Magnetic properties of single atoms of Fe and Co on Ir(111) and Pt(111)

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In using the fully relativistic versions of the embedded cluster and screened Korringa-Kohn-Rostoker methods for semi-infinite systems the magnetic properties of single adatoms of Fe and Co on Ir(111) and Pt(111) are studied. It is found that for Pt(111) Fe and Co adatoms are strongly perpendicularly oriented, while on Ir(111) the orientation of the magnetization is only out of plane for a Co adatom; for an Fe adatom it is in plane. For comparison, the so-called band energy parts of the anisotropy energy of a single layer of Fe and Co on these two substrates are also shown. The obtained results are compared to recent experimental studies using, e.g., the spin-polarized STM technique.

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The potential application in nonvolatile data storage devices is one of the driving forces behind research into magnetic nanostructures. In state-of-the-art hard disk drives a collection of a few hundred of single-domain particles (grains) are used to hold one bit of information. If materials can be manufactured, which exhibit sufficiently large anisotropies and thermal stabilities, it may become possible to store one bit in a single grain.[1] Such storage devices will require magnetic structures of precise atomic arrangement, as—if in addition the lateral dimensions of grains are further reduced—the influence of the perimeter atoms becomes increasingly important[2,3] and, as is known from previous studies, the magnetic properties of each atom in a nanostructure are highly influenced by its local environment.[1–4]

Using scanning tunneling microscopy structures can be precisely tailored and their magnetic properties determined. In recent scanning tunneling spectroscopy experiments[3,5] it has become possible to measure not only the Lande g factor of individual atoms but also their magnetic anisotropy. The findings suggest that the anisotropy energy of a single atom may eventually be large enough to use the magnetic state of an atom as a storage unit, pushing the ultimate limit for data storage density even further. Since the magnetic properties of small clusters and single adatoms differ strongly from those of bulk systems and even monolayers—e.g., showing a much enhanced magnetic anisotropy energy—they do not only generate interest for their technological relevance but also from a fundamental point of view.

In this paper we present a study of the magnetic moments and the angular dependent band energy part of the magnetic anisotropy energy of single atoms of Fe and Co, which—in order to investigate the influence of different substrates—have been deposited on Pt(111) and Ir(111). The calculations have been performed by means of the embedded cluster method (ECM), a scheme based on the fully relativistic screened Korringa-Kohn-Rostoker (SKKR) method, in which we can treat impurities embedded into a two-dimensional translationally invariant semi-infinite host. This approach makes use of multiple scattering theory in which the electronic structure of a cluster of embedded atoms is described by the so-called scattering path operator given by the following Dyson equation:[6,7]

$$\tau_c(\epsilon) = \tau_h(\epsilon)[1 - (t_h^{-1}(\epsilon) - t_c^{-1}(\epsilon))\tau_h(\epsilon)]^{-1}, \qquad (1)$$

where $\tau_c(\epsilon)$ and $\tau_h(\epsilon)$ account for all the scattering events within the embedded cluster and the host, and $\mathbf{t}_c^{-1}$ and $\mathbf{t}_h^{-1}$ denote the single-site scattering matrices for the "impurity" and for the host atoms, respectively. Once $\tau_c(\epsilon)$ is known, all corresponding local quantities, i.e., charge and magnetization densities, spin and orbital moments, as well as the total energy, can be calculated.

In order to perform self-consistent calculations within local density functional theory,[8] for the calculation of the t matrices and for the multipole expansion of the charge densities (needed to evaluate the Madelung potentials), a cutoff for the angular momentum expansion of $l_{max}=2$ was used. The potentials were treated within the atomic sphere approximation (ASA). In all self-consistent calculations the orientation of the magnetization was chosen to point uniformly along the surface normal (z axis). Structural relaxations of the cluster-substrate distance, which may, in principle, affect the magnetic properties,[9–12] have been neglected. The host and the impurity sites refer to the positions of an ideal fcc lattice with the experimental lattice constants of Pt ($a=3.92$ Å) and Ir ($a=3.84$ Å). The self-consistent calculations were performed using 102 $k_\parallel$ points in the irreducible surface Brillouin zone integrations and 16 energy points for the energy integrations along a semicircular contour in the complex energy plane by means of a Gaussian quadrature. To guarantee that all the perturbed host atoms with nonnegligible influence on the calculated properties are taken properly into account, we have increased the number of self-consistently calculated perturbed atoms around the adatom from 12 (the first atomic shell around the impurity) up to 85 (the fourth atomic shell). It should be noted that the perturbed atoms refer to substrate atoms and empty spheres (part of the vacuum region).

