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Abstract. The magnetocrystalline anisotropy energies of one Fe monolayer in Cu (Ag, Au) have been calculated from first principles. The spin-polarized relativistic linear muffin-tin orbitals (SPR–LMTO) method is used. The electronic contribution to the magnetic anisotropy energy is found to dominate in these systems and it favours an easy axis of magnetization perpendicular to the Fe monolayer plane. In contrast, the calculated magnetic dipolar interaction contribution favours an in-plane magnetization orientation but its magnitude is, respectively, about three, six and five times smaller than the electronic contribution.

Ultrathin transition-metal films show many unusual magnetic properties such as enhanced magnetic moments and a perpendicular magnetic anisotropy [1]. These interesting magnetic properties arise not only because of the two-dimensional nature of the film, but also as a result of the electronic structure at the interface. The magnetic properties of these ultrathin films have been a subject of considerable scientific and technical interest in recent years [1]. Of particular interest and importance at present is to understand the origin and nature of the magnetic anisotropy and to know how it varies as a function of, for example, number of monolayers and lattice spacing.

In this work we study the electronic structure and magnetocrystalline anisotropy of Fe monolayers in noble metals (Cu, Ag and Au) from first principles. The aim is to try to identify the source and the size of the magnetic anisotropy of these systems. Self-consistent electronic structure calculations have been carried out using the fully relativistic spin-polarized linear muffin-tin (SPR–LMTO) method [2, 3]. In this paper we present the results of our calculations for one Fe monolayer in noble metals.

Although the first attempts to understand the origin of the magnetic anisotropy of 3d ferromagnetic materials were made more than 50 years ago [4], the *ab initio* determination of the magnetic anisotropy of these bulk magnetic materials remains unresolved [5, 3]. The magnetic anisotropy energy (moment) is the energy (moment) change due to a change of magnetization direction. In the past decade, density functional theory with the local spin density approximation (LSDA) has proved very successful in describing many physical properties of many-electron systems in condensed matter. Thus, in principle, the magnetic anisotropy may be obtained from these first principles LSDA calculations. However, it has been established that the magnetic anisotropy is primarily due to the *simultaneous* occurrence of relativity (spin–orbit

coupling) and spin-polarization in the magnetic solids. Therefore, a detailed under-standing would need a formidable total energy study of relativistic many-electron systems. Recently, the extension of the LSDA for the relativistic spin-polarized many-electron systems has been explored [6], and several relativistic spin-polarized band methods have been developed [7, 2]. Magnetic anisotropy calculations for bulk Fe, Ni and Co from first-principles spin-polarized relativistic band theory have also been attempted [8, 5, 3]. These calculations show that because of its smallness (in the or-der of magnitude of 10^{-6} eV/atom), the magnetocrystalline anisotropy is a sensitive function of the fine details of the electronic structure of the solid. Consequently, the results obtained depend strongly on the approximations made, the numerical tech-niques used and whether they are converged with respect to, e.g., the size of the basis set and the numerical integration in k space [5, 3]. Indeed, whilst Fritsche *et al* [8] and Strange *et al* [8] obtained a magnetocrystalline anisotropy energy of cor-rect sign for Ni, Daalderop *et al* [5] and Guo *et al* [3] obtained a magnetocrystalline anisotropy energy with the wrong sign for Ni. Compared with bulk magnetic metals, ultrathin magnetic films usually have a much larger magnetic anisotropy because of their strong anisotropic property. It is, therefore, of interest to study the possibility of first-principles determination of the magnetic anisotropy of these magnetic systems by means of the spin-polarized relativistic band theory.
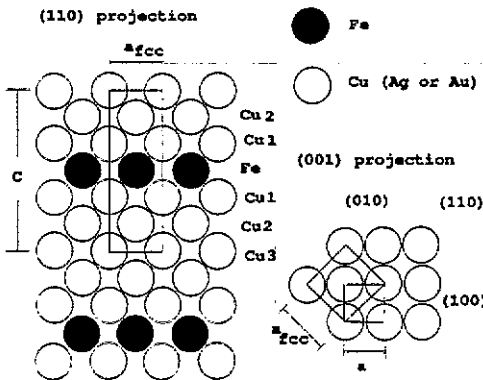

Figure 1. Hypothetical tetragonal crystal structure of one Fe monolayer in noble metals (Cu, Ag and Au) used in the present supercell calculations.

