Magnetocrystalline Anisotropy Energy of a Transition Metal Monolayer: A Non-perturbative Theory

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Abstract

The magnetocrystalline anisotropy energy $E_{\text{anis}}$ for a monolayer of Fe and Ni is determined using a fully convergent tight-binding calculation including $s$-$d$ hybridization. The spin-orbit interaction $\lambda_{so}$ is treated non-perturbatively. Remarkably, we find $E_{\text{anis}} \propto \lambda_{so}^2$ and important contributions to $E_{\text{anis}}$ due to the lifting of degeneracies near the Fermi-level. This is supported by the calculated decrease of the anisotropy energy with increasing temperature on a scale of several hundred K. Our results clarify the present debate on the origin of $E_{\text{anis}}$.

75.30.Gw, 75.70.Ak, 73.20.Dx, 71.70.Ej

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Despite increasing theoretical effort, the origin of magnetic anisotropy in ferromagnetic transition metals has not been clearly identified. Actually, present theoretical analyses are controversial [1,2]. It remains to determine clearly how the magnetocrystalline anisotropy energy $E_{\text{anis}}$ depends on the spin-orbit coupling (SOC) strength $\lambda_{so}$ and whether the level crossings at the Fermi-level $E_F$ play an important role for $E_{\text{anis}}$ or alternatively whether they have to be excluded as stated by Wang et al. [1]. It is important to present calculations without using the state-tracking method by Wang et al. [1], the validity of which was disputed by Daalderop et al. [2]. Due to increased recent experimental activity on magnetic anisotropy at surfaces, interfaces and thin films [3,4], there is need of a theory without too many restrictive assumptions in order to get a systematic understanding of $E_{\text{anis}}$.

In this paper, we present a theory treating $\lambda_{so}$ non-perturbatively and determining the electronic bandstructure within the combined interpolation scheme [5]. We investigate a simple quadratic Fe and Ni monolayer epitaxially grown on the Cu(001) surface and neglect further interactions with the substrate. Our calculation permits us to identify clearly the contributions to $E_{\text{anis}}$ resulting from level-shifts and lifting of degeneracies near $E_F$. In particular, the latter give important contributions to $E_{\text{anis}}$. We find for these that generally $E_{\text{anis}} \propto \lambda_{so}^2$ is valid. The degeneracies do not only appear at high symmetry points of the Brillouin zone (BZ) [2] but also along lines in $k$-space. It is very important that we obtain convergent results for $E_{\text{anis}}$ without applying state-tracking or excluding surface-pair coupling as was necessary in previous analyses by Wang et al. [1]. Furthermore, we find the characteristic scale for the temperature dependence of the magnetic anisotropy to be $\lambda_{so}$, rather than the bandwidth, again indicating the significance of the lifting of degeneracies at $E_F$ by $\lambda_{so}$.

We start our theory by defining the magnetic anisotropy energy as

$$E_{\text{anis}}(n) := E_{\text{tot}}(\theta = 0; n) - E_{\text{tot}}(\theta = \pi/2, \phi_0; n),$$

where $E_{\text{tot}}(\theta, \phi; n)$ is the ground-state energy per atom of the monolayer with a total of $n$ 3d- and 4s-electrons per atom and $N$ atoms and is given by

$$E_{\text{tot}}(\theta, \phi; n) = \frac{1}{N} \sum_{m,k} E_{mk}(\theta, \phi) f_0(E_F(n) - E_{mk}(\theta, \phi)).$$
The angles $\theta$ and $\phi$ denote the direction of the magnetization $\hat{\zeta}$. $f_0(\Delta E)$ is the Fermi-function at zero temperature and $E_F(n)$ is the Fermi-energy, which, for a given bandfilling $n$, is determined self-consistently by

