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Basic Magnetism (II. Magnetization processes)

Towards the macro-world of magnetics

Magnetic anisotropies: 1 - crystal anisotropy

Origin

Temperature behaviour

Crystal anisotropy (single-ion)

The Heisenberg exchange hamiltonian is isotropic, depending on the mutual directions of spins S_i and S_i :

$$\mathcal{H} = -\sum_{i \neq j} \mathcal{G}_{ij} \mathbf{S}_i \cdot \mathbf{S}_j = -\sum_{i \neq j} \mathcal{G}_{ij} \left(S_{xi} S_{xj} + S_{yi} S_{yj} + S_{zi} S_{zj} \right)$$

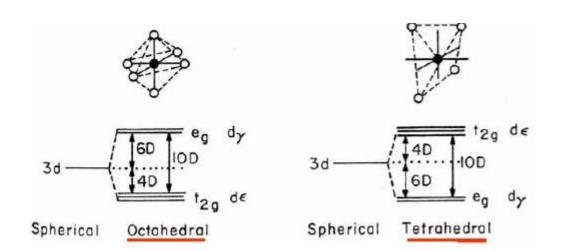
Real magnetic materials, however, exhibit a *crystal magnetic anisotropy*, which is basically related to spin-orbit coupling.

Spin-orbit coupling correlates the direction of spin with the orientation of electron orbits



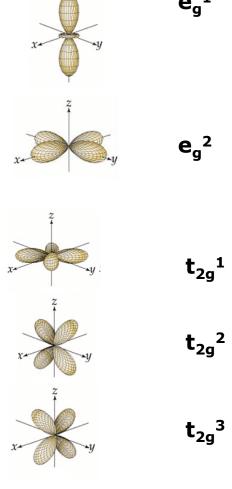
Energies of electron orbitals are influenced by crystal symmetry – therefore, the *spins* preferentially align in order to minimize the *orbit* energy, which depends on *crystal symmetry*

The **crystal field** – already introduced to explain the quenching of orbital momentum - is responsible for the emergence of such a magnetic anisotropy (*single-ion anisotropy*).



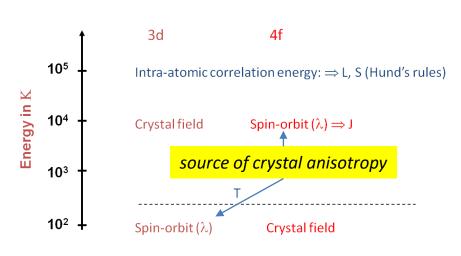
The energy of the system is markedly affected by the actual arrangement of neighboring atoms/ions.

As a result, there will be preferred (= low-energy) directions spontaneously taken by **M**



For transition metal ions, magnetic anisotropy is usually treated by evaluating the crystal field splitting and adding spin-orbit coupling as a perturbation. Crystal-field splitting is much larger than spin-orbit coupling for 3d electrons.

Instead, in rare-earth (RE) metals and RE-intermetallics, crystal-field splitting is much weaker than spin-orbit energy. Large S.O. coupling → large magnetic anisotropy of RE metals/intermetallics.



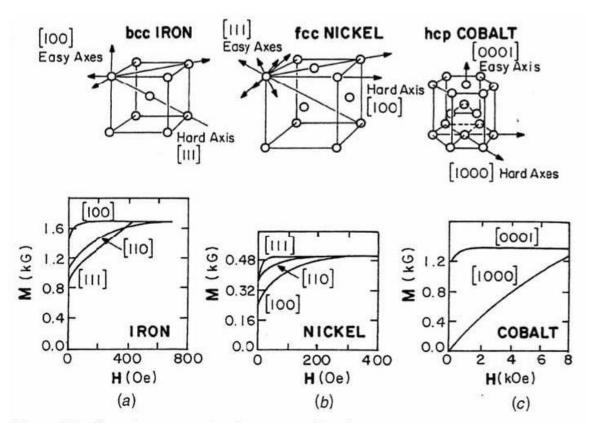
Two-ion crystal anisotropy

An anisotropic two-ion coupling is given by the classical magnetic dipole—dipole interaction → very weak (orders of magnitude less than isotropic exchange) - but extremely long-range.

Note: the dipole sum is extended over the entire lattice, and \rightarrow 0 for certain ideal lattices (e.g., all *cubic* lattices).

Phenomenology of the magnetic crystal anisotropy

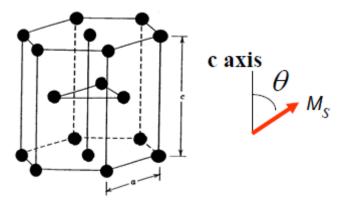
Favorable / unfavorable directions of the magnetization vector are usually called easy/hard axes.



