

Tight-binding approach to the orbital magnetic moment and magnetocrystalline anisotropy of transition-metal monolayers

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A perturbative theory of magnetocrystalline anisotropy and orbital moment in itinerant ferromagnets is presented that clearly outlines the close connection between these two quantities. The theory is used to study the magnetocrystalline anisotropy in transition-metal monolayers. The importance of the crystal-field energy and of the filling of the valence band is emphasized. For the first time the orbital contribution to the magnetization in monolayers is estimated; it is shown that it may produce an anisotropy in the magnetization of the order of $0.1\mu_B$ per atom.

I. INTRODUCTION

The possible appearance of a large magnetocrystalline surface anisotropy pointed out by Néel¹ and its potential applications in perpendicular magnetic recording have stimulated great current interest in surface anisotropies.²⁻⁶ However, although the basis of a theory of the anisotropy in itinerant ferromagnets were given by Brooks⁷ many years ago and widely applied to bulk materials,⁸⁻¹³ there are still very few theoretical papers on the anisotropy of ultrathin films.

In the 1970s, Bennett and Cooper,¹⁴ followed by Takayama, Bohnen, and Fulde¹⁵ studied the magnetic anisotropy of a Ni(001) monolayer in a tight-binding perturbative model. Because of rather crude approximations and inaccurate knowledge of the band structure, they obtained only a reasonable order of magnitude for the magnetocrystalline anisotropy.

Very recently, Gay and Richter published an *ab initio*, self-consistent calculation of the anisotropy of Fe(001) and Ni(001) monolayers¹⁶ and of a Fe(001) overlayer on Ag(001).¹⁷ These calculations are much more complicated and require an enormous amount of computer time, because a very large number of k points (more than 5000) must be taken to achieve convergence when integrating over the two-dimensional (2D) Brillouin zone.

Beside the anisotropy energy, the magnetic moment of ultrathin films is a quantity of fundamental interest and has been widely investigated both experimentally and theoretically. However, up to now, the theoretical papers did not take into account the spin-orbit coupling and therefore neglected the orbital contribution to the magnetic moment. Although the latter is largely quenched in transition metals, it is not negligible if one wants to compare accurately theory and experiments; moreover, as we already know that spin-orbit coupling is able to induce very large anisotropy energies in ultrathin films (as compared to bulk materials), anisotropic effects can also be reasonably expected for the orbital magnetic moment.

With respect to the above considerations, our study will be carried out rather in the spirit of the early papers,^{14,15} and, consequently, will suffer the same lack of accuracy. However, the aim is not to achieve realistic calculations for a given system, but rather to provide orders of magni-

tude, as well as looking for qualitative trends throughout a wide range of systems. In Sec. II, from a second-order perturbative treatment of the spin-orbit coupling, general formulas are derived which give the anisotropy constants and orbital moment as functions of the unperturbed band structure. The numerical calculations are thus very fast and convenient, and indeed we were able to perform them on a PC microcomputer. The results derived in Sec. II are used in Secs. III and IV in a tight-binding model to study spin-orbit effects in ultrathin films. More precisely, the parameters entering the model are varied in order to study their influence on the anisotropy energy and orbital moment. It turns out that a surface anisotropy of the order of 1 erg cm^{-2} can be expected. This anisotropy is strongly dependent on the crystal-field parameters and on the filling of the $3d$ band. Finally, an anisotropy as large as $0.1\mu_B$ is predicted for the magnetic moment.

II. PERTURBATIVE THEORY OF THE MAGNETO-CRYSTALLINE ANISOTROPY AND ORBITAL MOMENT

A. The spin-orbit coupling

The spin-orbit coupling, responsible for the magnetocrystalline anisotropy and orbital moment of ferromagnets, has been discussed by various authors^{8,18} who showed that it can be approximated by a one-electron term $\xi \mathbf{L} \cdot \mathbf{S}$, where ξ , the spin-orbit constant, is of the order of 0.05 eV. This is small as compared with the $3d$ bandwidth (a few eV) and justifies a perturbative treatment.

