C 2 Reduced Dimensions II: Magnetic Anisotropy

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1 Manifestations of the magnetic anisotropy

Without the effect of the magnetic anisotropy, magnetism would have been hard to discover. Almost all applications of magnetic materials – in some way or the other – depend on the fact that it is more favorable to magnetize a magnetic material in a certain direction than in another direction. This difference makes the material magnetically anisotropic. We all know, that a compass needle tends to be magnetized in the needle direction and not perpendicular, therefore it responds to the magnetic field of the earth. In this magnetic field, the needle will keep this magnetization direction and align itself in the direction of the magnetic poles. Would it be magnetically isotropic, the earth’s magnetic field would simply change the magnetization of the compass needle.

Apart from this simple (quasi low-dimensional) example, the magnetic anisotropy manifests itself also in other magnets of any shape and dimensionality. It is responsible for the occurrence of easy and hard axes (in our example parallel and perpendicular to the needle direction), stabilizes magnetic order in dimensions were the exchange interaction alone would not suffice, and limits the width of magnetic domain walls. These aspects will be treated in the first section.

The microscopic origins of the anisotropy will be discussed in section 2, and we will discuss their relative importance in various systems of low dimension in section 3.

1.1 Phenomenology: hard and easy axes

Physically we have seen that the energy of a magnetic system changes as a function of the direction of the magnetization with respect to the crystal axes. The free energy $F$ of a system with a magnetization $M$ can be expanded in terms of azimuthal and polar angles $\theta$ and $\phi$ of the magnetization direction. This can be done either in an expansion in spherical harmonics, or, usually, in terms of the directional cosines $(\alpha_1, \alpha_2, \alpha_3) = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ of $M$ with respect to the crystal axes:

$$F(M) = K_0 + K_1 f_1(h_1, k_1, l_1) + K_2 f_2(h_2, k_2, l_2) + \ldots$$  \hspace{1cm} (1)

where $h_i$, $k_i$, and $l_i$ will depend on the symmetry of the crystal lattice. Terms of the same order will be grouped together in the same function $f_i$. Generally, the coefficients $K$ will also be a function of the value of the magnetization, $M$, as well as of the temperature $T$ and other variables.

Suppose, we apply now an external magnetic field, $H$, and measure the change in the magnetization in the direction of the applied field, up to saturation (left of figure 1). The change in the Gibbs free energy ($G = F - M \cdot H$) can be expressed as

$$dG(T, H) = - SdT - M \cdot dH,$$

so that \[ \frac{\partial G}{\partial H} \bigg|_T = -M \]  \hspace{1cm} (2)

where $S$ is the entropy of the sample. The change in energy is then given by

$$\int_0^H M dH = \int_0^H -\frac{\partial G}{\partial H} dH = M_s H_s + F(0) - F(H_s)$$  \hspace{1cm} (3)

where $M_s$ and $H_s$ are the saturation magnetization and saturation fields respectively. From measurements in different crystallographic directions it is then possible to obtain the anisotropy coefficients $K$ in Eq.(1).
Fig. 1: Graphical representation of Eq.(4) for two different values of $K_1$: if $K_1$ is negative (left), the easy axis is the [111] direction (or equivalent), the hard axis is in [001] (or equivalent) (e.g. in Ni), if $K_1$ is positive (middle), the situation is reversed (like in Fe). The magnetization curves for the latter case are shown on the right.

For a single crystal in the absence of external magnetic fields it can be shown that in Eq.(1) no odd powers of the cosines can appear. This is due to time-inversion symmetry which states that the laws of physics remain unchanged when we substitute $t$ by $-t$. If some symmetry is present in the crystal, other restrictions on the values of $\alpha_i$, $k_i$, and $l_i$ will result. For example in a cubic lattice, the first terms of Eq.(1) read:

$$F(M) = K_0 + K_1 \alpha_1^2 \alpha_2^2 + \alpha_1^2 \alpha_3^2 + \alpha_2^2 \alpha_3^2 + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2 + \ldots$$

$$= K_0 + \frac{K_1}{64} \{(3 - 4 \cos 2\theta + \cos 4\theta)(1 - \cos 4\phi) + 8(1 - \cos 4\theta)\} +$$

$$+ \frac{K_2}{256}(1 - \cos 2\theta - 2 \cos 4\theta + \cos 6\theta)(1 - \cos 4\phi) + \ldots$$

In a spherical harmonics expansion, the expansion of $F$ for a cubic crystal would involve only terms like $Y_{l,m} = Y_{0,0}, Y_{4,0}, Y_{4,4}, Y_{6,0}, Y_{6,4}, \ldots$. A graphical representation of $F$ in cubic systems is given in figure 1 (middle and right).

In contrast to cubic systems, that show no single crystal axis that is non-equivalent to other axes, tetragonal or hexagonal lattices have a unique high symmetry axis (in these cases the $c$-direction). In these uniaxial systems the expansion of $F$ is given by

$$F(M) = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta + \ldots$$

Since all two- and one-dimensional systems are in this sense uniaxial, we will mostly refer to this definition of the anisotropy constants in the following.

If we now compare anisotropy constants for several materials collected in table 1, we see, that cubic materials generally have smaller $K$’s than uniaxial systems. This is understandable, since for cubic systems the anisotropy constants refer to higher order expansions in the $\alpha$’s than for

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*Note, that the presence of a magnetic field seems to break this symmetry and inhomogeneous samples (e.g. made of hard- and soft-magnetic material) may show unidirectional anisotropy. If one considers that magnetic fields are caused by the motion of electric charge, one sees, that time-reversal also reverses the magnetic fields and in total time-inversion symmetry is preserved.*
Table 1: Magnetic anisotropy constants \( K_1 \) and \( K_2 \) for some cubic and uniaxial magnetic materials in J/m\(^3\) at \( T = 4.2 \) K (Ref. [1])

<table>
<thead>
<tr>
<th>Class</th>
<th>Material</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d Metals</td>
<td>Fe</td>
<td>( 5.2 \times 10^4 )</td>
<td>(-1.8 \times 10^4 )</td>
<td>cub.</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>( 7.0 \times 10^6 )</td>
<td>( 1.8 \times 10^5 )</td>
<td>uni.</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>(-1.2 \times 10^6 )</td>
<td>( 3.0 \times 10^4 )</td>
<td>cub.</td>
</tr>
<tr>
<td>4f Metals</td>
<td>Gd</td>
<td>(-1.2 \times 10^5 )</td>
<td>( 8.0 \times 10^4 )</td>
<td>uni.</td>
</tr>
<tr>
<td></td>
<td>Tb</td>
<td>(-5.7 \times 10^7 )</td>
<td>(-4.6 \times 10^6 )</td>
<td>uni.</td>
</tr>
<tr>
<td></td>
<td>Er</td>
<td>( 1.2 \times 10^7 )</td>
<td>(-3.9 \times 10^6 )</td>
<td>uni.</td>
</tr>
<tr>
<td>Hard Magnets</td>
<td>Sm Co(_5)</td>
<td>( 7 \times 10^6 )</td>
<td>—</td>
<td>uni.</td>
</tr>
<tr>
<td></td>
<td>Nd Co(_5)</td>
<td>(-4 \times 10^7 )</td>
<td>—</td>
<td>uni.</td>
</tr>
<tr>
<td>Spinel Ferrites</td>
<td>Fe(_3)O(_4)</td>
<td>(-2 \times 10^4 )</td>
<td>(-9 \times 10^3 )</td>
<td>cub.</td>
</tr>
<tr>
<td></td>
<td>Cr Fe(_2)O(_4)</td>
<td>( \approx 10^6 )</td>
<td>—</td>
<td>cub.</td>
</tr>
</tbody>
</table>

uniaxial systems. We also note, that 4f metals or its compounds can have rather high anisotropy constants. One exception is Gd that has a 4f shell that is half filled and has an anisotropy similar to Co. (Both Co and Gd, as well as Tb and Er crystallize in hcp structure.) We will discuss the role of the localized 4f electrons in more detail in subsection 2.3. The hard magnets contain both 4f elements and a 3d element to obtain also a high Curie temperature.

