Local spin correlations in ultrathin Fe/W(100) films

G. A. Mulhollan, R. L. Fink, J. L. Erskine, and G. K. Walters*
Physics Department, University of Texas at Austin, Austin, Texas 78712
(Received 1 August 1990)

The temperature dependence of the valence-band energy-distribution curves of ultrathin Fe/W(100) films has been measured with use of spin- and angle-resolved photoemission. Majority and minority features at $\bar{\Gamma}$ are stationary with increasing temperature; apparent peak broadening is caused by the emergence of "extraordinary" peaks. Comparison with a cluster calculation suggests that short-range ferromagnetic order ~ 4 Å exists above T_C in the 1.5-monolayer film.

The study of phase transitions in quasi-two-dimensional systems plays a central role in modern surface physics.[1] A dominant theme is the attempt to understand the link between the short-range microscopic interactions and their long-range macroscopic manifestations. One technique is to map the valence-band structure as a characteristic order parameter, e.g., the magnetization, tends to zero. The first work of this type was done by Eastman, Himpsel, and Knapp on a (bulk) Ni(111) surface using angle-resolved photoemission.[2] The observed departure of the d-band splitting from the functional form of $M(T)$ is a subject that has received much scrutiny to date.[3–6] Progress in the synthesis of ultrathin magnetic films has provided the means to approach this issue anew. The lower critical temperatures of these quasi-two-dimensional systems permit access to the magnetic phase transitions without the ancillary problems of contaminant segregation to the surface common in studies of bulk materials. However, since truly two-dimensional freestanding ferromagnetic films will probably never be realized, it becomes necessary to understand effects due to substrate-overlayer interactions.

The characteristics of thin ferromagnetic films which are responsible for the ground-state ($T=0$) properties, e.g., reduced atomic coordination, manifest themselves also in the properties of such systems at elevated or finite temperatures. In particular, the Curie temperature T_C, at which the spontaneous magnetization disappears, depends strongly on the specific boundary conditions involved.[7,8] Simply put, the thermodynamic correlation, ξ, diverges as $T \rightarrow T_C$ inasmuch as system finiteness permits.[9] Lengths characterizing short-range order (SRO), however, are nearly temperature independent above T_C.[10] The modification of these correlation lengths via substrate-overlayer band hybridization is a topic that has only been investigated to date in a Ni(111)/W(110) overlayer system.[6] The results of that study were inconclusive in determining the degree of SRO present in the Ni overlayers.

In this light, the Fe/W(100) system has a number of interesting characteristics. Thermal desorption, low-energy electron diffraction (LEED) and Auger studies have shown Fe grows on the W(100) and W(110) surfaces in a pseudomorphic, thermodynamically stable way at the monolayer (ML) level.[11,12] Our surface magneto-optic Kerr effect (SMOKE) studies of Fe/W(100) have evinced dramatic adsorbate-induced effects on the macroscopic magnetization.[13] Furthermore, total-energy ground-state calculations predict a strong degree of hybridization between monolayer Fe overlayers and W substrates.[14] Thus Fe/W(100) is a prime candidate for studying substrate-induced critical behavior modifications.

An electron-beam cell was used to grow iron overlayers at a rate of ~ 0.2 ML/min on a spark cut W(100) surface aligned to $\pm 1°$ accuracy by an x-ray Laue camera. The first monolayer was grown at 1000 K, with all subsequent growth at $T \leq 300$ K. Our LEED I-V and spot profile experiments confirm the pseudomorphic growth model by clearly establishing the existence of translational symmetry. Spot profile analysis of the (10) LEED beams indicates that the second ML grows as large patches in the low coverage limit, reaching a mean island size ≈ 100 Å at $\Theta=0.5$ (1.5 ML). The films were pulse magnetized along $\langle 11 \rangle$, the easy magnetization direction as determined by SMOKE measurements, and all data were acquired in remanence. No evidence for out-of-plane magnetization in remanence was observed for 1.5-ML film thickness. The 1–3-ML Fe/W(100) near-ground-state and adsorbate-covered system electronic properties, along with some additional sample preparation and characterization details, will appear elsewhere.[15]

Our spin-polarized photoemission experiments were conducted on the U5 undulator beam line at the National Synchrotron Light Source, Brookhaven National Laboratory. The apparatus has previously been described in detail.[16] Briefly, monochromatized first harmonic radiation with $h\nu=60$ eV was used to excite photoelectrons from the even symmetry bands of Fe/W(100) overlayer systems with subsequent energy and spin analysis. Energy and angular resolutions were 0.3 eV and $\pm 1.5°$, respectively. The data were acquired with an incident angle of 36°, i.e., with primarily s-polarized light.

