Uniaxial Magnetocrystalline Anisotropy of Metal/Semiconductor Interfaces: Fe/ZnSe(001)

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A theoretical study of the magnetic moments and the in-plane magnetic anisotropy of an interface between a cubic ferromagnet and a cubic semiconductor, Fe/ZnSe(001), is presented. Theory confirms the observed, much debated, uniaxial anisotropy of the iron film. This result is important since the calculations are for perfect interfaces with squarelike environments, proving that the fourfolded symmetry of the interface Fe atoms is broken beyond the nearest neighboring semiconducting layer, effects that are usually assumed small. It is demonstrated how the uniaxial anisotropy is produced by the directional covalent bonds at the interface, even without atomic relaxations.

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Heterostructures consisting of ferromagnetic materials layered with semiconducting materials (FM/SC) show a range of new and interesting features, with potential use in spin electronics [1]. It has been suggested that an appropriate utilization of such materials will result in novel technologies based on spin-FET (field effect transistor), spin-LED (light emitting diode), etc. In addition, such heterostructures are expected to stand as strong candidates in the search for the next generation of giant and colossal magnetoresistance materials, where the transport properties are heavily dependent on an applied field [2].

Recently, Fe films grown on semiconductors in the cubic zinc-blende structure, e.g., ZnSe, GaAs, or InAs, have been in focus as potentially useful material combinations [3–7]. One of the key scientific issues has been identified with the atomistic/microscopic properties of the interface of these materials. In contrast to the expected fourfold local symmetry of the interface, an in-plane uniaxial magnetic anisotropy (UMA) was observed for thin Fe layers, with easy axis along [110] or $[1\bar{1}0]$, depending on the specific system [3–7]. As the thickness of the Fe layer increases, the symmetry changes gradually into the fourfold symmetry of bulk bcc Fe, with equivalent easy axes along the $\langle 100 \rangle$ azimuths. The effect has been found for various semiconductor substrates, and, in particular, for Fe/GaAs and Fe/ZnSe.

There have been many theories attempting to explain the microscopic origin of this UMA. Some of them, such as those based on the formation of an interface alloy or a large density of interface steps, have been ruled out. Today, the most favored explanation involves the reconstruction of the SC surface, due to the dimerization of its dangling bonds. These reconstructions lead to atomic rows along either [110] or $[1\bar{1}0]$, depending on the termination. The argument is that these reconstructions of the substrate remain after the growth of the FM film, which would produce a large uniaxial strain in the magnetic film. This strain in turn causes a uniaxial anisotropy through the magnetoelastic effect. Alternatively, the origin of the UMA has been attributed to the anisotropic interface bonding. For instance, by means of electronic structure calculations it was found that the two Fe atoms at the interface, although showing very similar densities of states, were affected by their inequivalent positions relative to the sp^3 bonds of the semiconductor [8].

In recent years, there have been experimental efforts to determine which of the two models causes the in-plane UMA. On one hand, Kneedler *et al.* [4] showed that the easy axis is independent of the direction of the surface reconstructions for two different Fe/GaAs systems, indicating that the strain in the Fe film has little effect. On the other hand, Xu *et al.* [5] deduced that it is the difference in the magnetoelasticity that causes the difference in easy axes observed for Fe/GaAs and Fe/InAs. Neither of these studies can completely rule out the competing model. However, if an interface with square geometry would show a UMA, the effect of any strain would only marginally affect its magnitude relative to the unstrained film. This is in contrast to the situation in, e.g., bcc Fe, where a symmetry breaking strain is crucial for the UMA.

It is the purpose of the present Letter, to show by means of first principles calculations, that ideal unstrained magnetic films in a FM/SC system do exhibit large in-plane UMA.

As a model system we have chosen Fe/ZnSe, since it has favorable qualities which simplifies comparisons with experiments; i.e., the system has a good lattice matching and, due to the lower reactivity of ZnSe as compared to, e.g., GaAs, has experimentally very clean interfaces. In addition, the surface reconstructions of this II-VI SC are comparatively simple. The Se-terminated surface has full coverage and is (2×1) reconstructed due to dimerization, while the Zn terminated surface only has half coverage leading to a $c(2 \times 2)$ structure [9].

Prior to this work there have been several theoretical studies of the Fe/ZnSe system. Continenza *et al.* performed semirelativistic spin-polarized calculations for three different Fe/ZnSe supercells, repeated to form multilayered structures [8]. The electronic structure and

the interlayer exchange coupling was calculated for the case of Fe/ZnSe superlattices by Jonge *et al.* [10], while the magnetic and transport properties as well as the out-of-plane magnetic anisotropy were calculated for Fe/ZnSe/Fe heterostructures by Herper *et al.* [11]. Finally, the relaxed positions of the atoms at the Fe/ZnSe(001) interface were thoroughly investigated by Sanyal and Mirbt [12]. However, the in-plane anisotropy was never considered in these studies; neither are we aware of such calculations for any other FM/SC combination.

