Onset of Magnetic Order in fcc-Fe Films on Cu(100)

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On the basis of an *ab initio* theory of metallic magnetism in layered materials, we investigate the onset of magnetic order in thin (2–8 layers) fcc-Fe films on and embedded in Cu(100) substrates. In particular, we find an oscillatory dependence of the Curie temperatures on embedding depth, in excellent agreement with experimental data. The thermally induced spin fluctuations are treated within a mean-field disordered local moment picture and give rise to layer-dependent "local exchange splittings" in the electronic structure even in the paramagnetic phase. These features determine the magnetic intralayer and interlayer interactions which are strongly influenced by the presence and extent of the Cu cap.

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Small numbers of Fe layers on and embedded in copper form one of the most challenging and controversial magnetic thin film systems. As noted by Qian *et al.* [1] in their description of their recent elegant experiments, the nature of the close correlation between magnetism and structure makes this system unique. Moreover, its satisfactory description provides an appropriate benchmark for theories of thin film magnetism [2]. Films with less than 10–12 monolayers (ML) on Cu take on the fcc structure of the substrate while thicker films revert to the bcc structure of bulk iron. When there are fewer than 4–5 ML, a ferromagnetic (FM) phase is observed while the thicker films of 6–11 ML seem to be antiferromagnetic (AF) with a net moment across the film. Adding covering layers of Cu to the films has a marked effect upon their magnetic properties. A single Cu ML suppresses the magnetic ordering temperatures T_c while the T_c's of 2 ML Cu-capped films are partly restored only to drop again as further Cu layers are added [3].

The "local moment" picture of itinerant magnets at finite temperature [4,5] is based on the premise that there is a separation between fast and slow electronic degrees of freedom so that local moments are set up and their orientations slowly vary. As well as the existence and behavior of the local moments being established by the fast electronic motions, their presence also affects the electronic motions. There is a mutual consistency. This basic picture has been investigated before for bulk materials [6–9] but has not been tested for systems of reduced dimension. In this Letter we address this by studying Fe films on and embedded in copper. We describe the local moment paramagnetic states of the Fe films of up to 8 ML thickness at finite temperatures and investigate both the growth of magnetic correlations and the onset of magnetic order. Moreover, we are able to extract intra- and interlayer "exchange" interactions and features of the electronic structure which set them up.

In magnetic metals, for times, τ, long in comparison with electronic "hopping" times, but short when compared with typical spin fluctuation times, the spin orientations of the electrons leaving an atomic site i are sufficiently correlated with those arriving that the magnetization integrated over a unit cell and averaged over τ is nonzero. These are the local moments which can change their orientations, described by a set of unit vectors $\{\hat{e}_i\}$, on a time scale longer than τ while their magnitudes fluctuate rapidly on the time scale τ. The electronic grand potential $\Omega\{\hat{e}_i\}$ of the system constrained appropriately for the configuration $\{\hat{e}_i\}$ is obtained from a generalization of spin density functional theory, and the long time average is replaced by an ensemble average with respect to the Gibbsian measure $P\{\hat{e}_i\} = Z^{-1} \exp -\beta\Omega\{\hat{e}_i\}$, and the free energy $F = -k_B T \log Z$ where the partition function $Z = \prod_i \int d\hat{e}_i \exp -\beta\Omega\{\hat{e}_i\}$. Evidently $\Omega\{\hat{e}_i\}$ plays the role of a classical "spin" (local moment) Hamiltonian, albeit a highly complicated one. By choosing a suitable reference single-site spin Hamiltonian $\Omega_0\{\hat{e}_i\} = \sum_i \omega_i(\hat{e}_i)$ and using the Feynman-Peierls' inequality [10] a mean-field or disordered local moment (DLM) theory is constructed [5,7]. The "first principles" formulation of the DLM picture can be implemented by an adaptation of the self-consistent field–Korringa Kohn Rostoker–coherent potential approximation (SCF-KKR-CPA) [5] method ideally suited for calculating the partial averages $\omega_i(\hat{e}_i)$. The approach can be further improved via the construct of a generalized Onsager cavity field [7].

