Magnetocrystalline Anisotropy Energy of Transition Metal Thin Films: A Non-perturbative Theory

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The magnetocrystalline anisotropy energy $E_{\text{anis}}$ of free-standing monolayers and thin films of Fe and Ni is determined using two different semi-empirical schemes. Within a tight-binding calculation for the 3$d$ bands alone, we analyze in detail the relation between bandstructure and $E_{\text{anis}}$, treating spin-orbit coupling (SOC) non-perturbatively. We find important contributions to $E_{\text{anis}}$ due to the lifting of band degeneracies near the Fermi level by SOC. The important role of degeneracies is supported by the calculation of the electron temperature dependence of the magnetocrystalline anisotropy energy, which decreases with the temperature increasing on a scale of several hundred K. In general, $E_{\text{anis}}$ scales with the square of the SOC constant $\lambda_{so}$. Including 4$s$ bands and 3$d$ hybridization, the combined interpolation scheme yields anisotropy energies that quantitatively agree well with experiments for Fe and Ni monolayers on Cu(001). Finally, the anisotropy energy is calculated for systems of up to 14 layers. Even after including $s$-bands and for multilayers, the importance of degeneracies persists. Considering a fixed fcc-Fe structure, we find a reorientation of the magnetization from perpendicular to in-plane at about 4 layers. For Ni, we find the correct in-plane easy-axis for the monolayer. However, since the anisotropy energy remains nearly constant, we do not find the experimentally observed reorientation.

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I. INTRODUCTION

The dependence of the total energy of a ferromagnetic crystal on the direction of magnetization originates from the magnetic dipole-dipole interaction as well as from spin-orbit coupling (SOC), as proposed by van Vleck. The magnetic anisotropy energy is expected to be enlarged in systems of low symmetry, i.e. at surfaces, interfaces, and thin films or in one-dimensional systems such as quantum corrals. Recently, a magnetization easy-axis perpendicular to the film plane has been observed for a wide variety of thin film systems, for example for thin films of fcc Fe on Cu(001). Some of these systems are promising candidates for magnetic high-density storage media.

In spite of many theoretical attempts, the relation between the electronic structure and magnetocrystalline anisotropy energy $E_{\text{anis}}$ could not be fully clarified so far. Some very important questions are subject to intense discussion: (i) Which bandstructure details lead to significant contributions to $E_{\text{anis}}$? Especially the treatment of degenerate bands near the Fermi level has been brought up controversially. (ii) How does $E_{\text{anis}}$ depend on the SOC strength $\lambda_{so}$? (iii) How is it influenced by the substrate lattice constant? Moreover, there is no unified thermodynamic and electronic theory to determine the temperature dependence of $E_{\text{anis}}$. Finally, the correct prediction of magnetic anisotropy for real systems still remains a challenge, since due to the quenching of orbital angular momentum in 3$d$ transition metal systems, $E_{\text{anis}}$ is several orders of magnitude smaller than other contributions to the total energy of a crystal (typically about 0.1 – 1 meV per atom in ultrathin films).

The magnetic anisotropy of thin films has been investigated using two essentially different approaches. In semiempirical calculations, the magnetocrystalline anisotropy energy $E_{\text{anis}}$ is determined by means of parametrized tight-binding bandstructures. Usually, spin-orbit coupling is restricted to second order perturbation theory. On the other hand, ab-initio calculations have been made and lead to realistic bandstructures. All calculations make use of the controversial force theorem. Convergence, however, is difficult to achieve; sometimes, additional assumptions are made in order to obtain converged results.

The structure of thin Fe films deposited on Cu(001) has been widely investigated, especially the dependence of the structure and magnetization orientation on the temperature. For films of less than 5 monolayers (ML) deposited at low temperatures, a distorted fcc-structure is found, with magnetization perpendicular to the film plane. At 5 ML, a transition to in-plane magnetization is observed, as well as a restructuration of the film. It is still not clear if this reorientation transition is an effect of the structural changes taking place in the film at 4-5 ML.

In this paper, we investigate a simple quadratic Fe and Ni monolayer and fcc multilayers systems up to 14 ML epitaxially grown on the Cu(001) surface and neglect further interactions with the substrate. The bandstructures are calculated within two different semi-empirical schemes, including SOC completely non-perturbatively without resorting to degenerate or non-degenerate perturbation theory of any order. A tight-binding calculation of the 3$d$-bands allows for a detailed, k-space resolved analysis of the role of degeneracies for $E_{\text{anis}}$. It is shown that degeneracies located near the Fermi level can yield significant contributions, if they occur along lines...
in \( \mathbf{k} \)-space. We find for these that generally \( E_{\text{anis}} \propto \lambda_{so}^2 \) holds. Including 4 \( s \)-bands by means of the \textit{combined interpolation scheme} and fitting the parameters to \textit{ab initio} calculations, we obtain the correct sign and values of \( E_{\text{anis}} \) for the systems considered with this fully convergent method. That could be achieved neither by a fit using bulk parameters nor by employing a real-space density of states calculation, the so-called recursion method. Moreover, we find the characteristic scale for the temperature dependence of the magnetic anisotropy to be \( \lambda_{so} \), rather than the bandwidth. This supports the significance of the lifting of degeneracies at \( E_F \) by \( \lambda_{so} \) and demonstrates the importance of contributions to magnetic anisotropy due to Fermi-edge smearing.

Finally, we calculate the anisotropy energy of multilayer systems. For systems of tetragonally-distorted Fe of 2 to 14 ML, we find a transition from magnetization perpendicular to the plane to in-plane magnetization at about 4 ML. We conclude from our calculation that the experimentally observed reorientation at 5 layers is not necessarily caused by a structural phase transition. For Ni, we find a nearly constant anisotropy energy from the fourth layer on, in disagreement with the results of Schneider and Baberschke, who find a reorientation from in-plane to parallel magnetization at 7 ML. In both cases, the degeneracies near the Fermi-level are found to play an important role for the dependence of the anisotropy energy on the film thickness.

This paper is organized as follows: In Section II, the interpolation schemes (II.A, II.B, II.C) and the determination of \( E_{\text{anis}} \) (II.D) are presented. The results for the tight-binding scheme for \( d \)-bands alone are shown in Section III.A, the role of degeneracies is analyzed in detail in III.B while the results for the complete \( s \)- and \( d \)-band calculation for Fe and Ni monolayers on Cu(001) and other substrates are given in section III.C. The influence of crystal field splitting is investigated. Some aspects of the temperature dependence of magnetic anisotropy are considered in III.D, and the results for multilayer systems are presented in III.E and III.F. Section IV sums up the most important results.

\section{II. Theory}

\subsection{A. Bandstructures}

The magnetocrystalline anisotropy energy \( E_{\text{anis}} \) depends sensitively on the electronic structure of the system. To simplify the analysis, the bandstructure of the monolayer is calculated in two steps. First, the 3\( d \)-bands are described within a tight-binding scheme. Although the resulting \( E_{anis} \) as a function of the 3\( d \)-bandfilling \( n_d \) shows already the most important features, the 4\( s \)-bands and \( s \)-\( d \)-hybridization have to be taken into account for a correct numerical evaluation of \( E_{\text{anis}} \).

