24.1

24. Physical origins and theoretical models of magnetic anisotropy

P. Bruno
Institut d'Electronique Fondamentale, CNRS UA 022
Bât. 220, Université Paris-Sud, F-91405 Orsay, France

1 Introduction

The primary property of a ferromagnet such as Fe, Co, or Ni, is the appearance of a spontaneous magnetization $\mathbf{M}$ below the Curie temperature $T_C$. The energy involved by this spontaneous breaking of symmetry is of the order of $kgT_C/\text{atom} \approx 0.1 \text{ eV/atom}$. The mechanism responsible for the appearance of ferromagnetism has been recognized by Heisenberg to be the Pauli principle, which prevents two electrons or parallel spins to occupy the same orbital state, so that the effective Coulomb repulsion for a pair of electrons with parallel spins is weaker than for antiparallel spins; this is known as the exchange interaction.

For a theoretical description of the basic properties of ferromagnetic materials, it is sufficient to use non-relativistic quantum mechanics. However, the spin is introduced here in an ad hoc manner, so that there is absolute freedom in the choice of the spin-quantization axis; in other words, non-relativistic quantum mechanics leads to a description of ferromagnetism in which the free energy of the system is independent of the direction of the magnetization (it is said to be isotropic). This is in contradiction with experience, which tells us that the magnetization generally lies in some preferred directions with respect to the crystalline axes and/or to the external shape of the body: this property is known as the magnetic anisotropy.

The energy involved in rotating the magnetization from a direction of low energy (easy axis) towards a one of high energy (hard axis) is typically of the order of $10^{-8}$ to $10^{-3} \text{ eV/atom}$. This anisotropy energy is thus a very small correction to the total magnetic energy; it actually arises from relativistic corrections to the Hamiltonian, which break the rotational invariance with respect of the spin quantization axis: these are the
24.2  

dipole-dipole interaction and the spin-orbit coupling.

Expressed in units of magnetic field, the magnetic anisotropy is of the order of 0.1 to 100 kOe, i.e. of the order of magnetic fields used in experimental situations. Thus, it appears clearly that these relativistic corrections should play an essential role; in particular, the magnetic anisotropy is a key property for applications where the magnetization must be pinned in a given direction, such as permanent magnets and media for magnetic storage of information. On a more fundamental point of view, the dipole-dipole interaction and the spin-orbit coupling are necessary to explain the very existence of ferromagnetism in two-dimensional systems such as ultrathin films: indeed, according to the Mermin-Wagner theorem, two-dimensional systems with short-range, isotropic exchange interactions, but without dipole-dipole or spin-orbit interactions, cannot sustain ferromagnetic order at non-zero temperature.

The present Chapter is devoted to the discussion of the physical origins and theoretical models of magnetic anisotropy. It is organized as follows: in Sec. 2, we present the phenomenological description of magnetic anisotropy, at a macroscopic level, with emphasis on symmetry considerations; Secs. 3 and 4 treat, at the microscopic level, the magnetic anisotropy arising, respectively, from the dipole-dipole interactions, and from the spin-orbit coupling.

Special emphasis will be given to the magnetic anisotropy of interface atoms in ultrathin films and multilayers, which is much larger than the one of bulk atoms, and is currently of very strong interest, from the fundamental point of view, as well as for storage applications. Although rare earth metals and rare earth-transition metals compounds have very large magnetic anisotropies, they will not be discussed here; rather, we will concentrate on transition metals (Fe, Co, Ni), in which the magnetic moment is carried by the delocalized 3d electrons (itinerant ferromagnetism). We note in passing that the spin-orbit coupling is also responsible for other properties of strong fundamental and technological interest, such as the magneto-optical effects, the magnetic circular dichroism, or the extraordinary Hall effect; they will not be discussed here. Throughout this Chapter, e.g.s. units will be used.

2  Phenomenology of Magnetic Anisotropy

2.1  Thermodynamic description

Let us consider a ferromagnetic body of magnetization \( \mathbf{M} = M \mathbf{\Omega}_M \), submitted to a uniform external field \( \mathbf{H} \). In order to unambiguously separate the magnetic anisotropy from energy contributions related to the exchange interaction (which are not of interest here), we restrict ourselves to situations where the unit vector \( \mathbf{\Omega}_M \) of the magnetization direction is uniform throughout the sample; in the following, \( \mathbf{\Omega}_M \) will be described either by its components \( (\alpha_1, \alpha_2, \alpha_3) \) with \( \alpha_1^2 + \alpha_2^2 + \alpha_3^2 = 1 \), or by the polar angles \( \theta \) and \( \phi \), defined in the usual manner. Also, we consider only temperatures well below the Curie temperature, so that magnetization fluctuations can be neglected.

The free energy density \( F(T, M, \mathbf{\Omega}_M, \varepsilon) \) is thus a function of the temperature \( T \), the magnetization magnitude \( M \), the magnetization direction \( \mathbf{\Omega}_M \), and the strain tensor \( \varepsilon \). One should realize that this free energy is not very convenient to use, essentially because \( M \) is not an externally controlled parameter. Actually, in a typical experimental situation, the magnetization is rotated from a direction to another one by rotating an external field of given magnitude; the magnitude of the magnetization \( M \) changes as the latter is rotated.
Clearly, one needs to change the free energy $F(M, \ldots)$ for a thermodynamic function having the external field as a natural variable. The appropriate Legendre transformation has been discussed by various authors [1]; the convenient thermodynamic potential $G$ is given by

$$G(T, H_M, \Omega_M, \varepsilon) \equiv F - H_M M,$$

where $H_M$ is the projection of the external field along the magnetization direction $\Omega_M$. Thus, apart from the temperature and the strain tensor, the natural variables of $G$ are $H_M$ and $\Omega_M = (\theta, \phi)$, and the corresponding partial derivatives are

$$\left( \frac{\partial G}{\partial H_M} \right)_{T, \theta, \phi, \varepsilon} = -M,$$

$$\left( \frac{\partial G}{\partial \theta} \right)_{T, H_M, \phi, \varepsilon} = M H_M,$$

$$\left( \frac{\partial G}{\partial \phi} \right)_{T, H_M, \theta, \varepsilon} = M H_M \sin \theta.$$

Except explicitly specified, the strain tensor $\varepsilon$ and the external field component $H_M$ along $\Omega_M$ will be taken equal to zero in the following, and the thermodynamic potential will be noted $G(\Omega_M)$; for simplification, $G$ will be referred to as the energy of the system. Note that taking $H_M = 0$ corresponds to experimental situations where the external field is perpendicular to the magnetization; this is somehow idealized, for in usual cases a non-zero field $H_M$ is necessary to maintain the system in a single-domain state.

It is also important to keep in mind that, as already mentioned, the magnetization magnitude $M$ itself is anisotropic, i.e. that it depends on $\Omega_M$. The anisotropy of the magnetization is related to the dependence of the anisotropy energy on $H_M$ by the Maxwell relations,

$$\left( \frac{\partial^2 G}{\partial H_M \partial \Omega_M} \right) = \left( \frac{\partial^2 G}{\partial \Omega_M \partial H_M} \right).$$

2.2 Shape versus crystalline anisotropy

As we have already mentioned in the Introduction, the energy depends the orientation $\Omega_M$ of the magnetization (i) with respect to the crystalline axes of the ferromagnetic body, and (ii) with respect to its external shape.

In order to unambiguously establish this distinction, let us perform the following gedanken experiment: we take a ferromagnetic material with a cubic crystalline structure and cut two samples, (a) a spherical one, and (b) a thin plate with the normal parallel to the [001] axis, as depicted on Fig. 1. The spherical sample is easily magnetized along the [001] and [100] directions (easy axes), whereas a larger field is needed to magnetize it along the [101] direction (hard axis); since the shape of the sample is isotropic, the observed anisotropy implies that the energy depends on the orientation of $\Omega_M$ with respect to the crystalline axes; this is known as the magnetocrystalline anisotropy. On the other hand, for the plate-shaped sample, different magnetization curves are reported for the [100] and [001] directions, which are respectively parallel and perpendicular to the plane; since these two axes are crystallographically equivalent, this indicates that the energy also depends on the orientation of $\Omega_M$ with respect to the shape of the sample. Thus the total anisotropy energy may be expressed as

$$G(\Omega_M) = G_{\text{cryst}}(\Omega_M) + G_{\text{shape}}(\Omega_M).$$
It is clear that the first term is an intrinsic contribution, depending only on the ferromagnetic material under consideration, whereas the second one is essentially of geometric character. In our gedanken experiment, we selected situations where the anisotropy arises entirely from one of these two contributions; however, in usual cases, both shape and magnetocrystalline anisotropy contributions are present. The general method to separate them will be discussed in Sec. 3.1.

The shape anisotropy arises entirely from the dipole-dipole interactions, while the magnetocrystalline anisotropy arises essentially from the spin-orbit coupling, but also, to a lesser extent, from the dipolar interactions.

