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Atomic and magnetic structure of fcc Fe/Cu(100)

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The atomic and magnetic structure of fcc Fe grown on Cu(100) are determined using spin-density-functional theory and the full-potential linear muffin-tin orbital method. Different types of interlayer and intralayer magnetism are investigated. For films of four up to eleven adsorbed Fe layers our *ab initio* total-energy calculations always give a ferromagnetic intralayer spin ordering of the Fe atoms. The surface and first subsurface layers couple ferromagnetically, whereas the deeper ones show interlayer antiferromagnetic coupling. This magnetic ordering is accompanied by a 3.9% expansion of the first layer spacing and a 1% contraction of the second, which agree well with low-energy electron diffraction analyses. We link the results to ground-state calculations for fcc iron.

Since the discovery in 1968 by Jesser and Matthews[1] that Fe grows in the fcc structure on Cu(100), a large number of experimental studies of this system have been made of many aspects of growth and structure. This system is of particular interest because it stabilizes at low temperatures the fcc phase of iron, which otherwise is only available as a stable phase in a temperature range of $\sim$ 1200–1650 K. Moreover the epitaxially grown fcc Fe film may differ in electronic and magnetic properties from the high-temperature phase. The latter is magnetically disordered and strictly cubic, whereas the former is magnetically ordered and slightly tetragonal because of lattice relaxation at the surface and in the "bulk," which usually begins at the third layer in fcc(100) metals. The calculation reported here finds this lattice relaxation.

The structure of films of a few atomic layers thickness is complicated and sensitive to growth conditions. Fortunately, however, relatively thick flat crystalline Fe films of 10 or more layers can be grown, which are thick enough so that electronic effects of the substrate can be neglected in discussing the Fe to vacuum interface. However, the films are strained in the plane of the film to the Cu lattice constant. The experimental situation is not completely clear, but some facts are well established. Low-energy electron diffraction (LEED) studies which analyzed intensities[2] found in films of eight or more layers a significant expansion of the first layer spacing compared to bulk and a contraction of the second spacing in the pseudomorphic growth region of 4–12 monolayers.

The magnetic properties are also not completely clear. Spin-polarized photoemission spectroscopy[3,4] determined thin Fe films to be ferromagnetic. Antiferromagnetism at low temperatures was found using Mössbauer spectroscopy.[5] An investigation using surface magneto-optic Kerr effect measurements together with LEED found ferromagnetic ordering on the surface, whereas inner Fe layers did not show a magneto-optic effect.[6]

There are few first-principles theoretical treatments of this complicated system, since it requires full-potential, spin-polarized total-energy calculations. Previous work[7,8] has given indications of the unusual magnetic structure of fcc Fe(100) constrained to the Cu lattice spacing in the plane, particularly of surface ferromagnetism and bulk antiferromagnetism, but these studies were restricted by the size of the treated system, and they did not relax the surface and bulk layers. Calculation of the relaxations provides a good quantitative check of the theory against experiment, since a consistent atomic structure is found in several LEED studies.[2] Hence a more extensive theoretical study which includes both the relaxations and the magnetic structure of the surface layers is timely, since it will help clarify the experimental situation.

We apply the full-potential linear muffin-tin orbital method[9] which has been previously applied, among many studies, directly to give accurate values of bulk and shear moduli of fcc Cu;[10] it has also been applied to the ground state of different Fe phases[11] and in its nonmagnetic version to the structural and electronic properties of transition-metal surfaces.[12] The local spin-density approximation (LSDA) is used with the exchange-correlation functional in the Vosko-Wilk-Nusair parametrization[13] of the Ceperley-Alder form[14] within the spin-density-functional formalism. The basis set consists of Hankel functions of s, p, and d character augmented to numerical solutions of the radial Schrödinger equation at three different energies. The charge density and the potential in the interstitial region are represented by basis-type functions fitted to the values and slopes on the atomic spheres.

In this work on the atomic and magnetic structure of the Fe/Cu(100) system in the intermediate growth range of 4–12 monolayers, which remained epitaxial in the experiments, we simulated the Fe/Cu(100) system by means of a slab construction of up to 11 Fe layers. The total energy is minimized with respect to the first-, the second-, and the bulk-layer spacings. The results match well those of the LEED analyses,[2] including the large expansion of the first-layer spacing over bulk. The layers are found to be individually ferromagnetic with the first and second layers coupled ferromagnetically. The first-layer moment is substantially greater than that of the deeper layers, which explains the expansion of the

first-layer spacing. The results are also consistent with magneto-optic observations.[6,15]