For the 3\( d \)-bands, the tight-binding formalism introduced by Fletcher and Slater and Koster is adapted to the monolayer. The Hamiltonian \( H^d = H_{at} + \Delta U \) is set up as a 10 \( \times \) 10 matrix with respect to the basis of Bloch wave functions

\[ \psi_{\mathbf{n} \mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i \mathbf{k} \cdot \mathbf{R}} \phi_{\mathbf{n}}(\mathbf{r} - \mathbf{R}). \]  

Here, \( H_{at} \) is the atomic Hamiltonian, \( \Delta U \) the additional crystal field in the monolayer. \( \phi_i, i = 1, ..., 5 \) (\( i = 6, ..., 10 \)) are the atomic 3\( d \) orbitals commonly denoted by \( xy, yz, zx, x^2 - y^2 \) and \( 3z^2 - r^2 \) respectively, together with the spin eigenstate \( |\uparrow\rangle \) (\( |\downarrow\rangle \)) with respect to the spin quantization axis \( z_M \). In the simple quadratic monolayer, only orbitals located on neighboring atoms are included. The extension to second nearest neighbors does not lead to further insight.

With the \( x \)- and \( y \)-axes oriented along axes connecting nearest neighbors in the monolayer, the spin-polarized Hamilton matrix has (within the three-center approximation) the form

\[ H^d_{ij} = \begin{cases} E_0 + \Delta^V_{\text{Fe}} & 2B_1(\cos 2\xi + \cos 2\eta) - J_{ex}/2 \\ E_0 + 2B_2 \cos 2\eta + 2B_3 \cos 2\eta - J'_{ex}/2 \\ E_0 + 2B_3 \cos 2\xi + 2B_2 \cos 2\eta - J'_{ex}/2 \\ E_0 + \Delta^V_{\text{Fe}} + 2B_4(\cos 2\xi + \cos 2\eta) - J_{ex}/2 \\ E_0 + \Delta^V_{\text{Fe}} + \Delta^V_{\text{Ni}} + 2B_5(\cos 2\xi + \cos 2\eta) - J_{ex}/2 \\ \end{cases} \]

and

\[ H^d_{ii} = H^d_{i-5,i-5} + J_{ex} \quad \text{for } i = 6, 10, \]
\[ H^d_{ii} = H^d_{i-5,i-5} + J'_{ex} \quad \text{for } i = 7, 8, 9. \]

Here, \( \xi = \frac{1}{2}k_x a \) and \( \eta = \frac{1}{2}k_y a \) are the normalized components of the crystal momentum \( \mathbf{k} \), \( a \) is the lattice constant of the simple quadratic monolayer. For qualitative results it is sufficient to use bulk values for the parameters of the paramagnetic bandstructure \( B_i \), the crystal field parameter \( \Delta^V_{\text{Fe}}/\text{Ni} \), and the spin splitting parameters \( J_{ex} \) and \( J'_{ex} \). For Ni, the parameters are taken from Wel and Callaway, for Fe from Pustogawa \textit{et al.} The \( B_i \) and \( \Delta^V \) are listed in the first column of table \ref{table1}. We have used \( J_{ex} = 0.1 \text{ eV} \) and \( J'_{ex} = 0.4 \text{ eV} \) for Ni and \( J_{ex} = J'_{ex} = 1.78 \text{ eV} \) for Fe. Due to the higher symmetry in fcc or bcc bulk crystals, only one crystal field parameter \( \Delta^V_{\text{Fe}}/\text{Ni} \) appears in the corresponding Fe (Ni) bulk Hamiltonian. For the monolayer, one would have to consider three different \( \Delta \) because of the reduced symmetry, but these parameters are not known. Hence, only \( \Delta^V_{\text{Fe}}/\text{Ni} \) has been considered in Eq. (2). The influence of further crystal field effects in \( E_{\text{anis}} \) in the monolayer, which was stressed by Bruno, is investigated in section III.C.

For a quantitative comparison with experiment, however, 4\( s \)-states have to be included, within the so-called “combined interpolation scheme” due to the strong overlap and hybridization between 3\( d \)- and 4\( s \)-bands in 3\( d \) transition metals. According to the pseudopotential
method by Harrison\cite{Harrison1989}, the 4s-electrons are described by a set of plane waves

$$\psi_{K_j, k}(r) = \frac{1}{\sqrt{N}} e^{i(k-K_j) \cdot r},$$

where the $K_j$ are a set of reciprocal lattice vectors. They have to be chosen such that at least the lowest eigenstates in the considered part of the two dimensional Brillouin zone (irreducible part, see below) are described. For simple quadratic monolayers, this yields $K_1 = (0, 0)$, $K_2 = \frac{2\pi}{a}(1, 0)$, $K_3 = \frac{2\pi}{a}(0, 1)$, $K_4 = \frac{2\pi}{a}(1, 1)$, $K_5 = \frac{2\pi}{a}(-1, 0)$ and $K_6 = \frac{2\pi}{a}(1, -1)$. To maintain the symmetry of the problem (and thus the correct occurrence of band degeneracies that turn out to be very important for $E_{anis}$), symmetry factors $F_{\xi} \xi$ have to be introduced into the Hamilton matrix. This leads to

$$H_{ij}^s = \langle \psi_{Kj, k} | H | \psi_{Kj, k} \rangle = \begin{cases} V_{00} + \alpha (k - K_j)^2 & \text{for } i = j, \\ V_{Kj-Kk} - F_{i} F_{j} & \text{else} \end{cases}$$

$V_{00}$, $V_{10}$, $V_{11}$, $V_{12}$ and $V_{20}$ are the Fourier components of the pseudopotential, $\alpha$ is the dispersion of the 4s-band. The symmetry factors are:

- $F_1 = 1$
- $F_2 = \sin 2\xi$
- $F_3 = \begin{cases} \sin 2\eta & \text{for } \eta \geq 0, \\ 0 & \text{else} \end{cases}$
- $F_4 = F_2 F_3$
- $F_5 = \begin{cases} \sin 2\eta & \text{for } \eta \leq 0, \\ 0 & \text{else} \end{cases}$
- $F_6 = F_2 F_5$

The s-d hybridization $H_{sd}$ between states of parallel spins is calculated according to Hodges et al.\cite{Hodges1990} with the parameters $B_1$ and $B_2$. To obtain accurate parameters, we perform a fit to the full-potential linear muffin-tin orbitals (LMTO) calculation for a free-standing Fe monolayer by Pustogowa et al.\cite{Pustogowa1996} and to the linear augmented plane wave (LAPW) calculation for a Ni monolayer by Jepsen et al.\cite{Jepsen1995}. The resulting parameters are listed in Table I. In order to reduce the number of free parameters in the fit, the d-band parameters $\tilde{B}_i$ and $\Delta_{ij}$ are still taken from the corresponding bulk crystals (see above). To obtain correct d-bandwidths, however, the $\tilde{B}_i$ are scaled with the fitted parameters $S^\dagger$ and $S^\dagger$ for the spin-up and spin-down bands, respectively. Finally, the s- and d-bandwidths and s-d-hybridization parameters are scaled with $t$ according to Harrison\cite{Harrison1989} to take into account the Cu surface lattice constant $a$:

$$a \left( \frac{a}{a_0} \right)^q = \left( \frac{t}{t_0} \right)$$

with $a_0$ the surface lattice constant of Fe or Ni, $t_0$ the corresponding hopping parameters, and $q$ being -5 for the $dd$ parameters, -2 for the $ss$ parameters and -7/2 for the $sd$ parameters. The in-plane lattice constant is taken to be that of the Cu-substrate for all considered systems ($a = 2.56$ $\text{rA}$). This is correct for Ni, which is known to have a large pseudomorphic growth range. For Fe however, both an in-plane nearest-neighbor distance similar to that of Cu and a smaller one have been reported.

