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LETTER TO THE EDITOR

Coherent epitaxy and magnetism of face-centred-cubic Fe films on Cu(100)

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Abstract. The epitaxy of face-centred-cubic (fcc) Fe layers on a Cu(001) substrate has been investigated by means of *ab initio* local spin-density calculations (including generalized gradient corrections) as a function of the thickness of the film. Fe films with a thickness varying between one and three monolayers (ML) adopt a ferromagnetic (FM) ground state. For thicker films with even numbers of Fe layers (4 ML, 6 ML and 8 ML), bilayer antiferromagnetic (AF) structures develop, while for odd numbers of Fe layers (5 ML, 7 ML and 9 ML), a variety of energetically almost degenerate spin structures each with a ferromagnetically coupled bilayer at the free surface are found. The magnetic structures of the films are strongly coupled to their crystal structures: the interlayer distance between ferromagnetically coupled layers is expanded, while that between antiferromagnetically coupled layers is reduced compared to the layer distance in the substrate and in ideal fcc Fe films. Our results explain the observed change from a tetragonally distorted structure in the ferromagnetic regime to thicker films that are almost fcc (on average) due to the antiferromagnetism in the deeper layers.

The structure and magnetism of face-centred-cubic (fcc) Fe films a few atomic layers thick, stabilized by epitaxial growth on a Cu(100) substrate, are currently subject to intensive investigation using both computational methods [1–4] and experiments [5,6]. Due to the small lattice mismatch of only ∼1–2%, the epitaxial growth of Fe layers on a Cu substrate allows the stabilization of a fcc-like phase of Fe (possibly tetragonally distorted) in thin films at room temperature, which is otherwise achievable for the bulk form only at high temperatures (above 1200 K). The strong interest in the fcc phase of Fe is related to its complex magnetic structure. It has been shown that, depending on the atomic volume, ferromagnetic (FM), antiferromagnetic (AF) and spiral magnetic structures can be stabilized [7]. The energy differences between these states are in the same range as that for thermal excitations of spin fluctuations that lead to the anomalous magneto-elastic properties [8].

For films prepared by room temperature (RT) deposition, many experiments agree to the extent of leading to similar structural and magnetic phase diagrams for Fe/Cu(100) films as functions of the thicknesses of the films and of temperature. These experiments distinguish three different regions:

(a) In region I with up to four monolayers of Fe ($t \leqslant 4$ ML), the ground-state spin configurations are FM, and recent LEED (low-energy electron diffraction) experiments [6] show that the film assumes a face-centred-tetragonal (fct) structure with an expanded atomic volume of $V_{at} \sim 12.1$ Å^3 (compared to an atomic volume of only 11.76 Å^3 in the substrate). For 4 ML films, in addition a three-dimensional lattice modulation of the top layers with sinusoidal lateral shifts and vertical buckling has been reported.

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(b) Films in region II (5 ML $\leqslant t \leqslant$ 11 ML) show only a very small overall tetragonal distortion (described as either compressed [9] or expanded [10]) of the fcc structure, and display ferromagnetism at the surface and antiferromagnetism in the deeper layers. The most recent tensor LEED experiments indicate that only the topmost two layers retain a larger interlayer distance, whereas the interior of the films relaxes into the 'isotropic' (on average) fcc structure [6].

(c) In region III ($t \geqslant$ 11 ML), the fcc structure becomes unstable and the films assume the body-centred-cubic (bcc) structure of α-Fe, with a bcc Fe(110)/fcc Cu(100) interface [11].

In this work, we present *ab initio* calculations of the structural and magnetic properties of Fe films on Cu(001). Firstly, we analyse briefly the magneto-elastic and strain properties of the FM and AF phases of fcc Fe biaxially strained to match the lattice of the Cu(001) surface. Secondly, we study the magnetic structure of thin films in regions I and II using supercell total-energy calculations modelling the Fe/Cu(100) system. Thirdly, we study the influence of the magnetic order on the relaxation of the films.