The present calculations have been performed using the full-potential linearized augmented-plane-wave method (APW + lo) [13], with the magnetization densities represented by a full vector field [14]. The exchange correlation energy is treated within the local spin density approximation.

The Fe/ZnSe(001) interface is described by a supercell, with five atomic layers representing the SC, terminated by a full layer of either Zn or Se. The structure is continued by three (five) layers of Fe, referred to as the 3 ML (5 ML) system, where half of the atoms in the bcc planes are positioned at crystal sites of the zinc-blende structure, and half of the atoms are located in the corresponding voids (see Fig. 2). This corresponds to the experimental situation in the case of a Se-terminated interface, neglecting any possible reconstructions. The Zn terminated interface will be discussed below. The lattice constant of the ZnSe structure is $a_{\mathrm{ZnSe}} = 5.7$ Å, while a_{Fe} is ideally chosen to be $\frac{1}{2}a_{\mathrm{ZnSe}}$. The distance between the SC and the first Fe layer is chosen as $d_{\mathrm{SC-Fe}} = 2.17$ Å, for both types of terminations. No efforts were made to optimize the structure, since we neglect any interface reconstructions. The Fe layers are in most calculations followed by a vacuum layer with the thickness a_{ZnSe}. The exception is the calculation with a multilayer structure, where the iron layer has two equally terminated SC on both sides. Calculations were also performed for the $c(2 \times 2)$ Zn terminated interface. The half coverage of Zn then replaces a quarter of the bcc positions in the first Fe layer, resulting in an Fe film with thickness 2.75 ML. In the latter calculation, the SC is reduced to 3.5 atomic layers.

In order to calculate the magnetocrystalline anisotropy energy (MAE), a scalar relativistic calculation is first performed for each system. The anisotropic energy differences are then found using the force theorem, where the spin-orbit coupling (SOC) is introduced in the last variational step. This procedure has proven to give a good estimate of the MAE [15]. In the present case with many different atomic sites, the SOC can be included on all atoms in the system, or artificially, on selected atoms in order to study atomic resolved anisotropy effects.

All calculations are performed with a plane-wave cutoff $K_{\max} = 3.5$ a.u.$^{-1}$, except for the case of the $c(2 \times 2)$ structure, where $K_{\max} = 2.7$ a.u.$^{-1}$ was used. A convergence test for the 3 ML Zn terminated interface showed that 72 k-points in the two-dimensional Brillouin zone (BZ) are sufficient to resolve the value of the MAE, while this number has to be increased to 784 k-points in the multilayer calculation. The smaller BZ of the $c(2 \times 2)$ system was sampled with 50 k-points. Variations in the used temperature broadening affect the MAE, but do not lead to any changes in easy axis. A Fermi-Dirac broadening of $k_B T = 0.14$ eV was used in the presented eigenvalue summations.

In Fig. 1(a), we show a selection of the results for the in-plane MAE. The first thing to notice is the large uniaxial component for the perfect square geometry Fe films. The magnitude of this UMA, defined as $E_{[110]} - E_{[1\bar{1}0]}$ [16], is for the 3 ML Zn terminated interface 100 μeV/interface Fe atom. The corresponding value for the 5 ML system (not shown) is 20 μeV. This reflects the fact that there are finite size effects at least in the 3 ML film. In order to truly separate the interface contribution a thicker film is needed. For both calculations, the direction with lowest energy is along $[1\bar{1}0]$. However, for the Se-terminated interface the easy axis is instead along the [110] direction. In addition, the MAE is stronger for this termination, 300 μeV in the case of a 3 ML Fe film. To appreciate the magnitude of these in-plane anisotropies, we note that the calculated out-of-plane MAE (not shown) is of the same order of magnitude, and that the MAE of bulk Fe is 2 orders of magnitude smaller. The calculated easy axis is in accordance with experiment for the case of Se termination [6], but for the case of Zn termination experiments observe the [110] direction as easy axis [7]. Our result, that the two terminations have different easy axes is, however, in accordance with the experimental observations for Fe films on GaAs. In the latter case the two terminations show similar stable surfaces, as regards reconstructions and vacancy formation.