2.3 Symmetry considerations

The general form of $G_{\text{Cryst}}(\Omega_M)$ for a given crystalline structure can be found by using some symmetry arguments. First, the invariance of the Hamiltonian with respect to time reversal implies that the expression of $G_{\text{Cryst}}(\Omega_M)$ must remain unchanged if $\Omega_M$ is replaced by $-\Omega_M$. The most convenient way to express the anisotropy energy is to expand it in spherical harmonics:

$$G_{\text{Cryst}}(\Omega_M) = \sum_{l \text{ even}} \sum_{m=-l}^{m=l} \kappa_l^m(H_M)Y_l^m(\Omega_M).$$

Another possibility is to expand the anisotropy energy in successive powers of the components $(\alpha_1, \alpha_2, \alpha_3)$ of $\Omega_M$.
In Eqs. (7,8), only those terms that are even in \( \Omega_M \) (i.e. compatible with the time-reversal symmetry) have been included. Although the expansions (7) and (8) are equivalent, the spherical harmonics present the advantage of forming a complete set of orthonormal functions; unfortunately, the tradition has established some expressions for \( G(\Omega_M) \) which do not possess this property. Similarly, the magnetization can be expanded in terms of, e.g., spherical harmonics,

\[
M(\Omega_M) = \sum_{l \text{ even } m=-l}^{m=l} M_l^m(H_M) Y_l^m(\Omega_M).
\]  

(9)

The anisotropies of the energy and of the magnetization are related by the Maxwell relations:

\[
M_l^m(H_M) = \frac{\partial E_l^m(H_M)}{\partial H_M}.
\]  

(10)

Experience shows that such expansions converge rapidly with increasing order, so that a few terms are enough to describe accurately the magnetocrystalline anisotropy. The explanation for this rapid convergence will appear clearly in Sec. 4.

The crystalline symmetry imposes some relationships between the coefficients of given order, thereby reducing the number of independent parameters. For example, in cubic systems such as Fe and Ni, terms of order 2 are forbidden and the first non-vanishing contribution to the crystalline anisotropy is of order 4. The usual expression for the anisotropy of cubic systems is

\[
G_{\text{cryst}}(\Omega_M) = K_0 + K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2 + \cdots
\]

\[
M(\Omega_M) = M_0 + M_1 \sin^2 \theta + M_2 \sin^4 \theta + (M_3 + M_4 \cos(6\phi)) \sin^6 \theta + \cdots
\]

(11)

with the coordinates axes taken along the cubic axes. For systems with hcp structure, like Co, the usual expression of the anisotropy is

\[
G_{\text{cryst}}(\Omega_M) = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta + (K_3 + K_4 \cos(6\phi)) \sin^6 \theta + \cdots
\]

\[
M(\Omega_M) = M_0 + M_1 \sin^2 \theta + M_2 \sin^4 \theta + (M_3 + M_4 \cos(6\phi)) \sin^6 \theta + \cdots
\]

(13)

(14)

where \( \phi \) and \( \theta \) are taken with respect to the \( a \) and \( c \) axes, respectively. Note that the traditional constants, \( K_1, K_2, \) etc., are somehow misleading; for instance, \( K_1 \) is a constant of order 4 in cubic systems, and of order 2 in hexagonal systems.

The values of the anisotropy constants of Fe, Co, and Ni are given in Table 1. The easy axes of Fe and Ni are respectively the [100] and [111] directions, while that of Co is along the \( c \) axis. It is worth noting that the anisotropy of hcp Co, which has a lower symmetry, is one order of magnitude larger than that of Fe and Ni, which have a cubic symmetry. Also, we can remark that the sign of \( M_1 \) is the opposite of that of \( K_1 \), which means that the magnetization is larger in the easy directions than in the hard ones. These points will be interpreted in Sec. 4.
24.6

Table 1: Anisotropy constants of Fe, Co, and Ni, at \( T = 4.2 \) K.\(^{(a)}\) Ref. [2]; \(^{(b)}\) Ref. [3]; \(^{(c)}\) Ref. [4]; \(^{(d)}\) Ref. [5]

<table>
<thead>
<tr>
<th></th>
<th>Fe (bcc)</th>
<th>Co (hcp)</th>
<th>Ni (fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_1 ) (erg cm(^{-3}))</td>
<td>( 5.48 \times 10^6 )(^{(a)})</td>
<td>( 7.66 \times 10^6 )(^{(b)})</td>
<td>(-12.63 \times 10^6 )(^{(a)})</td>
</tr>
<tr>
<td>( K_1 ) (eV atom(^{-1}))</td>
<td>( 4.02 \times 10^6 )</td>
<td>( 5.33 \times 10^6 )</td>
<td>(-8.63 \times 10^6 )</td>
</tr>
<tr>
<td>( K_2 ) (erg cm(^{-3}))</td>
<td>( 1.96 \times 10^6 )</td>
<td>( 1.05 \times 10^6 )</td>
<td>( 5.78 \times 10^6 )</td>
</tr>
<tr>
<td>( K_2 ) (eV atom(^{-1}))</td>
<td>( 1.44 \times 10^6 )</td>
<td>( 7.31 \times 10^6 )</td>
<td>( 3.95 \times 10^6 )</td>
</tr>
<tr>
<td>( K_3 ) (erg cm(^{-3}))</td>
<td>( 0.9 \times 10^9 )</td>
<td>(-1.2 \times 10^9 )</td>
<td>( 3.48 \times 10^9 )</td>
</tr>
<tr>
<td>( K_3 ) (eV atom(^{-1}))</td>
<td>( 6.6 \times 10^9 )</td>
<td>( 2.38 \times 10^9 )</td>
<td>( )</td>
</tr>
</tbody>
</table>

\( M_0 \) (G) | \( 1749.7 \)\(^{(b)}\) | \( 1459.5 \)\(^{(d)}\) | \( 524.8 \)\(^{(b)}\) |
| \( \mu_B \) atom\(^{-1}\) | \( 2.215 \) | \( 1.729 \) | \( 0.615 \) |
| \( M_1 \) (G) | \(-4.3 \times 10^{-1} \)\(^{(a)}\) | \(-6.75 \)\(^{(d)}\) | \( 5.1 \times 10^{-1} \)\(^{(a)}\) |
| \( \mu_B \) atom\(^{-1}\) | \(-5.4 \times 10^{-1} \) | \(-8.0 \times 10^{-3} \) | \( 6.0 \times 10^{-4} \) |

2.4 Volume versus interface anisotropy

So far, we have implicitly supposed that the system under consideration is large enough for the surface contributions to the energy to be negligible. This is however not the case in systems of small dimensions, such as ultrathin films; in such systems, the total thermodynamic potential must be written as the sum of a volume term, and of a surface (or interface) contribution, i.e.

\[
G(\Omega_M) = \int_V dV \, G^V(\Omega_M) + \int_S dS \, G^S(\Omega_M),
\]

where \( G^V(\Omega_M) \) is the energy per unit volume (this the one we have discussed so far), and \( G^S(\Omega_M) \) is the energy per unit interfacial area. The latter usually depends on the materials in contact at the interface and on the crystalline orientation of the latter.

It was first pointed out by Néel [6] that the atoms located near an interface have a different environment as compared to bulk atoms, and that they give additional contributions to the magnetic anisotropy. In particular, since the symmetry of an interface is often lower than that of the bulk, anisotropy terms that are forbidden in the bulk may be present at an interface.

The expression of the surface contribution to the magnetocrystalline energy is

\[
G^S_{\text{cryst.}}(\Omega_M) = K_1^S \sin^2 \theta + (K_2^S + K_2^S \cos(4\phi)) \sin^4 \theta + \cdots,
\]

for a cubic (001) surface (tetragonal symmetry),

\[
G^S_{\text{cryst.}}(\Omega_M) = (K_1^S + K_1^S \cos(2\phi)) \sin^2 \theta + \cdots,
\]

for a cubic (110) surface (orthorhombic symmetry), and

\[
G^S_{\text{cryst.}}(\Omega_M) = K_1^S \sin^2 \theta + K_2^S \sin^4 \theta + (K_3^S + K_3^S \cos(6\phi)) \sin^6 \theta + \cdots,
\]

for a cubic (100) surface (tetragonal symmetry).
Figure 2: Magnetization curves at $T = 10$ K of Au/Co(0001)/Au(111) sandwiches, measured perpendicularly (left) or parallel (right) to the film plane, for various values of the Co thickness $t_{Co}$: the easy axis is perpendicular to the plane $t_{Co} < t_s \approx 12 \text{ Å}$. From Ref.[7]

for a cubic (111) or an hcp (0001) surface (hexagonal symmetry). In the above equations, the angle $\theta$ is measured with respect to the surface normal.

