Theory of Magnetocrystalline Anisotropy Energy for Wires and Corrals of Fe Adatoms: A Non-Perturbative Theory

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The magnetocrystalline anisotropy energy $E_{anis}$ for free-standing chains (quantum wires) and rings (quantum corrals) of Fe-adatoms $N = (2...48)$ is determined using an electronic tight-binding theory. Treating spin-orbit coupling non-perturbatively, we analyze the relationship between the electronic structure of the Fe $d$-electrons and $E_{anis}(n_d)$, for both the chain and ring conformations. We find that $E_{anis}(N)$ is larger for wires than for rings or infinite monolayers. Generally $E_{anis}(n_d)$ decreases in chains upon increasing $N$, while for rings $E_{anis}(n_d)$ is essentially independent of $N$. For increasing $N$, $E_{anis}(n_d)$ in corrals approaches the results for freestanding monolayers. Small rings exhibit clear odd-even oscillations of $E_{anis}(N)$. Within our theoretical framework we are able to explain the experimentally observed oscillations of $E_{anis}(n_d)$ during film growth with a period of one monolayer. Finally, a generalization of Hund’s third rule on spin-orbit coupling to itinerant ferromagnets is proposed.

75.30.Gw, 73.20.Dx, 85.42.+m

I. INTRODUCTION

Over the past decades information technology has been determined by semiconductor applications. However, recently the technology of such devices is limited due to the optical wavelength. Thus, quantum structures on the nanoscale can offer new perspectives for electronic applications. Manipulations at this scale require to develop nanotools: Low-temperature scanning tunneling microscopes allow not only for the probing of metallic surfaces with atomic resolution, but also for single-atom manipulation on surfaces. It has recently been demonstrated that lateral structures of adatoms can be generated by the scanning tunneling microscope (STM) tip (Crommie et al., Meyer et al., Rieder et al.). Modern STM-techniques allow now for the preparation of quantum corrals (QC’s). Examples of QC’s which have been prepared are rings of 48 Fe adatoms or stadia. The latter shape is motivated by the search for quantum-chaotic behavior, which so far has not been successful due to strong scattering of the electrons by the corral atoms. However the magnetic moment and magnetocrystalline anisotropy for these nanoscopic structures have not yet been determined in experiment. The QC of adsorbate atoms sets the boundary condition for the wave function of the substrate surface state. The quantum mechanical electron distribution of this state can therefore be measured by STM and is found to be in remarkable agreement with standard predictions of quantum mechanics.

In this paper, however, we are not interested in the surface state but rather in the magnetic anisotropy properties of the quantum corral itself. Since it is known that the magnetocrystalline anisotropy energy $E_{anis}$ is enhanced in thin magnetic films compared to three-dimensional bulk media, one might speculate about a further increase of $E_{anis}$ upon reduction of the dimensionality to 1D. Thus, we calculate $E_{anis}$ for QC’s and quantum wires (QW’s). These chains are frequently realized by the enhanced adsorption probability of adatoms on step edges.

We analyze for chains and rings for different numbers $N$ of Fe-adatoms how the magnetocrystalline anisotropy energy $E_{anis}$ depends on the electronic structure. To our knowledge, the first attempt of this kind has been made by Wang et al. for a pair of two Fe-atoms to explain the dependence of the electronic states. While Wang et al. treated spin-orbit coupling (SOC) in second-order perturbation theory, we include SOC completely non-perturbatively without resorting to degenerate or non-degenerate perturbation theory of any order. It is shown that for the diatomic pair there are important contributions to the magnetocrystalline anisotropy energy as a function of the number $n_d$ of $d$-electrons per atom $E_{anis}(n_d)$ due to the different lifting of band degeneracies for different magnetization directions. We find that $E_{anis} \propto \lambda^2_{so}$ is valid for the diatomic pair. However, $E_{anis}(n_d)$ can change its sign with respect to $\lambda_{so}$ due to level crossings in the energy level scheme of the diatomic pair. In the same way we calculate $E_{anis}(n_d)$ for chains and rings with different numbers $N$ of Fe-atoms. In small rings there are oscillations of $E_{anis}(N)$ between rings with an even or odd number of atoms. For our calculation we use two models:

(i) an extension of the diatomic pair model $E_{anis}$ to $N$ atoms,
(ii) a conventional tight-binding description of the wires and corrals including SOC.

Our paper is organized as follows: In Sec. II, the diatomic-pair model (II.A) and the tight-binding model (II.B.) are presented together with the determination of SOC (II.C) and $E_{anis}$ (II.D.). Results for the diatomic-pair model are shown in Sec. III.A, while results for the tight-binding model are discussed in Sec. III.B.
II. THEORY

A. Diatomic-pair model

We follow the ideas of Wang et al. and extend their diatomic-pair model to the case of N atoms. We start from the following Hamiltonian:

$$H = \sum_{i,\gamma,\sigma} \epsilon_{i\gamma} c_{i\gamma\sigma}^\dagger c_{i\gamma\sigma} + \sum_{(i,j)\gamma,\beta,\sigma,\sigma'} t_{ij\gamma\beta} c_{i\gamma\sigma}^\dagger c_{j\beta\sigma'}$$  \hspace{1cm} (1)

The summation is taken over N sites i, while the second sum is over pairs of nearest neighbors. As usual \(c_{i\gamma\sigma}^\dagger\) creates (destroys) an electron with spin \(\sigma\) at site \(i\) and orbital \(\gamma\). Furthermore \(\epsilon_{i\gamma}\) is the on-site energy of an electron at site \(i\) and orbital \(\gamma\). For simplicity we set \(\epsilon_{i\gamma} = 0\), since we consider only orbitals of the 3d type. The basis functions \(\phi_k\), \(k = 1,\ldots,5\) (\(k = 6,\ldots,10\)) are the atomic 3d orbitals conventionally denoted by \(xy, yz, zx, x^2 - y^2\) and \(3z^2 - r^2\), where \(z\) denotes the interatomic axis, together with the spin eigenstates \(|\uparrow\rangle\) and \(|\downarrow\rangle\) with respect to the spin quantization axis \(z_M\). The complete ferromagnetic tight-binding Hamiltonian is

$$H_{tb} = H + H_{ex},$$  \hspace{1cm} (2)

with the diagonal on-site matrix \(H_{ex} = \sum H_{ex}^{(i)}\) and

$$H_{ex}^{(i)} = \begin{pmatrix} H_{ex}^{(1)} & 0 & \cdots & 0 \\ H_{ex}^{(1,2)} & H_{ex}^{(2)} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & H_{ex}^{(N-1,N)} \end{pmatrix},$$  \hspace{1cm} (3)