In this work, we consider one Fe monolayer with a square lattice sandwiched in between two Cu (Ag, Au) (001) surfaces. This is motivated partly by the fact that in many experiments the magnetic properties of Fe monolayers on noble metals are often measured with Fe monolayers covered by a thin layer of noble metals [9]. Furthermore, the magnetic properties of Fe monolayers in noble metals are interesting in their own right. To use the conventional bulk band structure method, the monolayer system is represented by a supercell geometry consisting of a periodic repetition of one Fe monolayer separated by a five-layer slab of Cu (Ag, Au) (written as M/Fe/M, M ≡ Cu (Ag, Au)) (see figure 1). Previous calculations [10] have shown that because of the short range of surface interface effects on noble metals, the slab containing five layers of noble metals is sufficiently thick to model the noble-metal substrates. No attempt is made to minimize the total energy with respect to the lattice spacing between the Fe

layer and neighbouring Cu (or Ag or Au) layers. Thus, the ideal FCC crystal structure is assumed and the supercell geometry is then equivalent to the noble metals with every sixth noble-metal layer in the [001] direction replaced by an Fe monolayer. The resultant system has the tetragonal symmetry with c/a equal to $3\sqrt{2}$ (see figure 1). Since the in-plane lattice constant (a) is mainly determined by the substrates, the observed FCC noble-metal lattice constants (a_{FCC}) are used to obtain the tetragonal lattice constants ($a_{FCC} = \sqrt{2}a$). Therefore, the tetragonal lattice constant (a) used is 2.557, 2.889 and 2.884 Å, respectively, for Cu/Fe/Cu, Ag/Fe/Ag and Au/Fe/Au.

Table 1. Calculated electronic and magnetic properties of Fe monolayer systems. m_s is the spin moment, m_o the orbital moment and m the total magnetic moment. g is the spectroscopic splitting factor, n_e the total electron charge in an atomic sphere. Cu (Ag or Au)n denotes Cu (Ag or Au) in the nth layer above or below the Fe monolayer (see figure 1).

		m_s (μ_B/atom)	m_o (μ_B/atom)	m (μ_B/atom)	g	Total charge n_e
Cu/Fe/Cu	Fe	2.435	0.068	2.503	2.053	25.894
	Cu1	0.030	0.005	0.035	—	29.070
($a = 2.557$ Å)	Cu2	−0.013	−0.001	−0.014	—	28.984
	Cu3	0.000	0.000	0.000	—	29.000
Ag/Fe/Ag	Fe	2.962	0.118	3.080	2.082	26.019
	Ag1	−0.025	0.002	−0.023	—	46.993
($a = 2.889$ Å)	Ag2	−0.008	0.000	−0.008	—	46.998
	Ag3	0.002	0.000	0.002	—	47.000
Au/Fe/Au	Fe	3.046	0.094	3.140	2.064	26.071
	Au1	0.001	0.015	0.016	—	78.958
($a = 2.884$ Å)	Au2	−0.010	−0.002	−0.012	—	79.008
	Au3	0.001	0.001	0.002	—	78.998

Self-consistent electronic structure calculations were carried out using the SPR–LMTO method. The magnetization direction is along [001] (perpendicular to the Fe monolayer plane). The usual local exchange-correlation potential of von Barth and Hedin was used [11]. The core charge densities were 'frozen' in the self-consistent cycles. The basis functions are s, p, d and f LMTOs. The same atomic radius was assumed for all atoms in the same system. The analytical tetrahedron technique was used for the Brillouin zone (BZ) integration with 364 k-points inside the irreducible wedge (IW) (1/16) of the tetragonal BZ sampled. The results of these calculations are summarized in table 1.

As expected, the calculated magnetic moments in these monolayer systems (table 1) are significantly enhanced (by 20–45% from the bulk Fe value (2.15 μ_B) [3]. So is the calculated spectroscopic splitting factor (g). This enhancement results from the reduced d bandwidth caused by the smaller number of near-neighbour Fe atoms in the Fe monolayer compared with the bulk Fe. Because there are no noble-metal d states around the Fermi energy to hybridize with the Fe d states, the neighbouring noble metal atomic layers, in particular, Ag or Au layers, are not very different from the vacuum at least as far as the magnetic moments are concerned. This observation is supported by the fact that the magnetic moment on the Fe sites in these monolayer systems (table 1) are close to that of the single Fe monolayer on, e.g., Ag (001) [12]. Similarly, due to lack of d band hybridization near the Fermi energy between Fe and the neighbouring noble metal atoms, the calculated induced magnetic moments on the

near neighbour Cu (or Ag or Au) are very small in comparison with, e.g., that in the single Fe monolayer on Pd [13].