Although the anisotropy energies are quite small for a bulk system like Fe, the magnetization of a macroscopic iron sample is nevertheless a quite stable quantity. Assuming that the spins at all atomic sites are coupled stiffly by the exchange interactions, turning the magnetization will require that all the spins are rotated simultaneously so that in total, a considerable amount of energy will be required. Taking the values for Fe from table 1, we see that \( K_1 \) is positive, therefore the easy axis is in the [001] (or any symmetry equivalent) direction. Now let us calculate the magnetic field needed to turn the magnetization direction from the easy axis into a [011] direction: From Eq.(4) we conclude that the needed energy amounts to \( \frac{\mu_B^2}{K_1} = 1.3 \times 10^4 \) J/m\(^3\). Assuming a density of 7.86 g/cm\(^3\) and a mass number of 55.85 g/mol, this corresponds to 0.9574 \( \times 10^{-6} \) eV/atom. Since the magnetic moment of Fe is 2.22\( \mu_B \) and the Bohr magneton is \( \mu_B = \frac{e\hbar}{2m_c} = 57.9 \times 10^{-6} \) eV/T, we see that fields in the order of \( 10^2 \) T are required, which can be produced easily in the laboratory. For hard magnets the required fields can increase up to a few Tesla.

1.2 Temperature and magnetic order

In a bulk system, like Fe, the magnetic order is stabilized by exchange interactions against temperature induced fluctuations. The high Curie-temperature \( T_C = 1043 \) K of Fe suggests already that the involved energy scale is about 100 meV (\( k_B = 8.617 \times 10^{-5} \) eV/K), and therefore five orders of magnitude larger that the anisotropy energy (see last subsection). Although the exchange interaction is strong, it is rather short-ranged and decays exponentially with the distance. Therefore, for two-dimensional systems, Mermin and Wagner [2] showed that no spontaneous magnetization will occur for finite temperatures if the magnetic order is stabilized by an interaction that decays faster than \( (\tau_i - \tau_j)^{-n} \) (where the \( \tau \)'s are the atomic positions and \( n \) is a
In nature, strictly two-dimensional systems do not occur. Even if only one monolayer of magnetic atoms is deposited on a weakly interacting substrate (like Ag), there is always some interaction between the magnetic atoms via the polarized substrate atoms. But even if this interaction did not exist, there is still a possibility to stabilize magnetic order in this monolayer – via the magnetic anisotropy. For a two-dimensional Heisenberg ferromagnet, Bander and Mills [3] demonstrated that there is indeed a critical temperature, if a uniaxial anisotropy is present in the system. If the anisotropy constant is $K$ and the transition temperature for the same Heisenberg ferromagnet in three dimensions is $T_{3D}$, the transition temperature of the two-dimensional system is given by:

$$T_{2D} = T_{3D} / \ln \left( \frac{3\pi \hbar T_{3D}}{4K} \right).$$

(6)

Although we introduced $K$ generally as a function of temperature and magnetization, we dropped this aspect in the above discussion and interpreted the anisotropy constants in a literal sense, i.e. as constants. But as experimental evidence has it, the temperature-dependence $K(T)$ is actually quite strong and the anisotropy vanishes much faster with $T$ than e.g. the magnetic moment.

Fig. 2: Left: temperature induced fluctuations of the magnetic moment around the easy [001] and a harder [011] axis. Right: variation of the magnetization and the anisotropy coefficient $k_2$ and $k_4$ with temperature. A critical exponent $\beta = 1/3$ was assumed.

In 1936 N. Akulov demonstrated, how for cubic systems a relation between $K_1(T)$ and $M(T)$ can be established [4]. Let us assume that the easy axis is in $z$-direction; from Eq.(4) we see that for a small variation $\delta \theta$ of the magnetization around the [001] and [011] directions (figure 2) we get:

$$F([001]) = K_0 + K_1(T = 0) \langle \delta \theta^2 \rangle \quad \text{and} \quad F([011]) = K_0 + \frac{K_4(T = 0)}{4} (1 - \delta \theta^2).$$

(7)

This variation $\delta \theta$ is related to the magnetization $M(T)$ by

$$\frac{M(T)}{M(0)} = \langle \cos \theta \rangle \approx \left\langle 1 - \frac{\delta \theta^2}{2} + \ldots \right\rangle$$

(8)
so that we get for this anisotropy:

\[ F([011]) - F([001]) = \frac{K_1(0)}{4} (1 - 5\delta^2) \approx \frac{K_1(0)}{4} \left( \frac{M(T)}{M(0)} \right)^{10}. \]  

(9)

Since \( \frac{K_1(T)}{K_1(0)} = F([011]) - F([001]) \), we see that

\[ \frac{K_1(T)}{K_1(0)} = \left( \frac{M(T)}{M(0)} \right)^{10} = (T_C - T)^{10/9}. \]  

(10)

where the relation \( M(T) = M(0)(T_C - T)^{3/2} \) has been used. While for cubic systems the exponent is very large (10), for uniaxial systems it can be shown to be only 3. If one expands the anisotropy energy in terms of Legendre polynomials by forming symmetry adapted linear combinations of spherical harmonics:

\[ F = \sum_l k_l g_l(\alpha) = \sum_l k_l \left[ \sum_{m=-l}^{l} A_{lm} Y_{lm}(\alpha) \right] \]  

(11)

this result can be generalized to

\[ \frac{k_l(T)}{k_l(0)} = \left( \frac{M(T)}{M(0)} \right)^{l(l+1)/2}. \]  

(12)

Since in cubic systems \( K_1 \) contains terms of order \( l = 4 \) the exponent is 10; in uniaxial systems \( K_1 \) is formed by terms with \( l = 2 \), leading to an exponent of 3. This result was derived classically by Zener[5], and on a quantum mechanical basis by Callen and Callen [6]. More aspects of finite-temperature effects can be found in the article of U. Nowak in this book.

### 1.3 Domain walls

In the preceding section we have seen that both exchange interaction and magnetic anisotropy contribute to the ordering temperature of magnets. Depending on the dimensionality of the system, one or the other quantity might dominate in influence. Another important example of the interplay between exchange and anisotropy is the formation of domain walls.

