteristic of fcc iron can be definitely identified. The location in energy, and change with iron thickness, of these photoemission EDC peaks is exactly as expected on the basis of self-consistent electronic structure calculations; and the change in work function (at room temperature) from copper is in close agreement with that calculated. Furthermore, magneto-optical (SMOKE) measurements, together with LEED and UPS measurements, show that there are two closely lying metastable states. fcc iron grown on copper at room temperature has a non-ferromagnetic state, while that grown at 190C adopts an expanded ferromagnetic state.

Acknowledgments:

This research has been supported by the U. S. Department of Energy and the West Virginia University Energy Research Center. H. M. Naik was supported in part by a Research Grant from AMOCO. We are indebted to the Center for Materials Science at Los Alamos National Laboratory for supplying time on a Cray 1 computer. Y. N. Darici, J. M. Marcano, and H. Min have provided valuable assistance in characterizing the samples.

## References

1. The Structures of the Elements, J. Donohue, John Wiley and Sons, New York, 1974.
2. U. Gradmann and P. Tillmanns, Phys. Stat. Sol. (a) 44, 539 (1977).
3. W. Wiartolla, W. Becker, W. Keune, and H. D. Pfannes, J. de Physique 45, C5-461 (1984).
4. S. D. Bader, E. R. Moog, and P. Grunberg, J. Mag. Magn. Mater. (in press).
5. G. W. Fernando, B. R. Cooper, M. V. Ramana, H. Krakauer, and C. Q. Ma, Phys. Rev. Lett. 56, 2299 (1986).
6. C. S. Wang, B. M. Klein, and H. Krakauer, Phys. Rev. Lett. 54, 1852 (1985).
7. O. K. Andersen, J. Madsen, U. K. Poulsen, O. Jepsen, and J. Kollar, Physica 86-88B, 249 (1977).
8. V. L. Moruzzi, P. M. Marcus, K. Schwarz, and P. Mohn, Phys. Rev. B34, 1734 (1986).
9. D. Bagayoko and J. Callaway, Phys. Rev. B28, 5419 (1983).
10. L. G. Peterson, R. Melander, D. P. Spears, and S. B. M. Hagstrom, Phys. Rev. B14, 4177 (1976).
11. J. Kübler, Phys. Lett. 81A, 81 (1981).
12. D. Wang, A. J. Freeman, and H. Krakauer, Phys. Rev. B26, 1340 (1982).

## Figure Captions

**Fig. 1.** Electron distribution curves (EDC's) showing relative number of electrons emitted (in arbitrary units, A.U.) as a function of energy (in eV), relative to the Fermi energy, for iron on copper (100). The numbers indicate the number of layers (ML) of iron on copper (100).

**Fig. 2.** Sphere-projected density of states (DOS) for a system consisting of a five-layer (100) slab of fcc Fe. The lattice constant has been taken as that of Cu. These curves have been smoothed by a Gaussian of full width at half maximum (FWHM) of 0.3 eV. The calculated work function for this system is 5.45 eV.

**Fig. 3.** Solid curves show sphere-projected density of states (DOS) for a system consisting of one layer of Fe on either side of 5 layers of Cu(100). The lattice constant for the entire 7-layer slab is taken as that of bulk Cu. (Dashed curves show DOS for 5-layer clean Cu(100).) Smoothing is as in Fig. 2. The calculated work function for this (unrelaxed) Fe-on-Cu system is 5.58 eV.

**Fig. 4.** EDC's on 5 layers of fcc iron on Cu(100) at 190C (top) and after cooling to 50C.

Fig. 5(a). SMOKE signal (magneto-optic reflected intensity) for iron-on-copper deposited at 186C. Presence of hysteresis unambiguously shows the presence of ferromagnetism.

(b). Behavior of sample in (a) on cooling to 96C in situ.

(c). Behavior of same sample on reheating to 190C in situ.