For bulk magnetic metals, DLM theory produces a local electronic structure which can possess a "local exchange" splitting even in the paramagnetic state [5] leading to the establishment of the local moment on each site. This means that an electron spin-polarized parallel to a local moment has a different density of states to that polarized antiparallel. When all orientations of the moments are averaged over in the paramagnetic state, the electronic

structure is inevitably unpolarized, but consequences from the presence of local moments can still be identified. This splitting can vary sharply as a function of wave vector and energy [5], a feature observed in spectroscopic experiments [11] on bcc Fe. In our generalization of the DLM theory to layered systems we find that the layer dependence of similar features in the electronic structure of paramagnetic Fe on or embedded in a Cu(100) substrate drives the onset of magnetic order and the form of the magnetic interactions between Fe layers.

We consider the response of the paramagnetic DLM state to the application of a small, external magnetic field, $\{\mathbf{h}_i\}$, varying from site to site, layer to layer. The induced magnetization is predominantly caused by the local moments changing their orientations to align with the field, and the site by site paramagnetic spin susceptibility [6] is the solution of the matrix equation $\chi^{ij} = (\beta/3)\mu_i^2\delta_{ij} + (\beta/3)\sum_k S_{ik}^{(2)}\chi^{kj}$ where $S_{ik}^{(2)}$ is the corresponding direct correlation function and μ_i is the magnitude of the local magnetic moment on the ith site. Expressions for $S_{ij}^{(2)}$ involving the electronic structure of the paramagnetic state and techniques for calculating them for bulk systems have been given elsewhere [6]. For layered systems with two-dimensional (2D) translational symmetry the magnitudes of the local moments, $\{\mu_i\}$, assume one value μ_P per site in a given layer labeled P but vary from layer to layer. A 2D lattice Fourier transform over sites within each layer gives $\chi^{PQ}(\mathbf{q}_\parallel) = (\beta/3)\mu_P^2\delta_{PQ} + (\beta/3)\sum_S S_{PS}^{(2)}(\mathbf{q}_\parallel)\chi^{SQ}(\mathbf{q}_\parallel)$, where $\mathbf{q}_\parallel$ is a wave vector in the 2D layer Brillouin zone. Once the $S_{PS}^{(2)}(\mathbf{q}_\parallel)$'s have been calculated and loaded into a $n \times n$ matrix, $S^{(2)}(\mathbf{q}_\parallel)$ (where n is the number of layers in the film), this set of equations is solved by a simple matrix inversion, i.e., $\chi^{PQ}(\mathbf{q}_\parallel) = [3k_BTI - S^{(2)}(\mathbf{q}_\parallel)]^{-1}_{PQ}\mu_Q^2$ (I is a unit matrix). For films in which the intralayer exchange coupling is ferromagnetic, as for the Fe films on Cu, the Curie temperature T_c is specified by the condition $\|3k_BT_CI - S^{(2)}(\mathbf{q}_\parallel = 0)\| = 0$. Full technical details on how $S^{(2)}(\mathbf{q}_\parallel)$ is calculated for layered systems will be provided elsewhere.

We use the spin-polarized screened KKR method [12] for layered systems adapted for the DLM picture. The lattice constants of the layers are taken to be the same as that of the substrate (6.83 a.u. for Cu). For each n, the electronic structure is calculated self-consistently using 78 $k_\parallel$ points in the irreducible part of the surface Brillouin zone. The moments and the effective "Weiss" field on each layer are then determined. By introducing a small change in the average magnetization on one particular layer and calculating the effective Weiss field on each layer we determine $S_{PQ}^{(2)}(\mathbf{q}_\parallel = 0)$, and hence the spin susceptibility, $\chi^{PQ}(\mathbf{q}_\parallel = 0)$, together with the T_c's for various thicknesses of both the Fe film and the Cu cap.