![Fig. 3: Schematic representation of a domain wall in a thin film. Through the domain wall, the orientation of the magnetization, \( \theta \), changes with a magnetization profile \( \theta(x) \).](image-url)
If a thin film has an easy axis perpendicular to the surface, the classical dipole interaction (cf. section 2.1) leads to the formation of magnetic domains on this film, i.e. areas, where the magnetization is in the direction of the surface normal, and others, where the magnetization is opposite. These areas form an “antiferromagnet on a large scale”, to minimize the effective stray field of the sample. Two such areas of opposite magnetization, the domains, are separated by a domain wall where the magnetization has to change its direction. The exchange interaction will favor very large domain wall where the spins turn slowly by an angle of $\pi$. Thereby neighboring atoms spins will be almost collinear and ferromagnetically coupled. The anisotropy, however, will favor a small domain wall width, such that only a few atoms spins are not aligned to the easy axis. As a consequence of this competition, the spin directions $\theta(x)$ in the domain wall will be given by the function $\theta(x)$ that minimizes the energy of the domain wall (cf. figure 3):

$$E_{\text{wall}} \sim \int_{-\infty}^{\infty} dx \left( A \theta'^2(x) + K \cos^2 \theta(x) \right).$$

(13)

Here, $A$ is the spin-wave stiffness, i.e. the second derivative of $E(\phi)$ at $\phi = 0$, when $E(\phi)$ is the energy of a spin-spiral where all the directions of the spins in neighboring planes of atoms differ by $\phi$ (here, these planes will be perpendicular to $x$). The function $\theta(x)$ and the domain wall width $w$ will then be given by:

$$\theta(x) = 2 \arctan \left( \exp \left( \sqrt{\frac{K}{A}} x \right) \right) - \frac{\pi}{2} \quad \text{and} \quad w = 2 \sqrt{A/K}.$$  

(14)

We see that large $K$ (due to the low symmetry) and small $A$ (due to the reduced coordination) lead to much smaller domain walls in thin films than in the bulk. E.g. for a monolayer Fe on W(110) a domain wall width of 0.6 nm was measured, for a double layer Fe on the same substrate $w$ was already 3.8 nm [7]. In bulk Fe, domain walls can get as large as a few hundred nanometers.

2 The Physical origin of the magnetic anisotropy

2.1 Classical dipole interaction

Classically, for a crystal with lattice vectors $R$ and atoms $\nu$ with localized magnetic moments $m_\nu$ at positions (within the unit cell) $\tau_\nu$, the dipole energy is

$$E_d = \frac{\mu_0 B^2}{2} \sum_{R,\nu,\nu'} \left( \frac{m_\nu \cdot m_{\nu'}}{|R + \tau_\nu - \tau_{\nu'}|^3} - 3 \frac{[(R + \tau_\nu - \tau_{\nu'}) \cdot m_\nu] [(R + \tau_\nu - \tau_{\nu'}) \cdot m_{\nu'}]}{|R + \tau_\nu - \tau_{\nu'}|^5} \right).$$

(15)

For a ferromagnet with only one atom in the unit cell, this expression simplifies to

$$E_d = \frac{\mu_0 B^2}{2} \sum_{i,j} \frac{m_i m_j}{R_{i,j}} \left( 1 - 3 \cos^2 \theta_{ij} \right)$$

(16)

where $\theta_{ij}$ is the angle between the direction of the magnetic moment and the vector connecting atoms $i$ and $j$. 

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Fig. 4: (a) Dipole-dipole interaction between two ferromagnetically aligned bar magnets at a constant distance (thin line). The thick line indicates the dipole-dipole interaction energy in a polar plot. (b) Same for antiferromagnetically aligned bar magnets. (c) “Chain” of four bar magnets: under the influence of a magnetic field, $H$, the chain will rotate by an angle $\theta$.

For a monoatomic chain, Eq.(16) is simple to evaluate and we see immediately, that the system prefers an orientation of the individual moments in the chain direction, while additional energy is required to magnetize the chain perpendicular to this direction. The situation is equivalent to the usual experience, that two bar-magnets prefer to orient such that the north-pole of the one is directed towards the south-pole of the other magnet (figure 4). In atomic units, the energy difference between in-chain and out-of-chain magnetization for a monoatomic chain with lattice constant $a$ and magnetic moment $m$ is given (in Rydberg per atom) by

$$\Delta E_d = \frac{\mu_B^2}{2} \left( 2 \sum_{j=1}^{\infty} \frac{1}{j^3} \right) \frac{m^2}{a^3} \frac{3}{3} \left[ \cos^2(0) - \cos^2(\pi/2) \right] \approx \frac{3 \cdot 1.202057 m^2}{137.0362 a^3} \approx \frac{m^2}{a^3} 0.192 \cdot 10^{-3}.$$

So, if $m = 2.22 \mu_B$ and $a = 4.84$ a.u. (e.g. for a Co chain deposited on a Cu(001) surface), we obtain $E_d = 8.35 \cdot 10^{-6}$ Ry or $0.114$ meV/atom. As we have seen above in the example of Fe, this energy is quite large as compared to anisotropy energies encountered in bulk systems.

For a monoatomic wire we have seen that the dipole-dipole interaction favors a magnetization in the wire axis. If this would be the only contribution to the magnetic anisotropy, the easy axis of this system would be in chain direction. In a similar way it is easy to show that the easy axis of an antiferromagnetically ordered chain is perpendicular to the chain direction, and for a ferromagnetically ordered film of one monolayer thickness the preferred direction is in the film plane. For an infinite bulk system there is of course no contribution of the dipole energy to the magnetic anisotropy. But any macroscopic sample of finite size is bounded by some surface, so that there will be a contribution from this surface region that is determined by the shape of the sample. Therefore it is often termed shape-anisotropy. Since the size of the magnetic moments at a surface can be quite different from the bulk, it is often difficult to determine from magnetization measurements. For a more detailed discussion of the magnetic anisotropy of bulk systems we refer the reader to ref. [8].

Although it might seem surprising at first sight, the classical dipole interaction is normally not included in ab-initio calculations starting from the Dirac- or Pauli equation (cf. the appendix).
that are based on effective single-particle theories (like the density functional theory). Jansen [9] derived the dipole-dipole interaction from the Hartree energy part of the Breit equation (cf. A.2), which can be written as

\[
\frac{\mu_0^2}{2} \int d^3r d^3r' \frac{1}{|r - r'|^3} \left[ M(r)M(r') - 3 \frac{(r - r')M(r)[(r - r')M(r']}{|r - r'|^2} \right] - \frac{4\pi\mu_0^2}{3} \int d^3r M(r)M(r).
\]

If we assume that the magnetization density \( M \) is localized at the atomic sites \( \tau_\nu \) as \( M(r) = \sum_\nu m_\nu \delta(r - \tau_\nu) \), and ignore the second part of Eq. (17), we recover the classical formula (15). We see, that the dipole-dipole interaction is taken into account by a mean-field type of approximation to the relativistic part of the two-particle interaction. Differences between the dipole energy calculated from the magnetization density (Eq. 17) and the classical dipole formula (15) are caused by the deviation of the actual distribution of \( M(r) \) from spherically centered around the atom sites. The anisotropic magnetic dipolar interaction between the spin moments of electrons of the same atom is called spin-spin coupling and dependent on shape of the orbits of the electrons in a particular state [10]. Normally, these deviations are small and the dipole energy is taken into account by the classical formula with magnetizations as calculated from \textit{ab-initio} methods.

### 2.2 Magnetocrystalline anisotropy

Spherical or elliptical samples, which should show no anisotropy stemming from the dipole-dipole interaction, nevertheless show hard and easy axes. In an infinite, three-dimensional periodic system there is still an anisotropy that comes from the relative orientation between the magnetization and the crystal lattice. To see, how the spin couples to the lattice, consider a free atom: an electron, traveling with a velocity \( \mathbf{v} \) on a classical trajectory around the nucleus, creates though its electric field \( \mathbf{E} \), like a current through a coil, a magnetic field, \( \mathbf{B} \approx -\mathbf{v} \times \mathbf{E} \). This field will couple to the magnetic (spin) moment \( \mu \) of the electron as \(-\mu \cdot \mathbf{B}\). If we assume, that in a solid the crystal field forces the electron to move e.g. in a certain crystallographic plane, the electron spin will be aligned in a direction normal to this plane. In such a way, a uniaxial anisotropy can arise regardless of the shape of a crystal.