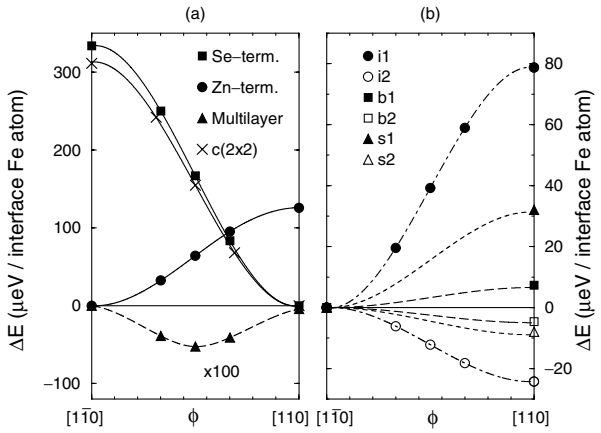

FIG. 1. (a) Total MAE for different 3 ML systems and the $c(2 \times 2)$ structure. (b) Local MAE for the 3 ML Fe film on a Zn terminated surface. The three Fe layers are referred to as interface (i), bulk (b), and surface (s). Positions with even numbers ($i2$, $b2$, and $s2$) correspond to voids in a continuation of the zinc-blende structure.

In order to study whether the disagreement between theory and experiment is due to the lower coverage of the Zn termination, calculations were performed also for a 2.75 ML Fe film on $c(2 \times 2)$ ZnSe. For this geometry the easy axis is directed along [110], see Fig. 1(a), in accordance with experiment [7]. Quantitatively, the calculated UMA for the 3 ML system is 1 order of magnitude larger than the experimental value, while the corresponding value for the 5 ML Fe film already approaches experimental results. Further, an experimental interface includes additional effects arising from strain and imperfections.

In Fig. 1, the MAE for the multilayer is also displayed (notice the different scale). Here the uniaxial component is missing, which results in a weak fourfold anisotropy, since the iron film has uniaxial contributions from both interfaces, that cancel exactly due to symmetry. This is true for all Fe thicknesses when the same SC stacking (i.e., same definition of [111] direction, see [16]) is used on both sides of the Fe layer. In the opposite case, where the second SC layer is a mirror image of the first, the two interfaces contribute to a doubled UMA in each Fe film. However, the contribution from consecutive films will cancel, resulting once again in a fourfolded anisotropy. Thus, the only way to achieve an enhanced UMA in a multilayer is to allow for both Zn- and Se-terminated interfaces.

As mentioned above, the atomic geometry of the interface has at first sight a perfectly square symmetry and, hence, the strong uniaxiality of the MAE is difficult to understand. However, as was pointed out in, for instance, Ref. [8], a closer inspection of the Fe atoms at the interface reveals that there are two different Fe positions. One Fe atom (Fe1) is situated at a site where a Se atom would have been situated if the zinc-blende structure was to continue across the interface. This atom follows an atomic geometry expected from sp^3-hybrid bonds. The other atom (Fe2) is situated at a position that corresponds to a void in the zinc-blende structure. The atomic geometry of the interface, hence, results in a reduced symmetry, although there are no atomic distortions. This deviation from square symmetry at the interface results in a large calculated (and measured) uniaxial component to the MAE.

Figure 1(b) shows the local contributions to the MAE when the spin-orbit coupling artificially is considered for only one Fe site at a time. As may be seen from this figure, the two different Fe atoms of the interface have different preferred easy axes. This difference prevails for the two inequivalent sites throughout the Fe film. The UMA coming from the surface atoms is enhanced, indicating that a surface layer close to the interface is more sensitive to the underlying uniaxiality than a nearby bulk layer.

The magnetic moments show no reduction for the Fe atoms at the interface. On the contrary, we calculate a slight enhancement, with spin and orbital moments of $2.6\mu_B$ and $0.08\mu_B$, which is in agreement with the calculations in Refs. [8,12], but in disagreement with those of Ref. [11]. There are small differences between the Fe1 and Fe2 sites of $0.04\mu_B$ and $-0.003\mu_B$, in spin and orbital moments, respectively. The surface spin and orbital moments are also enhanced, $2.9\mu_B$ and $0.07\mu_B$, while the interior of the film has atomic moments around $2.0\mu_B$ and $0.04\mu_B$. The orbital moments are all for the quantization axis along the easy axis, and display an anisotropy in accordance with the local anisotropies above. In Ref. [7], the hyperfine fields of the Fe atoms at the interface were reported to deviate very little from the bulk value.

As pointed out earlier, the square symmetry of the interface Fe atoms is broken beyond the nearest neighboring semiconducting layer. We will now analyze how these effects, that are usually assumed small, can give rise to a large UMA for Fe/ZnSe. As observed in Fig. 1(b), the two inequivalent Fe sites at the interface favor different directions: one perpendicular (Fe1) and the other parallel (Fe2) to the directions of the two unsaturated tetrahedral bonds of the sp^3 hybrid of the atoms of the ZnSe interface. Both for the case of Zn- and Se-terminated interfaces the global easy axis was found to be perpendicular to the direction of the sp^3-like bonds between the

