Two Magnetically Different, Closely Lying States of fcc Iron Grown on Copper (100)

Pedro A. Montano,[1,4] Gayanath W. Fernando,[1,5] Bernard R. Cooper,[1,3] E. R. Moog,[2] H. M. Naik,[2] S. D. Bader,[2] Y. C. Lee,[1] Y. N. Darici,[1] H. Min,[1] and J. Marcano[1]

[1]*Department of Physics, West Virginia University, Morgantown, West Virginia 26506*

[2]*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

[3]*Center for Materials Sciences, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

[4]*Department of Physics, Brooklyn College, City University of New York, Brooklyn, New York 11210*

[5]*Physics Department, Brookhaven National Laboratory, Upton, New York 11973*

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Two closely lying (in energy) states of fcc iron grown on copper (100) have been identified by magneto-optic and photoemission experiments. The as-grown state at 460 K exhibits in-plane surface ferromagnetism in magneto-optic measurements. Ferromagnetism parallel to the plane is not observed for the room-temperature state; its absence is supported by a comparison of our calculated and measured work functions and by the photoemission results. LEED shows expanded interplanar spacing at the surface. The temperature behavior and effect of fresh iron deposition indicate that the thermal transition between the two states is first order.

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Understanding the mechanisms that select the crystal structures of the elements is one of the fundamental questions of solid-state physics. This is especially interesting for iron because of the question of the "competition" between bcc and fcc structures and the role of magnetism in this competition. The ability[1,2] to prepare fcc iron films by epitaxial growth on copper has provided the opportunity to study directly the electronic structure of fcc iron.[3-5] Interestingly, quite conflicting conclusions have been reached as to the magnetic state of fcc iron grown on Cu(100).[3,4]

We have identified and characterized two closely lying (in energy) states of fcc iron grown on copper (100). On state (state L) has no ferromagnetism parallel to the surface and occurs at room temperature. The documentation for the nature of state L consists of the observations that the surface magneto-optic Kerr effect[6] (SMOKE) gives vanishing intensity (no hysteresis characteristic of ferromagnetism parallel to the surface) and that the work function increases relative to Cu. The work-function increase shows the same trend as that predicted by our self-consistent electronic-structure calculations for paramagnetic fcc iron relative to Cu or to bcc Fe or magnetically ordered fcc Fe. The second state (state H) is ferromagnetic and occurs when the sample is kept at its growth temperature (420–460 K); however, the experimental behavior indicates that the ferromagnetism is confined to the surface layer. This is consistent with our spin-polarized electronic-structure calculations which indicate the existence of a magnetically ordered state with ferromagnetism at the surface, but antiferromagnetism in the interior. The documentation for the ferromagnetic nature of state H consists of (a) a significant SMOKE intensity (hysteresis) identifying ferromagnetism parallel to the surface at 460 K, (b) a decreased work function compared with state L, consistent with the calculated trend predicted for magnetically ordered as compared with paramagnetic fcc iron, and (c) an indication of the presence of exchange splitting, shown by the ultraviolet photoemission spectroscopy (UPS) behavior at 460 K. Below we give a detailed description of this study and relate our results to those of other workers.

The absence of ferromagnetism parallel to the surface at room temperature was definitively recognized by the absence of any SMOKE intensity throughout the thickness range of about twenty layers where the iron grew in the fcc structure. (The SMOKE geometry used detects ferromagnetism parallel to the surface.) At greater iron thicknesses, when the structure reverts to bcc, we detect the presence of ferromagnetism through the occurrence of SMOKE intensity. Furthermore, the absence of detectable exchange splitting in the energy distribution curves (EDC's) in angular-integrated UPS measurements is consistent with the absence of *any* magnetic ordering. The UPS results (using HeI radiation, 21.2 eV) at room temperature are shown in Fig. 1 as a function of iron coverage.[5]

We have carried out fully warped, all-electron, self-consistent, film linearized muffin-tin orbital (FLMTO) electronic-structure calculations[7] for five layers of (100) fcc iron using the Cu lattice constant. The calculations are for both paramagnetic and spin-polarized states using 28 k points in the irreducible $\frac{1}{8}$ of the Brillouin zone. The calculated density of states (DOS) in the different layers of the five-layer paramagnetic (100) fcc iron slab (solid curves), as well as of a five-layer slab of paramagnetic bcc iron (dashed curves), are shown in Fig. 2.