In practice, only the first terms (order 2) are taken into account. Their order of magnitude is typically of 0.1 to 1 erg.cm$^{-2}$; in terms of microscopic units, this amounts to about $10^{-4}$ to $10^{-3}$ eV.(interface atom)$^{-1}$, which is considerably larger than the anisotropy of bulk atoms. The sign of the surface magnetocrystalline anisotropy may be positive or negative, depending on the interface under consideration.

The situation where $K_s^2$ is positive is of particular interest in ultrathin films: indeed, as we will see in Sec. 3, the volume anisotropy of films is dominated by the shape contribution which favors a in-plane orientation of the magnetization; the latter is competed by the surface anisotropy which favors a perpendicular magnetization for $K_s^2 > 0$. Thus, at large thickness, the bulk term dominates and the magnetization lies in the plane, whereas the relative weight of the surface terms increases with decreasing thickness, so that eventually, below a critical thickness of the order of 10 Å, the magnetization becomes perpendicular to the plane. An example of this behavior is shown on Fig. 2. This is of strong interest for technological applications in magneto-optical disks.
24.8

2.5 Strain-induced anisotropy and magnetostriction

In the above discussion, we have taken the strain tensor $\epsilon$ to be zero. If the latter is not zero, new energy terms must be considered. Some of them are purely elastic, i.e. they depend only on the strain tensor $\epsilon$. However, in a magnetized body one also has energy terms that depend both on $\epsilon$ and on $\Omega_M$: the magneto-elastic energy. In all this Section, we shall consider only volume terms, and consequently drop the corresponding $V$ indices.

As usual, for small deformations, one can formally expand this energy in powers of the deformation and in spherical harmonics of $\Omega_M$ (or powers of the $a_i$'s). The non-vanishing terms of lowest order are linear with respect to $\epsilon$ and quadratic with respect to the $a_i$'s. Thus the most general expression for the magneto-elastic energy density is

$$G_{\text{magn.el.}}(\Omega_M, \epsilon) = \sum_{i,j,k,l} B_{ijkl} \epsilon_{ij} a_i a_j + \cdots .$$

As for the magnetic anisotropy, the crystalline symmetry imposes some relationships between the coefficients $B_{ijkl}$. Thus, for cubic systems, the standard expression of the magnetoelastic energy is:

$$G_{\text{magn.el.}}(\Omega_M, \epsilon) = B_1 (\epsilon_{11} a_1^2 + \epsilon_{22} a_2^2 + \epsilon_{33} a_3^2) + 2B_2 (\epsilon_{12} a_1 a_2 + \epsilon_{23} a_2 a_3 + \epsilon_{31} a_3 a_1) + \cdots ,$$

and for hcp crystals:

$$G_{\text{magn.el.}}(\Omega_M, \epsilon) = B_1 (\epsilon_{11} a_1^2 + 2\epsilon_{12} a_1 a_2 + \epsilon_{22} a_2^2) + B_3 (1 - a_3^2) + B_4 (\epsilon_{23} a_2 a_3 + \epsilon_{31} a_3 a_1) + \cdots .$$

As the symmetry is generally lowered under strain, the magneto-elastic energy may contain anisotropy terms that are forbidden in the unstrained state; for instance, cubic crystals under strain acquire anisotropy terms of order 2. The magneto-elastic constants $B_1$, $B_2$, etc., of Fe, Co, and Ni are listed in Table 2. The latter are considerably larger than the volume magnetocrystalline anisotropy constants; as a consequence, small strains may give rise to an important anisotropy. In particular, this strain-induced anisotropy plays a very important rôle in ultrathin films, where considerable strains may result from the epitaxial growth of the film onto a substrate having a different lattice parameter. A detailed discussion of this problem is given in Ref.[7].

As a system under strain acquires some magnetic anisotropy, conversely, the existence of a non-zero magnetization $M$ along a given direction $\Omega_M$ induces an anisotropic strain of the ferromagnetic body. This particular case of the thermodynamic reciprocity relations is called magnetostriction. The explanation of this behavior is quite simple: as the magneto-elastic energy is linear with respect to the strain $\epsilon$, it is always possible for the system to lower its energy by acquiring a non-zero strain; this trend is competed, of course, by the elastic energy, which is quadratic with respect to the strain. The magnitude of this spontaneous strain is given by the competition between the elastic and magnetoelastic terms, and it depends on the magnetization direction. As the elastic constants are of the order of $10^{12}$ erg cm$^{-3}$, i.e. considerably larger that the magneto-elastic energy, the magnetostriction (relative change of length of the ferromagnetic body) is of the order of $10^{-5}$. For a cubic system and an hexagonal system, the expressions of the elastic energy
Table 2: Magneto-elastic constants of Fe, Co, and Ni, at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>Fe (bcc)</th>
<th>Co (hcp)</th>
<th>Ni (fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$ (erg.cm$^{-3}$)</td>
<td>$-3.44 \times 10^7$</td>
<td>$-8.10 \times 10^7$</td>
<td>$8.87 \times 10^7$</td>
</tr>
<tr>
<td>(eV.atom$^{-1}$)</td>
<td>$-2.53 \times 10^{-4}$</td>
<td>$-5.63 \times 10^{-4}$</td>
<td>$6.05 \times 10^{-4}$</td>
</tr>
<tr>
<td>$B_2$ (erg.cm$^{-3}$)</td>
<td>$7.52 \times 10^{-4}$</td>
<td>$-2.90 \times 10^8$</td>
<td>$1.02 \times 10^8$</td>
</tr>
<tr>
<td>(eV.atom$^{-1}$)</td>
<td>$5.56 \times 10^{-4}$</td>
<td>$-2.02 \times 10^{-3}$</td>
<td>$6.97 \times 10^{-4}$</td>
</tr>
<tr>
<td>$B_3$ (erg.cm$^{-3}$)</td>
<td>$-2.82 \times 10^8$</td>
<td>$-2.96 \times 10^3$</td>
<td>$-2.82 \times 10^8$</td>
</tr>
<tr>
<td>(eV.atom$^{-1}$)</td>
<td>$-2.94 \times 10^8$</td>
<td>$-2.82 \times 10^8$</td>
<td>$-2.94 \times 10^8$</td>
</tr>
</tbody>
</table>

are, respectively,

$$G_{el} (\varepsilon) = \frac{1}{2} C_{11} (\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + C_{12} (\varepsilon_{11} \varepsilon_{22} + \varepsilon_{22} \varepsilon_{33} + \varepsilon_{33} \varepsilon_{11}) + \frac{1}{2} C_{44} (\varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{31}^2),$$

and

$$G_{el} (\varepsilon) = \frac{1}{2} C_{11} (\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + C_{12} \varepsilon_{11} \varepsilon_{22} + \frac{1}{2} C_{33} \varepsilon_{22}^2$$

$$+ C_{13} (\varepsilon_{11} + \varepsilon_{22}) \varepsilon_{33} + \frac{1}{2} C_{44} (\varepsilon_{12}^2 + \varepsilon_{23}^2) + (C_{11} - C_{12}) \varepsilon_{12}^2.$$  

It is then straightforward to minimize the sum $G_{el} (\varepsilon) + G_{magn.el} (\Omega_M, \varepsilon)$ with respect to $\varepsilon$. One obtains the relative spontaneous magnetostriction (relative change of length) along the direction $\mathbf{u} \equiv (\beta_1, \beta_2, \beta_3)$ as a function of the magnetization direction $\Omega_M = (\alpha_1, \alpha_2, \alpha_3)$; for cubic systems, one gets

$$\frac{\delta l}{l} = \frac{3}{2} \lambda_{100} \left( \alpha_1 \beta_1^2 + \alpha_2 \beta_2^2 + \alpha_3 \beta_3^2 - \frac{1}{3} \right)$$

$$+ 3 \lambda_{111} \left( \alpha_1 \alpha_2 \beta_1 \beta_2 + \alpha_2 \alpha_3 \beta_2 \beta_3 + \alpha_3 \alpha_1 \beta_3 \beta_2 \right),$$

where $\lambda_{100}$ and $\lambda_{111}$ are the magnetostriction constants along the [100] and [111] directions, respectively, given by

$$\lambda_{100} = - \frac{2B_1}{3(C_{11} - C_{12})},$$

$$\lambda_{111} = - \frac{B_2}{3C_{44}};$$

and for hexagonal systems,

$$\frac{\delta l}{l} = \lambda_A \left[ (\alpha_1 \beta_1 + \alpha_2 \beta_2)^2 - (\alpha_1 \beta_1 + \alpha_2 \beta_2) \alpha_3 \beta_3 \right]$$

$$+ \lambda_B \left[ (1 - \alpha_3^2)(1 - \beta_3^2) - (\alpha_1 \beta_1 + \alpha_2 \beta_2)^2 \right]$$

$$+ \lambda_C \left[ (1 - \alpha_3^2) \beta_3^2 - (\alpha_1 \beta_1 + \alpha_2 \beta_2) \alpha_3 \beta_3 \right]$$

$$+ \lambda_D (\alpha_1 \beta_1 + \alpha_2 \beta_2) \alpha_3 \beta_3 ,$$

(27)
Table 3: Magnetostriction constants of Fe, Co, and Ni at room temperature. (a) Ref. [8]; (b) Ref. [9]; (c) Ref. [10]