The Curie temperature is the phase point where the global magnetization becomes zero. Near T_C, the magnetization follows the power law $M(T)=M(0)(1-T/T_C)^{\beta}$. It is not *a priori* clear that the measured valence-band polarization $P(T,\mathbf{k})/P(0,\mathbf{k})$ is equal to $M(T)/M(0)$.[17] In fact, the local electronic structure

may alter this strictly linear relationship. However, it is evident that $P(T)/P(0)|_{T_C}=M(T)/M(0)|_{T_C}=0$. Thus measurements of $P(T,\mathbf{k})$ can be used to establish the Curie temperature and to probe the temperature dependence in $E(\mathbf{k},\sigma)$.

We have measured the temperature-dependent valence-band energy-distribution curves (EDC's) for a 1.5-ML film. T_C for this film was established to be 330±20 K from $P(T)$ measurements. A more precise measurement using SMOKE yields a value of $T_C=323$ K. The Curie temperature is very sensitive to small (less than 0.1 ML) changes in film thickness. Films less than 1 ML thick exhibited zero in-plane remanent polarization at $T=115$ K. Further magneto-optic studies of these near monolayer thickness systems are in progress to better define their low-temperature magnetic character.

One possible explanation for the disappearance of the polarization is a superparamagnetic (SP) collapse in which the individual 2-ML islands retain their ferromagnetic nature but no longer couple through the ML-thick Fe between the 2-ML patches.[18] The moments of the individual patches would fluctuate along different easy axes such that the measurement-time-averaged magnetization becomes zero. It is well known that SP coupling usually occurs when the matrix in which the ferromagnetic particles are embedded is itself paramagnetic. A number of observations exclude SP collapse as a possibility. The magnetic hysteresis as obtained by SMOKE measurements is similar in shape at elevated temperatures to that at low temperatures (see Fig. 1), i.e., it is open and easily saturated ($H_{\text{sat}}<100$ Oe) with a nonzero remanence. The squareness of the loops is clear evidence of a system which is ferromagnetic. If the film were composed of SP coupled islands, the 2-ML patches would be sufficiently decoupled at elevated temperatures that there would be incomplete coherence upon switching the magnetizing field direction. In other words, the hysteresis loops would collapse and exhibit a linear dependence on applied field at even higher temperatures; a nonlinear response to the applied field typical of ferromagnetic systems is observed up to the point where the remanent magnetization goes to zero. Furthermore, from these same SMOKE measurements, it is clear that the shape of $M(T)$, as shown in Fig. 1, which depends only on the intrinsic microscopic properties of the system, is indicative of a second-order (ferromagnetic) phase transition. The magnetization of paramagnetic systems exhibits a linear dependence on temperature in the low-field limit.

Figure 2 shows the spin-integrated EDC's from the 1.5-ML film at $\bar{\Gamma}$ as a function of temperature. Very little change is seen in the shape of the curves though the relative intensities of the different peaks exhibit a minor temperature dependence. However, the spin-resolved intensities shown in Fig. 3 clearly exhibit strong temperature-dependent changes, unequivocally illustrating the difficulty in determining the behavior of ferromagnetic bands near T_C without spin analysis.

Before discussing the temperature dependence of the spin-resolved data, it is necessary to describe briefly the band assignments of the near-ground-state ($0.35T_C$) 1.5-ML film photoemission results. The $\bar{\Gamma}$ majority spin-resolved valence-band spectrum of Fig. 3(a) exhibits three peaks; the one at 1.4-eV binding energy, which also clearly shows up in the minority spectrum, Fig. 3(b), and in the spectrum for clean W(100), we ascribe to emission from the W Δ_5 band. The two other peaks in the majority spectrum at 0.8- and 2.4-eV binding energy are due to emission from the states localized in the Fe overlayer. Film-thickness-dependent spectra indicate that these bands are the precursors to the bulk Δ_1 and Δ_5 symmetry bands, respectively. The minority state conjugate to the 0.8-eV majority state is located above the Fermi level and is best accessed by inverse photoemission.[19] In the minority spin spectrum, in addition to the W feature, we see a sharp peak at 0.5-eV binding energy which we as-