The UPS EDC's (see Fig. 1) show markedly different features from those[8] of bcc iron. The EDC's show peaks at -1.1 and -3.2 eV for iron coverages of three to ten layers. The 3.2-eV peak is clearly due to Cu, and, as expected, diminishes and broadens with iron coverage. In

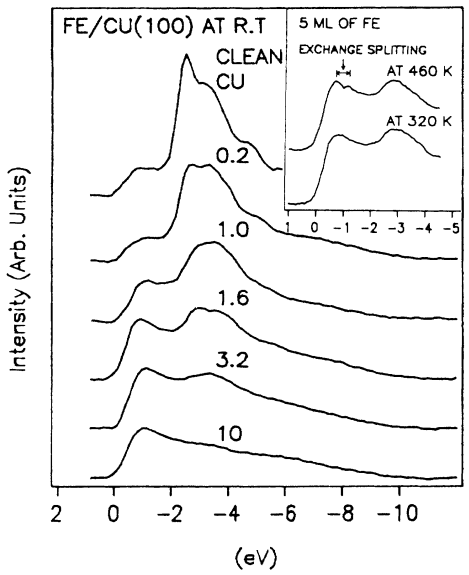

FIG. 1. Electron distribution curves showing relative number of electrons emitted (in arbitrary units) as a function of energy (in eV), relative to the Fermi energy, for iron on copper (100). The numbers indicate the number of monolayers (ML) of iron on copper (100). Inset: Energy distribution curves (EDC's) for five layers of fcc iron on Cu(100) at 460 K (top) and after cooling to 320 K (bottom).

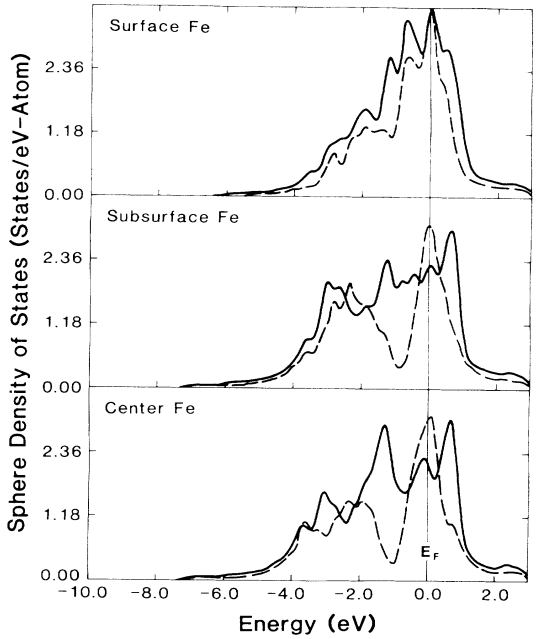

FIG. 2. Comparison of sphere-projected density of states (DOS) for *paramagnetic* (solid curves) fcc and (dashed curves) bcc iron. Solid curves: Sphere-projected (DOS) for a system consisting of a five-layer (100) slab of paramagnetic fcc Fe. The lattice constant has been taken as that of Cu. These curves have been smoothed by a Gaussian of FWHM of 0.3 eV. The calculated work function for this system is 5.3 eV. Dashed curves: DOS of a five-layer (100) slab of paramagnetic bcc Fe. The calculated work function for this system is 4.8 eV.

marked contrast, the feature at 1.1 eV below E_F is seen to grow sharply with higher Fe coverages. This feature is not due to surface states; no significant changes in peak intensity or position after O_2 and CO exposures were observed. This 1.1-eV peak is characteristic of fcc iron having approximately the same lattice constant as fcc Cu. Our calculated fcc Fe sphere-projected DOS curves in Fig. 2 show a sharp peak located quite close to the same energy, and this DOS peak is sharpest in the center layer. Kubler's[9] calculated bulk fcc Fe DOS has a peak at a slightly lower energy than our result, but we believe that it is the same feature. Neither the experimental[8] EDC's nor the calculated[7] DOS of bcc iron shows any sharp features around 1.1 eV below E_F. (The weak feature at 6 eV below E_F in Fig. 1, observed for thicker films, is probably associated with traces of oxygen on the surface.)

The calculated work function for the paramagnetic fcc iron slab of Fig. 2 is 5.3 eV. Our earlier calculated results[7] for (100) paramagnetic bcc iron and for (100) fcc copper were 4.8 and 4.9 eV, respectively. We have also calculated the electronic structure for a spin-polarized five-layer fcc iron slab. The work function predicted for the magnetically ordered state is lower: 5.1 eV. [Our calculated work function for ferromagnetic bcc Fe(100) is 4.6 eV.]