<table>
<thead>
<tr>
<th></th>
<th>Fe(a) (bcc)</th>
<th>Co(b) (hcp)</th>
<th>Ni(b) (fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{100}$</td>
<td>$24 \times 10^{-6}$</td>
<td>$-50 \times 10^{-6}$</td>
<td>$-66 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\lambda_{111}$</td>
<td>$-23 \times 10^{-6}$</td>
<td>$-107 \times 10^{-6}$</td>
<td>$-29 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

with

$$
\lambda_A + \lambda_B = \frac{2B_2C_{12} - (2B_3 + B_1)C_{33}}{C_{33}(C_{12} + C_{13}) - 2C_{13}^2}
$$

$$
\lambda_A - \lambda_B = \frac{B_1}{C_{12} - C_{11}}
$$

$$
\lambda_C = \frac{B_2(C_{12} + C_{13}) - (2B_3 + B_1)C_{33}}{C_{33}(C_{12} + C_{13}) - 2C_{13}^2}
$$

$$
4\lambda_D - (\lambda_A + \lambda_B + \lambda_C) = \frac{B_1}{C_{44}}
$$

The magnetostriction constants of Fe, Co, and Ni are given in Table 3. The magnetoelastic constants of Table 2 were obtained from these data [8-10] and from the elastic constants given in Ref.[11].

3 Anisotropy Arising from Dipolar Interactions

In the present Section, we aim to discuss, at a microscopic level, the magnetic anisotropy due to the dipolar interactions. In an itinerant ferromagnet like Fe, Co, or Ni, the magnetic moment is not localized, so that one has to consider the local density of magnetization $\mathbf{m}(r)$ (it should not be confused with the macroscopic magnetization density $\mathbf{M}(r)$, which is averaged over a large number of atomic cells). The dipole-dipole interaction has been discussed by Jansen [12] from the point of view of relativistic density functional theory, which is the appropriate starting point for this problem. The expression of the dipole-dipole Hamiltonian is

$$
\mathcal{H}_{\text{dip}} = \frac{\mu_B^2}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|^3}
$$

$$
\times \left( \mathbf{\hat{m}}(\mathbf{r}) \cdot \mathbf{\hat{m}}(\mathbf{r}') - \frac{3[(\mathbf{r} - \mathbf{r}') \cdot \mathbf{\hat{m}}(\mathbf{r})][(\mathbf{r} - \mathbf{r}') \cdot \mathbf{\hat{m}}(\mathbf{r})]}{|\mathbf{r} - \mathbf{r}'|^2} \right),
$$

where $\mathbf{\hat{m}}(\mathbf{r})$ is the magnetization density operator, expressed in $\mu_B$ per unit volume. This result is clearly interpreted as resulting from the interaction between the magnetization and the dipolar field created by the magnetization from the whole ferromagnet. It is a many-body Hamiltonian, which we treat in a Hartree approximation, so that the dipolar $E_{\text{dip}}$ is obtained by replacing in $\mathcal{H}_{\text{dip}}$, the operator $\mathbf{\hat{m}}(\mathbf{r})$ by its expectation value $\mathbf{m}(\mathbf{r})$. 


24.11

That the dipole-dipole interaction is a relativistic correction appears clearly, for it is proportional to $\mu_B^2 \sim c^{-2}$.

If the magnetization distribution within each atomic cell is not spherical, then its expansion in multipoles includes not only a dipolar moment, but also higher multipoles like quadrupoles, octupoles, etc. However, in 3d transition metals, the magnetization distribution is almost spherical, and can safely be replaced by the dipolar magnetic moments $m_i$ (i being the atom index), so that the dipolar energy writes

$$E_{\text{dip.}} = \frac{\mu_B^2}{2} \sum_{i \neq j} \frac{1}{r_{ij}^3} \left( m_i \cdot m_j - \frac{3 (r_{ij} \cdot m_i) (r_{ij} \cdot m_j)}{r_{ij}^2} \right).$$

(33)

Remembering that all moments are parallel, as a consequence of the dominating exchange interaction, $E_{\text{dip.}}$ may be rewritten as

$$E_{\text{dip.}} = \frac{\mu_B^2}{2} \sum_{i \neq j} \frac{m_i m_j}{r_{ij}^5} \left( 1 - 3 \cos^2 \theta_{ij} \right),$$

(34)

where $\theta_{ij}$ is the angle between $\Omega_{ij}$ and the direction $u_{ij}$ of the pair $(i,j)$; the latter expression clearly displays the fact that dipole-dipole interaction contributes to the magnetic anisotropy. For a given pair $(i,j)$ the dipolar energy is minimum when the moments are parallel to $u_{ij}$.

3.1 Shape anisotropy

A striking feature of the dipole interaction is that it decreases slowly as a function of the distance $r_{ij}$ (like $r_{ij}^{-3}$); thus the summation over the pairs $(i,j)$ converges very slowly. As a consequence, the dipolar field $H_{\text{dip.}}(i)$ experienced by a given moment $m_i$ depends significantly on the moments located at the boundary of the sample, and this results in the shape anisotropy.

Intuitively, we feel that the contribution to $H_{\text{dip.}}(i)$ of atoms that are very far from $i$ should not depend on their exact positions at the atomic level, so that one can safely replace the individual moments by the (macroscopic) continuous magnetization distribution $M(r)$; this, however, does not hold for moments that are close to $i$. These considerations are accounted for quantitatively in the Lorentz method for calculating $H_{\text{dip.}}(i)$, which is sketched in Fig. 3. In order to calculate $H_{\text{dip.}}(i)$, Lorentz decomposes the sample into two parts: in a spherical cavity of radius $R$ centered at site $i$, the discrete moment distribution is retained; in the rest of the sample, the moment distribution is approximated by the macroscopic magnetization density $M(r)$. Of course, the larger $R$, the better the approximation. For a continuous magnetization distribution, the dipolar field may be expressed as due to pseudo-magnetic charges with a volume density $\rho = -\nabla M$ and a surface density $\sigma = n \cdot M$, where $n$ is the normal to the surface.

If the magnetization is uniform, then only the surfaces carry some pseudo-charges. Thus, $H_{\text{dip.}}(i)$ can be written

$$H_{\text{dip.}}(i) = H_{\text{cav.}} + H_L + H_d,$$

(35)

where $H_{\text{cav.}}$ is due to the dipoles inside the cavity, $H_L = (4\pi/3)M$ (the Lorentz field) is the field created by the pseudo-charges at the surface of the cavity, and $H_d$ (the demagnetizing field) is due to the pseudo-charges on the external surface. The sum of the cavity
and Lorentz fields converges rapidly enough (like a sum over $r_{ij}^{-3}$) to be estimated with a moderate cavity radius $R$; it contributes to the magnetocrystalline anisotropy, and will be discussed further in Sec. 3.2. The shape anisotropy is entirely due to the demagnetizing field $H_d$.

Thus, the shape anisotropy is given by

$$G_{\text{shape}}(\Omega_M) = -\frac{1}{2} \int_V dV \mathbf{M}(r) \cdot \mathbf{H}_d(r).$$

(36)

The magnitude $M(r)$ is essentially constant, equal to the bulk value $M_V$ throughout the sample, and zero outside; however, near the interface, it can deviate from $M_V$ (this deviation accounts for the possible enhancement or reduction of $M$ in the ferromagnet as well as for the possible induced magnetization in the neighboring material). Thus, we can separate the total shape anisotropy into a volume term and a surface term. The volume term is obtained by taking $M$ equal to its bulk value, whereas the surface term is due to the departures from $M_V$ near the interface.