### B. Spin-orbit coupling

Spin-orbit coupling (SOC) between the $d$-states, leading to magnetocrystalline anisotropy, is introduced in the usual form as $H_{so} = \lambda_{so} \mathbf{l} \cdot \mathbf{s}$. It can be expressed by the components of the orbital momentum operator $\mathbf{l}$ in the rotated frame $(x_M, y_M, z_M)$. Here, $z_M$ is the spin quantization axis, which is parallel to the direction of magnetization $(\theta, \phi)\text{.}$

$$H_{so} =: \begin{pmatrix} H_{so}^{11} & H_{so}^{12} \\ H_{so}^{21} & H_{so}^{22} \end{pmatrix} = \frac{\lambda_{so}}{2} \begin{pmatrix} l_{xM} + il_{yM} & l_{zM} - il_{zM} \\ l_{zM} + il_{yM} & -l_{xM} - il_{zM} \end{pmatrix}$$

Expressed in the basis of Eq. (3), $H_{so}$ is a matrix function of the magnetization direction $(\theta, \phi)$. The SOC constant $\lambda_{so}$ is taken from the corresponding atom: $\lambda_{so} = 70$ meV for Ni and 50 meV for Fe.\cite{Fröhlich1960}

Unlike in usual tight-binding calculations\cite{Jepsen1995, Pustogowa1996}, SOC is included non-perturbatively in our treatment. Thus, we obtain important new information on how $E_{anis}$ scales with the SOC constant $\lambda_{so}$, which contributes to our analysis of the origin of $E_{anis}$ in terms of bandstructure properties (see below).

### C. Multilayers

We build up the Hamiltonian of a system of $l$ layers by coupling $l$ monolayer Hamiltonians $H_{mono,i}^l$ together. The coupling of the layers is described within the tight-binding nearest-neighbor formalism used for the monolayer. Because of the missing periodicity in z-direction, we obtain terms that depend only on $\xi$ and $\eta$. For the sake of simplicity, we take only $\sigma$-bonds into account and obtain the following terms for the coupling of the orbital $j$ of the monolayer $i$ with the orbital $k$ of the monolayer $i+1$, $H_{j,k}^{i,i+1}$:

$$H_{j,k}^{i,i+1} = -2\tilde{B}_i \cos 2\eta$$

$$H_{j,k}^{i,i+1} = -2\tilde{B}_i \cos 2\xi$$

with $i=1...l$. The $(18l \times 18l)$ coupling matrix thus has only elements in the $(l-1)$ $(18 \times 18)-$blocks just above and below the diagonal. The parameter $\tilde{B}_i$ is the same as used for the monolayers, but it yet has to be scaled to the interlayer distance of the tetragonally-distorted system, according to Eq. (3). We consider equidistant layers.
For Ni, we take into account the reported compression of 3.2% to scale the interlayer hoppings. For Fe, we assume an expansion of about 5% as reported by Müller et al. 

D. Anisotropy energy

The magnetic anisotropy energy per atom is defined as

$$E_{anis}(n) := E_{tot}(\theta = 0; n) - E_{tot}(\theta = \pi/2, \phi; n),$$

(5)

where $E_{tot}(\theta, \phi; n)$ is the ground-state energy per atom with a total of $n$ 3d- and 4s-electrons per atom, and the magnetization direction is denoted by $(\theta, \phi)$. The in-plane angle $\phi$ is chosen such that the resulting $|E_{anis}|$ is the largest possible. At first, the anisotropic dipole-dipole interaction is neglected, since it does hardly depend on the electronic structure. Nevertheless, it may be of the same order of magnitude as the magnetocrystalline anisotropy resulting from SOC and will thus be included later to obtain quantitative results. The total energy per atom $E_{tot}$ (with the $k$-space resolved energy $E_k$) is given by

$$E_{tot}(\theta, \phi; n) = \frac{1}{N} \sum_k E_k(\theta, \phi; n)$$

$$= \frac{1}{N} \sum_{m,k} E_{mk}(\theta, \phi) f_0 (E_{mk}(\theta, \phi) - E_F(\theta, \phi; n)) .$$

(6)

with $N$ the number of atoms. $f_0(\Delta E)$ is the Fermi-function at zero temperature and $E_F(\theta, \phi; n)$ is the Fermi-energy which, for a given bandfilling $n$, is determined self-consistently by

$$n = \frac{1}{N} \sum_{m,k} f_0 (E_{mk}(\theta, \phi) - E_F(\theta, \phi; n)) .$$

$E_{mk}(\theta, \phi)$ is the $m$-th eigenvalue with crystal momentum $k$ and magnetization along $(\theta, \phi)$ of the Hamiltonian

$$H_{mono} = H^d + H_{so}$$

for the monolayer in the tight-binding scheme and

$$H_{mono} = H^s + H^d + H^{sd} + H_{so}$$

for the monolayer in the combined interpolation scheme. For multilayer systems, we have the following Hamiltonian:

$$H = H_{mono}^1 \oplus ... \oplus H_{mono}^n + H_{coupling}$$

In Eq. (1), we use the so-called force theorem, the validity of which has been assumed in all calculations of the magnetocrystalline anisotropy so far. The complete Brillouin zone (BZ) summation over $k$ is performed as a weighted summation over the irreducible part of the BZ (for an arbitrary direction of magnetization). For the $d$-electrons with SOC, that means a summation over 1/4 of the BZ. About 2000 points of the 1/4 BZ are then sufficient to achieve convergence. Note that we do not have to exclude any parts of the BZ to obtain convergence, unlike Wang et al. Adding $s$-electrons and $s$-$d$ hybridization implies a coupling of non-SOC coupled states with the SOC-coupled $d$-states and results in a reduced symmetry. It is then necessary to perform the summation over 1/2 of the BZ. We then need 150 000 points to obtain the correct fourfold symmetry of the in-plane anisotropy energy as a function of the magnetization direction in the plane (cos4\phi). Fortunately, the out-of-plane anisotropy energy $E_{anis}$ as defined by Eq. (5), which is larger by two orders of magnitude in our calculation ($E_{anis}^{\text{in-plane}} \approx 1.2$ meV for Fe) already converges for about 7000 points, so that calculations for systems of up to 14 layers are feasible.

III. RESULTS AND DISCUSSION

A. Monolayers within the tight-binding scheme

In Figs. 1 and 2 results for $E_{anis}$ as a function of the 3d-bandfilling $n_d$ are presented (solid lines) for the parameters of Fe and Ni monolayers, respectively. We use the lattice constant of 2.56 Å to simulate epitaxial growth on Cu(001). These figures demonstrate the correspondence between electronic structure and magnetic anisotropy and show that our method will yield convergent results for the whole transition metal series and for large (Fe) and small (Ni) exchange coupling. They will be analyzed in the following. Yet, the numerical value of $E_{anis}$ for Fe and Ni monolayers cannot be extracted from these figures until the 4s-electrons are included (see III.C), since the exact 3d-bandfilling of the monolayers is not known.

