

***Ab initio* magnetocrystalline anisotropy calculations for Fe/W(110) and Fe/Mo(110)**X. Qian<sup>1</sup> and W. Hübner<sup>1,2</sup><sup>1</sup>Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany<sup>2</sup>Institut für Theoretische Physik, Karl-Franzens-Universität Graz, Universitätsplatz 5, A-8010 Graz, Austria

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First-principles full-potential linearized augmented plane-wave calculations were performed to evaluate the magnetocrystalline anisotropy energy for Fe monolayers and bilayers on Mo(110) and W(110) substrates. In-plane  $[1\bar{1}0]$  easy axes were found for these systems due to the large in-plane interface anisotropy. Our theoretical results compare well with previous experimental observations.

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Magnetic anisotropy is of great interest in the magnetic recording industry. It is also scientifically challenging and demanding to compute the magnetic anisotropy energy due to the fact that this quantity is usually on the order of 1 meV/atom or less for the uniaxial systems.<sup>1–5</sup> It is even smaller (on the order of 1  $\mu$ eV) for higher-symmetry bulk materials such as Fe and Ni.<sup>6,7</sup> The magnetic anisotropy energy consists of contributions from the magnetocrystalline anisotropy energy mainly arising from spin-orbit coupling and the shape anisotropy energy from the magnetic dipolar interaction. For magnetic thin films such as Fe, the magnetocrystalline anisotropy energy (MAE) competes with the shape anisotropy energy, thereby making the perpendicular easy axis a possibility. However, shape anisotropy eventually will dominate for the thicker films, and the easy axis will lie in the film plane. Due to the delicate balance between these two contributions as a function of the lattice parameter and film thickness, it is nearly impossible to predict the magnetic easy axis without detailed and precise calculations. The reason for a specific easy axis for a particular system is even more elusive. It is still unresolved whether the contribution to the MAE is mainly due to the lifting of degeneracy at high-symmetry points in the Brillouin zone (BZ) or the non-high-symmetry points in the BZ making an equally important contribution to the MAE. A further question concerns the contribution from bands away from the Fermi surface. The relative significance of these contributions will depend on the detailed electronic structure of the system. The electronic structure is a function of the atomic configuration, the in-plane and vertical lattice parameters, and the thickness of the thin films. The impact of the surfaces and interfaces on the MAE comes from their modification of the electronic structure due to the missing bonds at the surface and the hybridization of the bands at the interface.

The experimentally observed magnetic properties of Fe thin films on W(110) substrates strongly depend on the coverage of Fe thin films and their preparation conditions. The Fe films are ferromagnetic when the Fe coverage is between 0.6 monolayer (ML) and 1.2 ML.<sup>8,9</sup> An in-plane easy axis was observed in this regime. When the Fe coverage is between 1.2 ML and 1.5 ML (sesquilayer), an out-of-plane easy axis was found for the double-layer islands by Elmers *et al.*<sup>10</sup> and Pietzsch *et al.*,<sup>11</sup> while Sander *et al.*<sup>9,12</sup> found an in-plane easy axis under all coverages. This difference in the magnetization direction needs to be understood, especially in this

intermediate coverage of 1.2–1.5 ML when the second layer is still grown pseudomorphically to the substrate. This subtle dependence of magnetic properties on the experimental conditions indicates a strong interplay between magnetism and structure. A theoretical study of magnetism by an *ab initio* method has to rest on a reliably optimized structure of the system.

In this paper, the WIEN97 code,<sup>13</sup> adopting the highly accurate and reliable full-potential linearized augmented plane-wave (FP-LAPW) method, was employed for calculating the magnetocrystalline anisotropy energies. The structures of 1 and 2 ML Fe/5 ML W(110) and Fe/5 ML Mo(110) were first optimized with the scalar-relativistic calculations.<sup>14,15</sup> The total energy of the system with a specific magnetization direction was calculated, incorporating spin-orbit coupling for the valence electrons based on the optimized and converged slab structures. The spin-orbit coupling was implemented with the second-variational procedure without self-consistency. The general gradient approximation (GGA) was used for the exchange potentials. Throughout this paper, the definition used for the MAE is

