Total Energy Spectra of Complete Sets of Magnetic States for fcc-Fe Films on Cu(100)

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Based on a total energy search among the complete set of 2^{n-1} collinear spin states for n ($n = 1, \ldots, 6$) monolayers (ML) of fcc Fe on Cu(100) by use of the generalized gradient approximation combined with the full-potential linearized augmented plane-wave method, we find ferromagnetism for 1, 2, and 3 ML fcc-Fe/Cu(100), bilayer antiferromagnetism for even numbers of layers (4 and 6 ML), and the coexistence of several spin states for an odd number of layers (5 ML). The results are consistent with the experimental situation and a possible spin-spiral ground state of fcc Fe. Effects of band narrowing, relaxations, interface mixing, and surface steps are addressed. [S0031-9007(97)03614-4]

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A few atomic layers of Fe on Cu(100) make up the single most complex and complicated ultrathin magnetic system of all. The atomic structure, the growth mode, the film morphology, and the magnetic properties are intimately interwoven and Fe on Cu has developed to the touchstone and testing ground of understanding the complexity of thin-film magnetism. Originally the interest sparked upon the discovery that Fe films on Cu(100) grow in the fcc phase [1], which is otherwise accessible only above ~1200 K. The interest was fueled by the theoretical finding [2] of the longitudinal spin-density instability of fcc-bulk Fe, just at the volume range, where fcc Fe is stabilized on the Cu(100) surface. At this volume, ferromagnetic (FM) high- and low-spin states as well as type-I antiferromagnetic (AFM) (CuAu structure) and nonmagnetic (NM) states are in close energetic vicinity, and thus the equilibrium magnetic structure depends critically on volume and symmetry.

Understanding the system Fe on Cu(100) has challenged experimentalists and theoreticians for more than a decade. The experimental work on the structure, magnetism, electronic structure, growth, and morphology [3–21] has accumulated to a vast experimental effort and slowly a consistent picture is emerging: There are two distinct preparation conditions, the low-temperature (LT) (<140 K) and the room-temperature (RT) deposition. The latter leads to a layer-by-layer growth mode with roughness decreasing with film thickness. For RT-grown films we distinguish three different regimes as a function of the Fe coverage Θ, which exhibit different magnetic and structural properties. In regime I [$\Theta < 4 \sim 5$ ML (monolayer)] the spin configurations are FM [4,14] throughout the film [8,9,19]. Fe takes a tetragonally distorted [3,8] fcc structure accompanied by a considerable three-dimensional (3D) lattice modulation [6,7] and an expanded atomic volume of 12.1 Å^3 (=1.06 × 11.4 Å^3). In regime II ($5 \leq \Theta < \sim 11$ ML) the film bulk is undistorted AFM fcc Fe [8,9,13], with an atomic volume of bulk γ Fe (11.4 Å^3) [6], and with a net moment across the film thickness. The top layer is reconstructed and the first interlayer distance is tetragonally expanded by 5% [4,7]. This is interpreted, supported by a recent experiment [15], as being due to a FM surface-to-first-subsurface coupling (FM surface-bilayer state) on an otherwise AFM Fe film, which accounts for the net moment of the film. For thicker Fe films ($\Theta > \sim 11$ ML) fcc Fe becomes unstable and transforms into FM bcc Fe(110) [4,5], which characterizes regime III.

On the other hand, it is fair to state that although *ab initio* theory had a big impact on the development of the field of ultrathin magnetic films and in stimulating the investigation of Fe/Cu(100) films, it contributed only with partial success to the understanding of the Fe/Cu(100) system. Up to now most *ab initio* calculations [22–24] focused on the type-I AFM state of regime II and provide the foundation for the FM surface bilayer model. The results can be summarized as follows: (i) 1 and 2 ML Fe on Cu(100) are FM, (ii) for n ML Fe on Cu(100), $n \geq 3$, AFM appears first in the third layer and continues in case of thicker Fe films as layered AFM structure [alternating FM (100) planes of opposite polarizations consistent with the type-I AFM state] at least up to the sixth layer. The magnetic moments at the surface are strongly enhanced over the bulk value and the lattice distortions [24] are in good agreement with the experimental data of regime II. Although the matter is still under debate, there seems now a general consensus that these results consistently explain experimental observations of RT-deposited films of regime II. However, several puzzling questions remain: (i) *Ab initio* calculations [25–27] for bulk fcc Fe show that a spin-spiral density wave (SSDW) has a lower energy than the AFM structure and experiments [28] revealed a SSDW for Fe precipitates in the Cu matrix. This should be also reflected in the ground state spin structure of fcc films in regime II. (ii) Experimentally, the transition from FM fcc Fe to AFM fcc Fe happens between 4 and 5 ML instead of 2 ML as predicted by theory, and (iii) there was never

an attempt to understand the magnetostructural transition from regimes I to II.