Splitting the spin-orbit coupling matrix $H_{so}$ into two parts, one of them ($H_{so}^{\text{par}}$) containing only coupling between states of parallel spin, the other one ($H_{so}^{\text{antipar}}$) between states of opposite spin, and recalculating $E_{anis}$ as a function of $n_d$ with either of the two matrices instead of $H_{so}$ itself, we obtain the curves $E_{anis}^{\text{par}}(n_d)$ and $E_{anis}^{\text{antipar}}(n_d)$, respectively (Figs. 1 and 2 dashed and dotted lines respectively). Note that to a good approximation $E_{anis}^{\text{par}}(n_d) + E_{anis}^{\text{antipar}}(n_d) \approx E_{anis}(n_d)$ is valid. For Fe parameters, $E_{anis}^{\text{antipar}}(n_d)$ is very small due to the large exchange splitting $J_{ex}$ that completely separates the spin subbands. Thus, $E_{anis}^{\text{antipar}}(n_d)$ is ineffective and may therefore be neglected for further analysis. The curve $E_{anis}^{\text{par}}(n_d) \approx E_{anis}(n_d)$ consists of two parts of equal shape, viz. for $n_d \in [0; 5]$ (spin-up band) and $n_d \in [5; 10]$ (spin-down band). In the case of Ni, $E_{anis}^{\text{par}}(n_d)$ and $E_{anis}^{\text{antipar}}(n_d)$ are of the same order of magnitude, since there is a considerable overlap between the spin-up and spin-down subbands.
The curves $E_{\text{anis}}(n_d)$ show a number of pronounced peaks (A, B, C, E, F in Figs. 1 and 2), the origin of which has to be clarified. Two possible contributions to $E_{\text{anis}}$ are discussed in the literature. (i) The SOC-induced shifting of occupied, nondegenerate bands leads to contributions to $E_{\text{anis}}$ in second-order perturbation theory with respect to the SOC constant $\lambda_{so}$. $E_{\text{anis}} \propto \lambda^2$. The first order vanishes due to time reversal symmetry. (ii) The contribution of the lifting of degenerate bands, which are shifted linearly with $\lambda_{so}$, depends on the fraction of states in $k$-space influenced by the degeneracy. Whether this fraction is of the order of $\lambda_{so}$, which would yield $E_{\text{anis}} \propto \lambda_{so}$, or this fraction is of lower order, $\lambda_{so}$, thus would yield important contributions to $E_{\text{anis}}$, has been a controversial question. Anyway, the scaling of $E_{\text{anis}}$ with $\lambda_{so}$ can present important information about the dominant contributions to $E_{\text{anis}}$. Thus, it is very useful not to restrict calculations to second-order perturbation theory as has been frequently done. Remarkably, we find $E_{\text{anis}}(n_d) \propto \lambda_{so}^2$ for most of the $n_d$ values in agreement with Wang et al. Nonetheless, this does not rule out contributions to $E_{\text{anis}}$ of the lifting of degeneracies (ii). In section III.B and Fig. 3, we show explicitly that such contributions play a very important role for $E_{\text{anis}}$ in the monolayers considered. This is true as well for the multilayers (s. Figs. 3, 14, and 13 and the discussion in sections III.E and III.F).

The dependence of $E_{\text{anis}}$ on scaling of all d-electron hopping parameters with a common parameter $t$ was checked. We found that the overall shape of the curves $E_{\text{anis}}(n_d)$ will not change if $t$ is varied. \[ |E_{\text{anis}}| \text{ increases for decreasing } t \text{ (decreasing bandwidth). This leads to the general trend: } |E_{\text{anis}}| \text{ increases with increasing lattice constant } a \text{ of the monolayer, since } t \text{ is proportional to } a^{-5} \text{ (see section III.C)}. \]

B. The electronic origin of $E_{\text{anis}}$

In this chapter we discuss in detail how the magnetocrystalline anisotropy energy can be related to the electronic bandstructure. A 3d-band degeneracy can make large contributions to $E_{\text{anis}}$, if (i) it is lifted by SOC for one direction of magnetization ($z_M$) and remains for another ($z_X$); (ii) it is located near the Fermi level $E_F$; (iii) it runs along a line in $k$-space and (iv) the degenerate bands have no or very little dispersion along this line. Before showing that such degeneracies indeed occur in the bandstructures, we estimate their contribution within a linearized ‘bandstructure’ (see Fig. 3). If $E_F$ is situated below or above the two subbands, no contribution to $E_{\text{anis}}$ results: $\Delta E_{\text{anis}} = 0$. The maximal contribution occurs when the degeneracy lies exactly at the Fermi level $E_F$ and amounts to:

\[ \Delta E_{\text{anis}} = \frac{\lambda_{so}}{2} F = \lambda_{so}^2 \left( \frac{\partial E}{\partial k_1} \frac{\pi}{a} \right)^{-1} \]

since the fraction $F$ of involved states in the irreducible quarter of the BZ is $F = \frac{\Delta k_1 \pi/a}{\pi/2} = 2\lambda_{so} \left( \frac{\partial E}{\partial k_1} \frac{\pi}{a} \right)^{-1}$. The preferred direction of magnetization is $z_M$.

Thus, $\Delta E_{\text{anis}}$ is proportional to $\lambda_{so}^2$, for a degeneracy that occurs along a line with the involved bands being non-dispersive along that line. This agrees with the scaling of $E_{\text{anis}}$ observed above. In their estimate of the contribution of degeneracies, Wang et al. implicitly assume that the degenerate bands are dispersive in either dimension of $k$-space. This would lead to $F \propto \lambda_{so}^2$ and $E_{\text{anis}} \propto \lambda_{so}^3$ and justify the exclusion of degeneracies from their calculation in order to improve convergence. In the light of our results, however, this assumption is incorrect and it neglects very important contributions to $E_{\text{anis}}$.

In Fig. 4 some degeneracies are shown in the bandstructure of the Fe monolayer. For example, the degeneracy A that occurs for $M \parallel \hat{z}$ and is lifted for $M \parallel \hat{x}$ is located at the Fermi level for $n_d = 7.6$ (dotted lines in Fig. 1) and leads to the peak $A$ in Fig. 4. It runs along a line in $k$-space, which is shown Fig. 3. According to Eq. (7), with $\frac{\partial E}{\partial k_1} = 0.6 \text{ eV} / \pi$ (taken from the bandstructure), this contribution should be $\Delta E_{\text{anis}} \approx 4 \text{ meV}$, which agrees in the order of magnitude with the calculated value $E_{\text{anis}}(n_d = 7.6) = 6 \text{ eV}$.

Several tests have been made to support that hypothesis. Excluding the states influenced by the degeneracy $A$ (4.3% of the total of 3d-states) from the calculation of $E_{\text{anis}}$, the height of peak $A$ is reduced to 40%. The $k$-space resolved analysis of $E_{\text{anis}}(n_d = 7.6)$ (Fig. 4) also shows clearly that $E_{\text{anis}}$ results from the states near the degeneracy.

Analogous degeneracies are found in the Ni bandstructure contributing to the peaks $E$ and $F$ (Fig. 4). Note that the lifting of degeneracies can favor in-plane as well as perpendicular magnetization. This is in contradiction to the results of Daalderop et al. for a Co(111) monolayer, who state that degeneracies should always favor perpendicular magnetization.