In principle, the magnetic anisotropy energy consists of two parts, namely, the difference in total energy $\Delta E_{\mu\nu}$ and in the magnetic dipole-dipole interaction energy ΔE_{dd} (shape
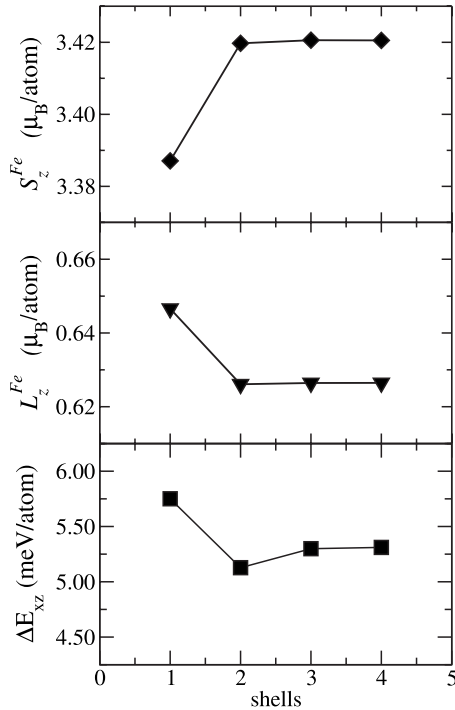
FIG. 1. Calculated spin (top) and orbital (center) magnetic moment, and magnetic anisotropy energy (bottom) of a single Fe adatom on Pt(111) as a function of the number of self-consistently treated atomic shells around the adatom.
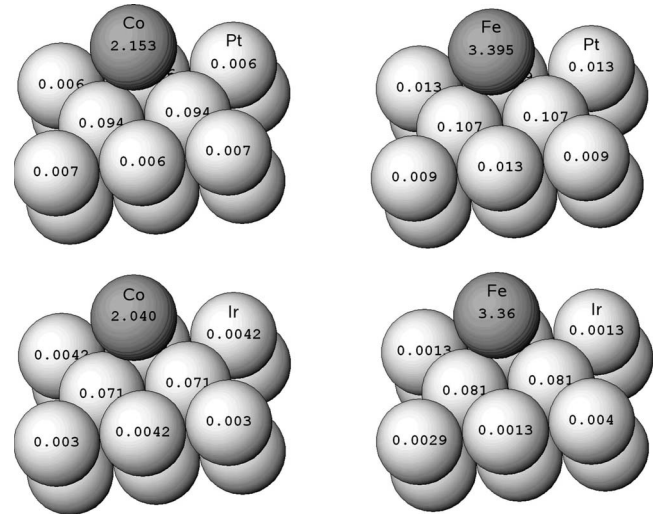

FIG. 2. Spin moments of the adatoms and induced spin moments in the topmost substrate layers. The values correspond to the size of the moments along the easy magnetization axis, which is out of plane in all cases except for the Fe/Ir system.

anisotropy) between two given uniform orientations μ and ν of the magnetization. Since for single adatoms the magnetic dipole-dipole interactions are of little importance, only $\Delta E_{\mu\nu}$ is considered, which in turn was calculated by means of the force theorem as the corresponding difference in band energies[13] (for details see Ref. 7). As can be seen from Fig. 1, reliable convergence of the spin and orbital moments of the adatoms with respect to the number of shells of neighbors used was obtained if only two shells of atoms were taken into account. For the calculations of the magnetic anisotropy energy up to four shells of atoms were required to obtain converged values as illustrated in Fig. 1.