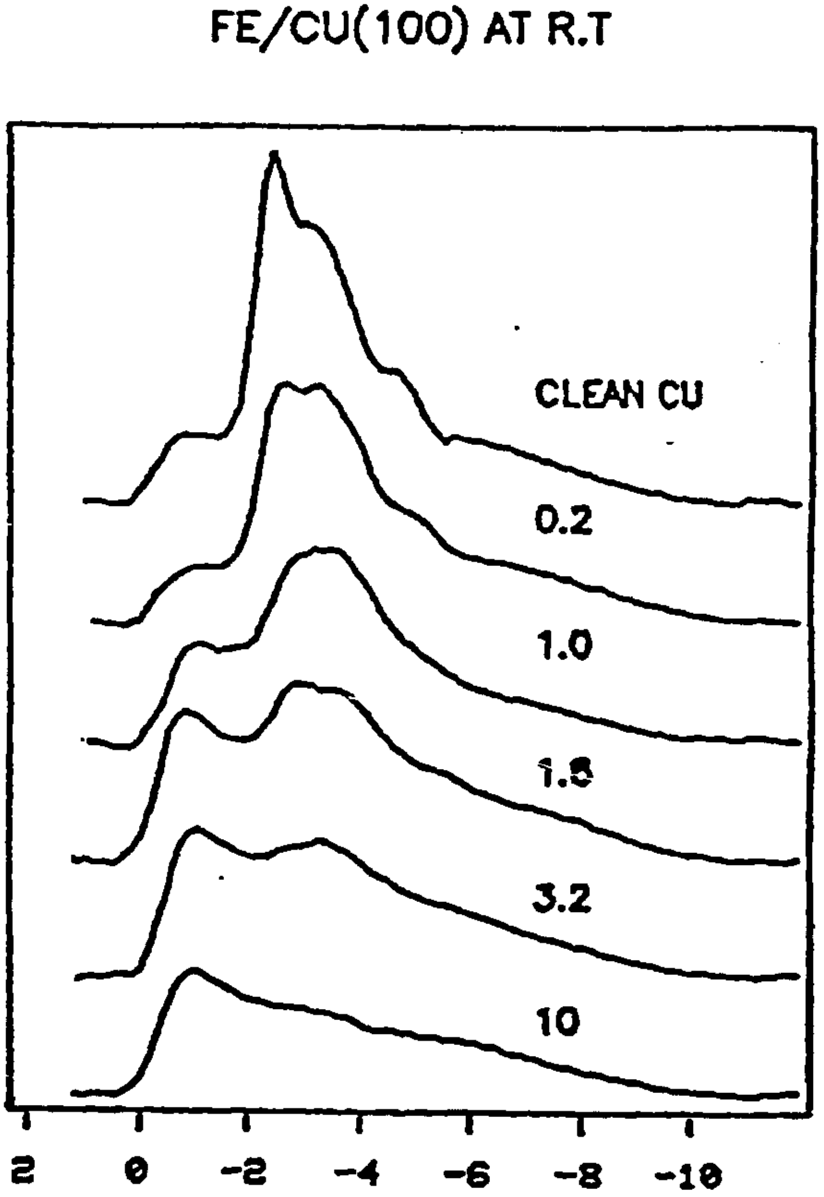


Fig. 1.

