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# Magnetism and Magnetocrystalline Anisotropy at fcc Fe (001) Surface

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**The size and surface effects on the magnetism of a fcc Fe (001) surface was investigated by performing first-principles calculations on 3, 5, 7, and 9 monolayers fcc Fe (001) single slabs with two different two-dimensional lattice constants, $a$ = 3.44 Å (System I) and 3.65 Å (System II), using the all-electron full-potential linearized augmented plane wave method within a generalized gradient approximation. The surface layers were coupled ferromagnetically to the subsurface layer in both systems. However, the magnetism of the inner layers was quite different from each other. While all the inner layers of System II were ferromagnetically coupled in the same way as the surface layer, the inner layers of System I showed a peculiar magnetism, bilayer anti-ferromagnetism. The calculated spin magnetic moments per Fe atom were approximately 2.7 and 2.9 $\mu_B$ at the surface for Systems I and II, respectively, due to the almost occupied Fe $d$-state being in the majority spin state and band narrowing. The spin orientations of System I were out-of-plane regardless of its thickness, whereas the orientation of System II changed from out-of-plane to in-plane with increasing thickness.**

**Keywords :** first-principles calculation, fcc Fe, thin film, surface

## 1. Introduction

Magnetic thin films exhibit significantly different magnetic properties from their bulk counterparts, such as magnetic crystalline anisotropy, enhanced magnetic moment and critical behavior. These differences are caused by the increasing influence of the reduced dimensionality with decreasing film thickness as well as by the strain induced by epitaxial constraint at the interface. For example, Kim *et al.* reported that a $MnPt_3$ alloy is in a stable anti-ferromagnetic (AFM) state at the (001) surface even through its ground state in the bulk is ferromagnetic (FM) [1]. In contrast to $MnPt_3$, $MnAu_3$ shows an opposite magnetic behavior [2, 3], *i.e.*, the (001) surface is stabilized in the FM state despite having an AFM ground state in the bulk. More recently, it was reported that the magnetism of a Pd thin film was dependent on its thickness and exhibited oscillatory behavior with film thickness due to quantum well states [4].

The ground state of bulk Fe in the bcc structure is FM. Metastable fcc-like Fe, which is the phase obtained at temperatures above 1186 K and can be synthesized artificially, exists in a variety of magnetic states, paramagnetic (PM), AFM, FM, and spin-spiral states, depending on the lattice constant and lattice distortion [5-11]. Theoretically, a first-principles study showed that the most stable magnetic state of fcc bulk Fe is AFM and the structure is tetragonally distorted from a cube [8, 9].

It was observed that fcc Fe can be stabilized by the epitaxial growth of Fe on a Cu (001) substrate whose lattice constant is close to that of fcc Fe [12-14]. This system has attracted considerable interest as a model for examining the correlation between the atomic structure and magnetism [15-18]. Most recent studies have reached a consensus regarding thermally deposited films, at least for those grown at room-temperature [12-14, 16-18]: (i) Below approximately 4 monolayers (ML), a FM face-centered-tetragonal (fct) Fe phase is obtained; (ii) for a middle range thickness film (from 5 to 11 ML) a third phase consisting of AFM fcc Fe covered with FM fct Fe surface layers is formed; (iii) finally, in thicker films, a bcc Fe phase is formed due to the phase instability of fcc-like Fe.

A recent first-principles calculation of bulk fcc-like Fe revealed its complex magnetic structure [9]. A key result from the calculation was that a high spin (HS) FM state can be stabilized at an expanded lattice constant (3.65 Å) with just slightly higher total energy (approximately 20 meV) than that of the ground fct AFM state. The mag-

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netic moment of the HS FM state was reported to be 2.64 $\mu_B$ and was predicted to be quite sensitive to tetragonal distortions. Therefore, it would be interesting to investigate the surface magnetism of the ground AFM and HS FM states. Accordingly, in this study we employed the bulk lattice constants of the ground AFM and HS FM states as two-dimensional lattice constants. The magnetic and atomic structures of the fcc Fe (001) surfaces with two different lattice constants were investigated using the highly precise all-electron full-potential linearized augmented plane-wave (FLAPW) method [19].