We note that the calculated magnetic moment on the Fe sites is larger in the Ag/Fe/Ag and Au/Fe/Au systems than in the Cu/Fe/Cu (table 1). This is mainly due to the larger lattice constants in the former systems. To see whether this is true, a self-consistent SPR–LMTO calculation was also carried out for the Cu/Fe/Cu with a lattice constant equal to that of the Ag/Fe/Ag. Indeed, we found that the spin moment on the Fe was increased to 2.96 μ_B. Finally, table 1 shows that the noble-metal atoms on the central layer (Cu3 or Ag3 or Au3 in figure 1 and table 1) are almost completely neutral and there is no induced magnetic moment. This indicates that the electronic structure of the central layer is close to that of the bulk noble metals [10], giving support to the statement made earlier that the slab containing five layers of noble metals is sufficiently thick.
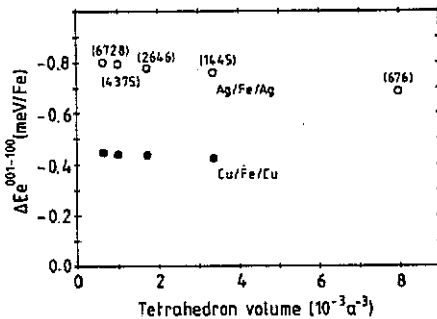

Figure 2. Calculated magnetocrystalline anisotropy energies, plotted as a function of the tetrahedron volume (see text). Numbers of the k-points in the irreducible wedge of the orthorhombic Brillouin zone sampled are given in round brackets.

When the magnetization direction is rotated from [001] to [100] (or [010] in-plane), the symmetry of the monolayer system is reduced to the orthorhombic one. Thus the IWBZ is now twice as large as that for the tetragonal system. Previous work [3, 5] has shown that to obtain reliable estimates of the magnetocrystalline anisotropy energy and moment, the BZ integration has to be carefully performed. To minimize the numerical uncertainties, we used the same IW of the orthorhombic BZ for both magnetization directions. The number of k-points inside the orthorhombic IWBZ used is 2646. This is obtained by dividing the ΓX line in the BZ into twenty intervals and the ΓZ line into five intervals. Self-consistent total energy calculations of this kind consume much computer time. Thus, to make computing effort tractable without losing much accuracy, we used the so-called 'force theorem' to obtain the magnetocrystalline energy and moment (i.e. the magnetocrystalline anisotropy energy is obtained as the difference in sums of single-particle eigenvalues for two different magnetization directions). Thus, we did one band structure calculation for each magnetization orientation using the self-consistent charge density obtained earlier for the magnetization along [001]. This approach has been shown to work well for a number of properties such as structural energy differences as well as magnetocrystalline anisotropy energies [14, 3]. The calculated magnetocrystalline anisotropy energy ($\Delta E_e^{001-100}$) and moment ($\Delta m^{001-100}$) are listed in table 2. The convergence of the BZ integration has to be checked. To this end we have calculated the magnetocrystalline anisotropy energy for

the Cu/Fe/Cu and Ag/Fe/Ag with a smaller basis set (s, p and d LMTOs only) for a number of different k-points inside the IWBZ (in other words, different tetrahedron volumes). The results are plotted as a function of the tetrahedron volume in figure 2. It is clear from figure 2 that as the tetrahedron volume approaches zero (the number of k-points sampled goes to infinity), the magnetocrystalline energy will not change significantly. The error in the data presented in table 2 due to the uncertainty of the BZ integration is estimated to be within 10%.

Table 2. Calculated magnetocrystalline anisotropy properties of Fe monolayer systems. $\Delta E^{001-100}$ is the total magnetic anisotropy energy, $\Delta E_{e}^{001-100}$ the electronic contribution and $\Delta E_{d}^{001-100}$ the magnetic dipolar contribution. $\Delta m^{001-100}$ is the anisotropy moment (the orbital contribution is given in round brackets).