$$\text{MAE}(\pi/2, \phi) \equiv E(\theta=0, \phi) - E(\theta=\pi/2, \phi),$$

where  $\theta$  is the polar angle and  $\phi$  is the azimuthal angle as shown in Fig. 1. In our calculations, the total energy was used to determine the MAE, while the earlier calculations mainly adopt the force theorem,<sup>2–4,6,17,18</sup> neglecting the electron-correlation energy differences for different magnetization directions. The theoretical bulk bcc W(110) and Mo(110) lattice constants were used as the in-plane lattice constants for the slabs of 1 and 2 ML Fe/W(110) and Fe/Mo(110), respectively.<sup>14,15</sup> The magnetic dipolar energy is not included in our MAE's. This part of the contributions had

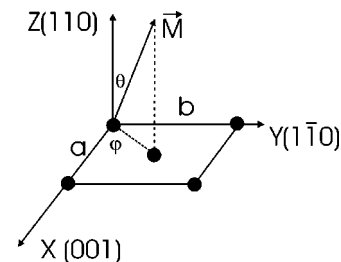


FIG. 1. Schematics of the bcc(110) surface.

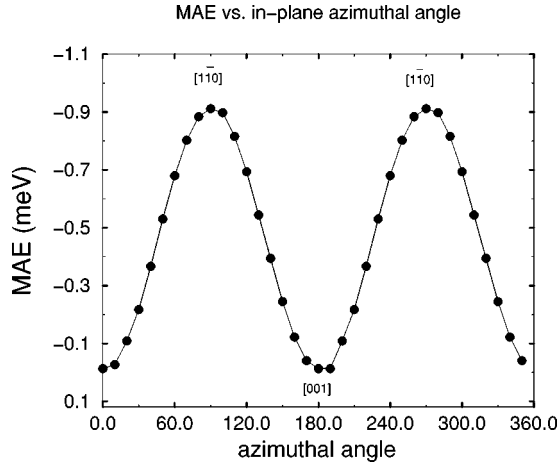


FIG. 2. MAE for the 1 ML free-standing Fe(110) with 420  $k$  points in the IBZ and with an in-plane lattice constant  $a = 3.163$  Å,  $b = 4.473$  Å. The in-plane [001] is the easy axis.

been calculated previously.<sup>16</sup> The dipolar energy is 0.08 meV for 1 ML Fe/W(110) and 0.26 meV for 2 ML Fe/W(110). The dipolar energy will make the magnetization direction slightly more favorable to the in-plane direction. The MAE energies for the free-standing thin films with bcc Fe(110) and Fe(100) orientations were also calculated (1) to compare with the previous available results and (2) to determine the effects of the film thickness, the symmetry of the thin films, and the lattice-constant change (magnetoelastic effect) on the MAE.

The numbers of  $k$  points in the irreducible Brillouin zone (IBZ) are 528, 435, 465, and 465 for 1 and 2 ML Fe/Mo(110), 1 and 2 ML Fe/W(110), respectively. The reduction of the symmetry due to the magnetization was taken into account. The total energy is converged to better than 20  $\mu$ eV.

The MAE for the free-standing bcc Fe(110) monolayer was calculated first. The in-plane lattice constant was chosen to be the same as the theoretical equilibrium value of the Mo(110) substrate with  $a = 3.163$  Å and  $b = 4.473$  Å.<sup>15</sup> Figure 2 plots the MAE value as a function of the in-plane azimuthal angle  $\phi$ . The easy axis is found to be in the in-plane [001] direction. Due to the in-plane  $D_{2h}$  symmetry, the MAE has a 180° period. If the free-standing monolayer can be considered to have two Fe/UHV interfaces, the phenomenological surface anisotropy constant  $K_{s,eff}$  can then be taken as one-quarter of the MAE energy. These results are shown in Table I. The  $K_{s,eff}$  values are in agreement with the values determined by Fritzsche *et al.*<sup>19</sup> In addition, the MAE value of this free-standing Fe(110) monolayer as a function of the in-plane lattice constant was calculated in the range

TABLE I. Fe(110)/UHV interface MAE results.