To treat this quantitatively on a quantum-mechanical basis, it is necessary to start from the Dirac equation (see appendix). In the Schrödinger equation – even for a magnetic system – there is no term that could differentiate the various magnetization directions. But if we include a certain term from the Pauli equation (a two-component approximation to the Dirac equation - see appendix A.1) we get

\[
\left[ E + eV(r) + \frac{\hbar}{2m} \nabla^2 - \frac{\mu_B}{2mc} \cdot (\mathbf{E}(r) \times \mathbf{p}) \right] \psi = 0.
\]

It is this relativistic correction (of order \( \frac{1}{c} \)) that leads to the coupling between spin-space (\( \sigma \)) and lattice (\( \mathbf{E}(r) \)). If we assume that the electric field is derived from a spherically symmetric

\[b\text{Although this interaction has the form of a Zeeman term (the interaction of the spin with an external magnetic field), due to kinematical effects this spin-orbit interaction is smaller by a factor of two. The origin of this effect is called Thomas-precession [11].}\]
potential (as occurs in the vicinity of an atomic nucleus), we can transform this term

$$\sigma \cdot (\mathcal{E}(r) \times p) = \sigma \cdot (\nabla V(r) \times p) = \frac{1}{r} \frac{dV(r)}{dr} \sigma \cdot (r \times p) = \frac{1}{r} \frac{dV(r)}{dr} (\sigma \cdot \mathbf{L}) = \xi \sigma \cdot \mathbf{L}, \quad (19)$$

where $\mathbf{L}$ is the orbital momentum operator. Therefore, this term is called the spin-orbit coupling (SOC) term with the spin-orbit coupling constant $\xi$. Since the radial derivative of the potential in a crystal will be largest in the vicinity of a nucleus, we can expect that the major contribution to the spin-orbit interaction will come from this region. For an atom $\nu$ then $r$ is the radial part of the vector $r_\nu = r - r_\nu$. Furthermore, since for small $r_\nu$ the potential will be Coulomb-like ($V = -\frac{Z}{r}$), its derivative $\frac{dV}{dr}$ is proportional to the nuclear number of the atom, $Z_\nu$. We thus expect that $\xi$ will be large for heavy atoms, but small for lighter ones.

The magnetocrystalline anisotropy energy (MAE) will then result from the anisotropy of the spin-orbit interaction, i.e. it is the difference of total energies obtained from Hamiltonians including the spin-orbit coupling term with the magnetization pointing in two different directions. Practically, one starts from a solution $\Psi_0$ of the Schrödinger equations (possibly including scalar-relativistic corrections, cf. appendix A.1), and then solves the Hamiltonian including the spin-orbit coupling term with the spin-quantization axis turned into the required direction by means of a spin-rotation matrix $U$:

$$\langle U\Psi_0|H_S + H_{so}|U\Psi_0 \rangle = \langle \Psi_0|H_S|\Psi_0 \rangle + \langle U\Psi_0|H_{so}|U\Psi_0 \rangle =$$

$$= \epsilon_0 + \xi \left( \begin{array}{c} \Psi_0^* \\ \Psi_0 \end{array} \right) U^\dagger \left( \begin{array}{cc} L_z & L_y - i L_x \\ L_y + i L_x & -L_z \end{array} \right) U \left| \begin{array}{c} \Psi_0 \\ \Psi_0^* \end{array} \right\rangle \quad (20)$$

If the orbital moment is small, the last part of Eq. 20 is only a small correction to the energy $\epsilon_0$ obtained from the Schrödinger equation and the magnetization direction of the solution will point into the direction of the spin-quantization axis described by $U$.

From the above equations it is clear that both, strong spin-orbit coupling and a sizeable orbital moment are necessary for a large contribution to the magnetic anisotropy. But it is also necessary that the spin-orbit interaction gives different energy contributions for different magnetizations of the sample. In principle there are two possibilities to imagine how this could happen: (i) the orbital moment is fixed to the lattice and its projection on the axis of the spin moment varies with the magnetization direction or (ii) the spin and orbital moments are collinear and depending on the magnetization direction the size of the orbital moment varies. Normally, we observe collinear spin- and orbital moments. The rotation of the orbital moment by an external magnetic field can then lead to structural changes of the crystal. This phenomenon is called magnetostriiction and is discussed e.g. in ref. [8].

Sometimes, in analogy to the Heisenberg Hamiltonian describing the exchange interaction in a crystal, the spin-orbit coupling is cast into a form $\sum_i \xi_i L_i S_i$ where $i$ is a particular atomic site. Then, evidently, another term coupling the spin of a site $i$ to the orbital motion at site $j$ is conceivable: $C_{ij} L_i S_j$. This spin-other orbit interaction is, like the dipole-dipole interaction, derived from the Breit equation (appendix A.2). In the Hartree approximation it was included in ab-initio calculations but was found to be much weaker than the formerly described spin-(same) orbit interaction [12].

Ab-initio calculations are a valuable tool to sort out the relative importance of the various contributions to the magnetic anisotropy. In most calculations only spin-orbit coupling (in an effective one-particle, Schrödinger-like theory, like Eq. 18) and the classical dipole-dipole energy (Eq. 15) have been included in a density functional theory framework. Typically, for bulk
systems like Fe or Co, the results or these calculations differ from the experimental values by a factor 2. Up to now, systematically going beyond these approximations (either by taking into account more terms of the Dirac-equation [13], or explicit inclusion of “two-particle” interaction terms [12]) could not significantly improve this agreement. Inclusion of “orbital polarization” terms [14] or correlation terms via the LDA+U method [15] improve the results in some cases, but a rigorous theory behind these correction terms is missing.

2.3 Orbital moments and single-ion anisotropy

In a bulk crystal of high symmetry (e.g. fcc or bcc), most orbitals of the valence electrons are directed in the nearest or next-nearest neighbor directions. The crystal environment of the atom confines the electrons then to directional bonds and effectively suppresses thereby orbital motion. Spin-orbit coupling tries to counteract this “quenching” of the orbital moments and – in some cases – a sizeable orbital moment can even occur in a bulk crystal.

As a prototypically example let us consider magnetite, Fe$_3$O$_4$, a classical magnetic material crystallizing in the inverse spinel structure. The O$^{2−}$ ions form a close packed cubic lattice and 1/8 of the tetrahedral sites are occupied with Fe$^{3+}$, while the remaining Fe$^{2+}$ and Fe$^{3+}$ ions each occupy 1/4 of the octahedral sites. In these crystal fields, the Fe $d$-levels will split up in $t_{2g}$ and $e_g$ levels. In the tetrahedral crystal field, the $e_g$ levels will have lower energy, while on the octahedral sites the $t_{2g}$ levels will be lower in energy. While in the free atom the orbitals could be classified according to their magnetic quantum number $m = -2, -1, 0, 1, 2$, the crystal field now forces the formation of new linear combinations to form orbitals with vanishing orbital moment (e.g. the $t_{2g}$ states $d_{xy}$ and $d_{xz}$ are linear combinations of the atomic $m = -1$ and $m = +1$ orbitals). Due to a small trigonal deformation, the $t_{2g}$ levels show an additional splitting in the spinel structure (cf. figure 5). Assuming that the Fe$^{3+}$ ions have a $d^5$ configuration and this half filled $d$ shell corresponds to a zero orbital moment, these atoms will not contribute much to the magnetocrystalline anisotropy. In Fe$^{2+}$, the additional electron will occupy the lowest, split-off level of the $t_{2g}$ states. When we substitute Fe by Co, we have another $d$-electron that can now occupy the remaining, doubly degenerate $t_{2g}$-like states. Since this electron is not involved in bonding, these states can now again form linear combinations with considerable orbital moments in a specific direction. As has been shown by Slonczewski [16], it is this orbital moment that leads to the pronounced difference in the magnetic anisotropy between magnetite and CoFe$_2$O$_4$ (cf. table 1).
It is important to realize in this context, that out of certain $d$-levels, only orbital moments pointing in a certain direction can be formed. E.g. a $d_{xy}$ and a $d_{x^2-y^2}$ orbital can only be combined to form an orbital moment in $z$ direction. An orbital moment pointing in $x$-direction has to be formed from electrons that can move in the $(y, z)$-plane, and this is impossible within only the $d_{xy}$ and $d_{x^2-y^2}$ orbitals. If now two appropriate orbitals are degenerate and occupied by a single electron (and thus forming the Fermi level), it is rather straightforward to identify the resulting direction of the orbital moment using group theory [17]. In a metal, where several bands are crossing the Fermi level, $\epsilon_F$, it is basically the sum of all contributions from bands near $\epsilon_F$ that determine the orbital moment. In second-order perturbation theory the expectation value of the orbital moment operator $L$ can be written as:

$$\langle L \rangle = \sum_{i,j} \frac{\langle \psi_i | L | \psi_j \rangle \langle \psi_j | H_{so} | \psi_i \rangle}{\epsilon_i - \epsilon_j} f(\epsilon_i) (1 - f(\epsilon_j)),$$

where $H_{so}$ is the spin-orbit coupling Hamiltonian and $f$ is the Fermi function ensuring that the wavefunction $\psi_i$ is occupied and $\psi_j$ is unoccupied. Van der Laan [17] has shown, that in the absence of spin-flip terms (i.e. when the majority and minority band are well separated by the exchange interaction), the spin-orbit coupling changes the total energy of a system in second-order perturbation theory as:

$$\delta E = \sum_{i,j} \frac{\langle \psi_i | H_{so} | \psi_j \rangle \langle \psi_j | H_{so} | \psi_i \rangle}{\epsilon_i - \epsilon_j} f(\epsilon_i) (1 - f(\epsilon_j)) \approx -\frac{1}{4} \xi \hat{S} \cdot \left[ \langle L^z \rangle - \langle L^x \rangle \right],$$

where $\xi$ is the radial part of the spin-orbit Hamiltonian (Eq. 19), $\hat{S}$ is the direction of the spin moment, and $L^x$ and $L^z$ are the orbital moment vectors of the spin-down and spin-up bands, respectively. If the spin-up band is completely filled, we see that energy change, $\delta E$, is proportional to the size of the orbital moment and the magnetocrystalline anisotropy energy (MAE), i.e. the difference of $\delta E$ for two different magnetization directions, will be proportional to the difference in the orbital moments. This relation between orbital moment anisotropy and MAE was first derived by Bruno [18].

For a given system it is often hard to tell which kind of effect, the dipole - dipole or the spin-orbit interaction, will give the major contribution to the anisotropy energy. For systems with very small orbital moment, like bulk Eu that has a half-filled 4$f$ shell ($S = 7/2, L = 0$) and only $s$-electrons in the conduction band, the spin-orbit interaction is weak (as can be inferred already from the fact that bcc Eu has a spin-spiral magnetic ground state). Therefore, the shape anisotropy is likely to dominate except for spherical or elliptical samples that can be easily magnetized in all different directions. Gd, too, has a half-filled 4$f$ shell, but one $d$-electron more than Eu. Its magnetic anisotropy is also small, but due to the additional $d$-electron the ordering temperature is much higher than in Eu. With again one more electron, hcp Tb has an orbital moment of $L = 3$ and there is no easy way to change the magnetization direction of a Tb crystal except for heating it up beyond the Curie-temperature and cooling under an external field in a symmetry-equivalent direction. In the compressed hcp lattice of Tb ($c/a = 1.59$) the flat, pancake-like minority 4$f$ electron is locked in the crystal lattice [19] and the easy axis is parallel to the $b$-axis. This strong anisotropy, that can be regarded as coming from a single atom is often referred to as single-ion anisotropy.

From the above discussion it should be clear, that orbital effects are most efficiently quenched in a bulk-like environment. There, the coordination is highest and high symmetry can additionally
reduce the magnetic anisotropy. But in (quasi) low-dimensional systems like thin films, chains and wires, or adatoms on a substrate spin-orbit coupling will be of much higher importance and large anisotropies can be expected.

3 Magnetic anisotropy in low dimensions

The most evident change that occurs, when going from the bulk material to lower dimensional structures, is the reduction of coordination. An atom in a closed-packed structure in three dimensions has twelve nearest neighbors, but only six in two dimensions (hexagonal film) or two in one dimension (wire). In a bulk material, most electrons are involved in bonding towards neighboring atoms and – since the Pauli principle requires that pairs of electrons of opposite spin form the bonds – most bulk materials are nonmagnetic. Normally, a lower coordination leads to less electrons involved in forming bonds and the “unbound” electrons can lead to magnetism. Put in a band-picture, we can also say that in low dimensions we get a smaller bandwidth and this favors (in the Stoner model) the formation of magnetic moments. A more detailed account of spin moments and exchange interaction in low-dimensional systems will be given in the article of S. Blügel of this volume.

Indeed, while of the main group elements only five are magnetic (Cr, Mn, Fe, Co and Ni), when deposited as thin films on surfaces also other elements like V, Ru or Rh become magnetic; as atoms, almost all are magnetic. So, we see that lower dimensionality favors an increase of the spin-moment. But it also enables the formation of large orbital moments, as can be seen from most atoms. Also in the case of the orbital moment the hybridization with some neighboring orbitals “locks” the electrons in place and quenches the orbital moment. Imagine a Sc atom
with only one \(d\)-electron: as an atom, according to Hund’s rules, the orbital moment will be maximized and antiparallel to the spin moment. But when Sc atoms are assembled in a square lattice, orbitals with \(m = -2\) and \(m = +2\) will form linear combinations to build \(d_{xy}\) and \(d_{x^2-y^2}\) orbitals of which the latter one will be occupied. The more these two levels are split in energy, the more difficult it will be for the electron to “circle” around the atom and, therefore, to form an orbital moment.

Table 2: Spin (\(\mu_s\)) and orbital (\(\mu_l\)) moments of Fe, Co and Ni as bulk materials (\(n=3\)), thin films (\(n=2\)), wires (\(n=1\)), and atoms (\(n=0\)). For film and wires the orbital moments parallel (\(\parallel\)) and perpendicular (\(\perp\)) to film-plane or wire-axis are given; the geometry is chosen as if the film or wire would have been grown epitaxial on a Pt(111) substrate. The column MAE indicates the order of magnitude of the magnetocrystalline anisotropy energy for different dimensions. The results were obtained in the generalized gradient approximation to the density functional theory.