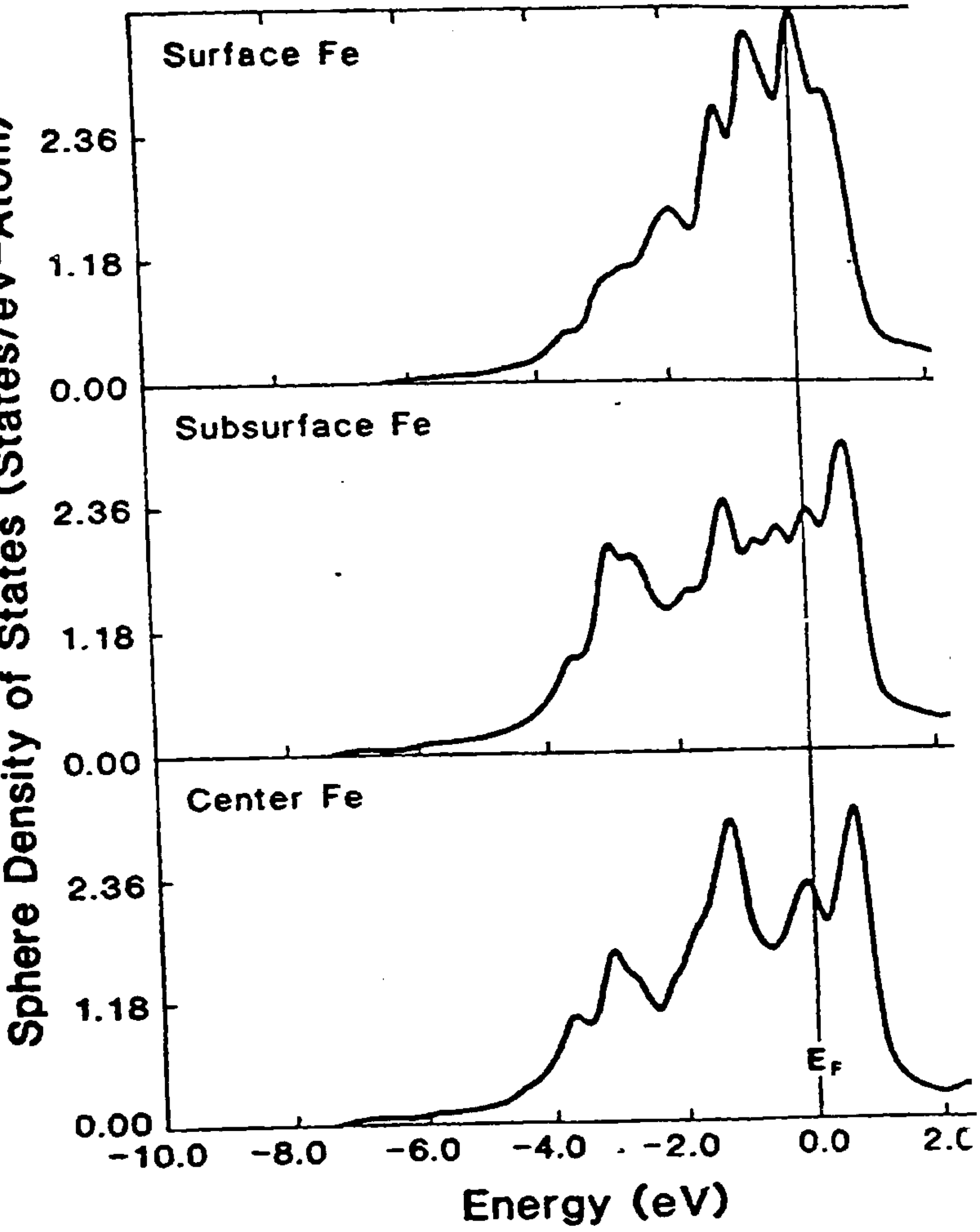

Surface Fe
Subsurface Fe
Center Fe
Sphere Density of States (States/eV–Atom)
2.36
1.18
0.00
2.36
1.18
0.00
2.36
1.18
0.00
−10.0
−8.0
−6.0
−4.0
−2.0
0.0
2.C
Energy (eV)
$E_F$