One reason for the modest impact of *ab initio* theory for the Fe/Cu problem is certainly caused by the well-known failure of the local spin-density approximation (LSDA) to the density functional theory to correctly predict the ground state of FM bulk bcc Fe [29], and in underestimating the lattice constant of bcc Fe by about 5%. Thus the application of LSDA casts serious doubts on the predictive power for such a delicate magnetostructural problem. Now it is well acknowledged [30] that these total-energy-related deficiencies of the LSDA can be satisfactorily improved by the generalized gradient approximation (GGA) [31,32] when combined with a full-potential electronic structure method [27,33] and the ground state structure, lattice constant, and magnetic energies are in good agreement with experiment.

In this work we present, to our knowledge, the first complete total energy search for the minimum-energy collinear spin structure for a finite number of layers of fcc Fe on Cu, and we address the puzzling structural and magnetic transition from regimes I to II for the RT-grown fcc Fe films. We calculate the total energy $E(\{\uparrow_i \downarrow_j\},\{d_{\mathrm{Cu}}\})_j$ for n ML of undistorted (interlayer distances $d_{ij} = d_{\mathrm{Cu}}$, between all adjacent layers i and j) fcc Fe on Cu(100) for $n = 1,2,3,4,5,6$, in the $p(1 \times 1)$ unit cell, taking into account the complete set of all possible $2^{(n-1)}$, $n \geq 2$, collinear spin configurations $\{\uparrow_i \downarrow_j\}$ between layers i and j. For a monolayer film ($n = 1$) we compared the energy of a $p(1 \times 1)$ FM film with a possible $c(2 \times 2)$ in-plane AFM (checkerboard arrangement of up and down spins) film, concluding (for details, see below) that we can safely discard $c(2 \times 2)$ films for $n \geq 2$. In total we calculated the total energy for more than 80 different spin configurations and all of them exist. The more than 380 different local Fe moments which result from these spin states are published elsewhere [34].

The results are obtained with the full-potential linearized augmented-plane-wave (FLAPW) method in film geometry [35] combined with the GGA proposed by Perdew and Wang (PW91) [32]. Converged total energy differences were obtained using roughly 80 symmetrized APWs per atom as variational basis set and ten [36] special $k_{\parallel}$ points to integrate over the irreducible wedge of the two-dimensional Brillouin zone. Prior to the n ML Fe/Cu(100) calculations we determined the theoretical (GGA-FLAPW) equilibrium lattice constant of bulk Cu as $a_0 = 3.82$ Å, close to the experimental value of 3.81 Å.

We find (cf. Fig. 1) n ML fcc Fe on Cu(100) are FM for $n \leq 3$ and AFM for $n \geq 4$. For $n \geq 4$ we find in agreement with previous calculations that the surface and subsurface atoms couple ferromagnetically, but the AFM structure of the film bulk atoms is much more complicated and the energetics is much more delicate than previously anticipated. For films with an even number of Fe layers we find a bilayer AFM structure, ($\uparrow\uparrow\downarrow\downarrow \mid$ Cu) and ($\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow \mid$ Cu), being the magnetic ground state, with

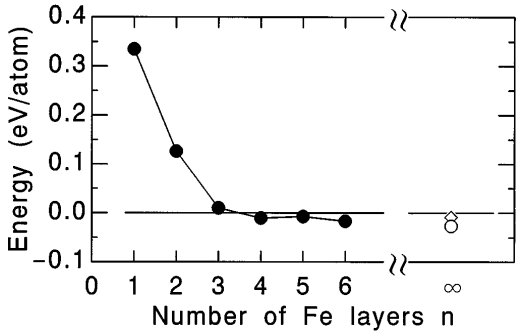

FIG. 1. Energy difference $\Delta E = E_{\mathrm{min}}(\mathrm{AFM}) - E(\mathrm{FM})$ between the minimum-energy AFM state and the FM state. $\Delta E > 0$ means the FM state is ground state. ($\diamond$) E(type-I AFM) $-$ E(FM) and ($\bigcirc$) E(SSDW) $-$ E(FM) [27] of bulk fcc Fe.