The following Fe systems were calculated in all of which the Fe lattice constant in the (001) plane was held at the Cu value: (1) a nonmagnetic (NM) Fe film, (2) intralayer antiferromagnetism of the Fe layers, and interlayer interaction allowing (3) ferromagnetic (FM) and (4) both FM and antiferromagnetic (AF) layer coupling. For the **k** summation we use up to 66 **k** points in the irreducible part of the surface Brillouin zone (BZ), depending on the system size. Bulk calculations were performed using 130 **k** points in the irreducible part of the BZ for nonmagnetic Cu (one atom per unit cell) up to 288 **k** points for antiferromagnetic fcc Fe (two atoms per unit cell). The energy eigenvalues were broadened by a Gaussian smearing of 5 mRy. Since relativistic corrections are known to worsen the agreement with experiment of various ground-state properties like the lattice constant or the bulk modulus of $3d$ and $4d$ transition metals,[11,16] they are not used in this work. A sufficiently large number of iterations was carried out to have the total energy converged to an accuracy better than half a mRy.

The starting point of this study is the determination of the theoretical equilibrium lattice constants of both fcc Fe and fcc Cu by calculating the total energy as a function of the atomic volume. For nonmagnetic fcc Cu, we find an equilibrium lattice constant of $a_0^{\mathrm{Cu}} = 6.82$ bohr, very close to the experimental value of 6.83 bohr. The results for the three different phases of fcc iron are plotted in Fig. 1. The AF phase begins with a second-order transition from the NM phase at about $a^{\mathrm{Fe}} = 6.45$ bohr. For larger values of a the AF phase is lower in energy than the NM phase. At the Cu lattice constant, the iron AF phase is energetically favored over both the NM and FM phases by 4.7 mRy/atom. The results agree well with previous calculations of Moruzzi *et al.*[17] Thus when fcc iron is constrained to the Cu lattice constant in the (001) plane and remains cubic, growth in the AF phase is expected. The calculation will show that the AF phase also occurs in the tetragonally distorted bulk.[18]

The density of states (DOS) of NM fcc Fe shows the general shape known for fcc transition metals (lowermost plot of Fig. 2). At the fcc Fe surface, the DOS exhibits two changes compared to the bulk. The upper three plots in Fig. 2 show the DOS for the surface, subsurface, and the Fe/Cu interface Fe atom calculated for four layers of Fe on seven layers of Cu. The bands get narrower due to the reduced coordination as one approaches the surface. The four layers of NM fcc Fe show a *contraction* of the first interlayer spacing d_{12} of 1.3% compared to its bulk spacing d_{34}. The high NM DOS at the Fermi energy will favor a ferromagnetic state according to the Stoner criterion. As is well known in ferromagnetic systems, the volume per atom is larger than in corresponding nonmagnetic systems. We therefore can understand the theoretical result that the layer spacings in the magnetic film are greater than in a nonmagnetic film.

The DOS of the interface Fe atoms (see Fig. 1) does not indicate a strong hybridization with the Cu substrate. Thus, interface effects at the sharp Fe/Cu boundary are not very important which implies that the Cu substrate serves mainly as an epitaxial constraint for the lattice constant in the (100) plane of the iron film. In the following we will change the surface unit cell to a size of four atoms, which allows for the study of intralayer as well as interlayer nearest-neighbor FM and AF coupling in the intermediate growth range of 4–12 monolayers. Considering 11 Fe layers with the parallel lattice constant

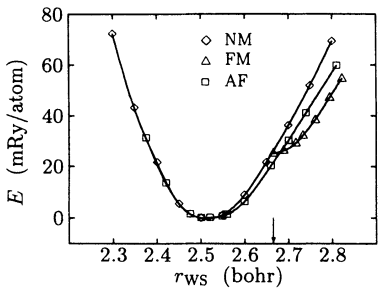

FIG. 1. Total energy of the nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AF) fcc iron. The energy difference $E^{\mathrm{NM}} - E^{\mathrm{AF}}$ is 4.7 mRy/atom at the Cu atomic volume, which is marked with the arrow. Further increase in the lattice parameter makes the FM more stable than the AF phase.