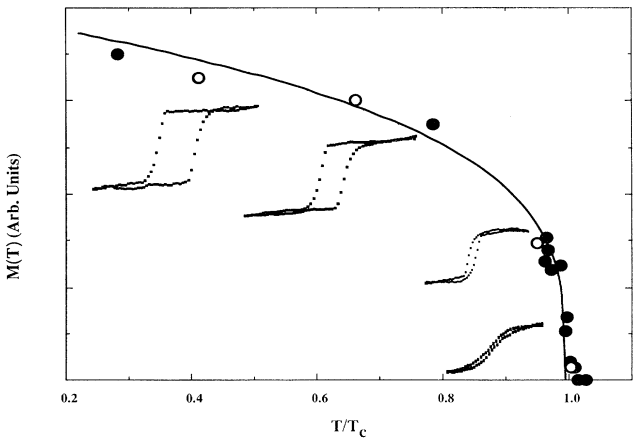

FIG. 1. Remanent magnetization vs reduced temperature for the 1.5-ML Fe/W(100) system. Hysteresis loops representative of those acquired at all temperatures are shown to further illustrate the ferromagnetic character of the phase transition. Open circles mark those values taken from the nearby hysteresis loops.

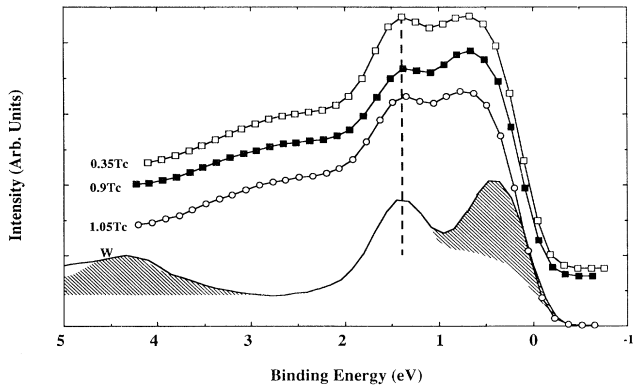

FIG. 2. EDC's for three temperatures of 1.5-ML Fe/W(100) film at $\bar{\Gamma}$: □, $T=0.35T_C$; ■, $T=0.9T_C$; and ○, $T=1.05T_C$ and for clean W(100). Shaded regions indicate W surface states quenched by 0.25-ML Fe (Ref. 15). Dashed line shows location of peak due to emission from the W Δ_5 band.

sign as the spin-exchange split partner to the 2.4-eV binding energy majority feature based on their symmetry properties; both are *s*-polarization sensitive. We see in this 1.5-ML film an exchange splitting of ~2.0 eV at $\bar{\Gamma}$, nearly that of bulk iron at Γ.[5]

Two additional finite temperature spectra for each spin direction also appear in Fig. 3. One was taken immediately below the Curie temperature, $0.9T_C$, and the other just above it, $1.05T_C$. A careful curve-fitting analysis of peak position shows that the Fe features shift very little with temperature. We can well reproduce the $0.9T_C$ majority spin data by a 70%-30% mixture of the majority and minority near-ground-state spectra and the minority spectrum is best fit by a 30%-70% mixture. However, the most dramatic effect is observed in a comparison of the $1.05T_C$ data with a calculated 50%-50% mixture of majority and minority spectra as is shown in Fig. 4. The agreement between the two curves is remarkably good. It is quite clear that the peaks originating from the spin-exchange split pair have not shifted from their low-temperature binding energies (no collapsing bands) and in fact the apparent broadening is most likely due to the appearance of "extraordinary" peaks, i.e., intensity from states of opposite spin.

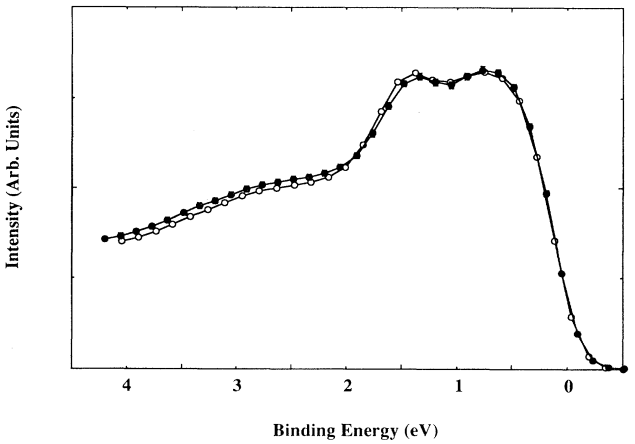

FIG. 4. EDC for ●, $T=1.05T_C$ and ○, 50%-50% mixture of $0.35T_C$ majority and minority spin-resolved EDC's.