The size of the magnetic moments of the adatoms exceed those of the respective bulk materials Fe and Co, and of (complete) monolayers of Fe and Co deposited on Ir(111) and Pt(111). This behavior, now quite well known to be characteristic for small magnetic clusters on top of metal substrates,[6,4] is due to the lower coordination of the surface atoms, which favors an incomplete quenching of orbital contributions. For both kinds of adatoms, Fe and Co, the magnetic moments are larger when deposited on a Pt substrate, a peculiar feature, which most likely is caused by the stronger polarization of Pt than that of an Ir substrate (see Fig. 2). In fact, the induced spin magnetic moments in the nearest neighbor atoms of the Pt substrate are by about $0.02\mu_B$ higher than for the Ir substrate, and the polarization rapidly decreases by one order of magnitude for the second and third nearest neighbors.

The spin and orbital moments of the adatoms are summarized in Table I. At first glance it can be realized that in relation to the bulk values the spin moments are considerably

increased. Compared to the (theoretical) value of bulk Co ($\mu_S^{hcp} = 1.6\mu_B$) the spin moments of the Co adatom are increased by a factor of approximately 1.3 if deposited on either substrate. For Fe, which has a bulk value of approximately $\mu_S^{bcc} = 2.1\mu_B$, this ratio is slightly larger, namely, 1.6. While it is known that for three-dimensional (3D) bulk systems, LSDA density functional calculations predict the spin moments rather accurately (underestimating the experimental values by only about $0.1\mu_B$), the orbital moments of Fe and Co, in particular, are off by about a factor of 2. Arguably, correlation effects may play a prominent role in predicting the size of the orbital polarization correctly.[14] The calculated values listed in Table I can therefore be expected to underestimate the actual size of the orbital moments of the adatoms. However, it is worthwhile to consider the amount by which these values are increased compared to the bulk values of LSDA calculations. The orbital moment of Co in bulk is $0.078\mu_B$ and that of Fe is $0.043\mu_B$. Due to the reduced coordination and the different chemical environment these values are increased for both an Fe and a Co adatom on the Ir substrate by a factor of approximately 6.3. In the case of a Pt substrate the Co and Fe orbital moments are 9.3 and 14.6 times larger, respectively. This increase of the orbital polarization is accompanied by an enhancement of the magnetocrystalline anisotropy.

Within our method it is possible to calculate the contributions of individual atoms to the total MAE and hence we can evaluate that portion of the anisotropy energy which is attributed to the substrate. The values obtained are illustrated in Fig. 3 for the adatom and atoms in the surface layer of the respective substrates. Interestingly, we find a significant dependence of these contributions on the type of deposited adatom. If Fe is deposited on Pt the substrate contributes only about 5.5%, whereas in the case of a Co atom the Pt atoms add 11.9% to the total MAE. In contrast, the atoms of an Ir substrate contribute 15.3% for the Co adatom, and even 25.5% if the adatom is Fe. The latter case is the only instance

TABLE I. Anisotropy energies (meV), spin and orbital magnetic moments (μ_B) of single monolayers of Fe and Co on Pt(111), and Ir(111) as compared to the corresponding adatoms values.

System			ΔE_{xz}	S_x	S_z	L_x	L_z
Pt(111)	Fe	ML	−0.710	3.018	3.016	0.093	0.113
		adatom	5.310	3.514	3.395	0.266	0.628
	Co	ML	0.123	1.987	1.988	0.117	0.147
		adatom	5.021	1.973	2.153	0.483	0.726
Ir(111)	Fe	ML	−0.063	2.828	2.827	0.117	0.121
		adatom	−2.655	3.359	3.341	0.267	0.243
	Co	ML	1.395	1.893	1.900	0.126	0.142
		adatom	2.982	2.008	2.040	0.427	0.494

when the preferred magnetization direction due to the MAE is perpendicular to the surface normal. In that case, interestingly, the major contribution of the substrate does not come from the atoms in the surface layer closest to the adatom, but from the subsurface layer ($S-1$, cf. Fig. 4).

Independent of the substrate for a Co adatom, $\Delta E_{\mu\nu}$ predicts strongly an out-of-plane orientation of the magnetization with the easy axis along the z direction (see Fig. 5), while for an Fe adatom (see Fig. 6), the choice of the substrate seems to be significant: on top of Pt(111) an out-of-plane orientation with an easy axis along z applies, while deposited on Ir(111) an easy axis along x is preferred.