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

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

$$H = H_s + H_d + H_{sd} + H_{so}.$$ 

$H_s$ refers to the $s$-electrons which are described by a set of properly symmetrized plane waves. $H_d$ refers to the $d$-electrons treated by spin-polarized tight-binding approximation using the Fletcher-Wohlfahrt parametrization [7,8] adapted to the monolayer. $H_{sd}$ denotes $s$-$d$ hybridization (in the conventional form of the combined interpolation scheme [5]) and $H_{so} = \lambda_{so} \mathbf{l} \cdot \mathbf{s}$ is the SOC between the $d$-electrons on the same site in the usual approximation with the SOC parameter $\lambda_{so}$. $H_{so}$ is a matrix function of the magnetization direction $\hat{\zeta}$. It can be expressed in terms of the orbital momentum operators $l_\xi$, $l_\eta$ and $l_\zeta$ with respect to the rotated frame $(\hat{\xi}, \hat{\eta}, \hat{\zeta})$ as [9,10]

$$H_{so} = \begin{pmatrix} H_{so}^{\uparrow\uparrow} & H_{so}^{\uparrow\downarrow} \\ H_{so}^{\downarrow\uparrow} & H_{so}^{\downarrow\downarrow} \end{pmatrix} = \frac{\lambda_{so}}{2} \begin{pmatrix} l_\zeta & l_\xi - il_\eta \\ l_\xi + il_\eta & -l_\zeta \end{pmatrix}.$$ (1)

For the numerical analysis, we employ for the $d$-electrons a basis of 10 two-dimensional Bloch-functions $\psi_i$, $i = 1, \ldots, 10$, for each possible crystal momentum $\mathbf{k}$, constructed from atomic $3d$-wave functions together with the spin eigenstates $|\uparrow\rangle$ and $|\downarrow\rangle$ of the Pauli matrix $\sigma_\zeta$, where $\hat{\zeta}$ is the spin quantization axis. Only nearest neighbors (4 in a simple-quadratic monolayer) are considered. To obtain accurate parameters, we perform a fit to the full-potential LMTO calculation for a free-standing Fe-monolayer by Pustogowa et al. [11] and to the LAPW calculation for a Ni-monolayer by Jepsen et al. [12]. The $s$- and $d$- bandwidths and hybridization parameters are then scaled to take into account the Cu surface lattice constant of 2.56 Å [13]. The complete BZ summation over $\mathbf{k}$ is performed as a weighted summation over the irreducible part of the BZ (1/8 of the quadratic BZ in the nonmagnetic case or for perpendicular magnetization and 1/4 for in-plane magnetization due to reduced
symmetry. To achieve convergence, about 1000 or 2000 points in the irreducible part of the BZ are sufficient. Note, we do not have to exclude any parts of the BZ to obtain convergence, unlike Wang et al. [1].

In Fig. 1 we present results for $E_{\text{anis}}$ as a function of the bandfilling $n$, in order to demonstrate the correspondence between electronic structure and magnetic anisotropy energy and to show that our method will yield convergent results for the whole transition metal series and for large (Fe) and small (Ni) exchange coupling. We use parameters for freestanding Fe and Ni monolayers and a lattice constant of 2.56 Å to simulate epitaxial growth on Cu(001). In particular, our results yield that Fe has a perpendicular easy axis with $E_{\text{anis}} = -0.32$ meV and Ni an in-plane easy axis (along an axis connecting nearest neighbors) with $E_{\text{anis}} = 0.1$ meV [14]. Experiment yields perpendicular anisotropy for ultrathin Fe-films [3]. However, comparison to experiment for a monolayer is difficult due to growth problems. In the case of Ni, even the calculated in-plane direction of the easy axis agrees with experiment [1]. Note, corresponding ab initio results for a free-standing Fe-monolayer yielded $-0.4$ meV [14], but previous tight-binding calculations gave $-5.5$ meV [16]. Although our numerical values of $E_{\text{anis}}$ depend on the choice of parameters, the sign and the order of magnitude of $E_{\text{anis}}$ are remarkably stable upon parameter variations: In agreement with Wang et al. [1] we find a perpendicular easy axis also for Fe monolayers taking (001) surface lattice constants of Pd, Ag, V, and W (2.77 Å, 2.89 Å, 3.03 Å, and 3.16 Å, respectively).