We have calculated the layer-dependent "local" magnetic moments in uncapped $Fe_n/Cu(100)$ films ($n = 2, \ldots, 8$) and find those on the topmost layer to be always the largest at around $2.5\mu_B$ followed by those on the Fe layer closest to the substrate next at roughly $2.2\mu_B$. In the films' interiors the moments are reduced to $1.7\mu_B$ close to that found for fcc-Fe for this lattice spacing [13]. The magnetic ordering temperatures have values 681, 532, 495, and 492 K for 2, 3, 4, and 5 ML and 485 K for 6 ML onwards. Table I shows the effective exchange interactions, i.e., the direct correlation function, $S_{PQ}^{(2)}$, which lead to these T_c's. Examples of 7 and 3 ML Fe systems are shown to bring out the dominant features. The intralayer couplings are ferromagnetic throughout. The top layers and those nearest the Cu substrate have the largest values owing to their reduced effective coordination. It is the interlayer couplings that show an important and interesting trend. The top two layers are strongly ferromagnetically coupled (positive values), whereas the coupling to nearest neighbor layers within the films is AF. There is also significant coupling to subsequent layers which alternates between FM and AF. Experimental data on the uncapped films have been interpreted [14] in terms of models in which the top two surface iron layers are FM coupled in an otherwise AF Fe film. This picture had been prompted by a series of *ab initio* $T = 0$ K electronic structure total energy calculations [15] and as shown in Table I is reinforced by our calculations.

Adding a copper cap to these films alters these results profoundly. Figure 1 highlights this for 3 and 7 ML Fe/Cu(100) films and shows T_c to have an oscillatory dependence on cap thickness. A single Cu ML suppresses

TABLE I. Intralayer $S_{PP}^{(2)}(\mathbf{q}_\parallel = 0)$ and interlayer $S_{PQ}^{(2)}(\mathbf{q}_\parallel = 0)$ ($P \neq Q$) effective "exchange" interactions in meV in an uncapped $Fe_7/Cu(100)$ system with the values for $Fe_3/Cu(100)$ shown for comparison in brackets. The Fe layer L_1 is adjacent to the substrate and L_n is the top layer.

	L_1	L_2	L_3	L_4	L_5	$L_{6(2)}$	$L_{7(3)}$
L_1	108.5 (108.4)	−7.5	8.5	−2.1	−0.8	−0.7 (−10.9)	−1.0 (25.1)
L_2	−7.5	19.6	−7.5	3.2	−2.2	−0.6	−0.7
L_3	8.5	−7.5	17.5	−7.2	2.1	−1.7	−0.7
L_4	−2.1	3.2	−7.2	18.8	−8.1	2.1	−2.1
L_5	−0.8	−2.2	2.1	−8.1	19.9	−10.0	9.8
$L_{6(2)}$	−0.7 (−10.9)	−0.6	−1.7	2.1	−10.0	33.2 (29.9)	50.0 (53.8)
$L_{7(3)}$	−1.0 (25.1)	−0.7	−0.7	−2.1	9.8	50.0 (53.8)	97.7 (96.7)

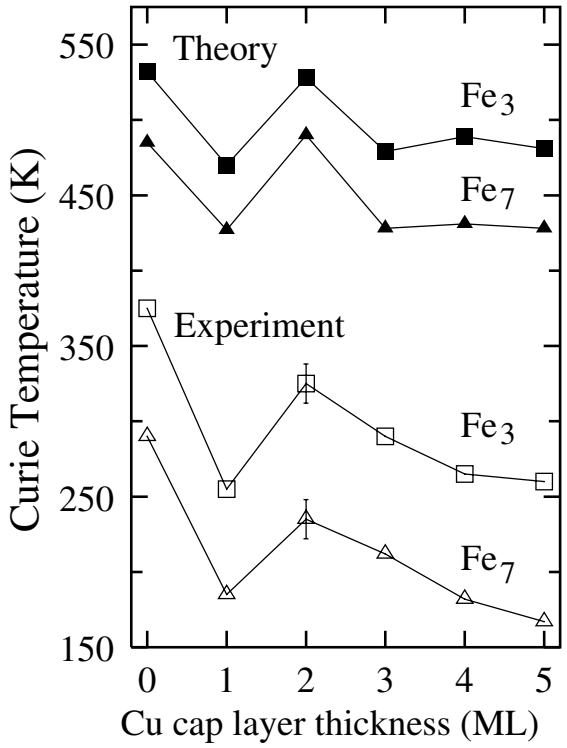

FIG. 1. The magnetic ordering temperatures for 3 and 7 layers of Fe on and embedded in Cu(100). Estimates of T_c's derived from Kerr data from Fig. 6 of Ref. [3] are also shown.