Finally, for matters of comparison to the single adatoms, $\Delta E_{\mu\nu}$ of a complete Fe and a Co monolayer ferromagnetically coupled[15] to the substrate was studied within the framework of the fully relativistic SKKR method.[7] The results of this study are displayed in Table I. One immediately observes that the orbital magnetic moments of the adatoms are more sensitive to the chemical environment than the spin moments and in the meantime, the orbital moment anisotropy is larger on the Pt substrate than on the Ir. In compar-

ing now Figs. 5 and 6 with the values in Table I, one easily can see that $\Delta E_{\mu\nu}$ is substantially larger for a Co adatom on Ir(111) or Pt(111) than for the corresponding monolayer. In the case of Fe adatoms one even has a reversed situation: according to our calculations and in a good agreement with experimental findings[16] a single monolayer of Fe on Ir(111) or Pt(111) exhibits an in-plane magnetic anisotropy while a single Fe adatom on Pt(111) is strongly perpendicularly oriented.

An additional contribution to the magnetic anisotropy comes from the magnetic dipole-dipole interaction energies (shape anisotropy), which is always negative[17] and consequently favors an in-plane orientation of the magnetic moments. For single magnetic monolayers on metal substrates the shape anisotropy is rather small (typically about−0.1 meV) and was not taken into account in the present calculations. It should be noted that the shape anisotropy becomes very important indeed, whenever the number of magnetic monolayers is increased and then very often is the cause for so-called reorientation transitions (see, for example, the discussion in Ref. 20). The numbers given in Table I compare the band energy contribution to the magnetic anisotropy energy of a monolayer with that of a single adatom.

Figure 7 shows the total spin resolved density of states (DOS) for the Fe and Co adatoms on the Pt and Ir substrate,
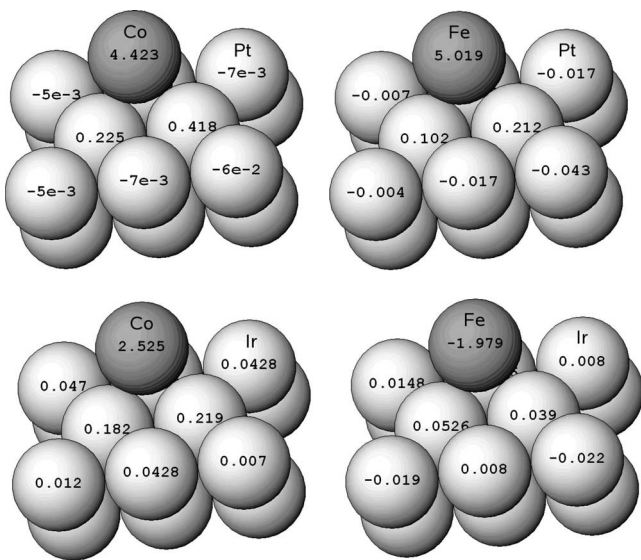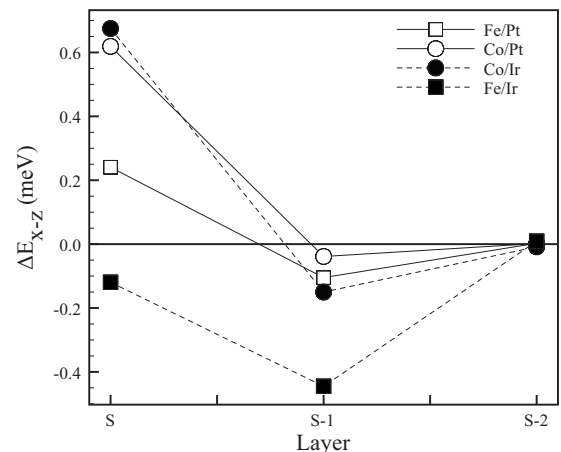

FIG. 3. Contributions to the MAE of the adatoms and the substrate. From left to right and top to bottom: Co/Pt, Fe/Pt, Co/Ir, Fe/Ir.