<table>
<thead>
<tr>
<th>(n)</th>
<th>(\mu_s)</th>
<th>(\mu_l)</th>
<th>(\mu_s)</th>
<th>(\mu_l)</th>
<th>(\mu_s)</th>
<th>(\mu_l)</th>
<th>MAE [meV]</th>
</tr>
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<tbody>
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<td></td>
<td>(\parallel)</td>
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<td>(\parallel)</td>
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<td>(\parallel)</td>
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<td></td>
</tr>
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<td>3</td>
<td>2.05</td>
<td>0.05</td>
<td>1.59</td>
<td>0.08</td>
<td>0.62</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
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<td>0.07</td>
<td>0.10</td>
<td>2.09</td>
<td>0.20</td>
<td>0.19</td>
<td>0.94</td>
</tr>
<tr>
<td>1</td>
<td>3.22</td>
<td>0.72</td>
<td>0.27</td>
<td>2.32</td>
<td>0.98</td>
<td>0.77</td>
<td>1.18</td>
</tr>
<tr>
<td>0</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>2</td>
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</table>

In table 2 some representative values of spin and orbital momentum have been collected. These are calculated results and, experimentally, films, wires and adatoms are normally deposited on some substrate, that will once more quench the values, especially for the orbital moments. But the trends are observable and we can see that in lower dimensions spin and orbital moment get increased. This, in turn, enhances the magnetic anisotropy. As the influence of the exchange interaction gets smaller (due to the reduced coordination), the influence of the anisotropy rises and it is fair to say that, as in bulk systems the exchange interaction dominates, in reduced dimensions much of the magnetic behavior is controlled by the magnetic anisotropy. Some typical examples will be presented in the next subsections.

### 3.1 Thin films

Thin magnetic films, deposited on a (probably nonmagnetic) substrate, provide ideal systems to test the concepts developed in the preceding paragraphs. Experimentally, X-ray magnetic circular dichroism (XMCD) spectroscopy is a powerful method to determine element-specific the charge, spin and angular momentum on a surface [20]. But also other experimental techniques, like magnetometric measurements and magnetic resonance provide insights into the magnetic properties of thin films. Together with ab-initio calculations already a very clear understanding of these structures has developed [21].

Let us first discuss the case of an unsupported, square \(d\)-metal monolayer, following J. Stöhr [20]. Assume that the \(d\)-band is substantially exchange split and more than half filled, so that we only have to consider the (partially filled) minority band. The \(d\) orbitals at each atom site experience
in the monolayer plane a crystal field, that leads to a splitting of these levels: if the surface normal is assumed to be in z-direction, the $d_{xy}$ and $d_{x^2-y^2}$ levels will experience a stronger field than the out-of-plane directed $d_{zx}$, $d_{yz}$, and $d_{z^2}$ orbitals. The crystal field leads to a splitting of $2V_\parallel$ for the in-plane oriented orbitals and $2V_\perp$ for the out-of-plane oriented ones. In a band-picture, these splittings can be translated into bandwidths, which will then be twice as large (cf. figure 7). Normally, $V_\parallel$ will be larger than $V_\perp$, so that $R = V_\perp/V_\parallel < 1$. (If, however, the monolayer is sandwiched between two slabs of nonmagnetic material the situation could be changed.)

Assume that – like in the case of Co – the minority band is half filled; the $d_{xy}$ and $d_{x^2-y^2}$ states will split symmetrically by $\pm V_\parallel$ around the Fermi level, the $(d_{zx}, d_{yz})$ and $d_{z^2}$ states by $\pm V_\perp$. In a band-picture, these splittings will of course depend on the considered $k$ point. Now we can use perturbation theory (Eq. 21) to calculate the orbital moments. The result [20]

\[
m_{\parallel \text{orb}} = \frac{\xi \mu_B}{2V_\parallel} \left( \frac{3}{R} + \frac{2}{R+1} \right) \quad \text{and} \quad m_{\perp \text{orb}} = \frac{\xi \mu_B}{2V_\parallel} \left( \frac{3}{R} + \frac{4}{R+1} \right)
\]

shows, that only the in-plane orbital moment, $m_{\parallel \text{orb}}$, depends on the splitting of the out-of-plane oriented states, while the out-of-plane orbital moment is only quenched by the in-plane crystal field. This is intuitively clear, since $m_{\parallel \text{orb}}$ corresponds to an in-plane motion of the electron, i.e. a hopping between the $d_{xy}$ and $d_{x^2-y^2}$ states that are separated by $V_\parallel$. For the calculation of the magnetocrystalline anisotropy energy we can use Eq.(22), that gives:

\[
E_{\text{MCA}} = \frac{\xi}{4\mu_B} (m_{\parallel \text{orb}} - m_{\perp \text{orb}}) = \frac{\xi^2}{8V_\parallel} \left( \frac{3}{R} + \frac{2}{R+1} - 4 \right).
\]

From this equation we see that, as long as $R < 1$, an in-plane magnetization is obtained, while for $R > 1$ an out-of-plane easy axis is possible. Indeed it is observed that Co-monolayers on a weakly interacting substrate (like Cu(001)) have an in-plane easy axis, while Co layer sandwiched in Pt has a perpendicular magnetization.

If more than one or two layers of magnetic material are deposited as thin film, the layers that are not forming an interface (to the vacuum and the substrate) will show more bulk-like properties. It is usual to separate the volume-like contributions to the effective anisotropy constants, $K^V$, from the surface- (or interface-) term $K^S$. If $t$ is the thickness of the film, the relation

\[
K^{\text{eff}} = K^V + 2K^S/t
\]

Fig. 7: Left: $d$-level splittings at a given $k$-point in a square monolayer. The density of states is shown on the right.
Fig. 8: Schematic drawing of a five monolayer Ni film on a Cu substrate; the bulk-like, surface and interface regions are marked as V, S, and I, respectively. Right: Schematic plot of the anisotropy (K) versus inverse film-thickness (1/t) plot: the volume-like contribution, $K_V$, is given by the intersection with the ordinate, the surface-like term, $K_S$, can be deduced from the slope of the curve. Together with the shape anisotropy, $K_{\text{shape}}$, these values determine the in-plane / out-of-plane / in-plane transition of the easy axis for Ni films on Cu(001).

is used, where we note that no difference between surface and interface term is made and they are summed up to $2K_S$. While for smaller thicknesses $K_S$ can dominate, for thick films $K_V$ can determine the easy axis. If these terms have different sign, a reorientation of the easy axis might occur. A well investigated example is the system Ni/Cu(001) [22]: For up to seven layers Ni, an in-plane easy axis of the Ni film is found. Then a reorientation to perpendicular magnetization sets in and only very thick films (more than 50 monolayers) show again in-plane magnetization. Here $K_2$ is negative, about $-85\mu eV/atom$ at room temperature, while $K_V$ is positive, approximately $30\mu eV/atom$. So we expect a reorientation between 5 and 6 monolayers, but actually the shape anisotropy contributes another $-10\mu eV/atom$ to $K_V$ (the shape anisotropy in thin films always favors in-plane magnetization). Therefore, the transition sets in between after 7 monolayer thicknesses. But we have to realize, that the value of $K_V$ is much larger than the bulk value of fcc Ni. In fact, LEED measurements demonstrated that Ni grown on Cu(001) is actually strained, the in-plane lattice constant is 1.6% larger than in fcc Ni. To compensate this strain, the spacing between the Ni layers is smaller than in the bulk. From the arguments of the last paragraph we would now suppose that $V_L > V_V$, therefore $R > 1$ and, indeed, $K_V$ favors perpendicular magnetization (although the band-filling of Ni does not correspond to the assumptions underlying Eq. 24). In very thick films, the structure of Ni relaxes back to fcc and the size of $K_V$ decreases until the influence of the shape anisotropy once more brings the easy axis back in-plane.