which is actually independent of \(i\). 1 and \(-1\) denote \(5 \times 5\) diagonal matrices, and \(O\) is a \(5 \times 5\) zero matrix. The matrix of the Hamiltonian \(H_{tb}\) is then given by:

$$H_{tb} = \begin{pmatrix} H_{ex}^{(1)} & H_{inter}^{(1,2)} & \cdots & \cdots \\ H_{inter}^{(1,2)} & H_{ex}^{(2)} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \vdots & H_{inter}^{(N-1,N)} \end{pmatrix},$$  \hspace{1cm} (4)

with the intersite Hamiltonian matrix

$$H_{inter}^{(i,j)} = \begin{pmatrix} H_{inter}^{(i)} & 0 \\ 0 & H_{inter}^{(j)} \end{pmatrix},$$  \hspace{1cm} (5)

where

$$H_{inter}^{(i)} = H_{inter}^{(i)} = \begin{pmatrix} V_{dd} & 0 & 0 & 0 \\ 0 & V_{dd} & 0 & 0 \\ 0 & 0 & V_{dd} & 0 \\ 0 & 0 & 0 & V_{dd} \end{pmatrix}. $$  \hspace{1cm} (6)

Due to the symmetry of the atomic 3d-orbitals, the dominant overlaps result from the \(d\)-orbitals of the same kind, thus yielding nonvanishing contributions only in the diagonal elements of the off-diagonal Hamiltonian \(H_{inter}^{(i,j)}\). Consequently the nearest neighbor hopping \(t_{ij}\) of Eq. (1) reduces to \(t_{i\gamma i\gamma}\), which is equivalent to the three independent nonvanishing interactions \(V_{dd\sigma}, V_{dd\pi}, V_{dd\delta}\) in Eq. (6). In rings, with periodic boundary conditions, the interaction between the first and last atom of the corresponding chain must be additionally included. As in ref. \([5]\) we use \(V_{dd\sigma} = -0.25\) eV, \(V_{dd\pi} = 0.18\) eV, \(V_{dd\delta} = -0.04\) eV, \(J_{ex} = 3.0\) meV, and lattice parameter \(a = 5.98\) a.u. which matches the fictitious W(001) substrate.

B. Tight-binding model

The main disadvantage of the diatomic-pair model is its unrealistic description of tilted \(d\)-bonds. To perform more realistic calculations of \(E_{anis}(n_d)\) in rings, we have to consider how the bond angles are changed between nearest neighbors of Fe-atoms. This aspect is taken into account in the tight-binding model, within the two-center approximation. The tight-binding Hamiltonian \(H_{tb}\) has the same structure for this model as the matrix in Eq. (4).

Only the elements of \(H_{inter}^{(i,j)}\) will change their values and positions, because the bond angles have changed. The Hamiltonian is parametrized in terms of the two-center integrals \(E_{dd}(l,m,n)\) of Slater and Koster, given in Table I, with \(d\) as one of the five 3d-functions \(x, y, z, x^2 - y^2\) and \(z^2\), the latter denoting \(3z^2 - r^2\) for simplicity. The direction of the vector \(R_j - R_i\), pointing along the bond from one atom to each of its nearest neighbors, is given by the direction cosines \(l, m, n\). Thus in the tight-binding model both blocks \(H_{inter}^{(i)} = H_{inter}^{(j)}\) of \(H_{inter}^{(i,j)}\) change to:

$$E_{xy,xy} \begin{pmatrix} E_{xy,xy} & 0 & 0 & E_{xy,x^2-y^2} \\ 0 & E_{xy,yz} & 0 & 0 \\ 0 & 0 & E_{zz,zz} & 0 \\ 0 & 0 & 0 & E_{zz,zz} \end{pmatrix}.$$

Since we take the \((x, y)\)-plane as the ring or chain plane, all direction cosines \(n\) must be zero, thus further simplify the nonvanishing two-center integrals of Table I. The other two direction cosines \(l\) and \(m\) are determined by the bond angle between the Fe-atoms.

If we calculate the magnetic anisotropy of single or double chains we assume them to lie also in the \((x, y)\)-plane and being parallel to the \(x\)-axis. We couple them either ferromagnetically or antiferromagnetically, by changing the sign of \(J_{ex}\).
C. Spin-orbit coupling

Magnetocrystalline anisotropy is caused by SOC between the d-states. SOC is introduced in the usual spherical on-site form as \( H_{so} = \lambda_{so} \cdot \mathbf{s} \), with the orbital and spin moment vectors \( \mathbf{l} \) and \( \mathbf{s} \) respective and the atomic spin orbit coupling constant \( \lambda_{so} \). Expressing the components of the orbital momentum operator \( \mathbf{l} \) in the rotated frame \( (x_M, y_M, z_M) \), where \( z_M \) is the spin quantization axis, which is parallel to the direction of magnetization \( (\theta, \phi) \), we may rewrite \( H_{so} = \sum_{n} H_{so}^{(i)} \) in the following form:

\[
H_{so}^{(i)} =: \begin{pmatrix} H_{so}^{↑↑} & H_{so}^{↑↓} \\ H_{so}^{↓↑} & H_{so}^{↓↓} \end{pmatrix} = \frac{\lambda_{so}}{2} \begin{pmatrix} l_{z_M} & l_{x_M} - il_{y_M} \\ l_{x_M} + il_{y_M} & -l_{z_M} \end{pmatrix}. \tag{8} \]

Here is \( H_{so}^{↑↑} = -H_{so}^{↓↓} \), and \( H_{so}^{↑↓} = - (H_{so}^{↓↑})^\ast \), with

\[
H_{so}^{↑↑} = \frac{\lambda_{so}}{2} \begin{pmatrix} 0 & iv & -iu & 2iw \circ 0 \\
-iv & 0 & iw & -i\sqrt{3}iu \\
iu & -iw & 0 & -iw \circ \sqrt{3}iv \\
-2iw & -iu & iw & 0 \circ 0 \\
0 & \sqrt{3}iu & -\sqrt{3}iv & 0 \circ 0 \end{pmatrix}. \tag{9} \]

The variables \( u, v, w, u', v' \), and \( w' \) are given by \( u = \sin \theta_M \cos \phi_M, v = \sin \theta_M \sin \phi_M, w = \cos \theta_M, u' = -\sin \phi_M + i \cos \phi_M \cos \theta_M, v' = \cos \phi_M + i \cos \phi_M \sin \phi_M \), and \( w' = -i \sin \theta_M \).