## 2. Numerical Method

In this calculation, the generalized gradient approximation (GGA) [20] was used for the exchange-correlation potential. Two different calculated values were used as the two-dimensional lattice constants, $a = 3.44$ Å and $a = 3.65$ Å, which correspond to the AFM ground state (System I) and HS FM state of bulk fcc Fe (System II), respectively [9]. Different thicknesses (3, 5, 7, and 9 ML) were used for the two systems to determine the effects of the surface and system size. The z-coordinates of all atoms were optimized through a total energy minimization procedure that was guided by atomic force calculations. Ten special $k$-points within the irreducible 2D Brillouin zone (BZ) were used for the systems. In the FLAPW calculations, energy cut-offs of 256 Ry for the charge density and potential and 11.56 Ry for the bases were chosen. The charge density and potential inside each muffin-tin (MT) sphere with a radius of 2.3 a.u. were expanded using $l \leq 8$ lattice harmonics. Self-consistency was assumed if the root-mean-square differences between the input and output charge and spin densities were less than $1.0 \times 10^{-4}$ $e$/(a.u.)$^3$.

## 3. Results and Discussions

First, the surface and the size effects of the Fe (001) thin film were determined by calculating the total energy of the fcc Fe (001) thin films composed of 3, 5, 7, and 9 ML for all possible collinear spin configurations. Surface relaxation was allowed for Systems I and II to determine the z-coordinates of the atoms in the systems. Fig. 1(a) and (b) show the calculated total energy difference, ΔE (in units of meV) (with reference to the corresponding FM state), for Systems I and II, respectively. The notations of + and – in Fig. 1 represent the spin-up and spin-down magnetic quantization directions, respectively. For example, (++–) denotes that the spin orientation of the subsurface parallel to that of the surface but opposite to that of the next inner layer.

The magnetism of System I, whose two-dimensional lattice constant is the calculated value of the AFM ground state of bulk fcc Fe, was examined. As shown in Fig. 1 (a), the most stable state of the 9 ML film showed peculiar magnetism, FM coupling between the two outmost layers at the surface and bilayer AFM coupling between the inner layers. This tendency was maintained regardless of the film thickness. Previously reported calculations of the magnetism of Fe/Cu (001) surfaces [16, 22] also showed similar results to the present ones, so called bilayer antiferromagnetism. However, the magnetism of System II with the expanded lattice constant was found to

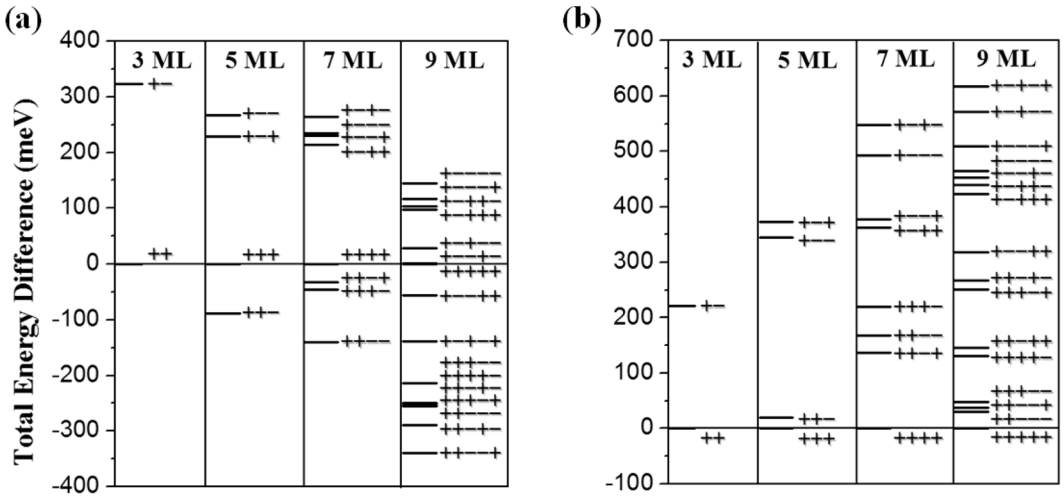


**Fig. 1.** Total energy difference ΔE for (a) System I and (b) System II in various collinear spin configurations in the relaxed systems, relative to FM (+++ ⋯) with 3, 5, 7, and 9 ML fcc Fe (001) surfaces. + (–) represents the spin-up (spin-down) magnetization direction, and the surface-to-inner-layers are read from left to right.