FIG. 4. Contributions of the substrate atoms in the surface layer (s) and the two layers below ($S-1, S-2$) to the total MAE.
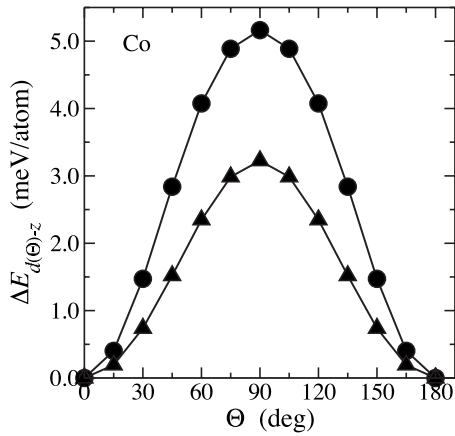
FIG. 5. Variation of the magnetic anisotropy energy of a single Co adatom on Ir(111) (triangles) and on Pt(111) (circles) as a function of the orientation of the magnetization with respect to the z axis, as specified by the polar angle Θ.

respectively. Note that the magnetic field was taken along the surface normal in all cases. As can be expected the DOS appears to be very similar for both Fe and Co, with the spin-up DOS always completely filled. The spin-down DOS of Fe and Co are of almost identical shape, but the peak is shifted slightly to lower energies for Co to accommodate the additional electron. Comparing the DOS on the Pt and Ir substrates, one can identify a broadening of the DOS on Ir, which results in the slightly lower spin moments S_z of Fe and Co (cf. Table I).

As has been shown in Refs. 18 and 19 the increase in the orbital moments, as compared to the bulk or the monolayer cases, is caused by the difference in the filling of the d_α ($\alpha = xy, xz, z^2, yz, x^2 - y^2$) orbitals.

It has been noticed quite some time ago[21,22] that in interfaces of Fe films with layers of the $5d$ elements the induced orbital moments can violate Hund's third rule. As a consequence of this rule the spin and orbital moments should align antiparallel for a less than half filled shell and parallel for a shell more than half filled. Even though strictly valid only for
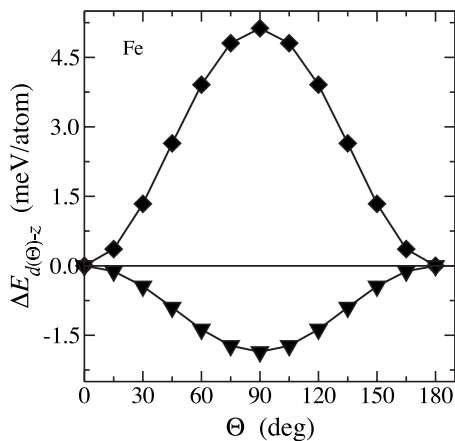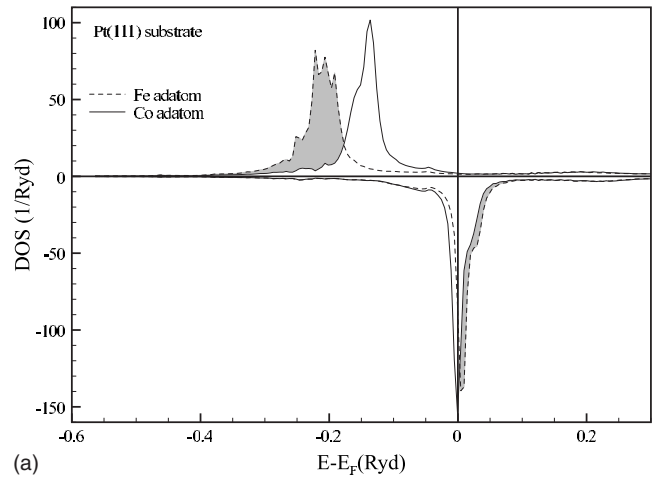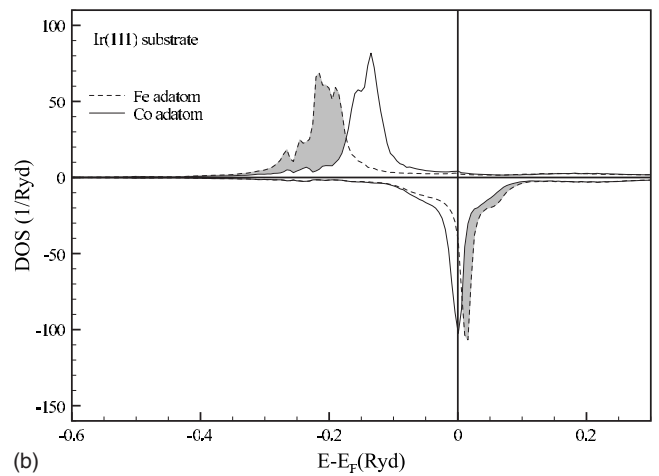

FIG. 6. Variation of the magnetic anisotropy energy of a single Fe adatom on Ir(111) (triangles) and on Pt(111) (diamonds) as a function of the orientation of the magnetization with respect to the z axis, as specified by the polar angle Θ.