The value for the SOC constant \( \lambda_{so} \) is taken from the Fe-atom. \( \lambda_{so} = 50 \) meV.

Now we have set up the Hamiltonian matrix in terms of the magnetization direction \( (\theta, \phi) \). Since SOC operates to a good approximation only on-site, the matrix elements of \( H_{so} \) occur exclusively in the diagonal blocks of \( H_{tb} \) in Eq. (4); consequently, the matrix elements really occur only in the diagonal and off-diagonal blocks of \( H_{so}^{↑↑} \). For chains, \( H_{so}^{↑↑} \) is independent of site \( i \), while for rings the situation is more complicated. If the magnetic moments are all parallel, \( H_{so}^{↑↑} \) is independent of the site index \( i \). However, if the magnetic moments have a radial configuration, \( H_{so}^{↑↑} \) is dependent on \( i \).

Now the total Hamiltonian \( H_{tot} \) is

\[
H_{tot} = H + H_{ex} + H_{so}. \]

In our treatment SOC is included non-perturbatively. So we get also contributions to \( E_{anis}(n_d) \) from higher order perturbation theory and may obtain information about the scaling behavior of \( E_{anis}(n_d) \) with the SOC constant \( \lambda_{so} \).

D. Anisotropy energy

In both models we define the magnetic anisotropy energy as the difference of energies for perpendicular magnetization \( E_{\perp} \) and parallel magnetization \( E_{||} \):

\[
E_{anis}(n_d) := E_{\perp} - E_{||}. \tag{11} \]

Note that for the diatomic pair-model (as defined in Sec. 2A) \( E_{\perp} (E_{||}) \) refers to magnetization perpendicular (parallel) to the interatomic bonds. For the tight-binding model (as defined in Sec. 2B) \( E_{\perp} (E_{||}) \), however, refers to magnetization perpendicular (parallel) to the plane of the QC, which is the (x,y)-plane. The QC’s in this case are assumed to lie in \( x \) direction. Thus \( E_{\perp} (E_{||}) \) refers to \( \mathbf{M} \parallel \hat{z} (\mathbf{M} \parallel \hat{x}) \).

We define the magnetic anisotropy energy per atom for the diatomic-pair model as:

\[
E_{anis}(n_d) := E_{tot}(\theta = \pi/2, \phi = 0; n_d) - E_{tot}(\theta = 0; n_d). \tag{12} \]

Due to the chosen coordinate system, there is no \( \phi \)-dependence of \( E_{anis}(n_d) \) in contrast to the tight-binding model. For the tight-binding model we define \( E_{anis}(n_d) \) as:

\[
E_{anis}(n_d) := E_{tot}(\theta = 0; n_d) - E_{tot}(\theta = \pi/2, \phi = n_d), \tag{13} \]

The in-plane angle \( \phi \) is chosen such that the resulting \( |E_{anis}| \) is the largest possible. \( E_{tot}(\theta, \phi; n_d) \) is the ground-state energy per atom of the chain or ring with a total of \( n_d \) 3d-electrons per atom, \( N \) Fe-atoms, and the magnetization direction denoted by \( (\theta, \phi) \). The total energy per atom \( E_{tot} \) is given by

\[
E_{tot}(\theta, \phi; n_d) = \frac{1}{N} \sum_{m} E_m(\theta, \phi) f_0 \left( E_m(\theta, \phi) - E_F(\theta, \phi; n_d) \right). \]

Here is \( f_0(\Delta E) \) the Fermi-function at zero temperature and \( E_F(\theta, \phi; n_d) \) is the Fermi-energy. For a given band-filling \( n_d, E_F(\theta, \phi; n_d) \) is determined self-consistently by

\[
n_d = \frac{1}{N} \sum_{m} f_0 \left( E_m(\theta, \phi) - E_F(\theta, \phi; n_d) \right). \]

The \( m \)-th eigenvalue of the total Hamiltonian \( H_{tot} \) with magnetization along \( (\theta, \phi) \) is given by \( E_m \).

Note that the magnetic-moment direction enters only by SOC and can be adjusted for each atomic site individually.

Concerning the anticipated magnetic order of the QW and QC in our electronic theory we remark the following:

(i) The interatomic distance in our model is chosen in accordance with the lateral lattice constant of a thin bcc-Fe film on a W(001) substrate, which is magnetically...
ordered. However, the STM-experiments produce QC with the interatomic distance of 8-10 rÅ, which probably would not order, except for possible indirect-exchange effects related to the substrate. Our interest, however, is mainly in small QC’s, which might be produced in the near future, with closer nearest-neighbor distances and magnetic order. Furthermore it is important to note that the assumption of magnetic long-range order in our electronic theory is not in contrast to the well known general theorems of the (ii) Ising- and (iii) Heisenberg-models

III. RESULTS AND DISCUSSION

A. Results from the diatomic-pair model

In Fig. 1, the magnetocrystalline anisotropy energy $E_{anis}(n_d)$ per for the Fe diatomic pair (dashed curve). First we note that, as expected, $E_{anis}$ is enhanced compared to Fe monolayers ($E_{anis} = 1...16$ meV for the dimer vs. $\approx 300$ µeV for an Fe monolayer), because of the symmetry reduction from 2D to 1D. This is in accordance with recent studies of magnetism in nickel clusters. Apsel et al. observe enhanced magnetic moments for small nickel clusters and find magnetization minima for clusters with closed geometrical shells and maxima for relatively open clusters.

In Fig. 1, also the dependence of $E_{anis}(n_d)$ on the scaling of all d-electron hopping parameters with a overall parameter $t$ for the diatomic pair is presented (dotted curve). The absolute value of the magnetic anisotropy energy $|E_{anis}(n_d)|$ increases for decreasing $t$ (decreasing bandwidth) for the easy axis perpendicular to the bond ($E_{anis}(n_d) < 0$), and decreases for the easy axis parallel to the bond ($E_{anis}(n_d) > 0$). Note that, contrary to the situation in thin films, no convergence problems occur in $E_{anis}$ due to our finite system. Our calculation is performed in real space, and we sum over discrete energy levels. Thus the change of the occupation number is $\Delta n_d = 0.5$, and we get 20 points for $E_{anis}(n_d)$ of the diatomic pair. When the band is completely empty or filled, no contribution to $E_{anis}$ results: $E_{anis}(n_d = 0; 10) = 0$. While this is trivially the case for an empty band, this relation holds with 14 significant digits for the completely filled case, which yields an independent check of our numerical accuracy. We find for Fe, with its atomic band filling $n_d = 6$, an in plane easy axis for $E_{anis}(Fe) = 6.1$ meV. Since the diatomic pair is a small system, it is not necessary to assume implicitly hybridization with $s$-electrons.