$\Delta E \approx -10$ meV/Fe atom lower in energy than the FM state $E(\mathrm{FM})$. This ($\uparrow\uparrow\downarrow\downarrow\cdots$) configuration bears some similarity to a spin-spiral state with $\vec{q} = 0.5\,\frac{2\pi}{a}\,(0,0,1)$, a wave vector $\vec{q}$ in close vicinity to the bulk value of fcc Fe of $\vec{q} = 0.6\,\frac{2\pi}{a}\,(0,0,1)$ [25–27], which is about 27 meV/Fe atom [27] lower than $E(\mathrm{FM})$. The bilayer AFM state is incompatible for films with an odd number of Fe layers and the ground state energy of the 5 ML film is less stable with respect to FM state ($\Delta E = -7$ meV/Fe atom) than the 4 or 6 ML film.

In detail, Fig. 2 contains the total energy spectra $E(\{\uparrow_i \downarrow_j\},\{d_{\mathrm{Cu}}\})_j$ of all $2^{(n-1)}$ collinear spin states for

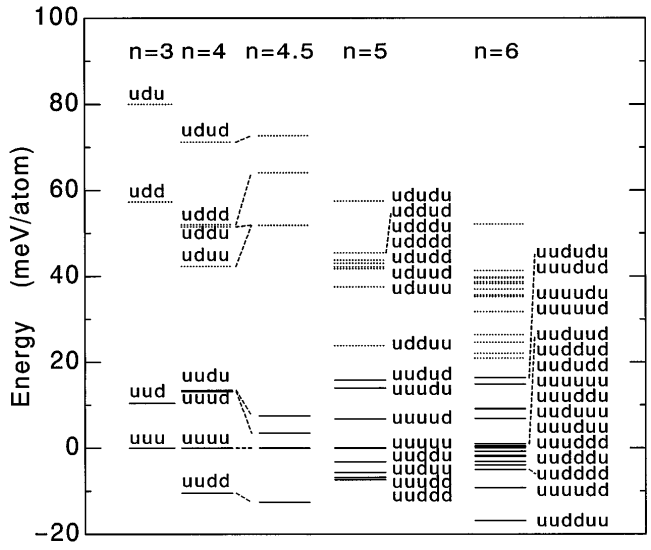

FIG. 2. Total energy $E(\{\uparrow_i \downarrow_j\})$ of all possible collinear spin states $\{\uparrow_i \downarrow_j\}$, relative to FM configuration ($uuu\ldots$), for n ML Fe on Cu(100), $n = 3,4,5,6$. For $n = 6$ only spin states with FM surface bilayers ($\uparrow\uparrow\cdots \mid$ Cu) are labeled. $n = 4.5$ indicates the 4 ML Fe/$c(2 \times 2)$FeCu/Cu(100) system. The labels of 4 and 4.5 ML are identical because the spin direction of Fe in the $c(2 \times 2)$FeCu plane and the adjacent Fe plane is always FM. Full [dotted] lines indicate ($\uparrow\uparrow\cdots \mid$ Cu) [($\uparrow\downarrow\cdots \mid$ Cu)] configurations. u, d denote the two possible spin configurations $u = \uparrow$, $d = \downarrow$, respectively, and the surface-to-inner-layers is read from left to right. The sequence of the labels and energy level are concurrent.