**Table 1.** Spin magnetic moments (in units of $\mu_B$) inside each of the muffin-tin (MT) spheres for 3, 5, 7, and 9 ML with two different systems.

| System | Layer | Fe(S) | Fe(S-1) | Fe(S-2) | Fe(S-3) | Fe(C) |
|---|---|---|---|---|---|---|
| | 3 (++) | 2.68 | · | · | · | 2.50 |
| System I | 5 (++−) | 2.68 | 2.20 | · | · | −1.70 |
| (3.43 Å) | 7 (++−−) | 2.70 | 2.25 | −2.09 | · | −2.45 |
| | 9 (++−−+) | 2.69 | 2.20 | −2.01 | −2.05 | 1.64 |
| | 3 (++) | 2.86 | · | · | · | 2.41 |
| System II | 5 (+++) | 2.90 | 2.52 | · | · | 2.50 |
| (3.65 Å) | 7 (++++) | 2.89 | 2.40 | 2.12 | · | 1.95 |
| | 9 (+++++) | 2.89 | 2.46 | 2.28 | 2.06 | 1.98 |

be totally different from that of System I. For System II [see Fig. 1(b)], the FM coupling over the whole layers are the ground states, irrespective of the film thickness. A FM fcc Fe thin film can be realized if a proper substrate is chosen. Further analysis will be required to determine the origin of the different magnetic structures between the two systems.

Table 1 lists the calculated layer-by-layer magnetic moments (in unit of $\mu_B$) inside each MT sphere for the 3, 5, 7, and 9 ML fcc Fe (001) thin films of Systems I and II in their magnetic ground states. The surface, the n-layers-away layer from the surface, and the center layers are denoted as S, S-n, and C, respectively. The top layers of the 9 ML films were closest to the bulk-terminated (001) surfaces. The magnetic moments at the surfaces of Systems I and II were close to 2.69 and 2.89 $\mu_B$, which are significantly enhanced, compared to those (1.64 and 1.98 $\mu_B$) of their center layers. The magnetic moment of the center layer in System II deviates significantly from that (2.64 $\mu_B$) of the bulk, whereas the magnetic moment of the center layer in System I was similar to the bulk value (1.63 $\mu_B$). This may be due to the sensitivity of the magnetic moment in the HS FM state to the tetragonal distortion. A detailed discussion of the origin of the deviation will be published elsewhere [23].

Total energy calculations of the 9 ML in System I guided by the calculated atomic forces revealed the interlayer spacings between the Fe layers to be different depending on the magnetic coupling between the neighboring layers. The interlayer spacing between the FM-coupled inner layers (1.93 Å) was higher than the bulk lattice spacing value (1.86 Å) [9]. On the other hand, the interlayer spacing (1.83 Å) between the AFM coupled layers was similar to that in the bulk. This result was expected considering that in the bulk, a FM metastable state has larger volume than the AFM ground state [9]. The interlayer spacing (1.91 Å) at the surface was slightly lower than that of the FM-coupled inner layers. The results are consistent with those of low-energy electron diffraction (LEED) analyses [14, 24], where a large expansion of the first-layer spacing over the bulk was observed.

The calculated layer- and spin-projected densities of states (DOS) of the 9 ML fcc Fe (001) thin film and bulk fcc Fe (for reference) are shown in Fig. 2(a) System I, (b) System II, (c) bulk fcc Fe in the AFM state, and (d) bulk fcc Fe in the HS FM state. Only the *d* states are presented in the figures in order to focus on the variation of the *d* states, which are responsible for the magnetism. The solid and dotted lines represent $t_{2g}$ (*xy*, *xz*, and *yz*) and $e_g$ ($z^2$ and $x^2$-$y^2$) states, respectively. The thick and thin lines indicate the in-plane (*xy* and $x^2$-$y^2$) and out-of-plane states (*xz*, *yz*, and $z^2$), respectively. The DOS of minority spin states were factored by −1 and the Fermi levels were set to zero. As shown in Fig. 2(a) (System I), majority *d*-states of Fe except for the *xy* orbital at the surface are fully occupied and exhibit band narrowing due to a surface effect, while the minority spin states show less occupation than those of Fe(C) for System I and the bulk AFM state [see Fig. 2(c)]. This effect will give rise to an enhanced magnetic moment (2.69 $\mu_B$) at the surface. For System II, the majority spin states were almost completely filled with the minority spin states being less filled. Hence, the magnetic moment at the (001) surface of the HS FM state was further enhanced.