At this point, some formalism should be introduced. Throughout this paper the Slater-Koster¹⁹ tight-binding formalism will be used, although the results derived in Sec. II are not restricted to any particular scheme.

The basis functions are orthonormalized atomic functions (Lowdin functions) $|j, \mu, \sigma\rangle$ where j labels the position, μ the $3d$ subband, and σ the spin. The $3d$ subbands yz , zx , xy , $x^2 - y^2$, $3z^2 - r^2$ are labeled 1, 2, 3, 4, 5, respectively. (x , y , z refer to the crystalline axes, Oz being chosen perpendicular to the film plane; the spin quantization is along an axis $O\zeta$, characterized by the standard

spherical angular coordinates θ and ϕ). The standard Bloch functions $|\mathbf{k}, \mu, \sigma\rangle$ are then introduced. The eigenfunction $|\mathbf{k}, n, \sigma\rangle$ of eigenvalue $\varepsilon_{n,\sigma}(\mathbf{k})$ is

$$|\mathbf{k}, n, \sigma\rangle = \sum_{\mu} a_{n,\mu,\sigma}(\mathbf{k}) |\mathbf{k}, \mu, \sigma\rangle. \quad (1)$$

One also introduces the generalized densities of states

$$n_{\mu_1,\mu_2,\sigma}(\mathbf{k}, \varepsilon) = \sum_n a_{n,\mu_1,\sigma}^*(\mathbf{k}) \times a_{n,\mu_2,\sigma}(\mathbf{k}) \delta(\varepsilon - \varepsilon_{n,\sigma}(\mathbf{k})), \quad (2a)$$

$$n_{\mu_1,\mu_2}(\mathbf{k}, \varepsilon) = \sum_{\sigma} n_{\mu_1,\mu_2,\sigma}(\mathbf{k}, \varepsilon), \quad (2b)$$

and the generalized spin-polarization densities

$$m_{\mu_1,\mu_2}(\mathbf{k}, \varepsilon) = n_{\mu_1,\mu_2,\uparrow}(\mathbf{k}, \varepsilon) - n_{\mu_1,\mu_2,\downarrow}(\mathbf{k}, \varepsilon). \quad (2c)$$

Then the spin-orbit term can be written

$$H_{s.o.} = \xi \sum_{\mu_1,\mu_2,\sigma_1,\sigma_2} \langle \mu_1, \sigma_1 | \mathbf{L} \cdot \mathbf{S} | \mu_2, \sigma_2 \rangle \times \sum_{\mathbf{k}} c_{\mu_1,\sigma_1}^{\dagger}(\mathbf{k}) c_{\mu_2,\sigma_2}(\mathbf{k}), \quad (3)$$

where c and c^{\dagger} are, respectively, annihilation and creation operators. The matrix elements $\langle \mu_1, \sigma_1 | \mathbf{L} \cdot \mathbf{S} | \mu_2, \sigma_2 \rangle$ (where $|\mu_1, \sigma_1\rangle$ and $|\mu_2, \sigma_2\rangle$ implicitly refer to the same point) are given in Ref. 15 as functions of the angles θ and ϕ .

The orbital moment is $\langle L_{\zeta} \rangle$, the expectation value of the \mathbf{L} component parallel to the spin quantization direction. It is very easy to prove that

$$\langle \mu_1, \sigma_1 | L_{\zeta} | \mu_2, \sigma_2 \rangle = 2\delta_{\sigma_1,\sigma_2} \langle \mu_1, \uparrow | \mathbf{L} \cdot \mathbf{S} | \mu_2, \uparrow \rangle. \quad (4)$$

$$\delta E = -\xi^2 \sum_{\mu_1,\mu_2,\mu_3,\mu_4} \langle \mu_1, \uparrow | \mathbf{L} \cdot \mathbf{S} | \mu_2, \uparrow \rangle \langle \mu_3, \uparrow | \mathbf{L} \cdot \mathbf{S} | \mu_4, \uparrow \rangle G(\mu_1, \mu_2, \mu_3, \mu_4), \quad (9)$$

with

$$G(\mu_1, \mu_2, \mu_3, \mu_4) = \sum_{\mathbf{k}} \int_{\varepsilon < \varepsilon_F} d\varepsilon \int_{\varepsilon_F < \varepsilon'} d\varepsilon' \frac{m_{\mu_1,\mu_4}(\mathbf{k}, \varepsilon) m_{\mu_3,\mu_2}(\mathbf{k}, \varepsilon')}{\varepsilon' - \varepsilon}. \quad (10)$$