Since the 3d-band degeneracies are so important for $E_{\text{anis}}$, we analyze in the following the occurrence and lifting of degeneracies in the bandstructure. It can be shown that, in terms of the basis of Eq. (3), the Hamilton matrix $H^d$ (Eq. (3)) has the simplest block diagonal form with only four off-diagonal elements (ODEs) $H_{55}^d = H_{54}^d$ and, equivalently, $H_{9,10}^d = H_{10,9}^d$. To find out which additional ODEs are introduced by SOC for a given direction of the magnetization $M$, we analyze the form of $H_{so}$ in Eq. (5). States with parallel spins are coupled if they contain equal orbital momenta with respect to the spin quantization axis $z_M$, whereas states with opposite spins must show a difference of one in the orbital momenta to yield nonvanishing ODEs. The real space components of the atomic states $\phi_i, i = 1, ..., 5$, are composed of eigenstates of $l_z$ with the eigenvalues (-2,2),
(-1,1), (-1,1), (-2,2) and 0, respectively. In terms of eigenstates of $I_z$, one has the eigenvalues (-1,1), (-2,2), (-1,1), (-2,0,2) and (-2,0,2), respectively. This yields a coupling for $\mathbf{M} \parallel \hat{z}$ within the groups of states $\psi_i$ with $i = 1, 4, 5, 7, 8$ and with $i = 2, 3, 6, 9, 10$, and, in the case of $\mathbf{M} \parallel \hat{x}$, within the groups of states $\psi_i$ with $i = 2, 4, 5, 6, 8$ and $i = 1, 3, 7, 9, 10$, respectively. In both cases, the Hamiltonian can be split into two $5 \times 5$ blocks, and subbands belonging to different blocks will intersect. Between states of the same block, the degeneracies will usually be removed. Especially the subbands $\psi_1$ and $\psi_5$ (and, correspondingly, $\psi_6$ and $\psi_7$) change their roles if the magnetization is changed from $\hat{z}$ to $\hat{x}$ and vice versa, because the orbitals $x_j$ and $y_j$ have different orbital momenta with respect to the $x$- and $z$-axes. These subbands will thus be involved in the lifting of degeneracies by altering magnetization and possibly, as shown above, yield important contributions to $E_{\text{anis}}$. In the case of Fe parameters, the situation is even simpler since coupling between states of opposite spin ($\psi_i$ and $\psi_j$ with $i \leq 5 < j$) can be neglected.

As an example, peak A in the curve $E_{\text{anis}}(n)$ of Fe at $n = 7.6$ (Fig. 3) results from the degeneracy A (Fig. 3) of the subbands corresponding to the states $\psi_7$ and $\psi_10$. Thus, it occurs for $\mathbf{M} \parallel \hat{z}$, and is lifted for $\mathbf{M} \parallel \hat{x}$, since in the second case the subbands belong to the same block of the Hamiltonian, whereas in the first they do not.

As a conclusion, it has been shown that 3d-band degeneracies along lines of constant energy result in important contributions to $E_{\text{anis}}$ if they occur near the Fermi level. They can favor in-plane and perpendicular magnetization and need not occur near high symmetry points of the BZ. Thus, for (001) layers, it is not sufficient to consider only bands at high symmetry points as was done by Daalderop et al. for a Co(111) monolayer. Furthermore, for such contributions from degeneracies, $E_{\text{anis}} \propto \chi_0^2$ and, approximately, $E_{\text{anis}} \propto 1/\partial E/\partial k$ is valid (the band dispersion $\partial E/\partial k$ is approximately proportional to the scaling $t$ of the hopping parameters) which agrees with the observations reported above. Note that the analysis is very simple due to the analytic form and low dimension of the 3d tight-binding matrix, which is an advantage of the semiempirical scheme. It remains valid if the extension to s-states is performed (see below).

C. The results of the combined interpolation scheme

Results for $E_{\text{anis}}(n)$ obtained from the combined interpolation scheme (including s- and d-bands as well as s-d hybridization) for the monolayer are presented in Figs. 3 and 4 for Fe parameters and Fig. 5 for Ni parameters with the lattice constant of the Cu(001) surface in both cases (solid curves; the discussion of the curves for two and three layers is postponed to section III.E and III.F). These results for the monolayer are similar to the curves for d-bands only (Figs. 6 and 7). $n$ is the total filling of the s- and d-band ($n = 8$ for Fe and $n = 10$ for Ni). We find for a Fe monolayer $E_{\text{anis}}(\text{Fe/Cu}) = -0.41$ meV per atom, for Ni $E_{\text{anis}}(\text{Ni/Cu}) = 0.10$ meV per atom. The dipole-dipole interaction is included under the assumption of a point dipole located at each site, carrying the magnetic moment of the unit cell. The (spin) magnetic moment per atom is calculated from the bandstructure ($m(\text{Fe/Cu}) = 3.3\mu_B$ and $m(\text{Ni/Cu}) = 0.91\mu_B$).

The dipole anisotropy (equivalent to the shape anisotropy in the monolayer) always prefers in-plane magnetization. Altogether, we obtain for the total magnetic anisotropy energy per atom of a Fe and Ni monolayer with the lattice constant of Cu(001)

$$E_{\text{anis}}(\text{Fe/Cu}) = -0.17 \text{ meV} \quad \text{and} \quad E_{\text{anis}}(\text{Ni/Cu}) = 0.12 \text{ meV}$$

with the easy axis perpendicular to the monolayer for Fe and in-plane for Ni. Note that corresponding ab-initio results for a free-standing Fe-monolayer yielded $-0.42$ meV, but previous tight-binding calculations gave the too large value of $-5.5$ meV.

In the case of Fe, the perpendicular easy axis of ultrathin Fe films on Cu(001) is reproduced correctly. Direct comparison with a Fe monolayer on Cu(001) is difficult due to film growth problems. It is common use to separate the anisotropy energy of thin films in a volume and a surface term $E_{\text{anis}}(d) = K_v + \frac{2K_s}{d}$. (8)

The first term, $K_v$, describes the thickness independent contributions to the anisotropy energy, and the second, $K_s$, the thickness dependent contributions and the surface effects. Fowler and Barth measure the following anisotropy constants $K_v = 0.132$ meV/atom and $K_s = 0.11$ meV/atom for the distorted fcc-films at 100 K. The value $K_v+2K_s = 0.352$ meV/atom is comparable to our result. This result has been calculated with the measured anisotropy field using the bulk saturation magnetization of bcc-Fe. For Ni, our result also agrees very well with experiments which yields $E_{\text{anis}}(\text{Ni/Cu}) = 0.125$ meV at 300 K. The anisotropy constants $K_v$ and $K_s$ are temperature dependent. Measurements of the anisotropy constants as a function of the reduced temperature have been made, but the correct extrapolation to $T=0$ K is not known yet. While in experiment, the values of $K_v$ and $K_s$ have to be compared at the same reduced temperature because of the thickness dependence of $T_c$, the theoretical values are for 0 K and thus independent of the difference of absolute and reduced temperature.

Note that in Fig. 6, the curve $E_{\text{anis}}(n)$ for the Ni monolayer (solid curve) has zeros near $n = 10$. Hence, the numerical result for Ni is not very stable and the excellent agreement with experiment should not be overemphasized. Nevertheless, for Fe and Ni, the sign and the order...
of magnitude of $E_{\text{anis}}$ turn out to be remarkably stable upon parameter variations: Sign changes do not occur upon variation of the pseudopotential and s-d hybridization parameters by as much as 10%. Moreover, we find in agreement with Wang et al. a perpendicular easy axis also for Fe monolayers taking (001) surface lattice constants imposed by substrates such as Pd, Ag, and V (2.77 rÅ, 2.89 rÅ, and 3.03 rÅ), respectively. This stability again demonstrates the validity of our results for $E_{\text{anis}}$. The good agreement of the results both with ab-initio theories and experiments is due to the fact that the parameters were obtained by a fit to ab-initio calculations for Fe and Ni monolayers rather than taking bulk parameters.