Our calculations have been performed within the local spin-density (LSD) approximation using the *Vienna ab initio simulation package* VASP [12]. VASP exists in a plane-wave version based on ultrasoft pseudopotentials (USPPs) [13, 14] and in an all-electron version based on the projector augmented-wave (PAW) method [15, 16]; for a detailed discussion of the one-to-one relationship between USPPs and PAWs, see Kresse and Joubert [16]. For transition metals with an open 3d shell (from Sc to Fe), the PAW total-energy functional leads to very accurate calculations of the magnetic energies which are slightly overestimated by the USPP method [14]. For the exchange–correlation functional, nonlocal corrections in the form of the generalized gradient approximation (GGA) of Perdew and Wang [17] were used; for the spin interpolation of the correlation energy, we use the Vosko–Wilk–Nusair parametrization [18]. We note in passing that the GGA is necessary for the correct prediction of the magnetic ground state of Fe [21]. Without the gradient corrections, the ground state of Fe in the LSD approximation is nonmagnetic hexagonal close-packed; the GGA leads to the correct ferromagnetic body-centred-cubic ground state and the correct magnetovolume effect [14].

Using the PAW method and the GGA functional, the equilibrium lattice parameter calculated for fcc Cu is $a_0 = 3.635$ Å, which is close to the experimental value of 3.614 Å. The computed fcc lattice parameters of FM (high-spin), AF and NM fcc Fe are 3.65 Å, 3.52 Å and 3.47 Å, respectively [14]. Therefore, coherent epitaxy on Cu(001) is achieved under a planar tensile stress for the NM and AF fcc Fe overlayers and under compressive stress for FM fcc Fe bulk-like layers. The epitaxial constraint produces a small strain both within the Fe/Cu interface and in the direction perpendicular to it.

The total-energy change as a function of the strain along the direction perpendicular to the interface for the FM, AF and NM states of fcc Fe biaxially strained to the lattice constant of the Cu(001) substrate is shown in figure 1. For the square-mesh constant $a_s = a_0/\sqrt{2}$ of the Cu(100) surface ($a_s = 2.57$ Å), both FM and AF Fe equilibrate in a body-centred-tetragonal (bct) Fe lattice with c/a_s ratios smaller than the fcc value of $\sqrt{2}$. The FM ground state is 0.05 eV/atom lower in energy than the AF solution, and the corresponding c/a_s values are 1.27 and 1.36, respectively. The smaller axial ratio for the FM state reflects a smaller volume and interlayer spacing ($d_0 = c/2$). When using the Perdew–Zunger (PZ) parametrization [19] of the spin-polarized local correlation energy, the total-energy difference between the FM and AF states reduces to 0.01 eV/atom and the presence of a stable AF ground state for bulk-like fcc Fe/Cu(001) cannot be ruled out.

The FM phase of Fe shows only a small variation of the total-energy curve as a function of the tetragonal axial ratio as compared to those for the AF and NM phases (see figure 1).