Similar formulas hold for $\langle L_{\zeta} \rangle$ by replacing in (9) ξ^2 by 4ξ , and $G(\mu_1, \mu_2, \mu_3, \mu_4)$ by

$$H(\mu_1, \mu_2, \mu_3, \mu_4) = \sum_{\mathbf{k}} \int_{\varepsilon < \varepsilon_F} d\varepsilon \int_{\varepsilon_F < \varepsilon'} d\varepsilon' \frac{1}{2} \frac{n_{\mu_1,\mu_4}(\mathbf{k}, \varepsilon) m_{\mu_3,\mu_2}(\mathbf{k}, \varepsilon') + m_{\mu_1,\mu_4}(\mathbf{k}, \varepsilon) n_{\mu_3,\mu_2}(\mathbf{k}, \varepsilon')}{\varepsilon' - \varepsilon}. \quad (11)$$

When the matrix elements of $\mathbf{L} \cdot \mathbf{S}$ are determined, one obtains

$$\begin{aligned} \delta E &= \xi^2 \frac{1}{4} \{ [I(1,2,1,2) + 4I(1,2,3,4) + 4I(3,4,3,4)] \\ &\quad + \sin^2\theta \{ I(1,2,1,2) - 4I(1,2,3,4) - 4I(3,4,3,4) + \frac{1}{2} [I(1,3,1,3) + I(1,4,1,4)] + \sqrt{3} [I(1,4,1,5) - I(2,4,2,5)] \\ &\quad + \frac{1}{2} [I(2,4,2,4) + I(2,3,2,3)] - \sqrt{3} [I(1,3,2,5) + I(1,5,2,3)] \\ &\quad + \frac{3}{2} [I(2,5,2,5) + I(1,5,1,5)] + [I(1,3,2,4) - I(1,4,2,3)] \} \} \\ &= K_0 + K_2 \sin^2\theta \end{aligned} \quad (12)$$

for (001) and (111) monolayers, and

$$\begin{aligned} \delta E &= K_0 + K_2 \sin^2\theta + \sin^2\theta \cos(2\phi) \xi^2 \frac{1}{4} \{ \frac{1}{2} [I(1,4,1,4) - I(1,3,1,3)] + \sqrt{3} [I(1,4,1,5) + I(2,4,2,5)] \\ &\quad + \frac{1}{2} [I(2,3,2,3) - I(2,4,2,4)] + \sqrt{3} [I(1,3,2,5) - I(1,5,2,3)] \\ &\quad + \frac{3}{2} [I(1,5,1,5) - I(2,5,2,5)] - [I(1,3,2,4) + I(1,4,2,3)] \} \\ &= K_0 + K_2 \sin^2\theta + K_2' \sin^2\theta \cos(2\phi). \end{aligned} \quad (13)$$

B. Perturbation treatment

We will perform it within the lowest order, i.e., second order for the energy correction (because the diagonal matrix elements of $H_{s.o.}$ are zero) and first order for the wave-function correction.

The corrections to the energy and wave function for the ground state are, respectively, given by the well-known formulas

$$\delta E = \sum_{\text{exc}} \frac{|\langle \text{gr} | H_{s.o.} | \text{exc} \rangle|^2}{E_{\text{gr}} - E_{\text{exc}}}, \quad (5)$$

$$\delta |\text{gr}\rangle = \sum_{\text{exc}} \frac{\langle \text{exc} | H_{s.o.} | \text{gr} \rangle | \text{exc} \rangle}{E_{\text{gr}} - E_{\text{exc}}}, \quad (6)$$

where $|\text{gr}\rangle$, $|\text{exc}\rangle$, E_{gr} , E_{exc} are, respectively, the ground state, excited state, and corresponding energies for the unperturbed system. Because the average value of L_{ζ} in the unperturbed ground state is zero, its expectation value is

$$\langle L_{\zeta} \rangle = \sum_{\text{exc}} \langle \text{gr} | L_{\zeta} | \text{exc} \rangle \frac{\langle \text{exc} | H_{s.o.} | \text{gr} \rangle}{E_{\text{gr}} - E_{\text{exc}}} + \text{c.c.} \quad (7)$$