To investigate crystal field effects, an additional parameter $\Delta$ is introduced to take into account the different effect of the monolayer geometry on orbitals that lie in the plane of the monolayer ($xy$ and $x^2 - y^2$) and out-of-plane orbitals ($yz$, $zx$ and $3z^2 - r^2$). Additional to Eq. (2), the on-site energies of the latter are lowered by $\Delta$ with respect to the first. The dependence of $E_{\text{anis}}$ on $\Delta$ is shown in Fig. 9 for Fe and Ni parameters (solid and dashed curve, respectively). Remarkably, $\Delta = 0$ changes the sign of $E_{\text{anis}}$ (for Fe/Cu) and $\Delta < 0$ (for Ni monolayer but employed for both Fe and Ni(001) monolayers). Pick and Dreyssé et al. state that for (001)-monolayers a crystal field parameter is not necessary. For Ni, this is supported by our result; even in Fe, our value of $\Delta$ is small compared to other bandstructure parameters. Cinal et al. report $\Delta = -0.14$ eV for the Ni(001) monolayer.

Finally, a detailed investigation of the bandstructure shows that the analysis given in section III.B for 3d-bands only is still valid for the combined interpolation scheme. As an evidence, consider Figs. 3 and 4 (solid curves): There is a one-to-one correspondence between the peaks in $E_{\text{anis}}$ in both curves. This correspondence can be shown to result from similar bandstructure details. In particular, the role of 3d-band degeneracies stressed in section III.B remains the same in the complete scheme.

D. Temperature dependence

One of the greatest challenges in the investigation of magnetic anisotropy is the calculation of reorientation transitions with temperature. Up to now, a complete electronic and thermodynamic theory is lacking. Here, one-particle effects of temperature are investigated. It turns out that they again support the role of degeneracies for magnetic anisotropy and, moreover, are comparable in order of magnitude with the many-particle aspects usually considered.

The free magnetic anisotropy energy $F_{\text{anis}}$ depends on temperature $T$ due to (i) the Fermi distribution of electronic states $f_T(\Delta E)$, (ii) the hopping integrals, which depend on $T$ because of the lattice expansion of the substrate, (iii) the entropy $S(T)$ and (iv) the effects of spin-waves, resulting in a temperature dependence of the magnetization $M(T)$. In this work, the first three effects are analyzed. More precisely, the thermal expansion (ii) of the lattice constant $a(T)$ is included by means of the empirical law $a(T) = a(T = 0)(\alpha T + 1)$. $\alpha = 2 \times 10^{-5}/K$ is the expansion coefficient for the Cu substrate. The expression for the entropy (iii) of non-interacting particles is:

$$S = -k_B \sum_{m,k} \langle n_{mk} \rangle \ln \langle n_{mk} \rangle + (1 - \langle n_{mk} \rangle) \ln(1 - \langle n_{mk} \rangle)$$

with $\langle n_{mk} \rangle = f_T(E_{\text{anis}}(\theta, \phi) - \mu(\theta, \phi; n))$. In analogy to Eq. (6), the free magnetocrystalline anisotropy energy $F_{\text{anis}}$ is defined as the difference in the free energy $F = E + T S$ for two different directions of magnetization.

Fig. 10 shows $F_{\text{anis}}(T)$ (d-band calculation for the monolayer, Fe parameters, $n_d = 6$). Including only Fermi statistics (i; dashed curve), the characteristic energy scale for the decrease of $|F_{\text{anis}}|$ with $T$ is about 1000 K (100 meV), which corresponds to the energy $2 \lambda_{so}$, but not to the 3d-bandwidth of approximately 3 eV. This becomes immediately plausible if one notices that the SOC-induced lifting of degeneracies occurs near the Fermi level. Thus, one expects a measurable effect on $F_{\text{anis}}$ due to Fermi statistics as soon as $k_B T$ becomes larger than or comparable to $2 \lambda_{so}$. In addition, we must conclude from our results that shifting of subbands far below the Fermi-level is not so important, since then $F_{\text{anis}}$ could not be essentially lowered on such a small temperature scale.

The characteristic increase of $|F_{\text{anis}}|$ with increasing temperature for $T < 500$ K is a direct result of the lifting of degeneracies. Consider again Fig. 1 for $M \parallel z_M^3$ (lifted degeneracy), which is the energetically favored case, Fermi statistics induces only little changes in the occupation of the electronic states, if $k_B T < \lambda_{so}$; for the degenerate bands ($M \parallel z_M^X$), however, states in the upper band are significantly occupied even for $k_B T < \lambda_{so}$. Thus, the total energy for $M \parallel z_M^X$ rises with respect to $T = 0$ in this temperature range. This leads to an increase of $|F_{\text{anis}}|$ with increasing $T$, if $k_B T < \lambda_{so} = 50$ meV ($T < 500$ K).

The inclusion of lattice expansion (ii; solid curve in Fig. 10) has only a small effect on $F_{\text{anis}}$. The narrowing of bands with increasing temperature due to the scaling of the hoppings leads to an increase in $|F_{\text{anis}}|$ for small $T$, which was already discussed for $T = 0$. For larger
$T$, the influence of Fermi statistics on narrowed bands is larger, leading to a stronger decrease of $|F_{anis}|$.

The entropy (iii; dotted curve) has a damping effect on the curve $F_{anis}(T)$, but maintains the features discussed above. This results from the fact that, in the case of degenerate bands, the entropy is larger than for nondegenerate bands, since states located nearer to the Fermi level have larger entropy. $F_{anis}(T)$ was also calculated for bilayers (Fig. 11), taking into account all three mentioned effects and shows a decrease with increasing temperature on the same scale as for the monolayer. Hence, this analysis of $F_{anis}(T)$ shows the significant contribution of temperature-induced changes of the degeneracies to the anisotropy energy. It is remarkable that the three temperature effects mentioned above, and particularly the electron temperature dependence of the Fermi-function, are of equal magnitude as the temperature effects of spin-waves on $M(T)$.

E. Fe Multilayers

Fig. 12 shows the calculated magnetic anisotropy energy for Fe films of 1 to 14 layers. Calculations for both 1/4 BZ and 1/2 BZ are included. The values obtained when the summation over $k$ is performed over 1/4 BZ lead to periodically recurring positive values of $E_{anis}$ (for films of 2, 6, 9 and 12 layers). The positive value for film of 2 layers can be traced back to the occurence of degeneracy $A$ at the Fermi-level. For the other positive values, easy and hard axis are found to be in-plane, an effect of the wrong symmetry resulting from the summation over $k$. We then obtain $K_v = -0.17 \text{meV per atom}$ and $K_A = -0.28 \text{meV per atom}$, which is in very good agreement with Fowler and Bart.

Including the dipole-dipole anisotropy energy as calculated by L. Szunyogh et al. we would expect for Fe a change of the easy-axis from perpendicular to in-plane at 4 ML ($F_{dip}^i(4 \text{layers})=0.59\text{meV}$). Our result indicates that the experimentally observed transition at 5 ML might be an intrinsic quality of fct-films grown at low temperature. L. Szunyogh et al. calculated the anisotropy energy of thin fcc-Fe films on Au (001) and also observed oscillations. They obtained a reorientation transition from perpendicular to in-plane magnetization at 4 ML.