(a)

(b)

FIG. 7. "Spin-projected" density of states of a single adatom of Fe (shaded area, dashed line) and of a single Co adatom (black line) on Pt(111) (top) and Ir(111) (bottom).

atoms it seems that Hund's rules are also applicable to solids, however, with exceptions. Since both Pt and Ir possess a more than half filled d shell, $\mathbf{J} = \mathbf{L} + \mathbf{S}$ has to be expected. The relative orientation of spin and orbital moments is explored in Fig. 8 where the atoms in the surface layer that occupy sites in the vicinity of the adatom are shown. A "+" indicates parallel and a "−" indicates antiparallel alignment of the moments. Note that the spin moments align parallel with the spin moments of the adatom, as also illustrated in Fig. 2. However, this is not strictly the case. Albeit not shown in this work, there are induced spin moments in the subsurface layer which align antiparallel to the spin of the magnetic adatom. Figure 8 shows that in a Pt substrate the spin and orbital moment are parallel with the Fe on top, and only a few moments are aligned opposite with the Co adatom on top. The situation is very much different for the Ir substrate, where many more atoms show antiparallel alignments. The arrangement of the atoms exhibiting this anomaly shows a symmetry according to the hexagonal two-dimensional (2D) lattice in the case of the Co adatom. However, for the Fe adatom this arrangement does not have the same symmetric pattern, because the easy magnetization direction is in plane
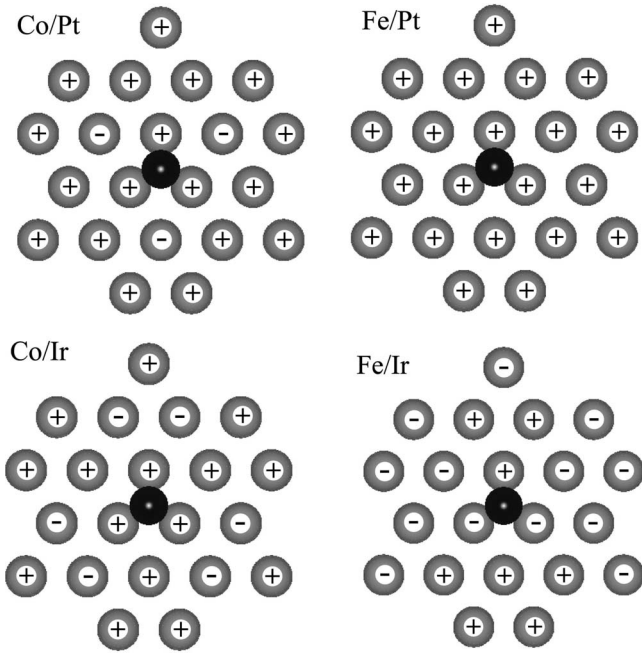
FIG. 8. Alignment of the spin and orbital moments in the surface layer of the Pt and Ir substrate. The sign "+" means that the induced moments are aligned parallel and "−" that they are aligned antiparallel. The central, black atom is the magnetic adatom. From left to right and top to bottom: Co/Pt, Fe/Pt, Co/Ir, Fe/Ir.
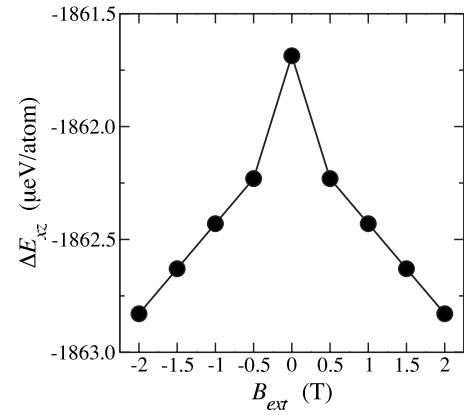

FIG. 9. Variation of the band energy part of the magnetic anisotropy energy of a single monolayer of Fe on Ir(111) as a function of an applied (constant) external magnetic field.