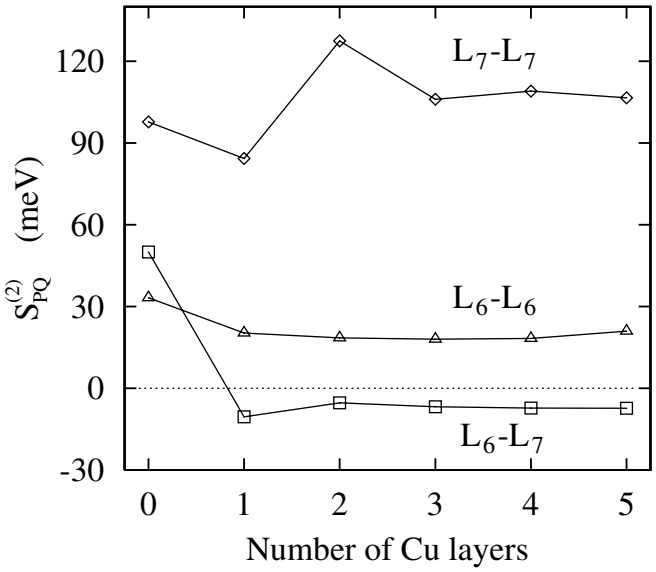

FIG. 2. The magnetic interactions (in meV) in and between the Fe layers nearest the surface or copper cap in a system of 7 Fe layers on Cu(100). "L_7-L_7" denotes the interactions within the top Fe layer (nearest the cap), "L_6-L_6" is for the second, and "L_6-L_7" is the coupling between these two layers.

T_c by some 50 K with the deficit being restored by a second layer. A third layer reduces T_c once again, and further layers cause minor oscillations about this lower value. This behavior is in excellent agreement with experimental data on the same systems by Vollmer *et al.* [3] (see their Fig. 6). Figure 2 shows the dominant changes to intra- and interlayer magnetic interactions to occur in the top two Fe layers nearest the cap. A single Cu ML cap switches the coupling between these layers from FM to AF, while further Cu layers strengthen the coupling within the topmost Fe layer.

We find a similar trend in the magnetic ground states (the $T = 0$ K limit of the theory). For example, Table II gives the relative total energies of all four collinear magnetic states of a Fe 3 ML film on and embedded in Cu. The most stable state of an uncapped film has the top two layers FM coupled and AF coupled to the Fe layer at the interface (↓↑↑) and more than 150 meV lower in energy than the states with AF-coupled top layers (↑↓↑, ↓↓↑). Adding a single Cu ML cap causes the one of these (↓↓↑) to become the most stable. The ↓↑↑ state again becomes the most stable with a second Cu ML, while the ↓↑↑ and ↓↓↑ states become roughly degenerate with increased cap thickness.

Recently Pajda *et al.* [16] constructed 2D effective Heisenberg models for Fe and Co monolayers on and embedded in Cu(100) using exchange interactions extracted from *ab initio* calculations of the spin wave spectra of the metals' low temperature FM states. A small anisotropy energy parameter was added. They found the T_c's substantially reduced when a more sophisticated approximation based on the random phase approximation is used in preference to a mean-field treatment (MFT). They also found an oscillatory behavior of the T_c's with Cu-capping thickness in both approximations. Interestingly, although our DLM approach requires no similar mapping to an effective Heisenberg model, we find the T_c of a single Fe layer on Cu(100) to be 1224 K and comparable to the MFT estimate of 1068 K of Pajda *et al.* [16]. Note, however, our calculations contain an account of the electronic structure which supports the magnetic fluctuations studied.