The dependence of $E_{anis}$ of Fe on the 3d- and 4s-bandfilling $n$ is shown in Fig. 6. For the monolayer at a s- and d-bandfilling $n=8$, we are near a zero of the curve, and at $n=8.2$ we already have a positive value of $E_{anis}$ caused by the growing influence of degeneracy $A$. We would thus expect a monolayer of a Fe$_x$Co$_{1-x}$ alloy to have an in-plane magnetization already at small Co concentrations. This was in fact measured by Dittshar et al. for $x=0.95$. We would predict an increase of the anisotropy energy with increasing Co concentration. For 3 layers, we would expect the same behavior, the structure of the curve $E_{anis}(n)$ near $n=8$ being similar to that of the monolayer. This alloying behavior found both theoretically and experimentally supports the relevance of degeneracies for the anisotropy energy, as claimed by Daalderop et al. and disputed by Wang, Wu and Freeman. In this case, there is no doubt that the magnetic moment persists.

F. Ni Multilayers

The magnetic anisotropy of Ni calculated for systems of 1 to 14 ML is shown in Fig. 6. We include again calculations using 1/4 of the BZ and 1/2 BZ, but this time no point has to be excluded. $E_{anis}$ of the second layer is much bigger than that of the monolayer, a fact which indicates that the influence of the substrate may not be neglected. The anisotropy then sinks again and remains approximately constant at a value of about 0.14 meV (which is still bigger as the value obtained for the monolayer). Schulz and Baberschke report for Ni a transition from in-plane to perpendicular magnetization at 7 ML, due to a large $K_v$, which favors perpendicular
orientation of the magnetization. Our theory does not reproduce this reorientation.

For Fe, the behavior of the films as a function of thickness could be related to the degeneracies occurring at the Fermi-level. The contribution of these degeneracies to the total anisotropy of the film would be expected to decrease with increasing number of layers, as their weight in the summation over all atoms (number of points in the BZ × number of layers) decreases: that is in fact what we find for Fe. For Ni, the contribution of the degeneracies to the anisotropy energy is not so evident, the minority and majority spin bands mix much more than in the case of Fe because of the small exchange coupling. This is a possible reason for the nearly constant anisotropy energy we obtain. The occurrence of a degeneracy of a $k$-times degenerated band would also probably lead to a thickness independent contribution to $E_{anis}$.

So far, no other monolayer calculation lead to the correct in-plane anisotropy for the Ni-monolayer. In a calculation for the fct-bulk, Eriksson finds a perpendicular easy-axis, which is correct for fct-Ni, but wrong for fcc-Ni. For Ni, we obtain the correct in-plane anisotropy for the monolayer, but the wrong $K_e$. So, a 3D calculation for fct-Ni does not really tackle the problem and explain the behavior of the magnetization.

Ni is a delicate system. Maybe many-body effects cannot be neglected (i.e. the force theorem does not work well). However, a total-energy calculation made by Eriksson still yields the wrong sign for $E_{anis}$ for fcc-Ni bulk. The dependence between the anisotropy energy and the bandstructure seem to be very subtle and the smallest details can influence the results.

IV. CONCLUSIONS

A calculation of the magnetocrystalline anisotropy energy $E_{anis}$ of Fe and Ni monolayers on Cu(001) is performed. In agreement with experiments, we find a perpendicular easy axis for Fe and an in-plane easy axis for Ni. The results are fully converged without any additional assumption to improve convergence. SOC is included non-perturbatively. It is an important result that large contributions to $E_{anis}$ can result from the SOC-induced lifting of degeneracies occurring along lines in k-space at the Fermi-level. The contributions of those degeneracies scale with the square of the SOC constant $\lambda_{so}$, as contributions from nondegenerate bands do. The occurrence and lifting of degeneracies in the 3$d$-band has been discussed in general. Evidence for the important contribution to $E_{anis}$ of the degeneracies at the Fermi-level are (i) the groove and the ring-shaped dip in the k-space resolved anisotropy for the monolayer in the tight-binding scheme and in the combined interpolation scheme respectively, (ii) the temperature dependence (the characteristic energy scale for the decrease of the free magnetocrystalline anisotropy energy $|E_{anis}|$ as a function of the temperature is determined by $\lambda_{so}$), (iii) the finite anisotropy energy at $T_c$ and (iv) the alloying behavior of Fe$_x$Co$_{1-x}$. We obtain for Fe a reorientation transition from perpendicular to in-plane magnetization at 4 ML, reorientation which is independent of any restructuration of the fct-film. Since it can be seen from Fig. 3 and Fig. 4 that both Fe and Ni do not exhaust the maximal anisotropy possible, our calculation of $E_{anis}$ should also be important for the technologically relevant maximization of magnetic anisotropy by appropriate surface-alloy formation.

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The parameters $A_i$ used by Weling and Callaway have to be transformed into the coordinate system used here by
\[
\tilde{B}_1 = A_4, \quad \tilde{B}_4 = -A_1, \\
\tilde{B}_2 = A_2 - A_3, \quad \tilde{B}_5 = -\frac{1}{\sqrt{3}}(A_4 + 4A_5), \\
\tilde{B}_3 = A_2 + A_3, \quad \tilde{B}_6 = \frac{2}{\sqrt{3}}A_6
\]
and $J_{ex} = J_{ex}(\epsilon_0)$, $J'_{ex} = J_{ex}(t_{2g})$.

The corresponding transformation formulas are
\[
\tilde{B}_1 = A_1, \quad \tilde{B}_4 = \left(\frac{1}{4}A_4 + \frac{1}{2}A_2\right), \\
\tilde{B}_2 = A_2, \quad \tilde{B}_5 = \left(\frac{1}{4}A_4 + \frac{1}{2}A_2\right), \\
\tilde{B}_3 = A_1, \quad \tilde{B}_6 = \frac{2}{\sqrt{3}}(A_2 - A_4)
\]
and $J'_{ex} = J_{ex}$.

$\theta$ denotes the angle between the magnetization direction $z_M$ and the surface normal $\hat{z}$. $\phi$ is the angle between the $x$-axis and the projection of $z_M$ in the plane of the monolayer.

$\theta$ is the angle between the magnetization direction $z_M$ and the surface normal $\hat{z}$.

Of course, SOC itself is part of a perturbation expansion, leading from the Dirac equation to the Pauli equation.

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TABLE I. Bandstructure parameters within the combined interpolation scheme for Fe and Ni (001)-monolayers with lattice constant $a$. The parameters $\tilde{B}_i$ and $\Delta V$ are taken from Pustogowa et al.$^{28,29}$ for Fe and from Weling and Callaway$^{26,27}$ for Ni (bulk parameters). The other parameters are obtained from a fit to ab-initio calculations for freestanding (001)-monolayers by Pustogowa et al.$^{31}$ for Fe and Jepsen et al.$^{32}$ for Ni.

|       | Fe     | Ni     |
|-------|--------|--------|
| $B_1$ (eV) | 0.0774 | 0.152923 |
| $B_2$ (eV) | -0.00816 | -0.015135 |
| $B_3$ (eV) | 0.0774 | 0.227635 |
| $B_4$ (eV) | -0.15324 | -0.25 |
| $B_5$ (eV) | -0.05652 | -0.071149 |
| $B_6$ (eV) | 0.08376 | 0.119380 |
| $\Delta V$ (eV) | 0.068 | 0.059360 |

$S^\uparrow$ | 2.06 | 1.33 |
$S^\downarrow$ | 2.63 | 1.52 |
$J_{xx}$ (eV) | 2.18 | 0.87 |
$J_{xx}'$ (eV) | 2.18 | 1.17 |
$E_0$ (eV) | -0.54 | -0.935 |

$\alpha$ (eV) | 20.0 | 25.2 |
$V_{60}$ (eV) | -4.20 | -4.60 |
$V_{10}$ (eV) | 1.2 | 0.4 |
$V_{11}$ (eV) | 1.0 | 2.0 |
$B_1$ (eV) | 7.5 | 5.0 |
$B_2$ (eV) | 5.1 | 12.8 |
$a$ (rA) | 2.76 | 2.49 |

FIG. 1. Dependence of the magnetocrystalline anisotropy energy $E_{anis}$ on the 3d-bandfilling $n_d$ for a monolayer with parameters referring to Fe, calculated within the tight-binding scheme (solid curve). Negative values of $E_{anis}$ yield perpendicular anisotropy. The origin of the peaks denoted by A, B and C can be traced back to degeneracies in the bandstructure (see text and Fig. 4). The dashed and dotted curves show the contributions $E_{anis}^{par}$ and $E_{anis}^{antipar}$ to $E_{anis}$ from the spin-orbit coupling between parallel spins and antiparallel spins, respectively.