Experimentally, an increase in the room-temperature work function (determined from the width of the EDC's) of fcc iron is observed, as compared with Cu(100), consistent with the predictions of the calculations for paramagnetic fcc iron. We measure a work function of 5.5 ± 0.1 eV for one monolayer of iron. [For Cu(100) the work function is 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. Our calculated electron-density maps help explain the work-function change when an Fe monolayer is put on the Cu substrate. The Fe orbitals which are less spatially localized compared with Cu and the stretched, near-surface Cu orbitals strengthen the surface dipole barrier, giving rise to the increase in the work function.

There is an indication of the presence of a small splitting of the *d* bands of about 0.5 eV at the as-deposited temperature 460 K (inset in Fig. 1), in contrast to the lack of such features at room temperature.[10] The splitting disappears on cooling to lower temperature (shown for cooling to 320 K in the inset to Fig. 1) and does not return upon heating back to 460 K. The appearance of this feature was observed reproducibly in numerous experiments. (By itself it does not provide conclusive evidence of ferromagnetism. Such conclusive evidence is

provided by SMOKE measurements.) The work function at 460 K for a freshly grown film is 4.9–5.0 eV, a decrease from its room-temperature value. This is in close agreement with our calculated value for the magnetically ordered state of fcc iron; however, one should bear in mind that the work function is, in any case, normally expected to decrease with increasing temperature. *The presence of ferromagnetism in the as-grown 460-K fcc iron on (100) copper was unequivocally identified by SMOKE measurements as shown in the upper and middle panels of Fig. 3.* There is a well-defined hysteresis[11] at 460 K as opposed to the absence of a hysteresis at lower temperatures such as 300 K, as shown in the lower panel of Fig. 3. As the temperature is lowered, say to 370 K, the SMOKE signal abruptly disappears and does not return when the sample is reheated to 460 K. The Auger spectra before and after the runs at 460 K do not show any increase in contaminants during and after cooling to room temperature.

The interplanar spacing behavior as found by LEED is quite unusual. The LEED measurements involve intensity versus energy (I-E) determination on thirteen spots. Multiple relaxation of the top three layers was allowed. For five layers of Fe on Cu(100) at room temperature, we find an interplanar distance of 1.81 Å for the top layer compared with 1.78 Å for fcc iron within the bulk, i.e., a surface interplanar expansion of about 1% or 2%. At 460 K, the surface interplanar spacing further increases to 1.83 Å, an expansion of an additional 1%. The intraplanar spacing remains equal to that of the Cu substrate.

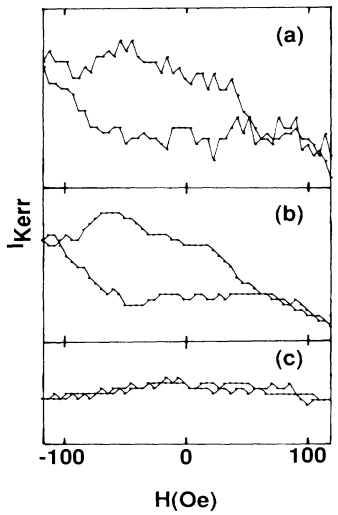

FIG. 3. (a) SMOKE ferromagnetic hysteresis loop at 460 K from three layers of Fe on (100) Cu grown at 460 K. (b) Average of eleven hysteresis loops on different runs from Fe films two and three layers thick, grown at 420 and 460 K and measured at $\geq 360\,^{\circ}$C. As shown in (c), the ferromagnetism disappears irreversibly upon cooling or after about an hour. (c) The eleven scans averaged after the ferromagnetism has disappeared.

There is strong evidence that the ferromagnetism at 460 K is confined to the surface fcc iron layer. When the SMOKE intensity disappears with time,[11] the SMOKE signal can be restored by fresh deposit of a single layer of iron. Furthermore, the SMOKE intensity does not vary with fcc iron thickness and corresponds to a monolayer-type signal level when compared with previous bcc-Fe-on-Au SMOKE measurements.[6]

It is interesting to consider this evidence for surface-only ferromagnetism in relationship to the results of our spin-polarized self-consistent LMTO calculations for a five-layer slab of fcc iron. The spin-polarized fcc-iron calculation was started by use of the self-consistent paramagnetic potential with an artificial spin polarization favoring ferromagnetic coupling between all layers. However, the final self-consistent result shows ferromagnetic alignment between the surface ($2.79\mu_B$) and subsurface ($2.30\mu_B$) moments, but the center-layer moment ($1.68\mu_B$) is aligned antiferromagnetically to the subsurface moment. This would indicate surface ferromagnetism coupled to bulk antiferromagnetism. The total energy for the magnetically ordered state is about 0.100 Ry below that for the paramagnetic state (our of some 12705 Ry).