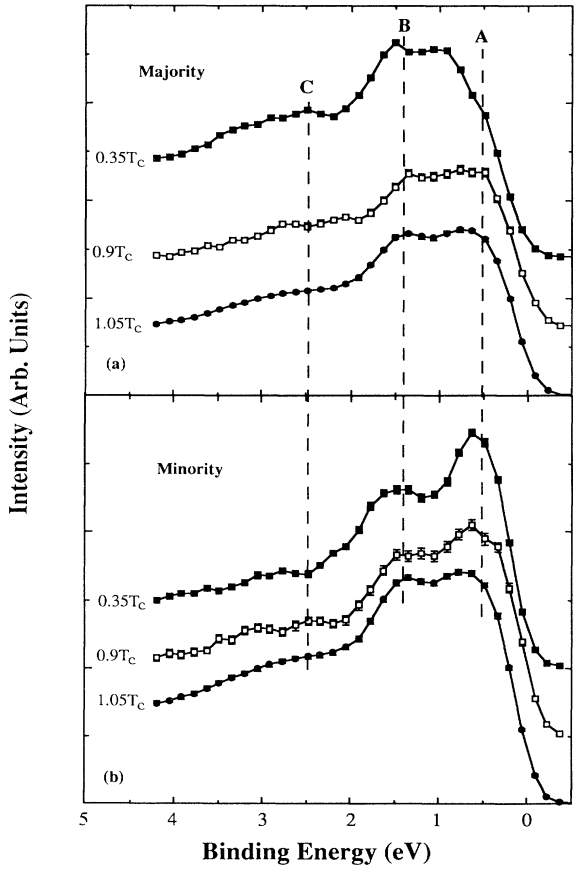

FIG. 3. Spin-resolved EDC's for (a) majority: ■, $T=0.35T_C$; □, $T=0.9T_C$; and ●, $T=1.05T_C$ and (b) minority: ■, $T=0.35T_C$; □, $T=0.9T_C$; and ●, $T=1.05T_C$ spins of 1.5-ML film at $\bar{\Gamma}$. The lines labeled *A*, *B*, and *C* mark the locations of the centroids of the Fe minority, W Δ_5, and Fe majority peaks, respectively.

The significance of the shape of the EDC above T_C becomes apparent when we examine the different demagnetization schemes. In the disordered local moment (DLM) model, it is assumed that the itinerant *d* electrons are sufficiently site localized that they may be treated as independently precessing spins near T_C, much as in the case of the rare-earth ferromagnets.[20] This individual randomness disallows any short-range order above T_C. The DLM model has failed to explain the observed, albeit disputed, spin waves in Ni and Fe in neutron scattering experiments.[21] In the fluctuating band (FB) model, on the other hand, the magnetization is dominated by the itinerant character of the *d* electrons to such an extent that local spin-split bands may exist even above T_C.[22] If the electron group velocity is sufficiently low compared to the mean electron hopping time, the electrons "feel" the local magnetization of the globally paramagnetic state. This group velocity dependence promotes a strong **k** dependence in the band structure near T_C.

An outgrowth of the local band model is the predicted existence of short-range order above T_C. It is clear that the momentum dependence makes it necessary to perform realistic calculations in order to determine the effects this ordering has on the band structure for different values of **k**. Such a calculation has been performed for a 2000 atom cluster of (bulklike) Fe using one-electron Green's functions to predict the photoemission intensities.[23] We compare our results at $\bar{\Gamma}$ with the results from this bulk Fe calculation at Γ, the only possible point of contact with our data. Naturally, this is not a completely accurate comparison, but the qualitative features should not be greatly in error since the overlayer majority and minority bands in the vicinity of $\bar{\Gamma}$ are relatively flat, as are the bulk Δ_5 bands at Γ. In the absence of SRO, these Δ_5 majority and minority bands at Γ

coalesce into a single peak centered at 1.8 eV, the same result as predicted by DLM calculations.[24] Our data clearly show that no such combination takes place. The presence of the well-separated 0.5-eV minority binding energy and 2.4-eV majority binding energy peaks is consistent with short-range order ~ 4 Å and the existence of local band structures. Further investigation of this phenomenon by mapping other high-symmetry points in the band structure as a function of temperature may be inconclusive until "cluster" calculations for this system become available.[6]

In conclusion, we have seen that the elevated temperature band structure at $\bar{\Gamma}$ of 1.5-ML Fe/W(100) films is consistent with the existence of local band structures above T_C. Comparison with a *bulk* calculation suggests that short-range order of at least 4 Å exists above T_C. Apparently the strong hybridization between the W 4*d* and Fe 3*d* bands does not act to quench this SRO, suggesting that substrate-overlayer interactions may not be very important in determining the above-T_C magnetic behavior of ferromagnetic thin films with large average moments per atom.