along the x direction. Small changes in the band filling have been shown to lead to such a behavior.[22]

Co nanostructures on Pt(111) were already studied in the past in terms of thin films of Co_n or $(CoPt)_n$ superstructures,[23] n denoting the number of atomic layers or repetitions and in the form of finite chains of Co atoms.[24,25] In Ref. 23 it was claimed that for a single layer of Co on Pt(111) an in-plane orientation of the magnetization is preferred with a very small anisotropy energy. In the spin dynamics study of Ref. 24, which is based on the same computational approach as used in here not only the value of the magnetic anisotropy energy agreed very well with experiment,[1] but also the direction of the canted magnetization. A recent study[26] of the structure of a thin film $Co/Pt_{13}/Co$ revealed that an fcc-type stacking of Co was more favorable than an hcp-type stacking, the interlayer distance between the Co and the first Pt layer being reduced by 10.1% as compared to that of bulk Pt. Although a film with two magnetic surfaces cannot be compared directly with a semi-infinite substrate coated with a monolayer of a magnetic metal (in the case of a semi-infinite system the Fermi energy is always that of the substrate, i.e., differs from that of a thin film), these results indicate that layer relaxation might in special cases be important for investigating magnetic anisotropies.

Experimentally, a study of Co nanostructures on Pt(111)[26,27] seems to lead to a rather complicated situation. In Ref. 26 an out-of-plane magnetization of Co wires and islands is found and—in order to explain the measured domain wall width in the wires—an effective anisotropy constant between 0.08 and 0.17 meV/atom for atoms within an island is proposed. In Ref. 27 the edge atoms of small islands are made responsible for their uniaxial out-of-plane magnetization. Of course none of these experimental results can be compared directly with results for a smooth Co monolayer on Pt(111) exhibiting two-dimensional translational symmetry. Finite Co nanostructures (single adatoms or finite wires) on Ir(111) and on Pt(111), however, do show a strong perpendicular anisotropy and support the experimental findings.

Up to now the case of using Ir(111) as a substrate is much less studied. From a spin-polarized STM study of (incomplete) monolayers of Fe on Ir(111) it was found[28] that the stacking of the Fe atoms seemed to be of fcc type. Furthermore, by applying an external magnetic field to the tip (and of course also to the sample) from the impact of this field, Bergmann et al.[28] concluded that "the observed superstructure is of magnetic origin with an out-of-plane magnetization". In order to check whether or not an externally applied field can be the cause for a possible misinterpretation of experimental results, the effect of such a field on the band energy part of the magnetic anisotropy energy was simulated by considering (non-self-consistently) a Kohn-Sham-Dirac Hamiltonian with the total magnetization pointing (a) along the surface normal,

$$H(\mathbf{r}) = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta m c^2 + V^{\text{eff}}(\mathbf{r})\mathbf{I}_4 + \beta \Sigma_z [B_z^{\text{eff}}(\mathbf{r}) + B^{\text{ext}}],$$

and (b) in plane. In the above equation α and β are Dirac matrices, $\boldsymbol{\Sigma}_z$ is the z component of the so-called spin operator, $\mathbf{I}_4$ is a four-dimensional unit matrix, and B^{ext} is a small constant external (magnetic) field. This simulation is displayed in Fig. 9 and very clearly shows that the fields applied in experiment most likely only marginally affect the size of the magnetic anisotropy. Possible sources of discrepancies between the weak in-plane anisotropy found in our calculations and the out-of-plane magnetization reported in Ref. 28 can be of quite different origin. For a smooth, two-dimensional translationally invariant Fe overlayer on Ir(111) the anisotropy energy is only slightly negative. Therefore layer relaxations as well as the finite size of the sample might be of importance. Complicated geometrical distortions due to the incompleteness of the atomic layers are very difficult to

take into account theoretically. Yet another possibility is that the experimentally found out-of-plane magnetization in Fe/Ir(111) is not caused by a perpendicular anisotropy but rather by other factors such as, e.g., a complicated chiral rotation of the magnetization due to higher order exchange interactions.[29] It might even turn out that perfect monolayers and single adatoms such as considered in here cannot reflect sufficiently well the actual situation mapped in a particular experiment.

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