FIG. 2. Dependence of the magnetocrystalline anisotropy energy $E_{anis}$ on the 3d-bandfilling $n_d$ for a monolayer with parameters referring to Ni, calculated within the tight-binding scheme (solid curve). Negative values of $E_{anis}$ yield perpendicular anisotropy. The origin of the peaks denoted by E and F can be traced back to degeneracies in the bandstructure (see text). The dashed and dotted curves show the contributions $E_{anis}^{par}$ and $E_{anis}^{antipar}$ to $E_{anis}$ from the spin-orbit coupling between parallel spins and antiparallel spins, respectively.
FIG. 3. Occurrence (full lines) and lifting (dashed lines) of a “line” degeneracy for two different directions of magnetization $z_M^X$ and $z_M^Y$, respectively. $k_1$ corresponds to one particular direction in $k$-space. Perpendicular to $k_1$ the intersecting bands are non-dispersive throughout the BZ. Note, the energy gained by the lifting of this degeneracy is given by $\Delta E_\text{anis} = \frac{\lambda_{so}}{2} \cdot F$, if $E_F$ falls in between the two subbands (dotted line). Here, $F$ is the fraction of the involved states in $k$-space. Apparently, if $E_F$ lies below or above the two subbands, $\Delta E_\text{anis}$ is zero.

FIG. 4. Bandstructure of the 3d minority spin band of the Fe monolayer, calculated within the tight-binding scheme. The magnetization $\mathbf{M}$ is directed along the layer normal $\mathbf{\hat{z}}$ (upper part) and in-plane along $\mathbf{\hat{x}}$ (lower part). The degeneracies denoted by $A$, $B$ and $C$ contribute to the peaks $A$, $B$ and $C$ in Fig. 1. The dotted lines denote the Fermi level for $n_d = 7.6$, respectively, $\Gamma = (0, 0)$, $X = (\pi/a, 0)$, $\Gamma = (0, \pi/a)$ and $M = (\pi/a, \pi/a)$ are the high symmetry points of the irreducible part of the Brillouin zone ($0 \leq k_x, k_y \leq \pi/a$; $a$ is the lattice constant of the monolayer) for the bandstructure of the Fe monolayer, $n_d = 7.6$ electrons per atom in the $d$-band, calculated within the tight-binding scheme. Positive values of $E_\text{anis}(k, n_d)$ favor in-plane magnetization.

FIG. 5. $k$-space resolved magnetocrystalline anisotropy energy $E_\text{anis}(k, n_d) = E_k(\theta = 0; n_d) - E_k(\theta = \pi/2, \phi = 0; n_d)$ in the irreducible part of the Brillouin zone ($0 \leq k_x, k_y \leq \pi/a$; $a$ is the lattice constant of the monolayer) for the bandstructure of the Fe monolayer, $n_d = 7.6$ electrons per atom in the $d$-band, calculated within the tight-binding scheme. Positive values of $E_\text{anis}(k, n_d)$ favor in-plane magnetization.

FIG. 6. Magnetic anisotropy energy of Fe as a function the $s$- and $d$-bandfilling for 1 layer (solid curve), 2 layers (dashed) and 3 layers (dotted). Peaks $A$ and $D$ are caused by the respective degeneracies in the bandstructure shown in Fig. 1.
FIG. 7. Magnetic anisotropy energy of Ni as a function the s- and d-bandfilling for 1 layer (solid curve), 2 layers (dashed) and 3 layers (dotted).

FIG. 8. Irreducible part of the two-dimensional Brillouin zone of Fe for the tight-binding scheme. a is the lattice constant of the monolayer. The main contribution to $E_{\text{anis}}$ at $n = 8.8$ (corresponding to $n_d = 7.6$ in the tight-binding calculation) results from the lifting of degeneracies along the line $LL'$.

FIG. 9. Dependence of the magnetocrystalline anisotropy energy $E_{\text{anis}}$ on the crystal field splitting $\Delta$ for the Fe monolayer on Cu(001), $n = 8$, (solid curve) and the Ni monolayer on Cu(001), $n = 10$, (dashed curve). Negative values of $E_{\text{anis}}$ yield perpendicular anisotropy. The vertical line denotes the best fit for $\Delta$ for the Fe monolayer. In the case of Ni, the fit cannot be improved by the introduction of $\Delta$ (see text).

FIG. 10. Temperature dependence of $F_{\text{anis}}(T)$ for a Fe-parametrized d-band calculation for the monolayer with d-bandfilling $n_d = 6$. For the dashed curve, only Fermi statistics is taken into account, for the solid curve the lattice expansion is added, and the dotted curve includes the effects of Fermi statistics, lattice expansion and entropy.
FIG. 11. Temperature dependence of $F_{\text{anis}}(T)$ for a Fe-parametrized $d$-band calculation for 2 layers with $d$-bandfilling $n_d = 6$. The calculation includes Fermi statistics, lattice expansion and entropy.

FIG. 12. Magnetic anisotropy energy of Fe as a function of the number of layers calculated in the combined interpolation scheme. The calculation for 1/4 BZ (dashed lines) yields periodic oscillations caused by the incorrect symmetry of $E_{\text{anis}}^{\text{in-plane}}$. Summation over 1/2 BZ corrects this problem. • and x are calculations with 15356 and 108228 points in the 1/2 BZ respectively.

FIG. 13. Monolayer bandstructure of the 3s- and 4s-band for Fe-parameters, calculated within the combined interpolation scheme with the magnetization $\mathbf{M}$ parallel to the layer normal $z$ in the upper part and in-plane parallel $x$ in the lower part. High symmetry points are the same as in Fig. 4.

FIG. 14. $\mathbf{k}$-space resolved anisotropy energy for the Fe monolayer at a 3s- and 4d-bandfilling of 7.8. The ring-shaped dip near the M-point is caused by degeneracy D.
FIG. 15. \textbf{k-space resolved anisotropy energy of Fe for 3 layers at a 3s- and 4d-bandfilling of 8.0. The negative peak near the M-point is caused by degeneracy D.}

FIG. 16. \textbf{Magnetic anisotropy energy of Fe as a function of the \textit{1/l} (\textit{l}: number of layers). Including the dipole-dipole anisotropy energy, we obtain in-plane magnetization from the fourth layer on. Linear least square fit yields $K_v = -0.17$ meV per atom and $K_s = -0.28$ meV per atom.}

FIG. 17. \textbf{Magnetic anisotropy energy of Ni as a function of the number of layers, calculated within the combined interpolation scheme.} $\square$ is a calculation for 1/4 BZ with 1722 points, the solid curve is a calculation for 1/2 BZ with 6188 points.