We gratefully acknowledge the aid of N. Brookes, A. Clarke, P. Johnson, and B. Sinković in this effort. This work was carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. This research was supported by the National Science Foundation under Grant Nos. DMR-8906935(MRG) and DMR-8922359.

---

*On sabbatical leave from Rice University, 1989–1990.

[1]M. N. Barber and K. Binder, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8.

[2]D. E. Eastman, F. J. Himpsel, and J. A. Knapp, Phys. Rev. Lett. **40**, 1514 (1978).

[3]C. J. Maetz, U. Gerhardt, E. Dietz, A. Ziegler, and R. J. Jelitto, Phys. Rev. Lett. **48**, 1686 (1982).

[4]H. Hopster, R. Raue, G. Güntherodt, E. Kisker, R. Clauberg, and M. Campagna, Phys. Rev. Lett. **51**, 829 (1983).

[5]E. Kisker, K. Schröder, W. Gudat, and M. Campagna, Phys. Rev. B **31**, 329 (1985).

[6]K.-P. Kämper, W. Schmitt, D. A. Wesner, and G. Güntherodt, Appl. Phys. A **49**, 573 (1989).

[7]D. P. Landau, Phys. Rev. B **13**, 2997 (1976).

[8]G. A. T. Allan, Phys. Rev. B **1**, 352 (1970).

[9]W. Dürr, M. Tamborelli, O. Paul, R. Germer, W. Gudat, D. Pescia, and M. Landolt, Phys. Rev. Lett. **62**, 206 (1989).

[10]H. Capellmann and V. Vieira, Solid State Commun. **43**, 747 (1982).

[11]X.-L. Zhou, C. Yoon, and J. M. White, Surf. Sci. **203**, 53 (1988).

[12]P. J. Berlowitz, J.-W. He, and D. W. Goodman (unpublished).

[13]J. Chen, M. Drakaki, C. Ballentine, and J. Erskine, Bull. Am. Phys. Soc. **35**, 199 (1990); and (unpublished).

[14]S. C. Hong, A. Freeman, and C. L. Fu, Phys. Rev. B **38**, 12 156 (1988).

[15]R. L. Fink, G. A. Mulhollan, J. L. Erskine, and G. K. Walters (unpublished).

[16]P. D. Johnson, S. L. Hulbert, R. Klaffky, N. B. Brookes, A. Clarke, B. Sinković, and M. Kelley (unpublished).

[17]E. Kisker, J. Chem. Phys. **87**, 3597 (1983).

[18]S. Mørup, J. Dumesic, and H. Topsøe, in *Applications of Mössbauer Spectroscopy,* edited by P. L. Cohen (Academic, New York, 1967), Vol. 2, p. 103.

[19]Q. Cai, R. Avci, and G. J. Lapeyre, in *Growth Characterization and Properties of Ultrathin Magnetic Films and Multilayers,* edited by B. T. Jonker, J. P. Heremans, and E. E. Marinero, MRS Symposia Proceedings No. 151 (Materials Research Society, Pittsburgh, 1989), p. 65.

[20]J. Staunton, B. L. Gyorffy, A. J. Pindor, G. M. Stocks, and H. Winter, J. Magn. Magn. Mater. **45**, 15 (1984).

[21]See P. J. Brown, H. Capellmann, D. Deportes, and K. R. A. Ziebeck, Solid State Commun. **52**, 83 (1984), and references cited therein.

[22]H. Capellmann, J. Phys. F **4**, 1466 (1979).

[23]E. M. Haines, R. Clauberg, and R. Feder, Phys. Rev. Lett. **54**, 932 (1985).

[24]P. J. Durham, J. Staunton, and B. L. Gyorffy, J. Magn. Magn. Mater. **45**, 38 (1984). It is interesting to note that this calculation predicts that the Fe bands at Γ with Δ_1 symmetry retain their splitting above T_C. A test of this prediction would require joint photoemission and inverse-photoemission experiments.