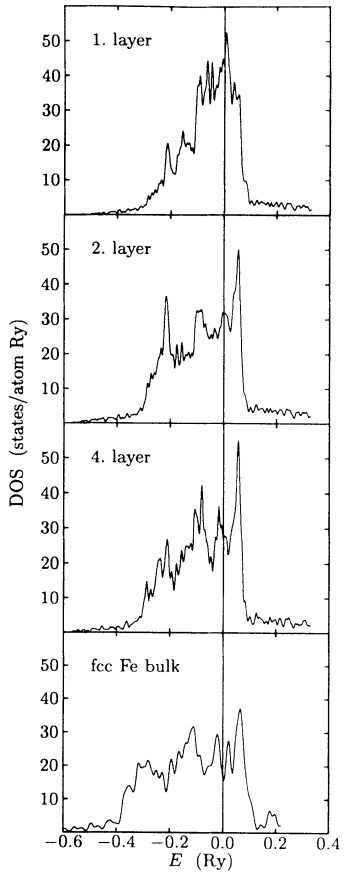

FIG. 2. Density of states (DOS) for bulk fcc NM iron and layer-resolved DOS for the surface (1. layer), the subsurface (2. layer) and the Fe/Cu interface (4. layer). Energies are referred to the Fermi level.

constrained to that of Cu(100), our supercell contains 44 atoms or 1144 electrons.

Since both interlayer and intralayer magnetic couplings are allowed, no constraints on the magnetic moments are imposed. The total energy of the whole system is determined as a function of the positions of the atoms in the first two layers at the vacuum interface. The total energy of the system is calculated for five positions each of the surface and the subsurface layer in steps of one percent of the lattice constant. For the resulting layer geometry which is lowest in energy the whole slab system including the bulk separation is allowed to undergo a tetragonal distortion and the two surface layers are adjusted again. These distortions must be studied, since the epitaxial strain on the fcc film will produce a tetragonal structure and also bulk AF systems like to undergo a tetragonal distortion which breaks the cubic symmetry.

For this 11-layer Fe system all majority-spin states are occupied in the first layer (see Fig. 3). The first interlayer spacing is *expanded* by about 3.9% over the bulk spacing and a large magnetic moment m of $2.80\mu_B$ is found for the surface atom. The first two layers show FM interlayer as well as FM intralayer coupling. Moving from the surface into the interior of the slab, the layers show AF coupling between layers, but FM coupling again is found within the layers.

The surface energy E_s of the NM unrelaxed slab, referred to bulk NM fcc Fe at the Cu lattice spacing, is 0.129 Ry per surface atom. Introduction of intralayer FM ordering reduces E_s to 0.104 Ry per surface atom and allowing interlayer AF coupling reduces E_s to 0.092 Ry per surface atom. Relaxation of surface and bulk layers of the 11-layer slab reduces E_s further to 0.087 Ry per surface atom. Table I shows that the calculated values for the layer spacings at the surface and in the bulk are in good agreement with LEED measurements. Values for the layer-resolved total charge and the magnetic moment, both in the muffin-tin (MT) sphere, are given in Table II. Charge density is accumulated in the second layer, whereas charge depletion is found for the surface atoms. The moment of the topmost Fe layer is strongly enhanced. The values of the moments of the next layers show AF oscillations with decreasing absolute values.

The quantitative agreement of the theoretical atomic structure with the LEED-determined structure is a valuable check on the accuracy of both results. The agreement holds for three structural parameters: the 3.9% expanded value of d_{12} over the bulk layer spacing, the small change in d_{23}, a 0.7% contraction in the theory—also found experimentally in Ref. 2(a), and the 2–3% decrease in c/a of the bulk, also found experimentally in Ref. 2. The importance of the constraint of the in-plane lattice constant to the copper substrate is clearly seen from the calculation. An unconstrained fcc(100) Fe surface becomes NM, the bulk lattice constant being at the NM value, which is 4.5% smaller than that of the FM phase (see Fig. 1), and d_{12} shows a further contraction from the bulk value.

The theoretical magnetic structure is also in general agreement with experiment since the Kerr effect measurements of Ref. 6 indicate ferromagnetic surface layers, but a paramagnetic bulk—which could be an antiferromagnetic phase above its Néel temperature. Both this work and previous theoretical work[7,8] show an enhanced ferromagnetic moment in the first layer compared to bulk ferromagnetic fcc Fe and a reduced ferromagnetic moment in the second layer oriented the same as the first layer. In addition all three studies show antiferromagnetic coupling in the third layer, which in the present case continues to the sixth layer. From the present work the effect of relaxation of the layer spacings on the moments can be found by comparing with Refs. 7 and 8, consisting of an increased first-layer moment and a considerably reduced second-layer moment. The moments of the deeper AF coupled layers are further reduced, but appear to rise in the fifth and sixth layer.