It is of considerable interest for the physical interpretation of the origin of magnetocrystalline anisotropy energy to study $E_{\text{anis}}$ as a function of $\lambda_{so}$ and the hopping parameters $t$. To a good approximation, we find quite generally $E_{\text{anis}} \propto \lambda_{so}^2$, which sheds light on previous analyses. This was calculated for Fe and Ni bandstructure parameters for fixed bandfilling $n$ and in the range of $\lambda_{so}$ from zero to the actual value (Fe: $\lambda_{so} = 50$ meV, Ni: $\lambda_{so} = 70$ meV). However, for very small $E_{\text{anis}}$ the dependence might be larger than $\lambda_{so}^2$.

Regarding the dependence of $E_{\text{anis}}$ on $\lambda_{so}$, the following remarks are of interest. Treating SOC as a perturbation, the lowest nonvanishing order of non-degenerate perturbation theory is $\lambda_{so}^2$ due to time reversal symmetry [10]. However, in the case of degenerate bands, a lifting of the degeneracy by SOC will complicate the situation. Degenerate bands can undergo a
lifting linear in $\lambda_{so}$ when SOC is introduced, and the resulting contribution to $E_{\text{anis}}$ depends on the area in $k$-space influenced by the degeneracy. Whether this area is of the order of $\lambda_{so}^2$, which would yield $E_{\text{anis}} \propto \lambda_{so}^3$ [1], or this area is of lower order and thus would yield an important contribution to $E_{\text{anis}}$ [2,17], has been a controversial question. This makes our result very interesting (see below).

Concerning the dependence of $E_{\text{anis}}$ on the $d$-electron hopping parameters $t$, note that the overall shape of the curves $E_{\text{anis}}(n)$ will not change if $t$ is varied. $|E_{\text{anis}}|$ increases for decreasing $t$ (decreasing bandwidth). This leads to the general trend: $|E_{\text{anis}}|$ increases with increasing lattice constant of the monolayer. This corresponds to an increasing substrate lattice constant, if one neglects hybridization effects between the substrate and the monolayer.

For the further physical interpretation of our results for $E_{\text{anis}}$ as a function of $n$ and $\lambda_{so}$, namely how $E_{\text{anis}}$ results from the bandstructure and especially how it is affected by the lifting of degeneracies in the bandstructure close to $E_F$, we neglect $s$-$d$ hybridization for simplicity. This is allowed since only $d$-state degeneracies matter; $s$-$d$ hybridization changes only the location of the degeneracies. The inset in Fig. 2 shows schematically that a special type of degeneracy (“line” degeneracy) leads to an important contribution to $E_{\text{anis}}$ if it occurs near $E_F$ for one direction of magnetization and is lifted by SOC for another. Estimating this contribution (see Fig. 2) yields $\Delta E_{\text{anis}} = \frac{1}{2} \lambda_{so} \cdot F$. The fraction $F$ of involved states in $k$-space is given by $F = \frac{\Delta k_1}{\pi} \cdot 1 = 2 \lambda_{so} \left( \frac{\pi \partial E}{a \partial k_1} \right)^{-1}$, since the intersecting bands are non-dispersive along one direction in $k$-space (perpendicular to $k_1$). Here, $a$ is the lattice constant, and $\frac{\partial E}{\partial k_1}$ is the dispersion of the intersecting bands near their intersection. Hence, the maximum energy gained by the lifting of the degeneracy amounts to

$$\Delta E_{\text{anis}} = \lambda_{so}^2 \left( \frac{\pi \partial E}{a \partial k_1} \right)^{-1}.$$  \hspace{1cm} (2)

It is important to note that such contributions are not caused by degeneracies at isolated points [18], but by degeneracies along lines in $k$-space. Our bandstructure calculations yield such degeneracies near $E_F$ for $n = 8.7$ using Fe parameters for the bandstructure and for $n = 5.9$ using Ni parameters.