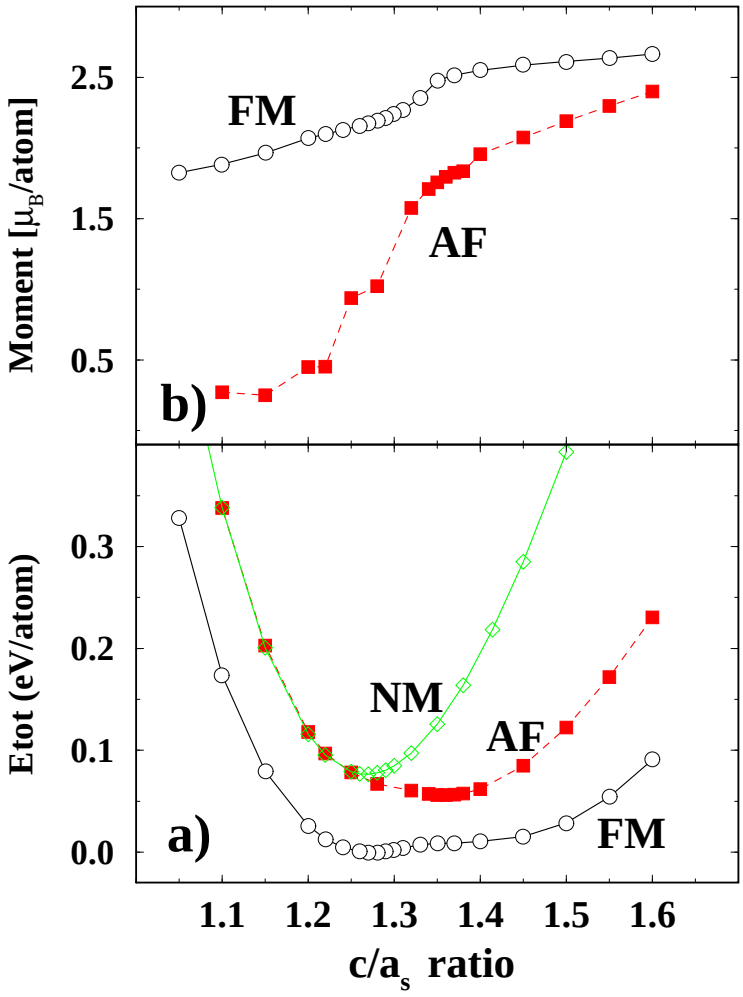

Figure 1. (a) The calculated total energy as a function of the c/a_s ratio for the FM, AF and NM states of fcc Fe biaxially strained to Cu(001). (b) Corresponding local magnetic moments of the FM and AF states.

This means that if upon temperature variation we allow fluctuations in energy ΔE of about 0.01 eV/atom, many FM states with expanded interlayer distances and large magnetic moments become accessible, and spin fluctuations may lead to different epitaxial equilibrium structures of the thick bulk-like fcc Fe films. AF and NM excited states display smaller volume fluctuations because the respective strain–energy curves are steeper around the corresponding equilibrium interlayer distance.

These calculations do not include effects related to the Fe/Cu and Fe/vacuum interfaces. Hence, to include these effects, we model the film + substrate system using vacuum/Fe/Cu supercells with a p(1×1) surface cell. The calculated GGA equilibrium lattice constant of fcc Cu has been used to fix the coordinates of the 'bulk layers' in our slab calculation. The number of Cu substrate layers is fixed at three and the thickness of the vacuum layer is 6 Å. The Brillouin zone integration has been performed using an ($8 \times 8 \times 1$) Monkhorst–Pack grid (ten k-points in the irreducible wedge) using smearing methods based on a Methfessel–Paxton

Table 1. Magnetic ground-state configurations of fcc Fe/Cu(001) films with up to nine monolayers. u = up and d = down indicate the orientations of the magnetic moment in a layer, starting at the free surface. The magnetic energy differences ΔE relative to the ground-state configuration are given in meV/atom.

1 ML	ΔE	2 ML	ΔE	3 ML	ΔE	4 ML	ΔE	5 ML	ΔE
u	0	uu	0	uuu	0	uudd	0	uuddd	0
		ud	137	uud	6	uuud	30	uuudd	2
				udd	44	uuuu	33	uuduu	7
				udu	91	uudu	36	uuuud	15
						uddd	62	uuudu	33
						uduu	63	uuuuu	62
						uddu	71		
						udud	97		
		6 ML	ΔE	7 ML	ΔE	8 ML	ΔE	9 ML	ΔE
		uudduu	0	uuudduu	0	uudduudd	0	uudududuu	0
		uuuudd	1	uududuu	26	uududuuu	30	uuudduudd	8
		uudddd	3	uududud	43	uuududud	45	uudduuddd	9
		uuuddd	7	uuuuuuu	80	uudududu	48	uudududud	14
		uududu	45						
		uuuuuu	84						

broadening function [12].

We consider first the magnetic ground state for idealized fcc Fe films. For a given number t of monolayers in the Fe film, we considered a number of different spin configurations (although for $t \geqslant 5$ it was not feasible to exhaust all of the $2^{(t-1)}$ possible spin configurations). The results are compiled in table 1. We find that the Fe films with thickness varying between 1 and 3 ML stabilize a FM ground state. However, in a 3 ML film the magnetic energy difference between the FM ground state and a configuration in which only the top two layers are ferromagnetically coupled while the third layer carries antiparallel moments (configuration uud with u = up and d = down) is already only 6 meV/Fe atom. On the other hand, to break the FM coupling in the surface bilayer costs a relatively large energy of $\geqslant$44 meV/Fe atom. For the 4 ML film we predict a bilayer AF structure (configuration uudd) as the ground state, which is 33 meV/Fe atom lower in energy than the FM configuration uuuu. This seems to contradict the experimental characterization of the 4 ML films as FM.