We find for the diatomic pair a mirror symmetry of $E_{anis}(n_d)$ with respect to half filling ($n_d = 5$), where the spin-up subband is completely full. However, the corresponding points of the curve are not totally symmetric, and a close inspection shows that there are deviations of this mirror symmetry of the order $10^{-5}$ eV. This small symmetry violation results from the combined action of SOC and hopping interaction. A detailed analysis shows that this asymmetry increases monotonously with increasing SOC. Especially for $n_d = 2.5$ and 7.5 this asymmetry is clearly visible in Fig. 1. To illustrate the origin of this asymmetry we split the spin-orbit coupling matrix $H_{so}$ into two parts $H_{so}^{para}$ and $H_{so}^{antipar}$, for the coupling between parallel and antiparallel spin states, and recalculate $E_{anis}(n_d)$ with either of the two matrices instead of $H_{so}$ itself:

$$H_{so} = \left( \begin{array}{cc} H_{so}^{para} & 0 \\ 0 & H_{so}^{antipar} \end{array} \right)$$

So we obtain the curve $E_{anis}^{antipar}(n_d)$ (solid curve) of Fig. 1, which exhibits a mirror symmetry with respect to half filling ($n_d = 5$). Due to the large exchange splitting $J_{xx}$, which completely separates the spin subbands, $E_{anis}^{para}(n_d)$ is very small and thus $E_{anis} \approx E_{anis}^{para}(n_d)$. The $E_{anis}^{antipar}(n_d)$ contribution prefers an easy magnetic direction perpendicular (parallel) to the molecule axis if the spin-down subband is less (more) than half-filled, and vice versa for the majority subband in agreement with the result of Wang et al. [5]. Also for larger chains $E_{anis}^{antipar}(n_d)$ changes it sign at $n_d = 2.5$ and 7.5, which seems to be a general trend also in Fe-monolayers. This is a generalization of Hund’s third rule on SOC which applies to itinerant magnetic systems (see Appendix).

While for Fe parameters the relation $E_{anis}^{para}(n_d) + E_{anis}^{antipar}(n_d) \approx E_{anis}(n_d)$ holds to a good approximation, small deviations are responsible for the asymmetry mentioned above. This asymmetry only occurs if we take into account at least the matrix elements of $H_{so}$ for the $\pi$- and $\delta$-bonds and is absent for all other combinations.

The electronic origin of $E_{anis}(n_d)$ of the diatomic pair can be explained from its energy level scheme in Fig. 1, for the two magnetization directions $E_{m}(\theta = 0)$ (parallel to molecule axis) and $E_{m}(\theta = \pi/2)$ (perpendicular to molecule axis). Only the spin-up states are shown in Fig. 1 for simplicity; due to the exchange splitting $J_{xx} = 3.0$ eV the spin-down states (not shown in the figure) are located symmetrically to these bands with respect to the zero of the energy scale. The individual levels of the spin-up subband have been labeled by the numbers 1...10 in the absence of SOC. Without SOC, the lowest bonding (level 1) and the highest antibonding states (level 10) result from the splittings caused by $V_{dd\sigma}$. Due to the inequalities $|V_{dd\pi}| > |V_{dd\sigma}| > |V_{dd\delta}|$ (Sec. II.B) the lowest bonding- and antibonding states are split by $2|V_{dd\sigma}|$, while in each case two doubly degenerate $\pi$-($\delta$)-bonding and antibonding states result from $V_{dd\pi}$ and $V_{dd\delta}$ (see Eq. 6). Thus the levels 2 and 3 (4 and 5) of Fig. 1 correspond to the $\pi$-($\delta$) bonding states, while the levels 8 and 9 (6 and 7) are equivalent to the corresponding antibonding states. These remaining degeneracies are lifted very strongly by SOC for $E_{m}(\theta = 0)$ and therefore level crossings may occur. For
$E_{an}(\theta = \pi/2)$ the degeneracies are only weakly lifted. The electronic origin of $E_{anis}(n_d)$ for the diatomic pair results from (i) different SOC-induced shifting of occupied, nondegenerate levels for the two magnetization directions, and (ii) different lifting of degenerate levels. Note that the lifting of degeneracies can favor a magnetization parallel as well as perpendicular to the bond axis.

Next we investigate the dependence of $E_{anis}$ on $\lambda_{so}$. We find $E_{anis}(n_d) \propto \lambda_{so}^2$ for all of the $n_d$ values of the diatomic pair in agreement with Wang et al., irrespective of the value of the spin-orbit coupling constant. To demonstrate this, we show in Fig. 3 the magnetocrystalline anisotropy energy $E_{anis}(\lambda_{so})$ for the bandfillings $n_d=1$ and $n_d=2.5$. In Fig. 3 however, we see a discontinuous change of the slope for $n_d=2.5$, because a level crossing (see Fig. 3) has occurred between the levels 5 and 6 for $\lambda_{so}=0.04$ eV. The inversion of these levels is indicated by the labeling in Fig. 3 for $\lambda=0.05$ eV. Thus $E_{anis}(n_d)$ can change its sign because of the level crossings. To explain for $n_d=1$ the dependence of $E_{anis}$ on SOC, we have to study the contribution of level shifts for different magnetization directions. We find that the shifting of nondegenerate states is for both magnetization directions proportional to $\lambda_{so}^2$. For the case of an perpendicular easy axis, the prefactor is larger. The shifting of degenerate states for magnetization parallel to the bond axis is in all cases proportional to $\lambda_{so}$ and for magnetization perpendicular to the bond axis proportional to $\lambda_{so}^2$. To illustrate this we show in the inset of Fig. 3 the dependence of the level shifts on $\lambda_{so}$ for the nondegenerate level 1 (this corresponds to $n_d=0.5$) and the degenerate level 2 ($n_d=1$), for both magnetization directions ($\theta = 0, \pi/2$) for the diatomic pair. For $\theta = \pi/2$ and small SOC there is a flat slope of the energy of both levels, while the slope increases with increasing $\lambda_{so}$. Otherwise, the slope of the energy of both levels for $\theta = 0$ is increasing less strongly with increasing $\lambda_{so}$. Thus in Fig. 3 the magnetic anisotropy energy $E_{anis}(n_d=1)$ decreases for larger SOC with increasing $\lambda_{so}$, as a result of the different position of the energy levels for the two magnetization directions entering the calculation of $E_{anis}(n_d)$. This yields another reason for the sign change of $E_{anis}(n_d)$.