	$K_{s,eff}(\pi/2, \pi/2)$ (meV)	$K_{s,eff}(\pi/2, 0)$ (meV)
Fe/UHV (Ref. 19)	-0.35	0.08
Fe/UHV (this work)	-0.23	+0.007

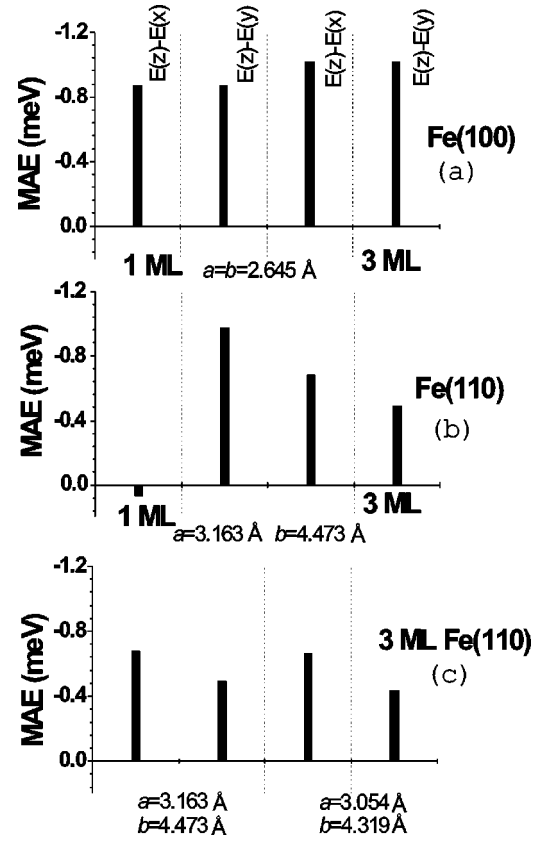


FIG. 3. Comparison of the MAE values for bcc Fe(100) 1 and 3 ML thin films with the same in-plane lattice constant. Comparison of the MAE values of bcc Fe(110) 1 and 3 ML thin films. Variation of MAE's for bcc Fe(110) 3 ML thin films with different lattice constants.

from  $a = 2.598$  Å and  $b = 3.674$  Å to  $a = 3.237$  Å and  $b = 4.578$  Å, keeping the  $b/a$  ratio fixed at  $\sqrt{2}$ . A systematic trend is not found for the MAE value with respect to the in-plane lattice constant. The magnitudes of the MAE's are very similar to one another. It shows that the magnetoelastic effect is a very complicated function of the electronic band structure. Its effect on the MAE energy for the free-standing Fe(110) monolayer is small when the  $b/a$  ratio is fixed. This agrees with previous theoretical results on free-standing Fe(100) monolayer systems.<sup>5</sup> When the symmetry is different as in the Fe(100) case or when the  $b/a$  ratio varies, more dramatic changes in the MAE values are expected due to the different splitting and degeneracies of the valence  $d$  orbitals. In contrast to an in-plane easy axis for the Fe(110) free-standing monolayer, an out-of-plane easy axis is found for the corresponding Fe(100) monolayer in agreement with previous calculations.<sup>5,17</sup>

The effect of symmetry and thickness of the Fe thin films on the value of the MAE is shown in Fig. 3. In this figure we compare the MAE for 1 and 3 ML Fe(100) and Fe(110) free-standing thin films. It is evident that Fe(100) and Fe(110) have very different MAE behaviors due to their symmetry differences. Moreover, the thickness of Fe thin films affects the two systems in very different ways. For the Fe(100) thin films, the thicker film only increases the MAE

magnitude. The MAE values are  $-0.8704$  meV and  $-1.02$  meV, respectively, for 1 and 3 ML systems with an in-plane lattice constant of  $2.645$  Å shown in Fig. 3(a). This result confirms earlier calculations<sup>17</sup> for the free-standing Fe(100) monolayer. However, these MAE values are quite different from the 1 ML and 3 ML Fe(110) free-standing monolayers as demonstrated in Fig. 3(b). For Fe(110), the additional layer of Fe enhances the overall trend of the perpendicular magnetization. Further, the hard-axis direction switches from the out-of-plane [110] direction to the in-plane [001] direction. Varying the in-plane lattice constant for the 3 ML Fe(110) free-standing thin films changes very little of the MAE magnitude as shown in Fig. 3(c) when the in-plane lattice constant is decreased from  $a=3.163$  Å,  $b=4.473$  Å to  $a=3.054$  Å,  $b=4.319$  Å with the same  $b/a$  ratio of  $\sqrt{2}$ . Once again we see the magnetoelastic effect on the MAE is small when the  $b/a$  ratio is fixed for 3 ML free-standing Fe(110) thin films.