For a body of arbitrary shape, the dipolar field $H_d(r)$ depends on the position $r$; however, if the body has the shape of an ellipsoid, $H_d$ has the striking property of being uniform (in magnitude and direction) throughout the sample. It is commonly expressed as

$$H_d = -4\pi \mathbf{D} \cdot M_V,$$

(37)

where $\mathbf{D}$, the demagnetizing tensor, can be shown to satisfy

$$\text{tr} \mathbf{D} = 1.$$

(38)

The shape anisotropy per unit volume then is

$$G_{\text{shape}}^V = -2\pi M_V \cdot \mathbf{D} \cdot M_V.$$

(39)
The demagnetizing tensor for simple limit cases may be found easily by symmetry arguments. For a sphere, one has

$$D = \begin{pmatrix} 1/3 & 0 & 0 \\ 0 & 1/3 & 0 \\ 0 & 0 & 1/3 \end{pmatrix};$$ (40)

for an infinite revolution cylinder of axis parallel to $z$,

$$D = \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 0 \end{pmatrix};$$ (41)

and for a plate of infinite lateral extension, with the normal parallel to $z$,

$$D = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. $$ (42)

Analytical expressions may also be obtained for an ellipsoid of revolution. Let $a$ be the polar semi-axis, and $b$ the equatorial semi-axis, with $m = a/b$; for a prolate ellipsoid ($m > 1$), one finds

$$D_a = \frac{1}{m^2 - 1} \left( \frac{m}{\sqrt{m^2 - 1}} \ln \left[ m + \sqrt{m^2 - 1} \right] - 1 \right),$$ (43)

and for an oblate ellipsoid ($m < 1$),

$$D_a = \frac{1}{1 - m^2} \left( 1 - \frac{m}{\sqrt{1 - m^2}} \arccos m \right);$$ (44)

the other tensor elements are obtained by using Eq. (38), i.e. $D_k = D_x = (1 - D_a)/2$.

The case of a plate of infinite lateral extension is relevant for layered systems such as ultrathin films and multilayers; for such systems, the volume shape anisotropy is

$$G_{\text{shape}}^V = K_{\text{shape}}^V \sin^2 \theta,$$ (45)

with

$$K_{\text{shape}}^V = -2\pi M_V^2,$$ (46)

and where $\theta$ is the angle between the normal to the plane and $\Omega_M$. It favors an in-plane orientation of $\Omega_M$. For Fe, Co, and Ni, $2\pi M_V^2$ is respectively equal to $1.92 \times 10^7$ erg.cm$^{-3}$ ($\equiv 1.41 \times 10^{-4}$ eV.atom$^{-1}$), $1.34 \times 10^7$ erg.cm$^{-3}$ ($\equiv 9.31 \times 10^{-5}$ eV.atom$^{-1}$), and $1.73 \times 10^6$ erg.cm$^{-3}$ ($\equiv 1.18 \times 10^{-4}$ eV.atom$^{-1}$). These values are larger than the volume magnetocrystalline anisotropy constants (compare Table 1), so that, in comparatively thick films, the shape anisotropy dominates both the volume and the surface magnetocrystalline contributions, and the magnetization lies in the film plane.

The surface contribution to the shape anisotropy is easily calculated by considering infinitesimal slices parallel to the surface, and one obtains, per unit area,

$$G_{\text{shape}}^S(\Omega_M) = K_{\text{shape}}^S \sin^2 \theta,$$ (47)
with

\[ K_{\text{shape}}^S = -2\pi \left( \int_{-\infty}^{0} [M^2(z) - M_v^2] \, dz + \int_{0}^{+\infty} M^2(z) \, dz \right) \]

\[ \approx -2\pi M_v M_S ; \]  

\[ \text{(48)} \]

in the above equation, \( z < 0 \) (respectively \( z > 0 \)) corresponds to the interior (respectively exterior) of the ferromagnetic body, and the excess surface magnetization \( M_S \) per unit area is defined by

\[ M_S = \int_{-\infty}^{0} [M(z) - M_v] \, dz + \int_{0}^{+\infty} M(z) \, dz . \]  

\[ \text{(49)} \]

The magnitude of the surface shape anisotropy can be obtained from electronic structure calculations of the layer-dependent magnetization near surfaces and interfaces. For instance, for Fe [13], the magnetization is enhanced at the surface Fe(001), and one obtains \( K_{\text{shape}}^S = -0.27 \text{ erg.cm}^{-2} \); the enhancement is slightly less at a Fe/Ag(001) interface, and one has \( K_{\text{shape}}^S = -0.12 \text{ erg.cm}^{-2} \). For Ni [14], one obtains \( K_{\text{shape}}^S = -0.017 \text{ erg.cm}^{-2} \) for the Ni(001) surface, and \( K_{\text{shape}}^S = 0.025 \text{ erg.cm}^{-2} \) for the Ni/Cu(001) interface, where the magnetization is reduced. These examples, as compared with the orders of magnitude of \( K^S \) given in Sec. 2.4, indicate that, although it is not completely negligible, the shape surface anisotropy contributes only weakly to the total surface anisotropy. In particular, in any case, the shape surface anisotropy can never lead to a perpendicular easy axis in ultrathin films.

3.2 Dipolar crystalline anisotropy

We consider now the contribution of the dipolar interactions to the magnetocrystalline anisotropy. Its calculation involves numerical summation of the dipolar field from the dipoles located inside the Lorentz cavity. To do this efficiently, sophisticated techniques must be used, such as the Ewald summation method, where the summation is performed partly in the real space and partly in the reciprocal space [15].

As may be seen from Eq. (34), the dipolar energy contains only terms of order 2 with respect to \( \Omega_M \). Thus, it contributes only to anisotropy constants of order 2. As a consequence, for structures of high symmetry (such as cubic structures) where terms of order 2 are forbidden, the net dipolar contribution to the magnetocrystalline anisotropy vanishes. Note that, for cubic systems, a non-zero anisotropy would arise from higher terms in the multipolar expansion of the magnetization density, but this is quantitatively negligible.

On the other hand, for structures of lower symmetry, where terms of order 2 are allowed, the dipolar crystalline is in general non zero. For bcc systems, the dipolar crystalline anisotropy is found to be exactly zero for the ideal ratio \( c/a = \sqrt{8/3} \approx 1.633 \) and to depart from zero as \( c/a \) departs from \( \sqrt{8/3} \); for Co, one has \( c/a = 1.622 \) and the dipolar contribution to \( K_1^V \) is \( K_1^\text{dip} = 5.7 \times 10^4 \text{ erg.cm}^{-3} (\equiv 4 \times 10^{-7} \text{ eV. atom}^{-1}) \) [24]. Quantitatively, this contribution to the volume anisotropy of bcc Co is negligible.

As was pointed out in Sec. 2.5, the symmetry of cubic crystal under strain is lowered, so that anisotropy terms of order 2 become allowed. Thus, the dipolar force
Table 4: Calculated dipolar contribution to the magneto-elastic constants of Fe and Ni; from Ref. [17].

<table>
<thead>
<tr>
<th></th>
<th>Fe (bcc)</th>
<th>Ni (fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$, dip. (erg.cm$^{-3}$)</td>
<td>$-7.3 \times 10^9$</td>
<td>$-5.0 \times 10^9$</td>
</tr>
<tr>
<td></td>
<td>(eV.atom$^{-1}$)</td>
<td>$-5.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>$B_2$, dip. (erg.cm$^{-3}$)</td>
<td>$2.4 \times 10^9$</td>
<td>$1.7 \times 10^8$</td>
</tr>
<tr>
<td></td>
<td>(eV.atom$^{-1}$)</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Table 5: Calculated values of the dimensionless parameter $k_S$ characterizing the magnitude of the dipolar contribution to the magnetocrystalline surface anisotropy, for various systems; from Ref. [18]

<table>
<thead>
<tr>
<th>system</th>
<th>sc</th>
<th>fcc</th>
<th>fcc</th>
<th>bcc</th>
<th>bcc</th>
<th>hcp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(001)</td>
<td>(111)</td>
<td>(001)</td>
<td>(110)</td>
<td>(001)</td>
<td>(0001)</td>
</tr>
<tr>
<td>$k_S$</td>
<td>0.039</td>
<td>-0.034</td>
<td>-0.118</td>
<td>-0.038</td>
<td>-0.218</td>
<td>-0.034</td>
</tr>
</tbody>
</table>

should contribute to the magneto-elastic constants $B_1$ and $B_2$ of cubic materials. Explicit calculations give [17]

$$B_1, \text{ dip.} = -3\alpha M_0^2$$
$$B_2, \text{ dip.} = \alpha M_0^2$$

with $\alpha \approx 0.8$ and 0.6 for the bcc and fcc structures, respectively. The corresponding results for Fe and Ni are given in Table 4. Again, these values are considerably smaller than the experimental ones, so that other contributions should dominate.

As emphasized in Sec. 2.4, the local symmetry is lowered at a surface, so that, even for cubic crystals, the dipolar interactions give a non-zero contribution to the surface crystalline anisotropy. As the Lorentz method cannot be used for atoms located near a surface, one needs another type of decomposition in this case [18]; the expression of the dipolar contribution to $K_1^S$ is

$$K_1, \text{ dip.} = -2\pi M_0^2 d k_S$$

where $d$ is the distance between atomic planes and $k_S$ is given in Table 5 for various surfaces. The largest value is obtained for the Fe(001) surface: $K_1^{S, \text{ dip.}} = 0.06 \text{ erg.cm}^{-2}$ ($\approx 6 \times 10^{-5} \text{ eV.atom}^{-1}$); again the dipolar interactions yield only a very small contribution to the observed surface crystalline anisotropies.