These results on the magnetic structure are clearly related to the bulk magnetic structure of Fig. 1. The expec-

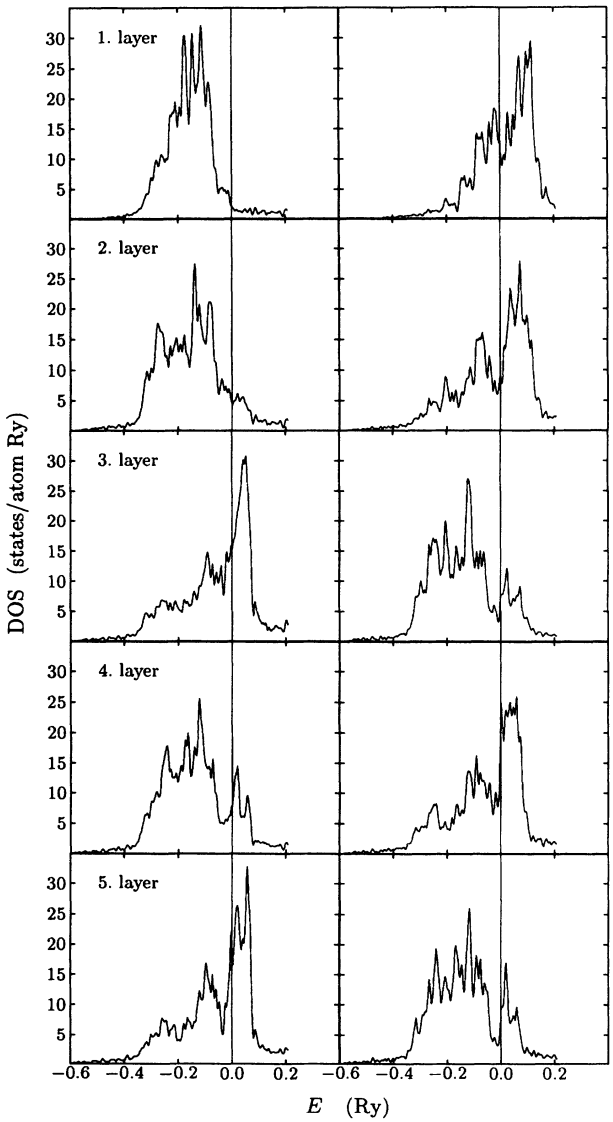

FIG. 3. Layer- and spin-resolved DOS from the 1. to the 5. layer of an 11-layer epitaxial Fe(100) system. All layers are internally FM. The first two layers couple ferromagnetically, whereas the inner layers are coupled antiferromagnetically.

TABLE I. Surface, subsurface, and bulk layer spacings compared to LEED analyses.

Spacing (bohr)	This work	Ref. 2(a)	Ref. 2(b)	Ref. 2(c)
d_{12}	3.44	3.48	3.42	3.50
d_{23}	3.27	3.33	3.36	3.40
d_{bulk}	3.31	3.35	3.36	3.35

TABLE II. Layer-resolved charge q and magnetic moment m inside the MT sphere for an 11-layer Fe slab.

Atom	L=6	L=5	L=4	L=3	L=2	L=1	Ref.
q (e)	7.05	7.04	7.05	7.13	7.17	6.95	this work
m (μ_B)	1.58	−1.61	1.40	−1.43	1.92	2.80	this work
				−1.45	2.31	2.68	7
				−1.68	2.30	2.79	8

tation that the tetragonally distorted bulk of a film held to the Cu lattice spacing in the (100) plane ($r_{\text{WS}} = 2.665$ bohr in Fig. 1) will be AF is demonstated. We note that the spacings of the inner layers found in three different ways all agree. The LEED values in Table I show that c/a is reduced by about 2% from the cubic value; this work finds 2.2% reduction; an elastic analysis based on stretching the Fe lattice from 6.78 bohr to 6.82 bohr in the (100) plane using a Poisson ratio $\nu = 0.44$ (estimated from the measured elastic constants of γ-Fe at 1400 K) (Ref. 19) also gives a reduction in c/a of 2%.

In conclusion we have performed extensive total-energy calculations to determine the atomic and magnetic structure of thin fcc iron films grown on Cu(100). The bulk of the Fe films is tetragonally distorted by about a 2% reduction in c/a from the exact fcc structure and the first-layer spacing expanded 3.9% compared to the bulk spacing. We find intralayer and interlayer ferromagnetism for the first two surface layers, whereas the deeper layers exhibit ferromagnetic intralayer and antiferromagnetic interlayer coupling.

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[19] The ratio of perpendicular to parallel strain equals $-2\nu/(1-\nu)$ and is derived and applied by F. Jona and P. M. Marcus, in *Surface Physics and Related Topics*, edited by F. Yang *et al.* (World Scientific, Singapure, 1991), p. 213. See also F. Jona and P. M. Marcus, Surf. Sci. **223**, L897 (1989).