An AF bilayer structure is also the ground state for thicker films with even numbers of layers (6 ML, 8 ML). The calculated magnetic energy differences demonstrate that a configuration with a bilayer sequence has only slightly higher energy, whereas AF coupling between monolayers is possible only at a much higher energetic penalty. As noted already by Asada and Blügel [2], these uudduu ... configurations bear some similarity to a spin-spiral state with a wavevector of $\vec{k} = 0.5(100)2\pi/a$ which is close to the value for bulk fcc Fe of $\vec{k} \sim 0.6(100)2\pi/a$ (see, e.g., reference [22]). In films with odd numbers of monolayers, the FM coupling in the surface bilayer is preserved in all energetically favourable magnetic configurations. In addition, we find that the formation of a ferromagnetically coupled bilayer is also favoured at the interface with the Cu substrate. In the interior of the films, monolayer and bilayer antiferromagnetism lead to very similar magnetic energies. Our results are in general agreement with previous *ab initio* calculations performed in the LSD approximation without [1, 3, 4] and including the gradient corrections [2], which also predict an AF bilayer structure for films with even numbers of monolayers.

However, the crucial question is that concerning the interplay of the magnetism and

Table 2. Magnetic moments m_i (in μ_B) and changes $\delta_{i,i+1}$ in the interlayer distances (in per cent) calculated for the magnetic ground states of Fe/Cu(100) films with up to seven monolayers. m and δ stand for the average magnetic moment and the average tetragonal distortion of the Fe film.

	1 ML	u	2 ML	uu	3 ML	uuu	4 ML	uudd	5 ML	uuddd	7 ML	uuudduu
i	m_i	$\delta_{i,i+1}$	m_i	$\delta_{i,i+1}$	m_i	$\delta_{i,i+1}$	m_i	δ_{i+i+1}	m_i	δ_{i+i+1}	m_i	$\delta_{i,i+1}$
1	2.79		2.87		2.82		2.89		2.90		2.86	
		0.74		1.23		0.62		0.70		0.99		0.59
2	0.04		2.68		2.61		2.34		2.39		2.62	
		1.51		3.05		3.53		−3.34		−3.99		3.47
3	−0.02		0.05		2.57		−2.27		−2.21		2.16	
				1.24		1.47		3.04		2.93		−4.66
4			−0.01		0.04		−2.67		−2.50		−2.24	
						0.04		1.97		3.87		2.34
5					−0.02		−0.04		−2.59		−2.26	
								0.70		1.68		−5.00
6							0.01		−0.04		2.19	
										0.47		2.90
7									0.02		2.65	
												1.51
8											0.03	
												0.52
9											−0.01	
	m	δ	m	δ	m	δ	m	δ	m	δ	m	δ
	2.79	0.75	2.78	2.14	2.67	1.87	0.07	0.59	−0.40	1.10	1.14	0.16

structural relaxation. In a third set of calculations, the interlayer distances in the Fe film and between the top two layers of the Cu substrate were allowed to relax in a p(1×1) surface geometry. The results for the magnetic ground-state configurations are compiled in table 2. For the FM films with up to 3 ML we find a strongly enhanced magnetic moment of 2.8 to 2.9 μ_B in the surface layer; even in the subsurface layers, the moments are larger than the bulk value of $\sim$2.2 μ_B. The very small moments in the Cu layers at the interface are the consequence of the strong d–d hybridization at the surface. The values of the magnetic moments are almost unchanged from those of the unrelaxed ideal fcc films. The equilibrium interlayer distances $d_{i,i+1}$ between adjacent FM Fe layers are larger than the interlayer distance d_{Cu} in the substrate ($d_{\mathrm{Cu}} = a_0/2 \approx 1.82$ Å). Because of surface relaxation, the expansion $\delta_{12} = (d_{12} - d_{\mathrm{Cu}})/d_{\mathrm{Cu}}$ of the distance between the surface and subsurface layers is smaller than the corresponding changes δ_{23} and δ_{34} of the deeper layers. We also find a small expansion of the top layers of the substrate. Thus the volume increases per atom for the FM 1, 2 and 3 ML Fe/Cu layers with respect to the bulk Cu value $V_{\mathrm{Cu}} = 12.007$ Å^3 are 0.75%, 1.40% and 1.26%, respectively.