From the numbers above we see, that the magnetic anisotropy of the Ni layers is almost one order of magnitude larger than the values encountered in the bulk (table 1). The tetragonal distortion in the film already changes $K_V$ from about $3\mu eV/atom$ (favoring the (111) direction) to $30\mu eV/atom$ (favoring the (001) direction). Directly at the surface, the values are still larger. It is the broken symmetry at the surface and the reduced coordination of the surface atoms that leads to these high values. While this suggests, that calculations of the anisotropy should be easier for surfaces than for bulks, in reality new problems arise: The reduced coordination and symmetry at the surface gives rise to relaxations or reconstructions of the atomic layers that influence the
magnetic anisotropy. Normally, the surface layer relaxed towards the bulk to compensate for the loss of nearest neighbors (by reducing the distance to its neighbors and, thereby, increasing the hybridization) and this counteracts exactly the mechanism that leads to an increased orbital moment at the surface, i.e. it enlarges the crystal field splitting. (The same is true for the spin-moment that is normally larger at surfaces, but then, again, reduced by relaxations.) The magnetocrystalline anisotropy is a quantity that is highly sensitive to structural changes, this has to be kept in mind when calculations that do not take into account relaxations are encountered. This sensitivity is of course also reflected in experiments, where different growth conditions can lead to different structural properties and, therefore, to seemingly identical thin films with different anisotropies.

Another note we must add here, that the substrate not always plays only a passive role, as Cu(001) did in the above example. Of course the magnetic moment of the interface substrate atoms, that is induced by the magnetic film, is rather small (typically \(1/20\) of the magnetic moment of the film). But when the nuclear number of the substrate atoms is large, the spin-orbit coupling constant \(\xi\) is also large (e.g. as compared to the 3d-element that forms the thin film). As we can see from Eq.(24), this constant enters quadratically in the expression for the magnetocrystalline anisotropy energy. So, even when the induced moment is tiny, a substrate like W or Pt can still have a significant effect on the MAE in thin films grown on these substrates. So, e.g. a single Fe monolayer on a W(110) substrate can have a significant effect on the MAE in thin films grown on these substrates.

### 3.2 Wires and chains

In the last years, the controlled growth of stripes and wires on step edges \([23]\) and semiconductor surfaces \([24]\) allowed the investigation of one-dimensional structures. Experimentally ferromagnetism was reported in Co chains deposited on Pt(997) step-edges: Gambardella et al. \([25]\) found an orbital moment for Co chains on Pt(997) of \(0.68 \, \mu_B\), the easy axis being tilted by \(43^\circ\) to the surface normal with an MAE of about \(2 \, \text{meV/atom} \) at \(45 \, \text{K}\). Depositing more than one strand of Co on this surface leads to an oscillation of the easy axis in the plane perpendicular to the wire direction \([26]\).

Let us first discuss the magnetic properties of a single Co chain: The shape anisotropy of chain has already been discussed in section 2.1. For an understanding of the orbital magnetism and the spin-orbit coupling in this system we start from a Co dimer. The schematic energy level diagram is shown in figure 9. For simplicity we only consider the minority 3d levels and their hybridization: Assuming that the dimer axis is in \(z\)-direction, we expect that the \(d_{z^2}\) orbitals will form \(\sigma\)-bonds, the \(d_{xy}\) and \(d_{yz}\) orbitals will combine to \(\pi\)-bonds, while the \(d_{xz}\) and \(d_{x^2-y^2}\) orbitals will be mainly non-bonding (since they are directed perpendicular to the dimer-axis). But since these non-bonding states are only singly occupied, now more “atomic-like” linear combinations can be formed. Remember, that the \(d_{xy}\) and \(d_{x^2-y^2}\) orbitals are linear combinations of the atomic \(m = +2\) and \(m = -2\) levels. This means, that a \(m = 2\) orbital can be formed, and, if occupied, an orbital moment of 2 can be obtained.

If we look now at the bandstructure (obtained with density functional theory in the local spin-density approximation (LSDA)) of an infinite Co chain (right picture in figure 9), we can more or less identify the bands corresponding to the Co-dimer levels: Bands with strong positive dispersion correspond to \(\sigma\)-bonds, those with negative dispersion to \(\pi\)-bonds. But most prominent at the Fermi level is the very flat band with small positive dispersion; this is the equivalent of
the non-bonding δ-states. Notice, that without spin-orbit coupling (left bandstructure) this band is doubly degenerate: there are no contributions in the LSDA functional that lead to an orbital polarization. But with spin-orbit coupling included, these bands can be seen to split: if the spin-quantization axis is parallel to the chain direction (middle bandstructure), one of the bands gets preferentially occupied. This is the band that – if fully occupied – leads to an orbital moment of $m = +2$. Actually a smaller orbital moment of $0.9 \mu_B$ is obtained. When the spin-quantization axis is perpendicular to the chain direction, other bands are mixing and the orbital moment is much smaller. As we know from our previous discussion, the anisotropy in the orbital moment is approximately proportional to the magnetocrystalline anisotropy and, therefore, the easy axis is parallel to the chain direction.

The fact, that experimentally of a Co chain on Pt(111) an easy axis perpendicular to the chain direction is observed, seems to be its cause in the interactions with the Pt substrate. Apart from its two nearest Co neighbors, a Co atom in a chain deposited on a (997) surface actually has five nearest Pt neighbors that give this system again a more surface-like character. Recent calculations [27, 28] indeed show an easy axis that has a large component perpendicular to the surface. Both, the experimentally observed MAE and the orbital moment are smaller than the LSDA results for an unsupported chain. One should note here that within LSDA normally both quantities are underestimated and several methods have been discussed in the literature how this deficiency can be overcome [29].

Also in the field of one-dimensional magnetic systems calculations indicate that a large number of metals that are nonmagnetic in the bulk can be magnetic in a one-dimensional arrangement. The experimental difficulties to prepare truly one-dimensional systems are even harder to overcome than in the two-dimensional case. New strategies, like coating or filling carbon nanotubes with magnetic atoms [30] are just evolving. Various methods to connect magnetic atoms by organic molecules to form chain-like structures have been developed [31], chain and wall-like structures can be synthesized out of metal-organic building blocks [32]. Although this is a
rapidly growing field with a high potential for new developments, one has to realize that the magnetic interactions mediated through the organic ligands are weak and magnetic order – if it exists at all – is only obtained at very low temperatures.

### 3.3 Adatoms and clusters

A single atom is of course the extreme case of a low-dimensional magnetic system. Here, the orbital magnetic moments can no longer be considered as some “side effect” of the spin magnetic moment, like in the bulk. Up to now, we only considered projections of the magnetic moments onto a selected axis \(m_s, m_l\), we never had to couple the vector quantities \((S, L)\) to a total angular moment \((J)\) as usual in the theory of atoms.

From the point of view of the magnetic anisotropy, of course, a free atom is uninteresting. If a single atom is put on a substrate, it will naturally lose some of its localized, atomic properties. Experiments have shown that, on (or in) alkali surfaces, impurities of Fe, Co or Ni show still almost unquenched orbital moments [33]. Ab-initio calculations [34] confirm these findings, but the question of the magnetic anisotropy was not addressed. A little bit more interaction between substrate and adatom than on alkali substrates can be expected on noble metals. Cu, Ag, and Au have mainly s-electrons at the Fermi level and especially in Ag the d-band is low. Calculations for several transition metal adatoms on a Ag(001) surface have shown [35], that all 3d-metals from Ti to Ni, and 5d-metals from Ta to Os are indeed magnetic and that their magnetocrystalline anisotropy energy should be (at least in some cases) very large. Due to their large nuclear number, of course the 5d-metals on average show larger anisotropies, even though the magnetic moments are of similar size as in the 3d-metals. Experimentally and theoretically a number of Co clusters on a Pt(111) have been investigated [36]. As expected, on a transition metal substrate the orbital magnetic moments are again lower. The evolution of orbital moment and magnetic anisotropy with increasing cluster size showed the expected decrease from more than \(1\mu_B\) and about 10 meV/atom for a single adatom to \(0.4\mu_B\) and 1 meV/atom for clusters of four or five atoms.