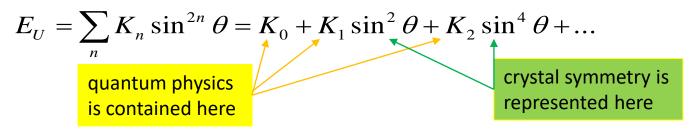
Types of magnetocrystalline anisotropy

Uniaxal anisotropy

Co crystals (hcp arrangement) show negligible anisotropy in the basal plane. Therefore, Co exhibits *uniaxial anisotropy* with a preference for magnetization to point along the c axis.



Uniaxial anisotropy energy (per unit volume) can be expressed as a power series containing *even powers* of $\sin\theta$ (energy does not change value under space inversion)

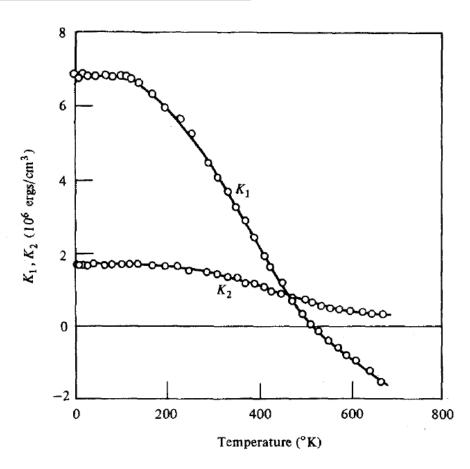


Usually, $K_1 > K_2 > K_3$... The c-axis is the easy axis if $K_1 > 0$.

	K_{u1} [J/m ³]	K_{u2} [J/m ³]
Со	4.1 × 10 ⁵	1.5 × 10 ⁵

The anisotropy constants K_1 , K_2 , ... are strongly temperature-dependent; they even intersect well above room temperature. K_1 changes of sign at high T.

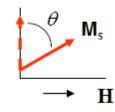
Crystal anisotropy becomes negligible at high temperatures Disappears at T_c



Anisotropy field

In uniaxial media, the magnetization process along the **hard** axis is described by adding the Zeeman energy - M_s H cos $(\pi/2-\theta)$ = - M_s H sin θ . Keeping only the K_1 term:

Easy axis



Hard axis

$$E = E_U - M_S H \sin \theta = K_1 \sin^2 \theta - M_S H \sin \theta$$

Equilibrium condition: take the derivative of $E(\theta)$ and put it equal to zero:

$$\frac{\partial E}{\partial \theta} = 2K_1 \sin \theta \cos \theta - M_S H \cos \theta = 0$$

$$2K_1 \sin \theta = M_S H$$

The field needed to rotate the M_S vector by 90° away from the easy axis (sin $\theta \to 1$) is

$$H=rac{2K_1}{M_S}$$
 . This quantity measures the anisotropy strength in terms of an internal fictitious field: the *anisotropy field*.

Cubic anisotropy

In cubic crystals, symmetry requires that the anisotropy takes the form:

$$E_A = K_0 + K_1 \Big(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2\Big) + K_2 \Big(\alpha_1^2 \alpha_2^2 \alpha_3^2\Big) + \dots$$
 quantum physics is contained here

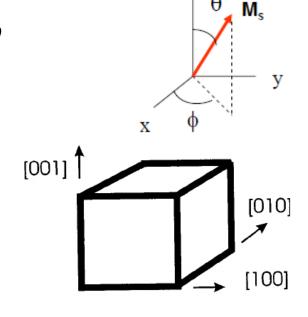
The direction cosines α_i are defined in terms of the Euler angles as:

$$\alpha_1 = \sin \theta \cos \phi;$$
 $\alpha_2 = \sin \theta \sin \phi;$ $\alpha_3 = \cos \theta$
 $\alpha_1^2 + \alpha_2^2 + \alpha_3^2 = 1$

Cubic systems: [100], [010], [001] crystallographic axes are equivalent.

Usually
$$|K_1| > |K_2| ... *$$

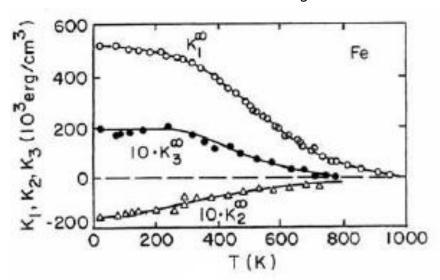
*exercise nr. 4



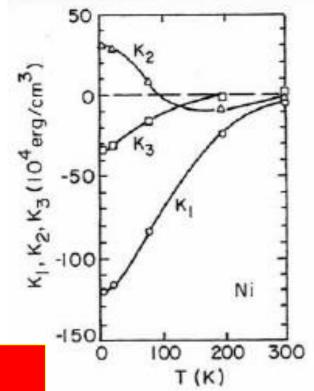
Room-temperature values of K_1 , K_2 and temperature dependence of K_1 , K_2 , K_3 for Fe and Ni single crystals.

$$\frac{K_i(T)}{K_i(0)} \approx \left(\frac{M_S(T)}{M_S(0)}\right)^{l(l+1)2}$$

I=2 for uniaxial anisotropy → M_s^3 I=4 for cubic anisotropy → M_s^{10}



	K_1 [J/m ³]	K_2 [J/m ³]
Fe	4.8×10^{4}	- 1.0 × 10 ⁴
Ni	-4.5×10^3	-2.3×10^3
Ni ₈₁ Fe ₁₉	~ 0	~ 0



Crystal anisotropy becomes negligible at high temperatures Disappears at T_c

Approaching magnetics

A ferromagnetic body is not indefinite; it has shape, surfaces...