An other important consequence of the levelcrossing can be seen in Fig. 1. The magnetic anisotropy energy $E_{anis}(n_d)$ of the quarter-band filling ($n_d=2.5$ and 7.5) of both subbands depends sensitively on the hopping parameters, because the level crossings then occur for smaller values of $\lambda_{so}$ (decreasing $t$) or, in the other case of increasing $t$ for larger values of $\lambda_{so}$.

In Fig. 1 (dashed curve), $E_{anis}(n_d)$ is shown as a function of 3d-band filling $n_d$ for the five-atom Fe ring. In the five-atom ring we find a translational symmetry of $E_{anis}(n_d)$ with respect to half filling. This symmetry behavior of $E_{anis}(n_d)$ is found in all rings with a small odd number $N=(3,7,9,11,..)$ of adatoms. In rings, with an even number of atoms and all chains irrespective on whether $N$ is odd or even, we find a mirror symmetry of $E_{anis}(n_d)$ with respect to half filling. This behavior is also valid in the tight-binding model and will be discussed again in Sec. III.B. If the number of atoms continues increasing ($N=45,47,..$), we then find a mirror symmetry of $E_{anis}(n_d)$ with respect to half filling also in odd rings.

B. Results of the tight-binding model

The tight-binding model is better than the diatomic-pair model, because it additionally allows to take into account the following points: (i) The change of the binding angles between nearest neighbors of adatoms in rings is considered in a realistic way. (ii) Due to the extra $\phi$-dependence of $E_{anis}(n_d)$ in the tight-binding model, it is possible to choose any magnetic-moment direction in the plane of the ring or chain. (iii) Furthermore, in the tight-binding model it is possible to couple the free-standing chains and rings to the substrate. This extension of the theory, however, has not been performed in this work.

For all chains it is easily checked that $E_{anis}(n_d)$ is equal in both models. There is a general trend that $E_{anis}(N)$ decreases with increasing number $N$ of Fe atoms in chains (compare Figs. 1 and 8). For rings this is not the case which will be discussed later.

The solid curve in Fig. 3 shows $E_{anis}(n_d)$ for the tight-binding five ring. Although this curve is different from the result in the diatomic-pair model, the translational symmetry survives. A detailed analysis yields that the tight-binding model has the same symmetry behavior for small odd rings as the diatomic-pair model. The translational symmetry can be traced back to the absence of a mirror symmetry between the levels in each of the two spin subbands with respect to $\pm J_{xx}/2$: In odd rings and chains both spin-subbands contain an odd number of electron states. If there the degeneracies of both subbands resulting from the exchange splitting are all lifted due to the hybridization, as is the case for odd rings, it is not possible to find a mirror symmetry in each of the two subbands. Since both spin-subbands have a translational symmetry with respect to the zero of the energy scale, $E_{anis}(n_d)$ has in this case also a translational symmetry with respect to half bandfilling. In all odd chains always five degeneracies (angular momentum algebra of 3d-states) are not lifted by hybridization. The remaining even number of the lifted degeneracies has a mirror symmetry around $\pm J_{xx}/2$ in both subbands, thus $E_{anis}(n_d)$ has also a mirror symmetry with respect to half bandfilling. In larger odd rings the translational symmetry of $E_{anis}(n_d)$ is lost. Due to the increased number of levels in both subbands the additional lifting of the five degeneracies, by closing of the corresponding odd chain to the ring, will not immediately destroy the mirror symmetry in both spin-subbands, as is the case for small odd QC's.

A very important point for the theory of small particles is the existence of shell structure. Here we discuss in par-
ticular the oscillations of $E_{\text{anis}}$ as a function of bandfilling $n_d$ for rings with an even or odd number of adatoms. If the magnetic moment is along the layer normal, it lies in planes perpendicular to all bonds of the ring. But if the magnetic moment lies in the ring plane (assuming exchange-enforced parallel moment alignment), it is \emph{twice} parallel to a bond axis in rings with an even number of $N$ and once in rings with an odd number of $N$. This is schematically illustrated in Fig. 7 for the trimer (5(a)), tetramer (5(b)), and hexamer ring (5(c)). In even rings, where $N$ is a multiple of four the moment lies also twice perpendicular to a bond axis (see Fig. 5(b)).

We investigate exemplarily for the four-Fe atom ring three different configurations of the magnetic moment direction, which are shown in Fig. 5. Since in larger rings the exchange interaction could possibly not enforce parallel alignment of all magnetic moments as assumed previously, we calculated $E_{\text{anis}}(n_d)$ for parallel magnetic moment alignment (p), radial moment configurations along the bonds (i) or half of the nearest-neighbor bond angle (h). Since there is a $\phi$-dependence of $E_{\text{anis}}(n_d)$ in the tight-binding model, we find the following in-plane symmetry in rings for the first two configurations (p) and (i):

$$E_{\text{anis}}(\theta; \phi = 0; n_d) = E_{\text{anis}}(\theta; \phi = 360/N; n_d). \quad (14)$$

Note this symmetry is absent for the case (h). In Fig. 6, $E_{\text{anis}}(n_d)$ is shown as a function of 3$d$-bandfilling $n_d$ of the four atom Fe ring, for the three configurations (p), (i), and (h). Especially for the $\pi$-bond, the magnetic anisotropy energy $E_{\text{anis}}(n_d)$ has the lowest values for the configuration (p). However, this is not the ground state configuration for Fe with atomic bandfilling $n_d=6$.

For all three configurations we get a parallel easy axis of $E_{\text{anis}}(\text{Fe})$, while its value is the largest where the magnetic moments are arranged in the configuration (h). This is the ground state of the three configurations for Fe with the lowest total energy. In order to determine the ground-state configuration for the case of bandfilling around $n_d=7.5$, we have to notice that we get a perpendicular easy axis for the two radial configurations and an in-plane easy axis for the configuration (p). In this case both radial configurations have the same total energy, which has to be compared with the total energy that results from the magnetization in-plane (p). A close inspection for all discrete bandfillings between $n_d=7$ and $n_d=8$ shows that the configuration (p) has the lowest total energy in this range.