For a 2D Heisenberg model magnetic long-range order is forbidden by the Mermin-Wagner theorem [17]. Presumably in our nonrelativistic electronic theory a similar principle is at work and so the above instability of the paramagnetic state of the monolayer is not expected to be a precursor to magnetic long-range order. However, in a relativistic version of our calculations we expect a crossover to an Ising-like universality class on account of spin-orbit coupling and dipolar interactions. Thus, although our calculated MFT T_c's are likely to be overestimates, they can be taken as indicative of what will happen in a more complete theory.

TABLE II. The dependence upon the number m of Cu capping layers of the difference of the total energies (meV) between three different magnetic states of 3 ML Fe film at $T = 0$ K and the remaining completely FM Cu(100)/ ↑↑↑ /Cu$_m$ one.

m =	0	1	2	3	4	5
Cu(100)/ ↓↑↑ /Cu$_m$	−54	−52	−60	−69	−67	−67
Cu(100)/ ↑↓↑ /Cu$_m$	101	−63	−22	−42	−38	−42
Cu(100)/ ↓↓↑ /Cu$_m$	113	−95	−37	−72	−64	−67

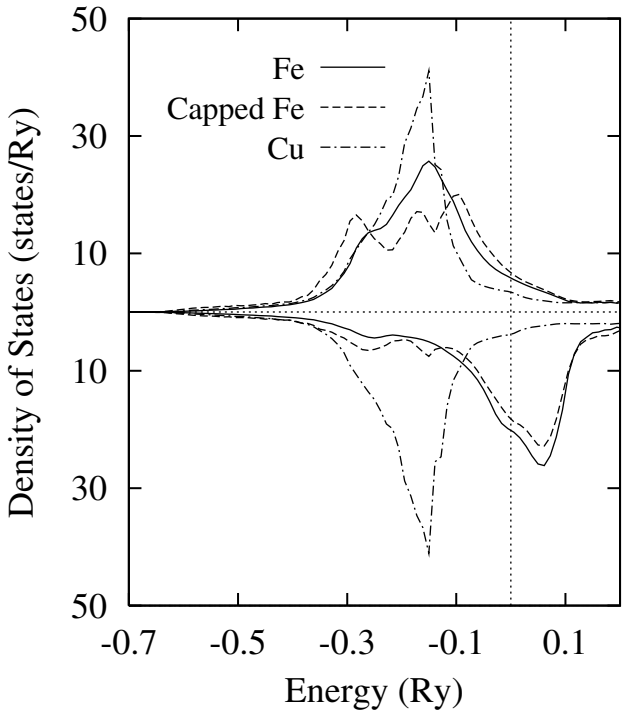

FIG. 3. The density of states (DOS) in the topmost Fe layer of a $Fe_7Cu(100)$ system without (full line) and with (dashed line) a single Cu ML cap. The dotted line shows the DOS for this Cu layer. The upper (lower) half shows the DOS for an electron spin-polarized parallel (antiparallel) to the local moment on a site.

Figure 3 compares the electronic density of states (DOS) of uncapped and 1 ML Cu-capped films in their DLM states. The former's DOS is "exchange split" over a large energy range. These states are nearly fully occupied and FM coupling between neighboring sites results. In the uncapped film these Fe states hybridize with quantum well states in the Cu cap formed between the vacuum and the Fe film causing the exchange splitting to collapse in the region of this hybridization. The remaining exchange-split states are roughly half-filled which leads to an AF coupling along the (100) direction as in bulk fcc Fe [13]. Figure 3 shows these effects in the DOS in the top layer of a $Fe_7/Cu(100)$ system both uncapped and capped by a single Cu ML. The narrow band of states in the Cu layer are also shown.

In conclusion, we note that the dramatic variations of interaction between local moments at different distances from the various surfaces and interfaces are itinerant effects, exemplified quintessentially by Fe films on and in Cu. As the much studied variation of the local moments near such planar defects show, they are due to the motion of the electrons not limited to an atom but confined by the geometry of the sample. In this respect they are manifestations of the same physics that is at work in the oscillatory magnetic coupling in metallic multilayers [18]. Moreover, our calculations provide significant new evidence that the DLM picture correctly captures the essential physics of magnetic order, due to mobile electrons, in the limit where local moments form. Moreover, they confirm and complement the results of Pajda *et al.* [16] for magnetic monolayers.

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