**Fig. 10:** Schematic structure of the molecular magnet \([\text{Co}_4 (\text{hmp})_4 (\text{CH}_3\text{OH})_4 \text{Cl}_4]\). The hmp (deprotonated hydroxymethyl pyridine) group is represented on the lower right. The local easy axis is indicated by the small arrow.
Like in the case of organometallic one-dimensional magnets, it is also possible to couple together several magnetic atoms by some organic ligands. These molecular magnets are typically quite large and complex, like the Mn\(_{12}\)-acetate that, in addition to a Mn\(_{12}\)O\(_{12}\) cluster in its core, contains 16 acetate radicals (attached to the outer eight Mn atoms of the cluster) and four water molecules. Such a cluster, consisting of eight Mn\(^{3+}\) and four Mn\(^{4+}\) ions that are coupled antiferromagnetically has a total magnetic moment of 20µB. The magnetic properties of molecular magnets normally is described by a quantum Heisenberg model. Experimentally, the tunneling of individual spins in the presence of a magnetic field can be observed. The second order contribution to the anisotropy energy that accounts for the tunneling barrier of a spin was determined to be in the order of 0.4 meV/atom in this system [37].

A molecular magnet with a simpler structure and a larger magnetic anisotropy is the Co cuban shown in figure 10. The core of this cluster is a cube of Co and O atoms, the local coordination of the Co atoms is sixfold and consists of a hydroxymethyl group, N, Cl and three O. Calculations have shown [38] that, depending on the exact structure, the MAE can be up to 15 meV, the local hard, medium and easy axis pointing in the directions of the O, N, and Cl atoms respectively.

A detailed discussion of molecular magnets can be found in this volume in the contribution of J. Schnack.

Appendices

A  The Dirac equation

A relativistic theory for an electron (of charge \(-e\)) in an external scalar potential \(V\) and a vector potential \(A\) can be formulated via the Dirac equation

\[ H\Psi = +i\hbar \frac{\partial}{\partial t} \Psi = E\Psi; \quad H = -eV(r) + \beta mc^2 + \alpha \cdot (cp + eA(r)). \]  

(26)

Here, \(\alpha\) is a vector of 4 \times 4 matrices, that can be written in terms of the Pauli spin-matrices, \(\sigma\), while \(\beta\) is a matrix of same rank, expressible in terms of the 2 \times 2 unit matrix \(I_2\):

\[ \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}, \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \]

The Hamiltonian acts on a four-component wavefunction \(\Psi\) that can be written as a 2-vector of the so-called large and small components, \(\psi\) and \(\chi\). For this components the Hamiltonian Dirac equation can be written as

\[ (E - 2mc^2 + eV(r))\psi = \sigma \cdot (cp + eA(r))\chi \]  

(27)

\[ (E + 2mc^2 + eV(r))\chi = \sigma \cdot (cp + eA(r))\psi \]  

(28)

where \(\sigma\) is the vector of Pauli matrices. In the non-relativistic limit, these equations reduce to the Schrödinger equation for the large component. Discussions of the Dirac theory are available in most textbooks on quantum mechanics, we follow here the book of Bethe and Salpeter [39].
A.1 Spin-Orbit coupling

Substituting Eq.(28) in (27) and retaining only terms up to order \((v/c)^2\), it is possible to formulate an equation (sometimes termed Pauli equation) for the large component only:

\[
\begin{align*}
E + eV(r) + \frac{\hbar}{2m} \nabla^2 + \frac{1}{2mc^2} (E + eV(r))^2 + \frac{\hbar}{mc} A(r) \cdot \nabla - \frac{e^2}{2mc^2} A^2(r) + \\
+i \frac{\hbar}{(2mc)^2} \mathbf{E}(r) \cdot \mathbf{p} - \frac{\hbar}{(2mc)^2} \sigma \cdot (E(r) \times \mathbf{p}) - \frac{\hbar}{2mc} \sigma \cdot \mathbf{H}(r) + \\
\end{align*}
\]

\[
\psi = 0 \tag{29}
\]

where the gradient of \(V\) and the curl of \(A\) have been written explicitly as electric (\(E\)) and magnetic (\(H\)) fields. In the non-relativistic limit the first three terms give the ordinary Schrödinger equation.

In the second line, the last term describes the interaction of the spin of the electron with an external magnetic field. Introducing the Bohr magneton, \(\mu_B = \frac{e\hbar}{2mc}\), as the unit of magnetic moment, this term can be written as a Zeeman energy \(\mu_B \sigma \cdot \mathbf{H}\).

If we rewrite the term containing the vector product in Eq.(29) as

\[
-\frac{\mu_B}{2mc} \sigma \cdot (E \times \mathbf{p}) = -\frac{\mu_B}{2} \sigma \cdot \left(\frac{1}{c} E \times \mathbf{v}\right) = -\frac{\mu_B}{2} \sigma \cdot \mathbf{H}' \tag{30}
\]

we see, that apart from a factor \(\frac{1}{2}\) this term has also the form of a Zeeman term. (For an explanation of this factor see e.g. ref. [40].) This is the interaction of the electron’s spin with the magnetic field that can be generated by its own motion. In a classical picture, an electron orbiting around a nucleus generates an orbital moment that couples to its spin moment via this term. Therefore it is called the spin-orbit interaction term.

It should be noted that the Pauli matrices \(\sigma\) couple the spin-up and spin-down part of the large component of the wavefunction. In the absence of vector potentials, the remaining terms of Eq.(29), accounting e.g. for the relativistic mass correction (fourth term), are sometimes called scalar-relativistic corrections since they do not lead to a coupling of the spin-components of the wavefunction.

A.2 Breit interaction

To generalize the Dirac equation (26) in order to introduce also the interaction between two particles one could be tempted to write

\[
(E + H_1 + H_2 + \frac{e^2}{r_{12}})\Psi = 0
\]

where \(H_1\) and \(H_2\) are the Hamiltonians of Eq.(26) and \(r_{12}\) is the distance between the two particles 1 and 2. This non-relativistic extension is not even approximately Lorentz invariant, and in fact a relativistic description of the two-electron problem is not easy. A well-established approximation is provided by the Breit equation,

\[
(E + H_1 + H_2 + \frac{e^2}{r_{12}})\Psi = -\frac{e^2}{2r_{12}} \left[ \alpha_1 \alpha_2 + \frac{\alpha_1 \cdot r_{12}}{r_{12}^2} \frac{\alpha_2 \cdot r_{12}}{r_{12}^2} \right] \Psi \tag{31}
\]

where the Dirac matrices \(\alpha_i\) act on particle \(i\) only.
While it would lead to far to discuss here all the approximations and consequences of this additional term, we just mention that it is possible to transform also this equation in a kind of Pauli equation (using similar approximations as in deriving Eq.(29)). Then, apart from several other terms encountered already in the last section (scalar relativistic corrections, spin-orbit coupling and Zeeman term), we find

\[
H_d = 4\mu^2 \left\{ -\frac{8\pi}{3}(s_1 \cdot s_2)\delta^{(3)}(r_{12}) + \frac{1}{r_{12}^3} \left[ s_1 \cdot s_2 - \frac{3(s_1 \cdot r_{12})(s_2 \cdot r_{12})}{r_{12}^2} \right] \right\} \tag{32}
\]

were \(\delta^{(3)}\) is the 3-dimensional (Dirac) delta function and \(s_i = \frac{3}{2}\sigma\) is the spin operator of particle \(i\). This term represents the interaction between the (spin) magnetic dipole moments of the two electrons.
References


[40] L. H. Thomas, Nature, London 107, 514 (1926); see e.g. Ref.[11]