For Fe(C) of System I, the features of the DOS were comparable to the bulk AFM state [see Fig. 2(c)], which means similar calculated magnetic moments. In contrast, the DOSs of Fe(C) of System II were quite different from those of the bulk HS FM state due to the tetragonal distortion near the center layer of the 9 ML thin film. As shown in Fig. 2(d), the fcc Fe of the bulk HS FM state contains degenerated $t_{2g}$ and $e_g$ orbitals due to the cubic symmetry and fully occupied in majority spin. However, the degeneracy of the states is broken and the states are split into *xy*, $x^2$-$y^2$, *xz*/*yz*, and $z^2$ states at Fe(C) in System II due to the 11 % reduced interlayer spacing [23]. For the Fe(C) in System II, the *xz*/*yz* and $x^2$-$y^2$ states shift to above the Fermi level in the majority spin compared to bulk HS FM state. Therefore the less occupied majority spin *d* state leads to a reduced magnetic moment of 1.98 $\mu_B$.

The mangetocrystalline anisotropy (MCA) originating from the spin-orbit interactions is one of the most fundamental and essential physical quantities in the field of magnetism. Here, the torque method, which provides very stable results [25], was used to calculate the MCA energy of the systems using a special 136 *k*-point in the irred-

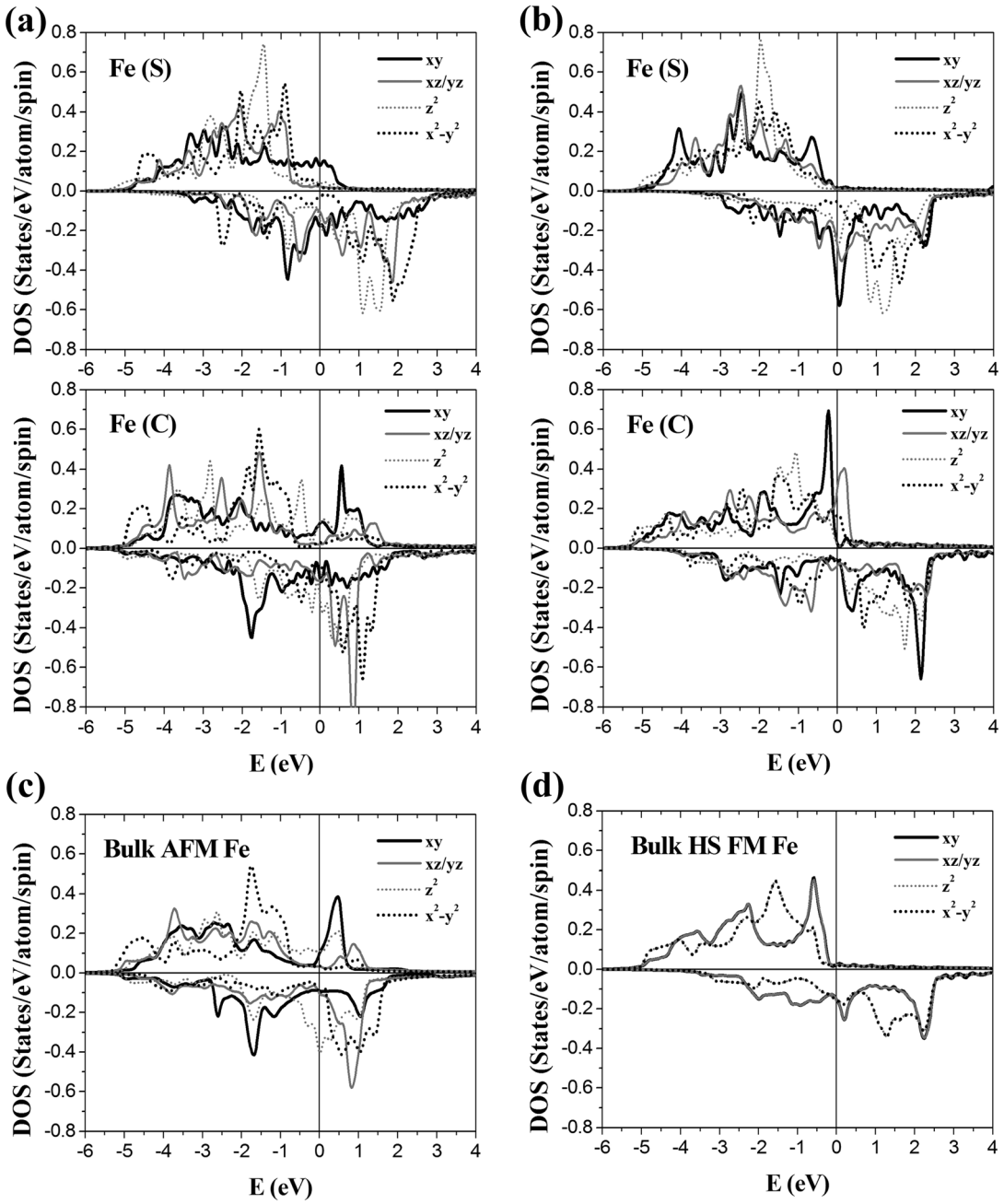


**Fig. 2.** Layer- and spin-projected DOS of the 9 ML fcc Fe (001) surface and center layer for (a) System I ($a$ = 3.44 Å), (b) System II ($a$ = 3.65 Å), (c) bulk AFM state, and (d) bulk HS FM state, respectively.

ucible 2D BZ. Table 2 lists the calculated $E_{MCA}$ (in units of $\mu$eV) for the 3, 5, 7 and 9 ML fcc Fe (001) surfaces with two different systems in their most stable magnetic structures. The positive magnetocrystalline anisotropy energy ($E_{MCA}$) means that the direction of magnetization is out-of-plane to the surface, while the negative one suggests in-plane magnetization. As shown in Table 2, the magnetic easy axis of System I was out-of-plane in the most stable magnetic structure with a significantly high