From the above results, it is apparent that the thickness affects the MAE values much more than the sheer lattice stretching with the same symmetry and  $b/a$  ratio in these systems. This difference is probably due to the fact that the electronic structure changes are quite different in these two instances. Obviously the electronic structure is only slightly affected when the lattice constant varies, particularly for the very thin films (1 and 3 ML here). However, the change in atomic environment and consequently the electronic structure is more dramatic when the thickness of the film increases from 1 to 3 ML.

The MAE's for Fe thin films on the substrates are expected to behave differently due to the Fe-W and Fe-Mo interface interaction. The interface W and Mo atoms are found to have an induced moment of  $0.1\mu_B$  which is antiferromagnetically coupled to the neighboring Fe overlayers.<sup>14,15</sup> This induced moment is most likely caused by the exchange interaction between the Fe  $3d$  electrons and W  $5d$  (Mo  $4d$ ) electrons. The charge transfer is found to be very small between the Fe and W(Mo) interface atoms. The presence of the interface (one consequence is symmetry breaking) is to cause a charge redistribution between the various valence  $5d(4d)$  orbitals. We found that the overall out-of-plane valence  $d$  charge ( $d_{xz}+d_{yz}+d_{z^2}$ ) is reduced, while the in-plane valence  $d$  charge ( $d_{xy}+d_{x^2+y^2}$ ) is enhanced. This agrees with the intuitive understanding that the overall in-plane bonding is strengthened and the out-of-plane bonding is weakened due to half of the missing bonds in the vertical direction. But the total number of  $d$  electrons remains unchanged. However, the valence  $d$  spin polarization is increased for the interfacial substrate atoms, but not for the inner substrate atoms which have no direct contact with the Fe overlayers. This induced moment on the neighboring substrate atoms could also be possibly caused by the  $spd$  orbital hybridization between the Fe overlayer and W(Mo) substrate. However, there is very little charge transfer observed. Orbital hybridization is a necessary but not sufficient condition for charge transfer for these metallic systems. The valence  $s$  and  $p$  electrons may still play a role in the interaction between the Fe and W(Mo) substrate. However, we found the valence  $s$  and  $p$  electrons of the substrate are only slightly

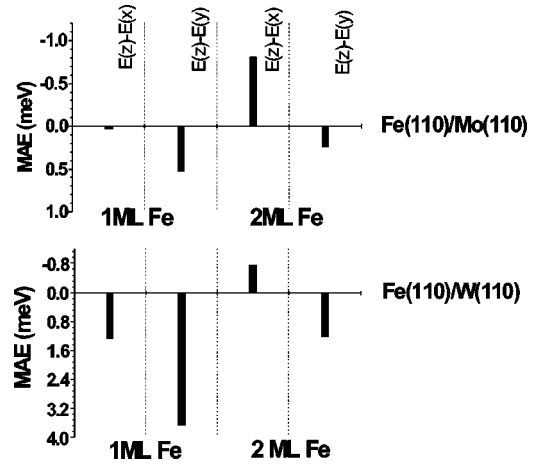


FIG. 4. MAE for the 1 and 2 ML Fe on Mo(110) (upper panel) and W(110) (lower panel) substrates.

polarized and contribute very little to the induced moment on the substrates. Further, the spin polarization for Fe  $4s$  and  $4p$  electrons stays the same with and without the presence of the substrate. Thus all our data point to the fact that the interaction between the Fe overlayer and the substrate is via the direct  $d-d$  interaction, probably not via the delocalized valence  $s$  and  $p$  electrons. This direct  $d-d$  interaction has already been predicted in theory<sup>3</sup> and observed in MXCD results for Co/Pt interfaces.<sup>20</sup>