When doing this calculation, we disregard any deformation of the Fermi surface. Kondorskii and Staube¹⁰ argued that the neglected contribution is of opposite sign so our results will probably be overestimated.

$H_{s.o.}$ is a one-electron operator diagonal in \mathbf{k} ; thus, the only excited states that need to be considered are of the form

$$|\text{exc}\rangle = c_{n_2,\sigma_2}^{\dagger}(\mathbf{k}) c_{n_1,\sigma_1}(\mathbf{k}) |\text{gr}\rangle, \quad (8)$$

with $\varepsilon_{n_1,\sigma_1}(\mathbf{k}) < \varepsilon_F < \varepsilon_{n_2,\sigma_2}(\mathbf{k})$.

By expanding the eigenstates over the basis states, and using the symmetry properties of the matrix elements of $\mathbf{L} \cdot \mathbf{S}$, one obtains

for (110) monolayers, with

$$I(\mu_1, \mu_2, \mu_3, \mu_4) = \text{Re}[G(\mu_1, \mu_2, \mu_3, \mu_4) + G(\mu_2, \mu_1, \mu_4, \mu_3) - G(\mu_1, \mu_2, \mu_4, \mu_3) - G(\mu_2, \mu_1, \mu_3, \mu_4)]. \quad (14)$$

For $\langle L_z \rangle$, we have similar results by replacing ξ^2 by 4ξ in (12) and (13), and the G 's by H 's in (14).

III. ANISOTROPY OF TRANSITION-METAL MONOLAYERS

A. Description of the band model

The band structure is calculated within the Slater-Koster tight-binding scheme,¹⁹ up to the second-nearest neighbors, using the hopping parameters given by Harrison.²⁰ We consider the $3d$ and $4s$ bands and take hybridization into account. The spin polarization is calculated in a simplified Hartree-Fock approximation. The Hartree-Fock Hamiltonian is

$$H^{\text{HF}} = \sum_{\mathbf{k}} \left[\sum_{\substack{\sigma \\ \mu_1, \mu_2 \in \{3d, 4s\}}} \varepsilon_{\mu_1, \mu_2, \sigma}(\mathbf{k}) c_{\mu_1, \sigma}^\dagger(\mathbf{k}) c_{\mu_2, \sigma}(\mathbf{k}) + \sum_{\substack{\mu \in \{3d\} \\ \sigma}} U_{\text{eff}}(n_{d, -\sigma}) \hat{n}_{\mu, \sigma}(\mathbf{k}) \right]. \quad (15)$$

The effective interaction parameter U_{eff} has been chosen equal to 1 eV in order to yield proper values for the spin polarization.

Important parameters that will be discussed below are the atomic potentials, i.e., the gravity centers of the $3d$ subbands. Because of the strongly reduced symmetry, the crystal-field shifts are much larger than in bulk materials. We assume that, as a first approximation, we can characterize the crystal-field effect by only one parameter, i.e., the energy difference Δ between orbitals pointing out of plane ($yz, zx, 3z^2 - r^2$), and orbitals lying in plane ($xy, x^2 - y^2$). For the spin-orbit constant, we chose $\xi = 0.05$ eV.

B. Results and discussion

The calculated anisotropy energies K_2 of Co and Ni fcc (001) monolayers for different values of the crystal-field parameter are reported in Table I.

One can see immediately that the calculated anisotropies (a few ergs cm^{-2}) are larger than what is generally observed in experiments (0.2–1 erg cm^{-2}). This may be

TABLE I. Anisotropy energy K_2 of Co and Ni fcc (001) monolayers for different values of the crystal-field parameter Δ .