Within our theoretical framework we are able to explain a recently discovered phenomenon, viz. oscillations of $E_{\text{anis}}(n_d)$ during film growth with a period of one monolayer. The in-plane lattice spacing during epitaxial growth of Co on a Cu(001) single-crystal substrate is found to oscillate as a function of coverage and produces anisotropy-oscillations. These oscillations are schematically illustrated in Fig. 8, which shows the connection between the change of the lattice spacing from $R_1$ to $R_1$ due to the growth and the corresponding change of $E_{\text{anis}}$. After starting the deposition, Co islands nucleate on the Cu surface. The Co atoms are relaxing in the direction of the center of the island. This gives rise to a reduced in-plane lattice spacing. If the growth of the N+1-layer is completed, $E_{\text{anis}}(N+1)$ nearly returns to the value of $E_{\text{anis}}(N)$. For uncompleted layers, however, the in-plane lattice constant is very different from that of complete layers and therefore oscillations occur in $E_{\text{anis}}(N)$ as expected. As a model assumption of this situation the four atom Fe-ring can be considered. We scale all d-electron hopping parameters belonging to one bond of the four-atom Fe ring with a parameter $t'$, while leaving the others unchanged. Then we find also anisotropy-oscillations, due to the changed position of some levels in the energy level scheme of the four atom Fe ring. For decreasing $t'$ for one bond, $E_{\text{anis}}(n_d)$ is increasing or decreasing dependent on $n_d$.

Finally we would like to discuss in this paper some results for larger QC’s and QW’s, in order to reach the experimental situation. In Fig. 8, $E_{\text{anis}}(n_d)$ is shown as a function of 3$d$-bandfilling $n_d$ of the 48 atom Fe ring (solid curve), for the p-configuration of Fig. 5. A comparison of the three configurations (p, i, h) shows only marginal deviations of the total energy for the 48 QC, thus we may assume the p-configuration to be the ground state. For an effective bandfilling of $n_d^\text{eff} = 6.6$ we find an in-plane easy axis with $E_{\text{anis}}(\text{Fe})=1.45$ meV, assuming implicitly a hybridization of the d-electrons with s-electrons for this larger system. The shape of the curve is very similar to that of the tight-binding calculations for free-standing Fe-monolayers. As can be seen from the comparison of Figs. 8, 4, and 6, $E_{\text{anis}}(N)$ is essentially independent of $N$.

Since metal atoms aggregating during film growth preferably on step edges (see ref.20 for Fe/W(110)) may cause one-dimensional metallization and new magnetic properties, it is of interest to calculate the magnetocrystalline anisotropy of larger QW’s. The origin of magnetic step anisotropies results from the modified local symmetry of step atoms compared to surface atoms. In Fig. 8, $E_{\text{anis}}(n_d)$ is shown as a function of 3$d$-bandfilling $n_d$ for the 48 atom Fe chain, for two different scalings of the hopping parameters (the dashed curve refers to the unscaled case $t=1$). The value of $E_{\text{anis}}(n_d)$ is considerably lower compared to the diatomic pair. However, it is still much larger than the values for freestanding Fe-monolayers. The shape of the curve for $t=1$ is very similar to the diatomic pair (see Fig. 5), irrespective of atomic number $N$. Thus we expect very large contributions to $E_{\text{anis}}(n_d)$ in all chains from SOC-induced lifting of degeneracies. Comparison of Figs. 8, 4, and 6 indicates that, upon decreasing $t$, the shape of the curve will change similarly for the 48 atom QW and for the dimer due to levelcrossings.

In order to show how sensitive the the magnetocrystalline anisotropy energy depends on spin configura-
tion, we calculate $E_{\text{anis}}(n_d)$ for two 48-atom Fe chains which are antiferromagnetically (AF) or ferromagnetically (FM) coupled to each other (Fig. 1). In these 96 atom systems $E_{\text{anis}}(N)$ has further decreased in both cases. In AF coupled chains $E_{\text{anis}}(n_d)$ is less dependent on the scaling of the interchain hopping than in FM coupled chains. Note that the shape of $E_{\text{anis}}(n_d)$ for AF coupled chains is similar to that of the 48 atom Fe chain. In this case the shape will not change if the interchain hopping $t_{l}$ is varied, in contrast to FM coupled chains. Thus the breakdown of the one dimensionality in two FM coupled chains will change $E_{\text{anis}}(n_d)$ very strongly. We find in this case a perpendicular easy axis with $E_{\text{anis}}(\text{Fe})=-0.36 \text{ meV} \ (t_{l}=1)$. This value is of the same order of magnitude as for Fe-monolayers. Experimental results showed that surface and step anisotropies are of the same order of magnitude, both exhibiting symmetry-breaking as was introduced by Néel’s phenomenological model. This is in agreement with our results for two FM coupled chains. The opposite sign and same order of magnitude for surface and step anisotropies is reproduced.

IV. SUMMARY AND OUTLOOK

A calculation of the magnetocrystalline anisotropy energy $E_{\text{anis}}(n_d)$ for free-standing chains and rings of Fe adatoms is performed. SOC is included non-perturbatively. $E_{\text{anis}}(N)$ for 1D chains is larger then for 2D rings, but in both cases $E_{\text{anis}}$ is enhanced compared to Fe-monolayers. Generally, very large contributions to $E_{\text{anis}}(n_d)$ result from the SOC-induced lifting of degeneracies. The shape of $E_{\text{anis}}(N)$ is in all chains very similar. In rings $E_{\text{anis}}(N)$ is essentially independent of $N$, while in chains $E_{\text{anis}}(N)$ generally decreases upon increasing $N$. For all chains and even rings, there is a mirror symmetry of $E_{\text{anis}}(n_d)$, while for small odd rings we find a translational symmetry. In small rings, there are odd-even oscillations of $E_{\text{anis}}(N)$, which might be of technological relevance for magneto-optical switching. Larger rings approach the results for freestanding Fe-monolayers. $E_{\text{anis}}(n_d)$ is found to be more sensitive to interchain hopping variation for two ferromagnetically than for two antiferromagnetically coupled chains. A generalization of Hund’s third rule on SOC is found. Oscillations of the magnetocrystalline anisotropy energy due the growth of Co on Cu have been explained.

Our results indicate that low-temperature scanning tunneling microscopy is a promising new tool for the preparation of atomic-scale nanostructures. These nanostructures exhibit interesting magnetocrystalline anisotropy properties which can be tailored by choosing appropriate atomic species and atom number, ring or chain conformations, and a suitable substrate. It will be of theoretical interest to incorporate the substrate degrees of freedom in the investigation of the magnetocrystalline anisotropy of quantum wires and corrals.