In the thicker layers each with a FM bilayer at the free surface and various types of antiferromagnetic ordering in the interior of the film, we find an expansion of the distance between ferromagnetically coupled layers of about 3% (reduced at the surface by inward relaxation) and a contraction of the distance between antiferromagnetically coupled layers by 4–5%. The moments are enhanced over those of the bulk at the surface and at the interface, but are bulk-like in the AF regions. Altogether, the Fe films in this region are almost fcc *on average*.

The relaxation also affects the magnetic energy differences between the ground state and the excited magnetic states. This is illustrated in table 3 for some selected config-

Table 3. Comparison between relaxed ground-state and excited configurations of 4 ML and 7 ML Fe/Cu(100) films. The magnetic moments m_i are given in μ_B and the changes in the interlayer distances $\delta_{i,i+1}$ in per cent of the ideal fcc interlayer distance of $d_{\mathrm{Cu}} = 1.82$ Å. m and δ stand for the average magnetic moment and tetragonal distortion in the Fe film. ΔE_{rel} gives the energy gain caused by relaxation (in meV/Fe atom) and ΔE_{mag} the magnetic energy difference relative to the ground state in meV/Fe atom. The numbers in parentheses give the energy differences for the unrelaxed films.

4 ML Fe/Cu(001)						
	uudd		uuuu		uuud	
ΔE_{rel}	5		30		5	
ΔE_{mag}	0		7(33)		30(30)	
	m_i	$\delta_{i,i+1}$	m_i	$\delta_{i,i+1}$	m_i	$\delta_{i,i+1}$
1 L Fe	2.89		2.81		2.87	
		0.70		−0.77		0.65
2 L Fe	2.34		2.52		2.61	
		−3.34		3.11		3.27
3 L Fe	−2.27		2.52		2.23	
		3.04		2.85		−4.33
4 L Fe	−2.67		2.58		−2.31	
		1.97		1.39		1.01
5 L Cu	−0.04		0.02		−0.06	
		0.70		0.58		0.44
6 L Cu	0.01		−0.03		−0.01	
	m	δ	m	δ	m	δ
	0.07	0.59	2.61	1.65	1.35	0.15

7 ML Fe/Cu(001)						
	uuudduu		uududuu		uududud	
ΔE_{rel}	7		5		4	
ΔE_{mag}	0(0)		28(25)		46(43)	
	m_i	$\delta_{i,i+1}$	m_i	$\delta_{i,i+1}$	m_i	$\delta_{i,i+1}$
1 L Fe	2.86		2.87		2.86	
		0.59		0.71		0.60
2 L Fe	2.62		2.37		2.39	
		3.47		−1.63		−1.17
3 L Fe	2.16		−2.03		−2.00	
		−4.66		−2.50		−2.11
4 L Fe	−2.24		1.88		1.86	
		2.34		−2.41		−2.39
5 L Fe	−2.26		−2.03		−2.16	
		−5.00		−3.49		−2.02
6 L Fe	2.19		2.26		1.83	
		2.90		3.37		−3.25
7 L Fe	2.65		2.63		−2.34	
		1.51		1.82		2.26
8 L Cu	0.03		0.03		−0.04	
		0.52		1.30		1.73
9 L Cu	−0.01		−0.02		0.00	
	m	δ	m	δ	m	δ
	1.14	0.16	1.14	−0.59	0.35	−1.15

urations of 4 ML and 7 ML films. Although the geometrical pattern of the relaxation remains the same (expansion between ferromagnetically coupled layers, contractions between antiferromagnetically coupled layers), the energy gain caused by relaxation may be substantially different: the FM 4 ML film gains 30 meV/Fe atom upon relaxation and assumes a structure with an average tetragonal distortion of about 1.7%, whereas for the AF bilayer ground state and for the excited AF uuud configuration, the relaxation energy arising from a much smaller distortion is only 5 meV/Fe atom. As a consequence, the relaxed FM configuration is only 7 meV/Fe atom higher in energy than the relaxed uudd ground state. This result has general validity: relaxation reduces the energy difference between the excited FM state and the partially AF ground state in region II. The example of the relaxed 7 ML film demonstrates that the contraction of the interlayer distance is particularly large (about 5%) between AF coupled bilayers, whereas between AF coupled monolayers it is only 2 to 3%. However, in both cases the average tetragonal distortion of the films remains small. For these thicker films, the influence of the relaxation on the magnetic energy differences is smaller.