	$\Delta E_{e}^{001-100}$ (meV/Fe)	$\Delta E_{d}^{001-100}$ (meV/Fe)	$\Delta E^{001-100}$ (meV/Fe)	$\Delta m^{001-100}$ (μ_{B}/Fe)
Cu/Fe/Cu	−0.428	0.136	−0.292	0.014(0.013)
Ag/Fe/Ag	−0.796	0.143	−0.653	0.026(0.025)
Au/Fe/Au	−0.743	0.149	−0.594	0.052(0.050)

The magnetocrystalline anisotropy energy discussed earlier is the electronic band structure (or simply, electronic) contribution to the magnetic anisotropy energy. This is due to the simultaneous occurrence of the electron relativistic interaction (spin–orbit coupling) and spin-polarization in the magnetic systems. The other important contribution to the measured magnetic anisotropy is the magnetostatic anisotropy [5, 15]. This may be thought of as the magnetostatic anisotropy energy resulting from the classical magnetic dipolar interaction. The magnetostatic anisotropy energy is zero for cubic systems and negligibly small for weak anisotropic systems such as cobalt [5]. However, for systems with a large anisotropy, such as ferromagnetic monolayers, this magnetostatic anisotropy energy cannot be neglected *a priori*. In fact, as our calculations reported later show, this magnetostatic anisotropy energy can be comparable with the electronic one for the ferromagnetic thin films.

Within the atomic sphere approximation, this magnetostatic energy E_d is just the magnetic dipole–dipole interaction energy and is given by (in atomic Rydberg units) [5]

$$E_{d} = \frac{1}{c^{2}} \sum_{qq'R}' \frac{1}{|R + q - q'|^{3}} \left\{ m_{q} \cdot m_{q'} - 3\frac{[(R + q - q') \cdot m_{q}][(R + q - q') \cdot m_{q'}]}{|R + q - q'|^{2}} \right\}$$

where q denotes the atom positions in one unit cell and m_q is the total magnetic moment in an atomic sphere around site q. For the ferromagnetic systems (i.e. $m_q \parallel m_{q'}$), this formula reduces to

$$E_{d} = \sum_{qq'} \frac{m_{q}m_{q'}}{c^{2}} M_{qq'}$$

and

$$M_{qq'} = \sum_{R}' \frac{1}{|R + q - q'|^{3}} \left\{ 1 - 3\frac{[(R + q - q') \cdot \hat{m}_{q}]^{2}}{|R + q - q'|^{2}} \right\}$$

where $M_{qq'}$ is called the ferromagnetic dipolar Madelung constant. We used the Ewald's lattice summation technique [16] to calculate these dipolar Madelung constants. The results for the Fe–Fe interaction in the supercell and also in a single monolayer are listed in table 3. Because of the smallness of the induced magnetic moments on the noble-metal sites, the contribution to the magnetic dipolar energy from the noble-metal layers is less than 1% and thus neglected. To evaluate the dipolar energy of one Fe monolayer in the noble metals, one must use the ferromagnetic dipolar Madelung constants for a single monolayer (not for the supercell) because the magnetic dipolar interaction is long range. Using the single Fe monolayer dipolar Madelung constants in table 3 and the Fe magnetic moments in table 1, we have obtained the magnetic dipolar anisotropy energy ($\Delta E_d^{001-100}$) for all the Fe monolayer systems considered (see table 2).

Table 3. Calculated ferromagnetic dipolar Madelung constant in units of a^{-3} (a is the tetragonal lattice constant) (see text and figure 1), for the Fe–Fe interaction in the supercell geometry (a) and in a free-standing monolayer (b).

m direction	Atom type	Fe (a)	Fe (b)
[001]	Fe	7.0590	9.0331
[100] or [010]	Fe	−3.5295	−4.5166

Our calculations predict that in all monolayer systems considered, the easy axis of magnetization is perpendicular to the Fe monolayer plane (see table 2). The origin of this perpendicular anisotropy is the large magnetocrystalline anisotropy of the electronic structure caused by the spin–orbit coupling. The magnetic dipolar anisotropy tends to give rise to an in-plane magnetic anisotropy. For the monolayer systems studied, however, the magnetic dipolar anisotropy is overcompensated by the electronic magnetic anisotropy. Like the magnetocrystalline anisotropy energy, the calculated anisotropy moments in these monolayer systems (table 2) are much larger (a factor of 100) than that of bulk Fe (10^{-4} μ_B). We note that these large anisotropy moments come mainly from the orbital moment contribution (more than 90%) (see table 2).