It is then to be expected to establish many of the phenomena successfully demonstrated in thin film magnetcism, also for one-dimensional magnetic systems, such as enhanced moments, giant magnetoresistance, quantum well oscillations, giant nonlinear Kerr rotation, or magnetic reorientation.

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APPENDIX: HUND’S THIRD RULE.

The curve of $E_{\text{anis}}^{\text{antipar}}(n_d)$ changes it sign at $n_d=2.5$ and 7.5 (see Fig.1). This sign change occurs exactly, when in each case the two subbands are half filled.

Wang et al. also found this behavior for SOC between the opposite spin states for the dimer which can be understood from the following equation ($z$ denoting the symmetry axis and $x$ an arbitrary direction in the perpendicular plane),

$$\Delta E_{\text{ud}} = E_{\text{ud}}(x) - E_{\text{ud}}(z) = \frac{\xi^2}{\Delta E_{\text{ex}}} \sum_{\sigma} < o^- | \frac{1}{2} (3L_z^2 - L^2) | o^- > . \quad (A1)$$

$\text{ud} \ (\sigma^-)$ represents SOC between the opposite spin states (represents occupied spin-down states), and $\Delta E_{\text{ex}}$ is the exchange splitting. The sign of $\Delta E_{\text{ud}}$ depends only on the axial component of the angular momentum. Three states ($L_z = 0, \pm 1$), which get first occupied, give negative contributions and two ($L_z = \pm 2$) contribute positively. Due to the hybridization, the two antibonding states with $L_z = \pm 2$, which contribute positively, will be occupied next, and therfore it comes to a sign change.

This behavior is also valid in larger chains and monolayers. If one spin-subband is half filled, there is $L=0$ and from this results no contribution to the anisotropy energy. The antibonding states will be occupied in reverse order and thus there is a sign change at $n_d=2.5$ and 7.5.
FIG. 1. Dependence of the magnetocrystalline anisotropy energy $E_{\text{anis}}$ on the 3d-bandfilling $n_d$ for a diatomic pair. While the dashed curve refers to the hoppings given in the text the dotted curve refers to hoppings scaled with an overall factor of $t=0.7$. Negative values of $E_{\text{anis}}(n_d)$ correspond to a perpendicular easy axis. The solid curve shows the contributions of $E_{\text{anis}}^{\text{antipar}}(n_d)$ to $E_{\text{anis}}(n_d)$ from antiparallel spins. As can be seen the main contribution to $E_{\text{anis}}(n_d)$ results from $E_{\text{anis}}^{\text{antipar}}(n_d)$, due to the large exchange splitting $J_{\text{ex}}$ in Fe. The zeros in $E_{\text{anis}}^{\text{antipar}}(n_d)$ at $n_d=2.5$ and 7.5 indicate a sign change imposed by a generalization of Hund’s third rule (see text).

FIG. 2. Energy levels of the diatomic pair for the two magnetization directions $E_m(\theta = 0)$ (magnetization in bond direction) and $E_m(\theta = \pi/2)$ (perpendicular to the bond axis). For simplicity only the spin-up states of the energy scale are shown in the plot. For magnetization perpendicular to the bond axis the degeneracies are very weakly lifted by SOC, in contrast to the case of magnetization in the bond direction, where SOC lifts the degeneracies so strongly, that level 5 and 6 intersect.

FIG. 3. The dependence of the magnetocrystalline anisotropy energy $E_{\text{anis}}$ on $\lambda_{SO}$ (eV) for $n_d=2.5$ (solid line) and 1 (dashed line) for the diatomic pair. For $n_d=2.5$ a discontinuous change of the slope occurs due to the crossing of levels 5 and 6 in the case of a magnetization parallel to the bond axis. For $n_d=1$ $E_{\text{anis}}$ decreases with increasing $\lambda_{SO}$. This behavior is explained in the inset of Fig. 3 (see text). The inset shows the shift of levels 1 ($n_d=0.5$) and 2 ($n_d=1$) as a function of $\lambda_{SO}$ for the diatomic pair and magnetization in bond direction ($\theta = 0$) and perpendicular to bond ($\theta = \pi/2$).

FIG. 4. The dependence of the magnetocrystalline anisotropy energy $E_{\text{anis}}$ on the 3d-bandfilling $n_d$ for the five atom ring calculated in the diatomic pair model (dashed curve) and the tight-binding model (solid curve). In both models, there is a translational symmetry with respect to half filling $n_d = 5$. In the tight-binding model all moments in-plane are chosen to be parallel to each other for this case.

FIG. 5. Odd-even oscillations of the rings (schematic).

FIG. 6. Dependence of the magnetocrystalline anisotropy energy $E_{\text{anis}}$ on the 3d-bandfilling $n_d$ for a four atom ring calculated in the tight-binding model for the three displayed magnetic moment configurations. In (p) all moments are parallel to each other, while in (i) and (h) the two radial configurations are given, where all moments are in the bond directions or half to these.

FIG. 7. Schematic sketch of anisotropy oscillations during the growth of Co on Cu. We expect that the change of the lattice spacing from $R$ to $R_1$ due the growth of the (N+1)-layer will produce oscillations of $E_{\text{anis}}$, which are found in the calculation for the four atom Fe ring, used to simulate this system.

FIG. 8. Dependence of the magnetocrystalline anisotropy energy $E_{\text{anis}}$ on the 3d-bandfilling $n_d$ for a 48 atom ring (solid curve) for the tight-binding model, with the configuration that all moments in plane are parallel to each other. The dashed (dotted) curves shows the dependence of $E_{\text{anis}}(n_d)$ for a 48 atom chain for two different scalings of the hopping $t=1$ (t=1/3).

FIG. 9. Dependence of the magnetocrystalline anisotropy energy $E_{\text{anis}}$ on the 3d-bandfilling $n_d$ for two antiferromagnetically (dashed curve) and ferromagnetically (solid and dotted curve) coupled 48-atom Fe chains for the tight-binding model.