Eq. (2) explains immediately the height of the peak at $n = 8.7$ shown in Fig. 1 (curve a). Taking from our bandstructure calculations (Fe parameters) $\frac{\partial E}{\partial k_y} \approx 1 \text{ eV}/\pi a$ we obtain
\( \Delta E_{anis} \approx 2.5 \text{ meV}. \) This is in excellent agreement with the exact result of our calculation \( E_{anis}(n = 8.7) = 2.7 \text{ meV}. \) In addition, a detailed k-space resolved calculation of \( E_{anis}(n = 8.7) \) shows that indeed only states near the corresponding degeneracy at \( E_F \) yield large contributions to \( E_{anis}. \) Furthermore, Eq. (2) shows that \( \Delta E_{anis} \propto t^{-1} \) since approximately \( \partial E / \partial k \propto t. \) Note, this is in agreement with our previous observation regarding the dependence of \( E_{anis} \) on the hopping parameters \( t. \)

Since the degeneracies are so important for \( E_{anis}, \) we outline in the following at some length the relationship between \( E_{anis} \) and the degeneracies and thus the crystal symmetry. For that purpose, we adapt our basis set of Bloch wave functions \( \psi_i, i = 1, \ldots, 10, \) in order to obtain a maximum number of zeros in the Hamiltonian matrix for the \( d \)-electrons. Expressed in terms of Bloch functions constructed from the cartesian atomic orbitals, the \( 5 \times 5 \) tight-binding matrix has its simplest block diagonal form with only two off-diagonal elements (ODEs) \( (H_d)_{4,5} = (H_d)_{5,4} \) (and equivalently \( (H_d)_{9,10} = (H_d)_{10,9} \)) if the \( x \)-axis is directed along an axis connecting nearest neighbors. To find out which additional ODEs are introduced by SOC for a given direction of the magnetization \( M \) (in the following, \( M \parallel \hat{z} \) and \( M \parallel \hat{x} \) are considered), we analyze the form of \( H_{so} \) in Eq. (3). We assume that different Bloch-states are orthogonal. States with parallel spins are coupled, if they contain equal orbital momenta with respect to the spin quantization axis \( \hat{\zeta}, \) whereas states with opposite spins must show a difference of one in the orbital momenta to yield nonvanishing ODEs. The cartesian orbitals \( xy, yz, zx, x^2 - y^2 \) and \( 3z^2 - r^2 \) (leading to \( \psi_1, \ldots, \psi_5 \) together with \( |\uparrow\rangle \) and to \( \psi_6, \ldots, \psi_{10} \) with \( |\downarrow\rangle, \) respectively) 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 \( l_x \) one finds the eigenvalues \((-1,1), (-2,2), (1,1), (-2,0,2) \) and \((-2,0,2), \) respectively. Hence, coupling exists, for \( M \parallel \hat{z}, \) 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 \( M \parallel \hat{x}, \) 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 ordinarily be removed. Especially the subbands \( \psi_1 \) and \( \psi_2 \) (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 \( xy \) and \( yz \) have different orbital momenta with respect to the \( x- \) and \( z- \) axes. So,
they will be involved in the lifting of degeneracies by altering magnetization and possibly, as shown above, yield important contributions to $E_{\text{anis}}$. As an example, the prominent peak in the $E_{\text{anis}}(n)$ curve of Fe at $n = 8.7$ results from a degeneracy of the subbands corresponding to the states $\psi_7$ and $(\psi_9, \psi_{10})$ for $\mathbf{M} \parallel \mathbf{\hat{z}}$, occurring along a line parallel to the $k_x$-axis in $\mathbf{k}$-space, that is lifted for $\mathbf{M} \parallel \mathbf{\hat{x}}$, because in the second case the subbands belong to the same block of the Hamiltonian, whereas in the first they do not.