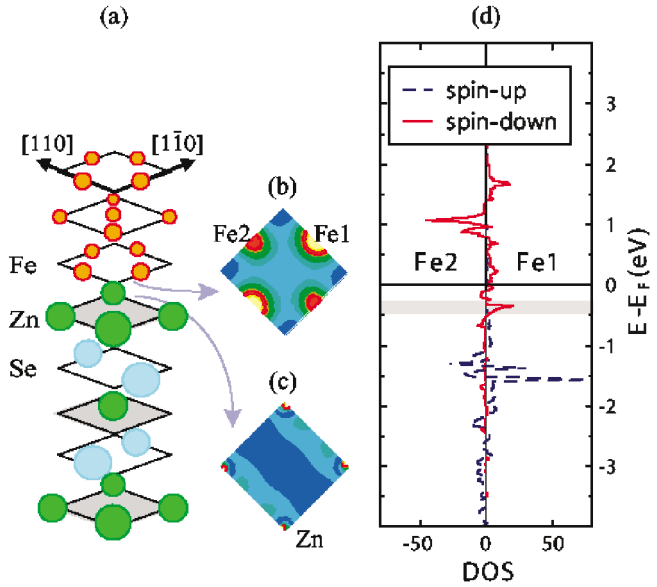

FIG. 2 (color). (a) Schematic picture of the 3Fe/ZnSe(001) structure. (b),(c) The spin-down orbital density is plotted for two slices parallel to the Zn terminated interface of the 3 ML Fe film: (b) 0.5 Å below the first Fe layer, towards the SC, and (c) 0.5 Å above the Zn layer, towards the FM. The densities are from the orbitals within the bonding energy interval around 0.4 eV below the Fermi energy, marked with a gray shade in Fig. 2(d). (d) Differences in d-projected density of states between the two Fe atoms at the interface. Fe1 is the atom in the "bonding" position, while Fe2 is placed in the "nonbonding" site.

SC and the first Fe layer. The sp^3-hybrids bond with d states at the Fe1 site, which results in a splitting into bonding and antibonding states. In order to illustrate this, we show in Fig. 2(d), for Zn termination, the difference in d projected density of states (DOS) between the two inequivalent Fe sites at the interface. There are three regions in the spin-down DOS that display conspicuous differences between the two Fe atoms. The states 1.0 eV above the Fermi energy (E_F) in the Fe2 atom are for the Fe1 atom split into regions of bonding (0.4 eV below E_F) and antibonding (1.6 eV above E_F) states. The effect of the stronger bonding of the Fe1 atom to the substrate is also reflected in the orbital density, calculated in the energy range of the bonding states, as shown in Figs. 2(b) and 2(c). Hence, one may detect a deviation from square symmetry both by inspection of the DOS as well as the charge density.

As mentioned, there exist several competing sources to the total UMA, both between the two sites within the Fe interface, and between sites with Se and Zn neighbors in, e.g., the $c(2 \times 2)$ Zn terminated interface. In reality there are also imperfections at the interface, such as steps, and regions with different interface structures, which will give rise to contributions with alternating sign to the UMA. Heinrich *et al.* [17] have shown that such local deviations from a uniform UMA give rise to a significant fourfold anisotropy component that has been observed experimentally. In this context we would like to discuss the recent observations in Mössbauer experiments on ^{57}Fe implanted at the interface of a 25 Å thick Fe film on Zn terminated ZnSe [7]. In these experiments a local uniaxial easy axis deviating with 30° from the [110] direction was observed. This deviation from the symmetry axis could occur due to a strong frustration at the interface from strong competing anisotropies, or from a strong fourfold anisotropy in the ^{57}Fe prepared sample. The transition from uniaxial to fourfold anisotropy takes place in a gradual manner, as a function of Fe thickness, as shown in Ref. [18].

In conclusion, we have provided a microscopical explanation to the observed large in-plane UMA of Fe films grown on zinc-blende SC. Since the large UMA is present also for ideal undistorted interfaces, our results indicate that strains in the Fe film, induced by possible reconstructions at the SC side of the interface, only would enhance (or reduce) its magnitude through the linear magnetoelastic effect. Hence, the anisotropic interfacial bonds are the microscopic mechanism causing the large UMA. For Fe/ZnSe, we calculate the same easy axis, [110], as observed in experiments [6,7], both for Se and Zn terminated interfaces when considering the experimental coverage. Our results stress the importance of the coverage of the surface of the SC substrate rather than its dimerized reconstruction.

It is demonstrated that an important ingredient for the MAE of Fe/ZnSe is the sp^3-like tetrahedral bonds from the substrate to the Fe atoms at the interface. Since it is known that the effect of the spin-orbit coupling of the interface atoms can be very important for the MAE, we predict that one can enhance the in-plane UMA by replacing Zn by the heavier isovalent element Hg, or simply Se by Te. We also predict that no high quality Fe/SC multilayer of equally terminated interfaces will display UMA, but instead they will all show a fourfold in-plane anisotropy.

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