TABLE I. The nonvanishing energy integrals in terms of two-center integrals, which we used for the tight-binding model.

| $E_{xy,xy}$ | $3l^2m^2(V_{dd\sigma}) + (l^2 + m^2 - 4l^2m^2)(V_{dd\pi}) + (n^2 + l^2m^2)(V_{dd\delta})$ |
| $E_{yz,yz}$ | $3m^2n^2(V_{dd\sigma}) + (n^2 + m^2 - 4m^2n^2)(V_{dd\pi}) + (l^2 + m^2)(V_{dd\delta})$ |
| $E_{zx,zx}$ | $3n^2l^2(V_{dd\sigma}) + (n^2 + l^2 - 4l^2n^2)(V_{dd\pi}) + (m^2 + l^2n^2)(V_{dd\delta})$ |
| $E_{xy,x^2-y^2}$ | $\frac{3}{4}l^2m(l^2-m^2)(V_{dd\sigma}) + 2lm(m^2-l^2)(V_{dd\pi}) + \frac{1}{4}l^2m(l^2-m^2)(V_{dd\delta})$ |
| $E_{xy,z^2}$ | $\sqrt{3}lm[l^2 - \frac{1}{2}(l^2 + m^2)](V_{dd\sigma}) - 2\sqrt{3}lmn^2(V_{dd\pi}) + \frac{1}{2}\sqrt{3}mn$ |
| $E_{yx,y^2,z^2}$ | $\frac{3}{4}(l^2-m^2)^2(V_{dd\sigma}) + |l^2+m^2-(l^2-m^2)^2|(V_{dd\pi}) + |n^2 + l^2m^2|$, $|n^2 + l^2m^2|$ |
| $E_{yx,x^2,y^2}$ | $\frac{1}{4}\sqrt{3}(l^2-m^2)[n^2 - \frac{1}{2}(l^2 + m^2)](V_{dd\sigma}) + \frac{1}{4}\sqrt{3}(1+n^2)(l^2+m^2)(V_{dd\pi})$ |
| $E_{zx,z^2}$ | $n^2 - \frac{1}{2}(l^2 + m^2)^2(V_{dd\sigma}) + 3n^2(l^2 + m^2)(V_{dd\pi}) + \frac{1}{2}(l^2 + m^2)(V_{dd\delta})$ |
*corresponding Author

1. M. F. Crommie, C. P. Lutz, and D. M. Eigler, SCIENCE 262, 218 (1993).
2. E. J. Heller, M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature 369, 464 (1994).
3. G. Meyer, B. Neu, and K. H. Rieder, Phys. Bl. 51, 105 (1995).
4. K. H. Rieder and A. Baratoff, Phys. Bl. 52, nr.1, 14 (1995).
5. Ding-sheng Wang, Ruqian Wu, and A. J. Freeman, Phys. Rev. B 47, 14932 (1993).
6. G. C. Fletcher, Proc. Phys. Soc. 65, 192 (1952).
7. J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).
8. H. Takayama, K.-P. Bohnen, and P. Fulde, Phys. Rev. B 14, 2287 (1976).
9. The angle $\theta$ denotes the angle between the magnetization direction $z_M$ and the molecule axis or surface normal $\hat{z}$. $\phi$ is the angle between the $x$-axis and the projection of $z_M$ in the plane of perpendicular magnetization or in the plane of the monolayer.
10. P. N. Argyres, Phys. Rev. 97, 334 (1955).
11. Of course, SOC itself is part of a perturbation expansion to the Dirac equation yielding the Pauli equation.
12. It is well known that the 1D Ising-model, which is applicable for QW's and QC's (with periodic boundary conditions) exhibits a phase transition only at $T=0$. However, in our case we may implicitly assume hybridization with the substrate, which introduces some 2D-character to our system.
13. The 2D Heisenberg model should exhibit no phase transition if no anisotropy is involved; the latter, however, is the subject of this work. Thus the assumption of magnetic long range order seems justified.
14. S. E. Apsel, J. Deng, and L. A. Bloomfield, Phys. Rev. Lett. 76, 1441 (1996).
15. Furthermore, Monte Carlo simulations for ferrofluids, where the only stable states for systems with few particles ($N<14$) are the ring and the chain, show that rings always have an absolute magnetic moment that is close to zero for both low and high temperatures and nonzero magnetic field (indicating a radial moment configuration such as (i) and (b)). Borrmann et al.\(^{10}\) expect that their results can also be transferred to nanocrystalline material.
16. P. Borrmann, H. Stamerjohanns, and E. Hilf, (1996 (preprint)).
17. J. Fassbender, U. May, B. Schirner, R.M. Jungblut, B. Hillebrands, and G. Güntherodt, Phys. Rev. Lett. 75, 4476 (1995).
18. W. Weber, C. H. Back, Ch. Würsch, A. Bischof, and R. Allenspach, Phys. Rev. Lett. 76,1940 (1996).
19. T. H. Moos, W. Hübner, and K. H. Bennemann, Sol. State Comm. 98, 639 (1996).
20. T. H. Moos, Diploma thesis, Freie Universität Berlin (1995). This justifies to use the same $n_{eff} = 6.6$ as introduced for monolayers by Moos.
21. M. Albrecht, T. Furubayashi, M. Przybylski, J. Korecki, and U. Gradmann, Journal of Magnetism and Magnetic Materials, 113, 207-220 (1992).
22. M. L. Néel, J. Phys. Radium 15, 225 (1954).
23. M. L. Néel, Compt.Rend. 237, 1468 (1953).
$E_{\text{anis}}$ (meV per atom)

number $n_d$ of 3d-electrons per atom
Fig. 7

\[ E_{\text{anis}} \text{ (meV per atom)} \]

\[ \text{Cu-atom} \]

\[ \text{Co-atom} \]

N-layer

N+1-layer

number of 3d-electrons per atom

\[ 0 \quad 2 \quad 4 \quad 6 \quad 8 \quad 10 \]

\[ E \quad (\text{meV per atom}) \]
$E_{\text{anis}}$ (meV per atom)

number $n_d$ of 3d-electrons per atom
$E_{\text{anis}}$ (meV per atom) vs $\lambda_{SO}$ (eV)

- $n_d = 1$ (dotted line)
- $n_d = 2.5$ (solid line)

$n_d = 1$

$n_d = 2.5$
\[
\lambda_{SO} (\text{eV})
\]

\[
\text{Energy (eV)}
\]

- \(n_q = 0.5; \theta = \pi/2\)
- \(n_q = 0.5; \theta = 0\)
- \(n_q = 1; \theta = 0\)
- \(n_q = 1; \theta = \pi/2\)
$E$ (meV per atom) vs. number $n$ of 3d-electrons per atom. 

- $t = 1$ (solid line) 
- $t = 0.7$ (dashed line)
E (meV per atom) vs number $n_d$ of 3d-electrons per atom

- **tight-binding model**
- **diatomic pair model**
Energylevels [eV] of the diatomic pair

- $E_m(\theta=0)$
- $E_m(\theta=\pi/2)$