Previous attempts to study the effect of a tetragonal distortion on the magnetic properties of fcc Fe films have been made by Kraft, Marcus and Scheffler [20] and by Asada and Blügel [2], but these calculations were restricted to symmetric free-standing films. Hence the ground state of a 5 ML film for example is uuduu and not uuddd as for the supported film, and there are only two and not six independent interlayer distances. As a consequence, there is qualitative agreement on expansion between adjacent FM layers and contraction between adjacent AF layers, but there is considerable quantitative disagreement on the precise amount of the interlayer relaxation.

In summary, we find that Fe films of thickness 1 to 3 ML are FM, while beyond 3 ML, AF mixed-spin states have the lowest energy. For an even number of Fe layers (for 4 ML, 6 ML and 8 ML) a bilayer AF ground state develops, while for an odd number of Fe layers (for 5 ML, 7 ML and 9 ML) various spin structures coexist. The spin configurations with the lowest energies display FM coupling of the Fe layers near the Fe/vacuum and Fe/Cu interface. In the ground-state spin configurations, the distances between FM coupled layers are slightly expanded, while distances between AF coupled layers are contracted relative to those in the ideal epitaxial structure. Hence Fe/Cu(100) films in region I with a ferromagnetic ground state are tetragonally distorted, whereas the partially antiferromagnetic films in region II are 'isotropic' fcc on average; both of these findings are in agreement with experiment.

There are two points where theory and experiment disagree.

The first concerns the ground state of a 4 ML film, which is predicted to be uudd and almost fcc in contrast to the experimental result of a tetragonally distorted ferromagnetic uuuu ground state. However, we have shown that the relaxation reduces the magnetic energy difference to only 7 meV/Fe atom. It is conceivable that a three-dimensional reconstruction as predicted by the tensor LEED experiments leads to a preference for the FM state. The *ab initio* calculation of such extended reconstructions is extremely time consuming; such studies are now under way. Another possibility is that the FM state of the as-grown films results from the growth on an already FM ordered underlayer and does not represent the true ground state. This view is supported by the fact that in 4 ML films the ferromagnetic/paramagnetic transition at the Curie temperature is irreversible and coupled to a structural transition [5, 23]. On cooling, the film does not return to the tetragonally distorted high-moment FM state, but assumes a more isotropic low-moment state. Evidently this is compatible with the coexistence of a metastable uuuu and an uudd ground state. The possibility of reversible and irreversible transitions between high- and low-moment states in Fe/Cu(100) films has been discussed by Spišák and Hafner [4], but the coupling of the magnetic to a structural transition has been ignored.

The second point where theory and experiment disagree is as regards the prediction of

only a modest expansion of $\leqslant 1\%$ in the ferromagnetically coupled bilayer at the surface in region II, in contrast to the experimental result [6, 24] of an expansion by almost 0.1 Å. Such a discrepancy between *ab initio* calculations (referring to zero temperature) and LEED analyses of the surface relaxation of metals (performed at room temperature) is not unusual—a much discussed example is that of Rh(100) surfaces, for which *ab initio* calculations agree on an inward relaxation of $\geqslant 3\%$, whereas LEED studies concluded that there is a much weaker relaxation ($1.2 \pm 1.6\%$) [25]. In this case it was demonstrated that the source of the discrepancy is in a strong anisotropic thermal expansion at the surface which compensates (or even overcompensates), with increasing temperature, for the inward relaxation predicted for the low-temperature limit [25]. Again the magnetic ordering makes finite-temperature calculations for the Fe/Cu(100) films much more difficult, so it must be left to future studies to verify whether the same mechanism also applies in the present case.

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