To summarize the present Section on the magnetic anisotropy due to dipolar interactions, we have examined in detail the contributions of the latter to the various terms of the total anisotropy energy $\mathcal{G}(\Omega_M)$. In all cases, we have given a quantitative estimate of the dipolar contribution. It turns out that the essential contribution of the dipolar interactions to $\mathcal{G}(\Omega_M)$ is the volume shape anisotropy $G_{\text{shape}}(\Omega_M)$. For all other terms (magneto-elastic anisotropy, volume and surface crystalline anisotropies), the dipolar contribution is quantitatively not important, and, as will be shown in the next Section, they must be attributed essentially to the spin-orbit coupling.
4 Anisotropy Arising from the Spin-Orbit Coupling

In this Section, we shall proceed in steps of increasing sophistication. After having presented the spin-orbit interaction, we propose a simple model for the magnetic anisotropy; then, we present the perturbation theory, and finally, we discuss the state-of-the-art of first-principles calculations of magnetic anisotropy. The discussion will be focused on a few selected examples, and we shall not attempt to mention all the works that have been published on this topic. Otherwise explicitly specified, in all this Section, the term magnetic anisotropy will refer to the contribution arising from the spin-orbit coupling.

4.1 The spin-orbit coupling

The relativistic theory of the electron relies on the Dirac equation. In the limit of low velocities (more precisely to order \( v^2/c^2 \)), the Dirac equation reduces to the Pauli equation, which is essentially a Schrödinger equation with relativistic corrections; the Pauli Hamiltonian writes

\[
\mathcal{H}_{\text{Pauli}} = \frac{p^2}{2m} - e\Phi - \frac{p^2}{8m^2c^2} + \frac{e\hbar^2}{8m^2c^2} \text{div} \mathbf{E} + \frac{e\hbar}{4m^2c^2} \mathbf{\sigma} \cdot (\mathbf{E} \times \mathbf{p}) .
\]  

The interpretation of the various terms is as follows: The first two terms are respectively the non-relativistic kinetic energy and the electrostatic potential energy; they form the non-relativistic Hamiltonian. The third term is the relativistic mass-velocity correction. The fourth term is the Darwin correction, which accounts for the fact that, within the relativistic theory, the electron is sensitive to the electric field \( \mathbf{E} \) over a lengthscale of the order of the Compton wavelength \( \lambda_C = h/(mc) \). The third and fourth terms are independent of the spin \( s = \sigma/2 \); they are often combined with the non-relativistic terms to form the so-called scalar-relativistic Hamiltonian. The last term in Eq. (52) is the spin-orbit coupling \( \mathcal{H}_{\text{S.O.}} \). It can be interpreted as the coupling between the spin of the electron and the magnetic field created by its own orbital motion around the nucleus. As the orbital motion itself is directly coupled to the lattice via the electric potential of the ions, this term provides a contribution to the magnetocrystalline anisotropy.

The spin-orbit term is large essentially in the neighborhood of the nucleus, where, to a fairly good approximation, the potential is spherically symmetric; then the electric field writes

\[
\mathbf{E} = -\frac{r}{r} \frac{d\Phi}{dr} ,
\]

so that the spin-orbit Hamiltonian may be expressed as

\[
\mathcal{H}_{\text{S.O.}} = -\frac{e\hbar}{4m^2c^2r} \frac{d\Phi}{dr} \mathbf{\sigma} \cdot (r \times \mathbf{p}) = \frac{e\hbar^2}{2mc^2r} \frac{d\Phi}{dr} \mathbf{l} \cdot \mathbf{s} = \xi(r) \mathbf{l} \cdot \mathbf{s} .
\]

As the magnetism of transition metals is due to the \( d \) electrons, it is sufficient to consider only the spin-orbit interaction for \( d \) electrons. Thus, the spin-orbit coupling finally writes

\[
\mathcal{H}_{\text{S.O.}} = \xi \mathbf{l} \cdot \mathbf{s} ,
\]

where \( \xi \), the spin-orbit constant, is the radial average of \( \xi(r) \) over \( d \)-orbitals. The calculated spin-orbit constants of transition metals are shown in Fig. 4. It appears that
\[ \gamma = \frac{(2s_z + l_z)/(s_z + l_z)}{(2s_x + l_x)/(s_x + l_x)} \]

where \( l_x = l_x \pm l_y \). It then a simple matter to calculate explicitly the matrix elements of \( \mathbf{I} \cdot \mathbf{s} \) between the various \( d \) orbitals \((xy, x^2 - y^2, \text{etc.})\) as function of the angles \( \theta \) and \( \phi \); the result may be expressed as

\[ \mathbf{I} \cdot \mathbf{s} = \begin{pmatrix} M & N \\ -N^* & M^* \end{pmatrix}, \]

where the \( 5 \times 5 \) matrices \( M \) and \( N \) are given in Table 7.

### 4.2 Simple physical picture

Before giving a detailed discussion of the microscopic theory of magnetic anisotropy, we first propose a simple physical picture. Let us consider the case where the exchange
Figure 4: Calculated values of the spin-orbit constant $\xi$ of transition metals; from Ref.[19]
Table 7: Matrix elements of $M$ and $N$; the labels 1 to 5 correspond respectively to the $xy$, $yz$, $zx$, $x^2-y^2$, and $3z^2-r^2$ $d$-orbitals; from Ref. [21].

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>$</td>
<td>1\rangle$</td>
<td>$</td>
<td>2\rangle$</td>
</tr>
<tr>
<td>1</td>
<td>$0$</td>
<td>$\frac{1}{2} i \sin \theta \sin \phi$</td>
<td>$-\frac{1}{2} i \sin \theta \cos \phi$</td>
<td>$i \cos \phi$</td>
</tr>
<tr>
<td>2</td>
<td>$-\frac{1}{2} i \sin \theta \sin \phi$</td>
<td>$0$</td>
<td>$\frac{1}{2} i \cos \theta$</td>
<td>$-\frac{1}{2} i \sin \theta \cos \phi$</td>
</tr>
<tr>
<td>3</td>
<td>$\frac{1}{2} i \sin \theta \cos \phi$</td>
<td>$\frac{1}{2} \cos \theta$</td>
<td>$0$</td>
<td>$-\frac{1}{2} i \sin \theta \sin \phi$</td>
</tr>
<tr>
<td>4</td>
<td>$-i \cos \theta$</td>
<td>$\frac{1}{2} i \sin \theta \cos \phi$</td>
<td>$\frac{1}{2} i \sin \theta \sin \phi$</td>
<td>$0$</td>
</tr>
<tr>
<td>5</td>
<td>$0$</td>
<td>$\frac{1}{2} \sqrt{3} i \sin \theta \cos \phi$</td>
<td>$-\frac{1}{2} \sqrt{3} i \sin \theta \sin \phi$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

$N$ | $|1\rangle$ | $|2\rangle$ | $|3\rangle$ | $|4\rangle$ | $|5\rangle$ |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0$</td>
<td>$\frac{1}{2} (\cos \phi$</td>
<td>$\sin \phi$</td>
<td>$-i \cos \theta \cos \phi$)</td>
<td>$-i \sin \theta$</td>
</tr>
<tr>
<td>2</td>
<td>$-\frac{1}{2} (\cos \phi$</td>
<td>$i \cos \theta \cos \phi$)</td>
<td>$0$</td>
<td>$-\frac{1}{2} \sin \theta$</td>
<td>$\frac{1}{2} (\sin \phi$</td>
</tr>
<tr>
<td>3</td>
<td>$\frac{1}{2} (-\sin \phi$</td>
<td>$i \cos \theta \cos \phi$)</td>
<td>$\frac{1}{2} \sin \theta$</td>
<td>$0$</td>
<td>$-\frac{1}{2} (\sin \phi$</td>
</tr>
<tr>
<td>4</td>
<td>$i \sin \theta$</td>
<td>$\frac{1}{2} (-\sin \phi$</td>
<td>$i \cos \theta \cos \phi$)</td>
<td>$\frac{1}{2} (\cos \phi$</td>
<td>$+i \cos \theta \sin \phi$)</td>
</tr>
<tr>
<td>5</td>
<td>$0$</td>
<td>$\frac{1}{2} \sqrt{3} (-\sin \phi$</td>
<td>$+i \cos \theta \cos \phi$)</td>
<td>$0$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

Splitting between the spin up and spin down bands is much larger than the crystal field splitting (or band width), so that we can neglect the matrix elements of $\mathcal{H}_{S.O.}$ that couple spin up and spin down states. Then, the effect of the spin-orbit coupling is equivalent to that of an effective magnetic field $\mathbf{H}_{\text{orb}}$, acting only on the orbital magnetic moment $\mathbf{m}_i = \mu_B \mathbf{l}$, i.e.

$$\mathcal{H}_{S.O.} = -\mathbf{m}_i \cdot \mathbf{H}_{\text{orb}},$$  

(58)

with

$$\mathbf{H}_{\text{orb}} = \pm \frac{\xi \Omega_M}{2\mu_B},$$  

(59)

where the sign + (respectively −) is for a $d$ band with more (respectively less) than 5 electrons.