Δ (eV)	$K_2(10^{-3} \text{ eV atom}^{-1})$	
	Co(001)	Ni(001)
-0.5	-0.47	0.12
0	-1.34	-0.16
0.5	-1.98	-0.86
1	-2.12	-1.14

due to our neglecting the deformations of the Fermi surface, that makes our results overestimated. A very important point is that the calculated anisotropy strongly depends on the crystal-field parameter Δ . This parameter is determined by the interelectronic interactions and correlations, and is not well known in ultrathin films. Its strong influence on the anisotropy indicates that much care should be taken to that point if one wants to make realistic calculations. For the following, we chose $\Delta = 0.5$ eV by comparison with the Ni(111) band structure calculated self-consistently by Wimmer.²¹

In Table II we report the calculated anisotropy K_2 of fcc (001) and (111) monolayers for various numbers N_v of valence electrons ($3d + 4s$). The strong variations of the anisotropy with N_v can be explained qualitatively: The second-order perturbation involves the inverse of the energy difference between levels located, respectively, above and below the Fermi level [Eqs. (9)–(11)]; the anisotropy is, therefore, strongly dependent on the neighborhood of the Fermi level and may change drastically as we move the latter by filling the valence band.

IV. ORBITAL MOMENT OF TRANSITION-METAL MONOLAYERS

As appears from formulas (9)–(11), there is a very strong connection between the anisotropy energy and the orbital moment. As the G 's and H 's can be expected to be of the same order of magnitude, with an anisotropy energy of 10^{-3} eV and a spin-orbit constant ξ of 0.05 eV, one can already estimate the anisotropic part of the magnetization to be roughly $0.1 \mu_B$. The same qualitative rule also holds for bulk materials, since for Ni and Fe (Ref. 22) one has $(E_{100} - E_{111}) / (M_{100} - M_{111}) \approx 0.02 - 0.12 \text{ eV} \approx \xi$.

Table III shows the calculated in-plane and out-of-plane orbital moments of fcc (001) and (111) monolayers, for various numbers N_v of valence electrons. Their signs and orders of magnitude are close to those of bulk materials (because of an important isotropic contribution, which is not strongly affected by the symmetry). Since these calculations are essentially parallel to those of magnetocrystalline anisotropy, and since the latter yielded orders of magnitude consistent with the *ab initio* calculations by

TABLE II. Anisotropy energy K_2 of fcc (001) and (111) monolayers vs the number N_v of $3d + 4s$ electrons.

N_v	$K_2(10^{-3} \text{ eV atom}^{-1})$	
	fcc (001)	fcc (111)
8 (Fe)	0.00	-0.61
8.5	-1.38	-1.12
9 (Co)	-1.98	-2.47
9.5	-2.11	-1.13
10 (Ni)	-0.86	-0.43

TABLE III. In-plane and out-of-plane orbital magnetic moment of fcc (001) and (111) monolayers vs the number N_v of $3d + 4s$ electrons.

N_v	fcc (001)		fcc (111)	
	$M_L^{\parallel} (\mu_B)$	$M_L^{\perp} (\mu_B)$	$M_L^{\parallel} (\mu_B)$	$M_L^{\perp} (\mu_B)$
8 (Fe)	0.16	0.13	0.19	0.10
8.5	0.26	0.12	0.22	0.09
9 (Co)	0.33	0.13	0.32	0.08
9.5	0.30	0.09	0.18	0.08
10 (Ni)	0.15	0.07	0.09	0.05

Gay and Richter,^{16,17} the present results for the orbital magnetic moment are likely to be of the correct order of magnitude.

The important point is that, as stated qualitatively above, there is a quite large anisotropy in the magnetization.

To our knowledge, this large magnetization anisotropy has never been predicted, nor experimentally observed. This deserves to be confirmed by other calculations including the spin-orbit coupling. On the experimental point of view, the magnetization anisotropy is in the range of 2×10^{-6} cgs emu for 1 cm^2 and seems likely to be detected by using modern magnetometry techniques (superconducting quantum interference device, alternating force magnetometer).

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