Fig. 2

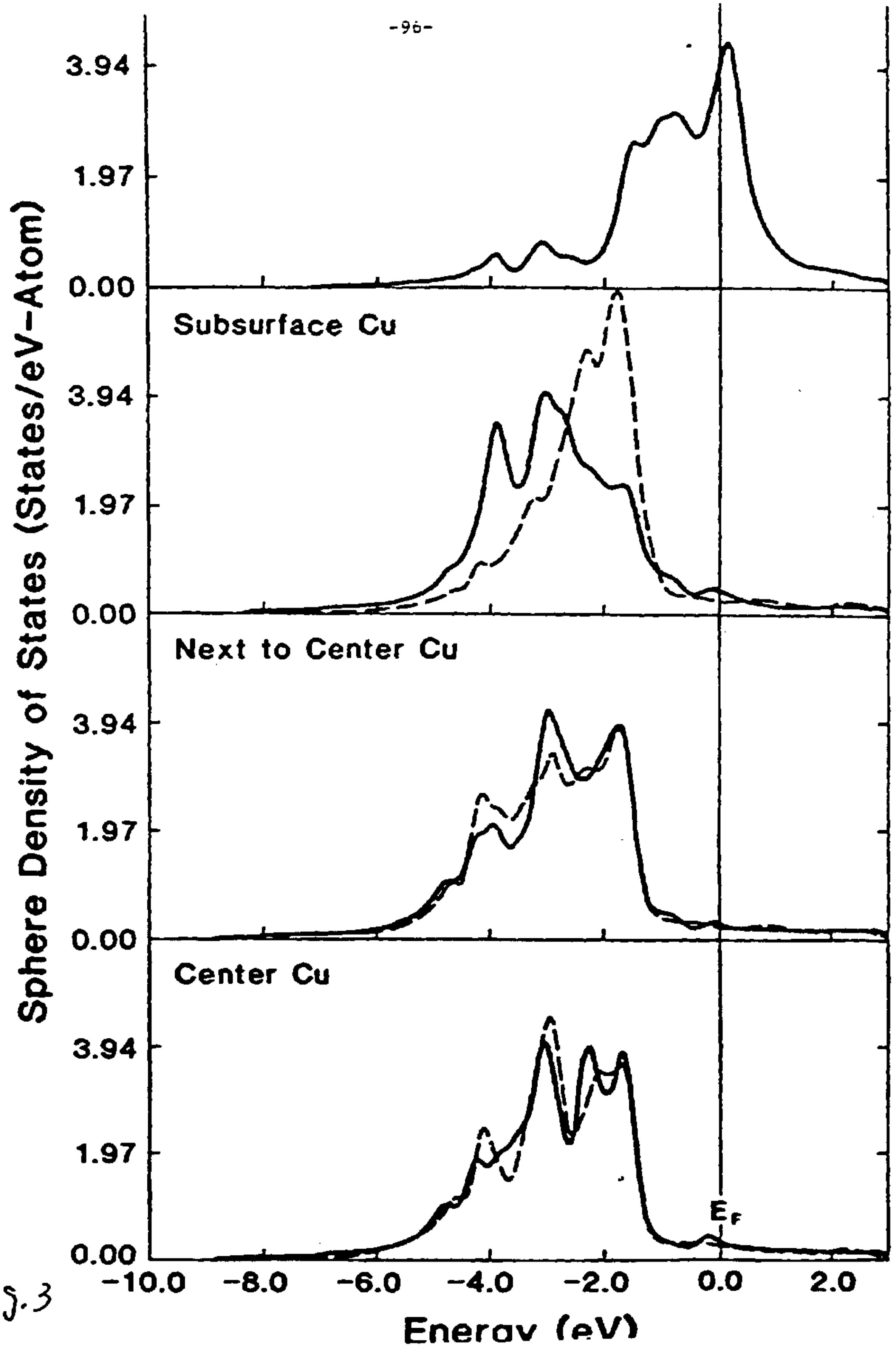

3.94
1.97
0.00
Subsurface Cu
3.94
1.97
0.00
Next to Center Cu
3.94
1.97
0.00
Center Cu
3.94
1.97
0.00
Sphere Density of States (States/eV–Atom)
$E_F$
−10.0
−8.0
−6.0
−4.0
−2.0
0.0
2.0
Energy (eV)

Fig.3