The effect of this effective field is described, to first order in $\mathbf{H}_{\text{orb}}$, by the orbital susceptibility (2nd order) tensor $\chi_{\text{orb}}^{(2)}$. Thus, to lowest order in $\mathbf{H}_{\text{orb}}$, the expectation value $<\mathbf{m}_i>$ of the orbital magnetic moment and the spin-orbit energy $E_{S.O.}$ are respectively given by

$$<\mathbf{m}_i> = \chi_{\text{orb}}^{(2)} \cdot \mathbf{H}_{\text{orb}},$$

$$= \pm \frac{\xi \Omega_{M}}{2\mu_B} \chi_{\text{orb}}^{(2)} \cdot \Omega_M,$$

(60)

and

$$E_{S.O.} = -\frac{1}{2} \mathbf{H}_{\text{orb}} \cdot \chi_{\text{orb}}^{(2)} \cdot \mathbf{H}_{\text{orb}}.$$
For a system of hexagonal or tetragonal symmetry, with the symmetry axis along \( O_z \), the orbital susceptibility writes

\[
\chi_{\text{orb.}}^{(2)} = \begin{pmatrix}
\chi^{(2)11}_{\text{orb.}} & 0 & 0 \\
0 & \chi^{(2)11}_{\text{orb.}} & 0 \\
0 & 0 & \chi^{(2)33}_{\text{orb.}}
\end{pmatrix};
\]

(62)

Thus, the orbital contribution to the magnetic moment writes

\[
m_t^\xi = \pm \frac{\xi}{2 \mu_B} \left[ \chi^{(2)33}_{\text{orb.}} + \left( \chi^{(2)11}_{\text{orb.}} - \chi^{(2)33}_{\text{orb.}} \right) \sin^2 \theta \right],
\]

(63)

and the spin-orbit energy is

\[
E_{\text{S.O.}} = -\frac{1}{2} \left( \pm \frac{\xi}{2 \mu_B} \right)^2 \left[ \chi^{(2)33}_{\text{orb.}} + \left( \chi^{(2)11}_{\text{orb.}} - \chi^{(2)33}_{\text{orb.}} \right) \sin^2 \theta \right].
\]

(64)

Of course for a cubic system, \( \chi^{(2)11}_{\text{orb.}} = \chi^{(2)22}_{\text{orb.}} = \chi^{(2)33}_{\text{orb.}} \), so that there is no anisotropy at this order. Thus, one must consider the non-linear orbital susceptibility, which is given by the 4th order tensor \( \chi^{(4)}_{\text{orb.}} \):

\[
m_t^\xi = \sum_{i,j} \chi^{(4)ij}_{\text{orb.}} H_i^j, \\
E_{\text{S.O.}} = -\frac{1}{2} \sum_{i,j} \chi^{(4)ij}_{\text{orb.}} H_i^j = -\frac{1}{2} \sum_{i,j,k,l} \chi^{(6)ijkl}_{\text{orb.}} H_i^k H_j^l H^k \]

(65)

For cubic symmetry, the only independent elements of \( \chi^{(4)}_{\text{orb.}} \) are \( \chi^{(4)1111}_{\text{orb.}} \) and \( \chi^{(4)1122}_{\text{orb.}} \), so that the expressions of \( m_t^\xi \) and \( E_{\text{S.O.}} \) for cubic systems are, respectively,

\[
m_t^\xi = \pm \frac{\xi}{2 \mu_B} \chi^{(2)11}_{\text{orb.}} \\
+ \left( \pm \frac{\xi}{2 \mu_B} \right)^2 \left[ \chi^{(4)1111}_{\text{orb.}} + 2 \left( 3 \chi^{(4)1122}_{\text{orb.}} - \chi^{(4)1111}_{\text{orb.}} \right) \left( \alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_4^2 \right) \right],
\]

(67)

\[
E_{\text{S.O.}} = -\frac{1}{2} \left( \pm \frac{\xi}{2 \mu_B} \right)^2 \chi^{(2)11}_{\text{orb.}} \\
- \frac{1}{2} \left( \pm \frac{\xi}{2 \mu_B} \right)^4 \left[ \chi^{(4)1111}_{\text{orb.}} + 2 \left( 3 \chi^{(4)1122}_{\text{orb.}} - \chi^{(4)1111}_{\text{orb.}} \right) \left( \alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_4^2 \right) \right]
\]

(68)

Similarly, higher order anisotropy terms are taken into account by considering higher order terms in the non-linear susceptibility.

Although the limit of large exchange coupling does not hold for Fe, Co and Ni, we may tentatively apply this model to the latter. For these metals, the effective field \( H_{\text{orb.}} \) is of the order of \( 5 \times 10^6 \) Oe. The orbital susceptibility of Fe, Co and Ni is given in Table 8. Data on the non-linear susceptibility are not available.
Table 8: Orbital susceptibility of Fe, Co, and Ni; (a) Ref. [2]; (b) Ref. [5]

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) $\chi_{\text{orb.}}^{(2)\text{II}}$ (emu.mole$^{-1}$)</td>
<td>$120 \times 10^{-6}$</td>
<td>$240 \times 10^{-6}$</td>
<td>$80 \times 10^{-6}$</td>
</tr>
<tr>
<td>(a) $\mu_B.\text{Oe}^{-1}.\text{atom}^{-1}$</td>
<td>$20 \times 10^{-9}$</td>
<td>$60 \times 10^{-9}$</td>
<td>$15 \times 10^{-9}$</td>
</tr>
<tr>
<td>(b) $\chi_{\text{orb.}}^{(2)\text{III}}$ (emu.mole$^{-1}$)</td>
<td>$-50 \times 10^{-6}$</td>
<td>$-50 \times 10^{-6}$</td>
<td>$-50 \times 10^{-6}$</td>
</tr>
<tr>
<td>(b) $\mu_B.\text{Oe}^{-1}.\text{atom}^{-1}$</td>
<td>$-9 \times 10^{-9}$</td>
<td>$-9 \times 10^{-9}$</td>
<td>$-9 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

The predictions of the present model are the following: (i) the orbital moment is of the order of $0.1 \mu_B\text{atom}^{-1}$, parallel to the spin moment (i.e. $g > 2$); (ii) $K_1$ and $M_1$ in Table 1 are of opposite sign, and the ratio $-2K_1/M_1$ is of the order of $H_{\text{orb.}}$; (iii) for Co, the moment anisotropy $M_1$ is of the order of $10^{-2} \mu_B\text{atom}^{-1}$. All these predictions are fairly well satisfied, both in sign and order of magnitude, which indicate that the simple physical picture proposed here is essentially correct.

4.3 Perturbation theory

Since the spin-orbit coupling $\xi$ is much smaller than the bandwidth and the exchange splitting, it is quite natural to attack the problem of calculating the magnetic anisotropy by using the perturbation theory.

As may be seen from Table 7, the matrix elements of $1 \cdot s$ are combinations of first order spherical harmonics of $\Omega M_1$; thus the matrix elements of $(1 \cdot s)^n$ are combinations of spherical harmonics of order $n$. So, in order to calculate an anisotropy constant of order $n$, one has to use perturbation theory of order $n$. For hcp crystals and ultrathin films, 2\text{nd} order perturbation is sufficient, whereas for cubic crystals magnetic anisotropy arises only in 4\text{th} order perturbation theory.

The change in energy to 2\text{nd} order in spin-orbit coupling is given by the well-known formula

$$\Delta E_{\text{SO}} = \sum_{\text{exc.}} \frac{|<\text{exc.}|H_{\text{SO.}}|\text{gr.}>|^2}{E_{\text{gr.}} - E_{\text{exc.}}}, \quad (69)$$

where the labels "gr." and "exc." refer to the unperturbed ground state and excited states, respectively. The only excited states one needs to consider here are those where an electron of momentum $k$ is raised from an occupied state into an empty state above the Fermi level, with or without spin flip.

Thus, a very rough estimate of $K_1$ for a uniaxial system, is

$$K_1 \sim \frac{\xi^2}{W}, \quad (70)$$

where $W$ is the $d$ bandwidth; similarly, one may estimate the anisotropy of cubic crystals from 4\text{th} order perturbation theory to be

$$K_1 \sim \frac{\xi^4}{W^3}. \quad (71)$$

Taking $\xi \approx 75$ meV and $W \approx 5$ eV, one obtains $K_1 \approx 1 \mu_B\text{atom}^{-1}$ for a uniaxial system, and $K_1 \approx 0.3 \mu_B\text{atom}^{-1}$ for a cubic system; these rough estimates are respectively
24.22

of the order of magnitude of the observed anisotropy in ultrathin films and bulk cubic
ferromagnets, respectively. Thus, the perturbation theory provides a simple explanation
for the order of magnitude of the magnetic anisotropy. Quite generally, we conclude that
anisotropy constants of order $\eta$ are given by powers of order $n$ of $\xi/W$ which is a small
quantity: this explains the rapid convergence of the expansion of the anisotropy energy
in spherical harmonics.