**Table 2.** The calculated magnetocrystalline anisotropy energies ($E_{MCA}$) (in $\mu$eV/Fe atom) for Systems I and II in the most stable magnetic structures (MS) at different thicknesses.

| System | | 3ML | 5 ML | 7 ML | 9 ML |
|---|---|---|---|---|---|
| System I | MS | ++ | ++– | ++–– | ++––+ |
| (3.44 Å) | $E_{MCA}$ | 163 | 201 | 163 | 144 |
| System II | MS | ++ | +++ | ++++ | +++++ |
| (3.65 Å) | $E_{MCA}$ | 12 | 9 | –4 | –77 |

$E_{MCA}$ (larger than 100 $\mu$eV) regardless of its thickness. However, at the expanded two-dimensional lattice constant (System II), the sign of $E_{MCA}$ changed depending on the film thickness. The spin orientation changed from out-of-plane to in-plane magnetization with increasing thickness. This suggests that the lattice size in the lateral plane has a significant influence on the magnetictocrystalline anisotropy. Hence, stable perpendicular magnetic anisotropy may be realized in ultra-thin Fe films on a Cu substrate.

## 4. Summary

This study investigated the magnetism and atomic structures of fcc Fe (001) surfaces, using the all-electron FLAPW method within GGA. The most stable state was calculated to be FM coupling of two adjacent Fe layers at the surface, and the inner layers was quite different from each other (Systems I and II). The calculated spin magnetic moment per Fe atom in Systems I and II was approximately 2.7 and 2.9 $\mu_B$ at the surface, respectively. This was attributed to the Fe *d*-state being almost occupied in the majority spin part and band narrowing from the DOS results. The calculated $E_{MCA}$ showed that the out-of-plane is an easy axis for System I. In contrast, the easy axis of System II changes to in-plane with increasing film thickness. System II with a large magnetic moment is achievable if the appropriate substrate is chosen.

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