$n = 3, 4, 5, 6$ ML fcc-Fe/Cu(100) (for a discussion of the $n = 4.5$ ML system, see below). Summarizing Fig. 2: (i) All possible spin states exist and are stable or metastable states. (ii) With an increasing number of layers n the energy difference between different spin states becomes increasingly smaller and for $n \geq 4$ multiple spin states are found within a temperature range of 300 K. (iii) The energy spectrum has a bimodal blocking of the spin states. Bilayer FM at the surface is always favored over surface-to-subsurface AFM $[E(\uparrow\uparrow\cdots|\,\mathrm{Cu}) < E(\uparrow\downarrow\cdots|\,\mathrm{Cu})]$. (iv) Within each block we find the same behavior for the magnetic coupling of two Fe layers adjacent to the inner Cu interface $[E(\cdots\uparrow\uparrow|\,\mathrm{Cu}) < E(\cdots\uparrow\downarrow|\,\mathrm{Cu})]$. (v) For $n \geq 4$, films with an even number of layers show a distinct energy gap of about 10 meV/atom to the next excited spin state, while for the 5 ML film superimposed spin states exist even for temperatures as low as 70 K.

The results are in agreement with the experimental data showing live surface magnetism of fcc Fe in regime II, but experiments at low temperatures may be required to reveal the magnetic structure for the inner Fe layers. The results also show that not only the surface atoms but also inner Fe layers may add to the net moment of regime II. In contrast to the experimentally observed transition from regimes I to II at $4 \sim 5$ ML, the theoretical one is between $3 \sim 4$ ML.

We explain the bilayer FM at the surface (iii) and interface (iv) as a result of the band narrowing of the electronic structure due to the reduced coordination number N_i at both interfaces (c.f. local density of state of fcc-Fe/Cu(100) [22] or fcc Fe(100) [24]). In bulk metals, complex spin structures occur when, in terms of a spin model, the nearest neighbor coupling constant J_1 becomes zero or small and the magnetic structure is determined by competing long-range interactions J_i, $i \geq 2$. The value of J_1 depends on the band-filling n_f and the volume. The critical value n_f^*, for which J_1 becomes small, is $n_f^* \approx 6$ (=Fe) or $n_f^* \approx 5.5$ for an fcc lattice or a monolayer on Cu(100), respectively. Thus with increasing band narrowing the critical regime of complex structures is moved towards Mn. This is also reflected in our data. Comparing an Fe atom in the film interior to an Fe atom at the Cu interface, or at the surface and the monolayer, the bandwidth decreases, and the energy difference for a spin flip of adjacent Fe atoms is increasing. Thus a reduction of N_i takes the same role as band narrowing caused by the lattice expansion of bulk fcc Fe, for which Mryasov *et al.* [25] has shown that J_1 changes sign from AFM to FM and increases upon lattice expansion stabilizing the FM phase for larger volumes.

We also investigated the total energy $E(\{\uparrow_i \downarrow_j\}\,|\,\{d_{ij}\})$ as function of the interlayer distances $\{d_{ij}\}$ for some typical spin configurations for 1 ML Fe/Cu(100), and analogous to [24] for symmetric free-standing 5 and 7 ML fcc-Fe(100) films with the in-plane lattice constant of Cu. We optimized the interlayer distance by energy minimization. For the 1 ML Fe/Cu(100), 5 ML, and 7 ML films there are one (d_{12}), two (d_{12}, d_{23}), or three (d_{12}, d_{23}, d_{34}) independent interlayer distances, respectively. We found for the 1 ML film (FM | 1.002), for the 5 ML film (NM | 0.876, 0.927), (FM | 1.000, 1.013), ($\uparrow_1\uparrow_2\downarrow_3\uparrow_2\uparrow_1$ | 1.019, 0.988), and for the 7 ML film (FM | 1.003, 1.033, 1.030), ($\uparrow_1\uparrow_2\downarrow_3\downarrow_4\downarrow_3\uparrow_2\uparrow_1$ | 1.018, 0.983, 1.032), with all values given relative to d_{Cu}. Summarizing, adjacent FM Fe layers show an interlayer expansion $d_{ij} > d_{\mathrm{Cu}}$, which is smallest at the surface due to surface relaxation, while interlayers of adjacent AFM Fe layers show a contraction, $d_{ij} < d_{\mathrm{Cu}}$. Thus the net volume per atom of fcc Fe in regime II is close to the bulk Cu value, and the volume of the FM structure is ~2% larger than the bulk Cu value. Importantly, we found in the case of the FM 7 ML Fe(100) film that certain paths in the d_{ij} space lead to rather small energy increases upon the expansion of interlayer distances d_{ij}. For the experimentally observed interlayer expansions of 5% [6], $E(\mathrm{FM}\,|\,1.05, 1.05, 1.05)$ is only 4.7 meV/atom higher than $E_{\min}(\mathrm{FM})$. We speculate that by including the 3D shear reconstruction, this energy can be easily gained, reconciling theory and experiment.