In the following, we restrict ourselves to uniaxial systems, i.e. to 2nd order pertur-

bation theory. By using the symmetries of the matrix elements of $\mathbf{I} \cdot \mathbf{s}$, one gets

$$
\Delta E_{SO} = \xi^2 \sum_{m_1, m_2, m_3, m_4} <m_1 \uparrow | \mathbf{I} \cdot \mathbf{s} | m_2 \uparrow | m_3 \uparrow | \mathbf{I} \cdot \mathbf{s} | m_4 \uparrow> G(m_1, m_2, m_3, m_4),
$$

(72)

where $G(m_1, m_2, m_3, m_4)$ depends only on the non-perturbed band structure, while the
matrix elements of $\mathbf{I} \cdot \mathbf{s}$ depend only on $\Omega_M$. More details may be found in Ref. [22].
Finally, one obtains

$$
\Delta E_{SO} = K_0 + K_1 \sin^2 \theta
$$

(73)

where $K_1$ is proportional to $\xi^2$. The virtue of the perturbation theory is that it allows to
calculate directly the anisotropy constants without calculating explicitly the total energy
of the system as a function of the direction of the magnetization. On the other hand,
it has the inconvenient of incorrectly handling degenerate levels and deformations of the
Fermi surface.

We give here an example of calculated magnetic anisotropies for the case of fcc
(001) and (111) monolayers [22]. The band-structure has been calculated by using the
tight-binding method, including 3d and 4s bands. Special attention must be paid to the
low convergence of the integration over the two-dimensional Brillouin zone: in the
present case it was necessary to perform the summation over more than 5000 k-points.
The results are shown in Fig. 5. In order to investigate the trends across the 3d series,
$K_1$ has been calculated as a function of the number $N_V$ of valence electrons, for $N_V = 7$
hypothetical ferromagnetic Mn) to $N_V = 10$ (Ni). The most striking trend (indicated by the
dashed line in Fig. 5) is a systematic variation with respect to $N_V$: for $N_V < 8$ the
anisotropy favors a perpendicular magnetization, while for $N_V > 8$ is favors an in-plane
magnetization. This trend has been interpreted in connection with a theorem stating that
$K_1$ must change of sign at least 4 times as the number of d electrons increases from 0 to
10 [23].

It is interesting to note that the sign of the fcc (111) Co monolayer is in contradiction
with the perpendicular magnetization observed in ultrathin fcc (111) or hcp (0001) Co
films: this point will be discussed further in the next Section.

4.4 First-principles calculations

The ab initio calculation of the magnetic anisotropy is a formidable task. The usual
procedure is to compute the difference of total energy for $\Omega_M$ along two non-equivalent
directions (for example [001] and [111] in a cubic crystal). In a (bulk) cubic crystal, the
anisotropy energy is of the order of $10^{-6}$ eV.atom$^{-1}$, while the total energy per atom
is about $40 \times 10^5$ eV.atom$^{-1}$; thus the total energy would have to be calculated with a
tremendous numerical accuracy. Such brute-force calculations are of course not feasible.
Fortunately, most contributions to the total energy remain (almost) unchanged upon
rotation; thus they can be skipped in the total energy. The frozen-core approximation
Figure 5: Calculated anisotropy constant $K_1$ of transition metals fcc (001) and (111) monolayers, as a function of the number $N_V$ of valence electrons; the dashed line is a guide for the eyes. From Ref. [22]

and the use of the force theorem allow to obtain the total energy difference as the difference between the sums of one-electron energies; the latter are of the order of 10 eV atom$^{-1}$, so that the calculation of the energy difference with an accuracy of 10$^{-6}$ eV atom$^{-1}$ remains extremely difficult. On the other hand, the magnetic anisotropy of interfaces is in the range of 10$^{-4}$ to 10$^{-3}$ eV atom$^{-1}$, and should be calculated much more reliably.

Thus, the usual procedure for calculating the magnetic anisotropy from first principles is: (i) perform a self-consistent spin-polarized calculation for the scalar relativistic Hamiltonian; (ii) perform a (non self-consistent) calculation including the spin-orbit coupling for various directions $\Omega_M$ and take the difference between the sums of one-electron eigenvalues. The band structure is generally calculated within the local spin-density approximation (LSDA), and the Schroedinger equation is solved by using a linear scheme such as the linear muffin-tin orbital (LMTO) method, or the linearized full-potential augmented plane wave (FLAPW) method.

For bulk transition metals, the most detailed calculations are due to Daalderop et al. [24], who used the LMTO method. In spite of extremely careful calculations (they used up to 500,000 k-points for the Brillouin zone integration), they did not obtain results in agreement with experimental data: for Ni and Co, they predict a wrong easy axis, while for Fe, they obtain the correct sign for the anisotropy, but a factor 3 too small. The order of magnitude is nevertheless correct. They have investigated the possible origin of the discrepancy between the calculated and experimental results, and suggested that the latter might be due to incorrect positioning of some degenerate bands near the Fermi surface.

As already outlined, the situation is much favorable in the case ultrathin films, where the anisotropy is several orders of magnitude larger than in bulk materials. We
shall discuss here the case of fcc (111) (or hcp(0001)) Co ultrathin films, which have been widely investigated experimentally, and exhibit a perpendicular magnetization when sandwiched between Au, Pd, or Pt.

The results of the calculations are presented in Table 9. One first remarks that the anisotropy of the free-standing Co (111) monolayer strongly favors an in-plane orientation of the magnetization, in agreement with the results of perturbation theory. This is in contrast with the case where the Co layer is in contact with a substrate (Cu, Ag, Pd, Pt): the anisotropy now favors a perpendicular magnetization; this tendency is particularly strong for Pd and Pt (note that for the latter, the anisotropy was calculated with only one Co/Pt interface, so that an even larger anisotropy may be expected for a Pt/Co/Pt sandwich). These results are essentially in agreement with experiment.

In order to understand the rôle played by the substrate in establishing the perpendicular anisotropy, it is important to note that both Pd and Pt have a large Stoner-enhanced susceptibility together with a large spin-orbit coupling. Thus, they acquire a sizeable spin-polarization at the contact of Co and give an important contribution to the anisotropy, due to their large spin-orbit coupling. This interpretation is supported by the fact that suppressing the spin-orbit interaction in Pd strongly reduces the calculated anisotropy of Pd/Co/Pd films [27].

On the other hand, Cu and Ag have filled d bands, and the induced spin-polarization is negligible; thus, they influence the anisotropy only via the s-d hybridization with the Co d bands, and their spin-orbit interaction does not play an important rôle.

Another very interesting case is that of fcc (111) Co/Ni multilayers, where both constituents are ferromagnetic metals. Daalderop et al. noted that since Ni is isoelectronic of Pd, a perpendicular anisotropy could be expected for this system as well: from LMTO calculations, they predicted a perpendicular easy axis for Co/Ni multilayers, a result which they confirmed experimentally [28]. The latter result is a brilliant success of the theory of magnetic anisotropy.

### 5 Outlook and Conclusions

In this Chapter, we have attempted to make clear the mechanisms by which small relativistic corrections to the Hamiltonian (the dipole-dipole interaction and the spin-orbit coupling) give rise to the important property of magnetic anisotropy. The order of magnitude of the various contributions have been estimated and compared with experimental...
The effect of the dipolar interactions appear to be almost entirely contained in the shape anisotropy, which depends on the magnetic material in a rather trivial way: via the magnitude of the (bulk) magnetization $M_y$.

The anisotropy due to the spin-orbit coupling, on the other hand is very subtle, and depends in a complicated manner on the band structure of the material, which makes its calculation a very difficult task.

Nevertheless, by using simple arguments, we can explain the relationships between the crystalline symmetry of the system and the magnitude of its magnetic anisotropy: thus, we have a satisfying explanation for the fact that low-symmetry systems, like ultrathin films, exhibit much larger anisotropies than bulk cubic materials. With the help of a simple model, we have been able to explain the connection between the anisotropy of the energy and those of the magnetization and orbital susceptibility.

The state-of-the-art of first-principles calculations of magnetic anisotropy for bulk materials is rather disappointing: more than half a century after the pioneering work of Brooks [29], we are not able to explain from first-principles why Fe, Co, and Ni are respectively magnetized along the $(100)$, $(0001)$, and $(111)$ axes! The situation looks better, however, for the case of low-symmetry systems where very encouraging success has been obtained, in particular for ultrathin films.
24.26

Textbooks and review articles on magnetic anisotropy that have been used for the preparation of these lectures


References

[29] H. Brooks, Phys. Rev. 58, 909 (1940)
NOTIZEN