Based on the optimized and converged structures of 1 and 2 ML Fe/5 ML Mo(110) and 1 and 2 ML Fe/5 ML W(110), the total energy was calculated including spin-orbit coupling for the valence electrons. The results are shown in Fig. 4 where a comparison between 1 and 2 ML Fe overlayers is made. For the Fe overlayers on Mo(110) substrate, a  $[1\bar{1}0]$  in-plane easy axis was found for both the 1 ML and 2 ML Fe coverages. However, the magnitude of this in-plane  $[1\bar{1}0]$  MAE is much reduced when there is an additional layer of Fe on top. Furthermore, the hard axis switches its direction from the out-of-plane [110] direction for the 1 ML Fe overlayer to the in-plane [001] direction for the 2 ML Fe coverage. In short, the overall strong in-plane surface anisotropy was compensated by the additional layer of Fe on top. This tendency towards a more out-of-plane magnetization direction when the Fe film is thicker is the same as for the free-standing Fe thin films if dipolar anisotropy is not taken into account. However, eventually the dipolar anisotropy will dominate and the magnetization direction will lie in plane if the film is thick enough. For Fe, the perpendicular magnetization only occurs with ultrathin films as has been demonstrated experimentally already. The MAE for the Fe overlayers on the W(110) substrate reveals a very similar characteristic except that the in-plane surface anisotropy is much stronger. As in the Mo case, the presence of the second layer of Fe reduces dramatically this in-plane MAE value. The hard axis also switches its direction from [110] to [100] as in the previous case. Since Mo and W belong to the same group and have very similar mechanical, atomic, and electronic properties, it is puzzling to understand why in the case of W there is a much more stronger interface anisotropy. The

answer may lie in the fact that W is a heavier atom than Mo. The W  $5d$  electrons are farther away from the nuclei compared to the Mo  $4d$  electrons; consequently, the  $5d$  orbitals are more influenced by and influence more strongly the neighboring atoms, as in this case the Fe atoms. The crystal-field splitting and the spin-orbit interaction for the W  $5d$  orbitals are larger than the Mo one. As a result, the anisotropy effect is stronger in W than in Mo. The origin of the magnetic anisotropy is the anisotropy of the lattice<sup>2,21</sup> together with spin-orbit coupling. The magnitude of the orbital moment and its anisotropy directly reflect the anisotropy of the crystal environment and the further distortion due to spin-orbit coupling. In agreement with the above argument, an increased orbital moment for W systems is observed compared to the Mo one due to the more anisotropic environment in W and stronger spin-orbit coupling. The orbital moments are found to be  $0.09\mu_B$  and  $-0.018\mu_B$ , respectively, for the neighboring Fe and W atoms in 1 ML Fe/5 ML W(110) when the magnetization direction is perpendicular to the film plane in agreement with recent calculations.<sup>16</sup> The orbital moments are  $0.067\mu_B$  and  $-0.005\mu_B$  for the neighboring Fe and Mo atoms, respectively, for the corresponding 1 ML Fe/5 Mo(110). Further, almost all of the orbital moments are from

valence  $d$  orbital contributions. Since magnetic anisotropy is mostly from valence  $d$  electron contributions, it is expected that the anisotropy is stronger for Fe/W(110) than Fe/Mo(110). There is another factor, i.e., a lattice misfit that may cause this difference.<sup>22</sup> The theoretical misfits are 10.5% and 11.6% between the Fe overlayer and Mo, W substrates, respectively. The Fe film is stretched slightly more on the W substrate than on the Mo substrate. This may affect the MAE values. But our earlier results of the MAE for free-standing Fe thin films show very little dependence on the lattice variation if the symmetry and  $b/a$  ratio are fixed. Experimentally,<sup>8-10</sup> it was found that 1 ML Fe/W(110) has a very strong in-plane anisotropy with an easy-axis in the  $[1\bar{1}0]$  direction. Our theoretical results agree with this experimental observation. Further, our calculation results show that for 2 ML Fe on the W(110) substrate, the easy axis still lies in the in-plane  $[1\bar{1}0]$  direction. However, the magnitude of this large in-plane anisotropy is reduced significantly.

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