Until now we discussed only systems with perfect Fe/Cu interfaces. In order to gain insight into the effect of atomic interface roughness or alloying at the interface on the stability of the magnetic structure and to extend the discussion to half integer (0.5 ML) film thickness, we investigated a system of 4 ML Fe on 1 ML of Fe and Cu arranged in a $c(2 \times 2)$ checkerboard structure deposited on Cu(100) (4 ML Fe/$c(2 \times 2)$FeCu/Cu(100) [37]) as a model for atomic interface roughness. The 4 ML film was selected because it is the critical thickness at the transition from regimes I to II. The in-plane magnetic coupling between the Fe atoms in the checkerboard arrangement is weak [38], and the magnetic interaction is dominated by the coupling of the Fe atom in the checkerboard structure with the Fe atoms at the adjacent layer, resembling an impurity problem, for which we know [39] that the magnetic interaction is FM. From this we can immediately estimate that a 3.5 ML Fe film is still FM. Thus, for searching the lowest energy spin structure of the 4.5 ML film we included all possible spin configurations but fixing the coupling of two most inner 1.5 Fe layers to be FM. In Fig. 2 the results, indicated by the column $n = 4.5$ ML, are compared to the ideal 4 ML Fe/Cu(100) system. The results are surprising. We find (i) the bilayer AFM ground state does not change and is even stabilized. (ii) The energy gap between the bimodel blocks of different surface spin arrangements is increased. From this result we deduce that the interface roughness described by the present model stabilizes the bilayer AFM state and is most likely not the source extending regime I beyond 3.5 ML.

At the end we shortly address the importance of the lateral fluctuation of the film thickness due to steps between different Fe terraces or due to steps at the Fe/Cu interface for the magnetism. At steps a problem may arise

due to the misalignment in the sequence of the magnetic moments between, i.e., a 3 ML($\uparrow\uparrow\uparrow$ | Cu)/4 ML($\downarrow\downarrow\uparrow\uparrow$ | Cu) Fe film (regime I/regime II) showing a misaligned magnetic moment at the subsurface layer of the 4 ML film or even more complicated misalignments may occur at steps between terraces of regime II films of different thickness [i.e., 4 ML($\uparrow\uparrow\downarrow\downarrow$ | Cu)/5 ML($\uparrow\uparrow\downarrow\downarrow\downarrow$ | Cu)]. The overall importance of this topologically induced magnetic frustration for the macroscopic magnetic properties depends on the terrace width. For RT-grown films we expect that the terrace width is sufficiently large and the energy stored in the magnetic frustration may well be released by forming a noncollinear magnetic structure similar to the Cr/Fe system [40] involving about 5 to 6 atomic rows off the step edge and the overall importance might be small. A more complex scenario may develop for rough films.

In summary, we calculated the total energy of all possible collinear spin configurations of n ML fcc Fe on Cu(100) for $n = 1, \ldots, 6$. We find 1, 2, and 3 ML fcc Fe on Cu(100) are ferromagnetic. Beyond 3 ML, for films with an even number of Fe layers (i.e., 4 and 6 ML) a bilayer ($\uparrow\uparrow\downarrow\downarrow\cdots$ | Cu) AFM state has the lowest energy. We conclude that atomic roughness at the Fe/Cu interface stabilizes this magnetic structure and does not explain why theory and experiment disagree on the transition coverage between regimes I and II. The bilayer AFM structure is incompatible to the atomic structure of films with an odd number (i.e., 5 ML) of Fe layers resulting in many different coexisting spin structures within an energy range of 70 K. The band narrowing is the origin of the FM fcc Fe phase characterizing regime I, and of the FM coupling of two adjacent Fe layers at the surface and interface. FM favors the lattice expansion, and we speculate by allowing for a 3D reconstruction of the film, that FM will be responsible for the observed 5% lattice expansion of regime I. Whether this extends the regime I to 4 ML needs to be seen. It remains an open question, whether this bilayer AFM structure will converge into the SSDW for thicker films, or whether undiscovered noncollinear magnetic structures in regime II are lower in energy than those found here.

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