Modern ultrahigh vacuum and epitaxy techniques have made it possible to prepare monolayer range ultrathin films. The magnetic anisotropy properties of these artificial systems can be studied via, e.g., surface magnetic-optic Kerr effect (SMOKE) and ferromagnetic resonance (FMR) [1]. Nevertheless, it is extremely difficult to fabricate, e.g., high-quality ultrathin Fe films of one or two monolayer thickness on Cu substrates. Characterization of some of these magnetic films is equally difficult. Experimentally determined values of the magnetic anisotropy usually vary a lot. It is believed that at present, only qualitative comparison of our calculations with experiments is possible. We note that many measurements indicate that Fe monolayers of up to three layer or more thickness, on (or in) noble-metal substrates show a magnetization direction perpendicular to the Fe monolayer plane. For example, in ultrathin FCC Fe (001) films on Ag (001) the magnetization is found to be perpendicular to the surface for films thinner than 2.5 monolayers but to lie in the surface for films thicker than 6 monolayers [17]. Liu *et al* [18] reported that in FCC Fe (001) on Cu (001), the magnetization orientation is perpendicular below a critical thickness of six monolayers or less. The perpendicular anisotropy is also observed for monolayer range FCC Fe (001) on Au (001) [19].

Previous magnetocrystalline anisotropy calculations for one Fe monolayer on Ag (001) have been carried out by Gay and Richter by means of a (pseudo) perturbational approach based on the local-orbit band method [20]. More recently, Li *et al* [21] also reported magnetocrystalline anisotropy calculations for one Fe monolayer on Ag (001) and Au (001) using, again, a perturbational approach based on the linear augmented plane wave (LAPW) method. The results of these calculations predict that in one Fe monolayer on Ag (001) and Au (001), the magnetocrystalline anisotropy favours an easy axis of magnetization perpendicular to the Fe monolayer plane. The magnetocrystalline anisotropy energy ($\Delta E_e^{001-100}$) for Fe on Au (001) obtained by Li *et al* [21] is about -0.56 meV/atom, not very different from our result (-0.74 meV/atom) (table 2). The magnetocrystalline anisotropy energy for Fe on Ag (001) reported in [20] and [21] is, respectively, about -0.11 and -0.06 meV/atom. If one adds to these calculated magnetocrystalline anisotropy energies the magnetic dipolar anisotropy energy ($\Delta E_d^{001-100}$) of 0.14 meV/atom for an Fe monolayer with a magnetic moment 3.08 μ_B, the resultant magnetic anisotropy energies ($\Delta E^{001-100}$) for Fe on Ag (001) prefer an in-plane magnetization orientation. Therefore, Li *et al* [21] would have obtained an in-plane magnetic anisotropy (instead of a perpendicular one) for Fe on Ag (001) if the magnetic dipolar anisotropy energy had not been neglected in their work. Furthermore, our values for the magnetic anisotropy energies of the Ag/Fe/Ag and Au/Fe/Au are very similar. In contrast, Li *et al* [21] found rather different magnetocrystalline anisotropy energies for these systems (i.e. -0.06 meV/atom for Fe on Ag (001) and -0.56 meV/atom for Fe on Au (001)). It is not clear whether the differences in the calculated magnetocrystalline anisotropy energies between this work and previous studies are due to the fact that in this work a single Fe monolayer in the noble metals is considered whilst in previous studies a single monolayer on Ag (Au) substrate was investigated. However, it should be pointed out that in [21] calculations were only carried out for an Fe and Ag (Au) double atomic layer which may be too simple to represent one Fe monolayer on noble-metal surfaces. In [20], although the substrate is represented by a five-Ag-layer slab sandwiched in between two single Fe monolayers, the unperturbed band structure was obtained non-relativistically. The energy shifts due to relativistic mass–velocity and Darwin correction terms can be as large as 1.0 eV for silver compounds, and thus, as pointed out by Gay and Richter [20], the calculated results for one Fe monolayer on Ag (001) in [20] are perhaps not reliable.

In summary, we have performed self-consistent fully relativistic spin-polarized electronic structure calculations for the Fe monolayer in Cu (Ag, Au). We have also calculated the magnetic anisotropy properties due to both the anisotropy in the electronic structure and the anisotropy of the magnetic dipolar interaction. The results of our calculations predict that in all systems considered, the magnetization direction is perpendicular to the Fe monolayer plane. The perpendicular anisotropy in these monolayer systems results from the large anisotropy in the electronic structure caused by the electron relativistic interaction (spin–orbit coupling), which overcome the in-plane anisotropy provided by the magnetic dipolar interaction.

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