In conclusion, the results reported above show that fcc iron as grown on (100) copper "chooses" between two states that lie close in energy. Both states show an unusual interplanar expansion at the surface. The work-function increase relative to copper observed for the lower-energy state (state L), and the photoemission evidence for decreased or vanishing exchange splitting suggests that state L is paramagnetic, rather than ferromagnetic with alignment perpendicular to the surface. If this is so, either there is a transition at lower temperature to the theoretically predicted magnetically ordered ground state, or having such a paramagnetic state as the experimental ground state would contradict the results of our zero-temperature total energy calculations (based on the local spin-density approximation). While the present calculations are for uniform interplanar spacing, one would expect expanded surface spacing to favor the magnetically ordered state even more.[12,13] The surface layer in the higher-energy state (state H) is ferromagnetic parallel to the surface. There is strong evidence that the thermal transition from state H to state L is first order. This is shown by the abrupt disappearance of the SMOKE signal on cooling, the failure to restore the ferromagnetism after cooling by cycling back up in temperature, and the ability to restore the ferromagnetism by deposition of iron at elevated temperature. The time decay[11] of the SMOKE intensity and of the exchange splitting provides evidence that state H, which is observed under as-grown conditions at 460 K, is *metastable* with respect to state L at that temperature. This could be characteristic of a metastable situation created by

growth conditions, e.g., by growth-induced strains which relax in time. For bulk ferromagnetic fcc iron, theory has predicted[12-14] a low-moment to high-moment transition with increasing volume. Moruzzi[13] has emphasized that the moment cannot show a gradual decrease to zero moment with decreasing volume. This would be consistent with great magnetic sensitivity to growth-induced strains, which may be strongly modifying the surface magnetic moment in magnitude and/or preferred alignment direction.

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[1]U. Gradmann and P. Tillmanns, Phys. Status Solidi (a) **44**, 539 (1977).

[2]W. Wiartolla, W. Becker, W. Keune, and H. D. Pfannes, J. Phys. (Paris), Colloq. **45**, C5-461 (1984).

[3]A. Amiri Hezaveh, G. Jennings, D. Pescia, R. F. Willis, K. Prince, M. Surman, and A. Bradshaw, Solid State Commun. **57**, 329 (1986).

[4]M. F. Onellion, C. L. Fu, M. A. Thompson, J. L. Erskine, and A. J. Freeman, Phys. Rev. B **33**, 7322 (1986).

[5]Sample preparation and characterization was as described by Y. C. Lee, H. Min, and P. A. Montano, Surf. Sci. **166**, 391 (1986).

[6]S. D. Bader, E. R. Moog, and P. Grunberg, J. Magn. Magn. Mater. **53**, L295 (1986).

[7]G. W. Fernando, B. R. Cooper, M. V. Ramana, H. Krakauer, and C. Q. Ma, Phys. Rev. Lett. **56**, 2299 (1986); C. Q. Ma, M. V. Ramana, B. R. Cooper, and H. Krakauer, Phys. Rev. B **34**, 3854 (1986).

[8]L. G. Peterson, R. Melander, D. P. Spears, and S. B. M. Hagstrom, Phys. Rev. B **14**, 4177 (1976).

[9]J. Kubler, Phys. Lett. **81A**, 81 (1981).

[10]References 3 and 4 both report angle-resolved photoemission for Fe on Cu(100). They differ as to the evidence for exchange splitting and, hence, ferromagnetism at room temperature. Reference 4 reports ferromagnetism, and Ref. 3 reports that no ferromagnetism is present.

[11]The splitting is a transient phenomenon, disappearing in a period of about 1 h. The SMOKE experiments also show the transient effect; the hysteresis indicative of ferromagnetism disappears in about 1 h.

[12]C. S. Wang, B. M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985).

[13]V. L. Moruzzi, Phys. Rev. Lett. **57**, 2211 (1986); V. L. Moruzzi, P. M. Marcus, K. Schwarz, and P. Mohn, Phys. Rev. B **34**, 1784 (1986).

[14]O. K. Andersen, J. Madsen, U. K. Poulsen, O. Jepsen, and J. Kollar, Physica (Amsterdam) **86B-88B**, 249 (1977).