Concerning the different behavior of $E_{\text{anis}}$ as a function of $n$ choosing Fe or Ni parameters (see Fig. 4), one should note that due to the large exchange splitting in Fe only the SOC between $d$-states with parallel spins contributes significantly to $E_{\text{anis}}$. Thus, $E_{\text{anis}}$ for a less than half-filled $d$-band ($n < 6.2$ in Fig. 4, curve a) mainly results from the majority-spin subband and $E_{\text{anis}}$ for a more than half-filled $d$-band ($n > 6.2$) from the minority-spin states. This explains the similar shape of these two parts of the curve $E_{\text{anis}}(n)$. For Ni, the contribution to $E_{\text{anis}}$ from SOC between opposite spin states is of equal magnitude, leading to a rather different behavior of $E_{\text{anis}}(n)$.

Apparently, the occurrence and lifting of degenerate subbands for different directions of magnetization is important for calculating the magnetic anisotropy energy. This should also be clearly seen from the temperature dependence of $E_{\text{anis}}$ due to the magnetization $M(T)$, the Fermi function $f_T(\Delta E)$, the hopping integrals $t(T)$, which depend on temperature due to lattice expansion, and the entropy $S(T)$. In particular, effects resulting from the latter three contributions are analyzed. We find a characteristic energy scale of the order of magnitude of $\lambda_{so}$ for the reduction of the free anisotropy energy $F_{\text{anis}} = E_{\text{anis}} - TS_{\text{anis}}$ with increasing temperature. This is demonstrated in Fig. 5 in a $d$-band calculation with Fe parameters ($d$-bandfilling $n_d = 6.0$), where $F_{\text{anis}}$ decreases over a temperature range of 500–1000 K (50–100 meV), which corresponds to the energy $\lambda_{so}$, but not to the $3d$-bandwidth of about 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 $F_{\text{anis}}$ if $k_B T$ becomes larger than $2\lambda_{so}$. Furthermore 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. Hence, this analysis of $F_{\text{anis}}(T)$ shows also the significant role of changes of the degeneracies giving an important contribution to
the anisotropy energy. It is remarkable that the three temperature effects mentioned above are of equal magnitude as the temperature effects due to $M(T)$.

In conclusion, a fully convergent calculation of the magnetocrystalline anisotropy energy $E_{\text{anis}}$ of Fe and Ni monolayers on Cu (001) is performed. We find a perpendicular easy axis for Fe and an in-plane easy axis for Ni. Large contributions to $E_{\text{anis}}$ result from the SOC-induced lifting of degeneracies at the Fermi-level, which is also supported by our calculation of temperature effects. In general, $E_{\text{anis}}$ scales with the square of the SOC constant $\lambda_{so}$. The main features of our analysis can be applied also to thicker films, which is of particular interest for the investigation of reorientation transitions.
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per atom. Including $E_{dip}$, we still find a perpendicular easy axis for Fe on Cu(001). For Ni, we obtain $E_{dip} = 0.02$ meV from $m = 0.91 \mu_B$. This confirms the in-plane easy axis.

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FIGURES

FIG. 1. Dependence of $E_{anis}$ on the 3$d$- and 4$s$–bandfilling $n$ for a monolayer with parameters referring to Fe (curve a) and Ni (curve b). Negative values of $E_{anis}$ yield perpendicular anisotropy. The vertical lines denote $n$ for Fe and Ni, respectively.

FIG. 2. Temperature dependence of $F_{anis}(T)$ for a Fe-parametrized $d$-band calculation with $d$-bandfilling $n_d = 6$. The inset shows the occurrence (full lines) and lifting (dashed lines) of a “line” degeneracy for two different directions of magnetization $M_1$ and $M_2$, 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 $\Delta E_{anis} = \frac{1}{2} \lambda_{so} \cdot F$, 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, $\Delta E_{anis}$ is zero.