- **Shape anisotropy**: nature, representation, practical consequences
- •Self-energy of a magnetized body and practical consequences:
- a. Ferromagnetic domains and domain structures
- b. Domain walls

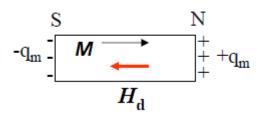
Shape anisotropy

A magnetized body produces a magnetic field



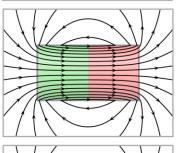


 $\vec{\mathsf{B}}$

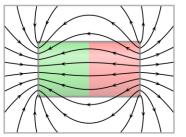


$$\nabla \cdot \mathbf{B} = 0$$

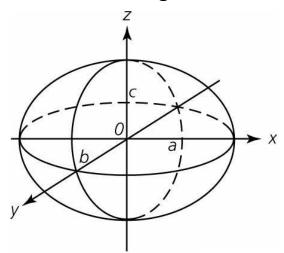
$$\nabla \cdot \boldsymbol{H_d} = -\frac{1}{4\pi} \, \nabla \cdot \boldsymbol{M}$$



Discontinuities of magnetization at surfaces act as sources of demagnetizing field \mathbf{H}_{d} . Generally speaking, \mathbf{H}_{d} =-N \mathbf{M} . The demagnetization factor N depends on body's shape. For an ellipsoid, three demagnetization factors can be defined:





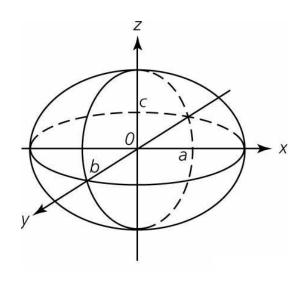


Gaussian system: $N_x + N_y + N_z = 4\pi$

$$H_{dx} = -N_x M_x$$

$$H_{dy} = -N_y M_y$$

$$H_{dz} = -N_z M_z$$



The magnetic energy (per unit volume) is given by:

$$\varepsilon_d = -\frac{1}{8\pi} \mathbf{M} \cdot \mathbf{H_d}$$

$$\varepsilon_d = +\frac{1}{8\pi} \left(N_x M_x^2 + N_y M_y^2 + N_z M_z^2 \right)$$

General rule: if a > b > c, then $N_x < N_y < N_z$

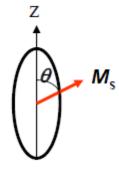


the longer the axis, the smaller N_{axis}

For an ellipsoid of revolution around z, $N_\chi = N_y = N_\perp \ (= 2\pi - \frac{N_z}{2})$

$$\varepsilon_{d} = +\frac{1}{8\pi} \left(N_{\perp} \left(M_{x}^{2} + M_{y}^{2} \right) + N_{z} M_{z}^{2} \right) = \frac{M_{s}^{2}}{8\pi} \left(N_{\perp} \sin^{2}\theta + N_{z} \cos^{2}\theta \right)$$

$$= const. + \frac{M_{s}^{2}}{8\pi} (N_{z} - N_{\perp}) \cos^{2}\theta$$



Shape anisotropy is **uniaxial**; easy axis is the *long axis* of ellipsoid (*)

*exercise nr. 5

Ferromagnetic domains & domain structures

$$H_{\mathbf{d}}$$
 $+\mathbf{q}_{\mathbf{m}} \stackrel{+}{+} \mathbf{N} \stackrel{\mathbf{M}}{\longleftarrow} \mathbf{S} \stackrel{=}{=} -\mathbf{q}_{\mathbf{m}}$

Magnetic poles (of field H_d) appear at sample surfaces

$$\nabla \cdot \boldsymbol{H}_d = -\frac{1}{4\pi} \, \nabla \cdot \boldsymbol{M}$$

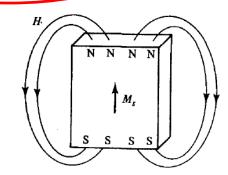
$$\varepsilon_d = -\frac{1}{8\pi} \mathbf{M} \cdot \mathbf{H_d}$$

The magnetostatic energy for a uniformly magnetized body can be written in either form:

$$E_d = -\frac{1}{8\pi} \int_{body} \mathbf{M} \cdot \mathbf{H_d} dV$$

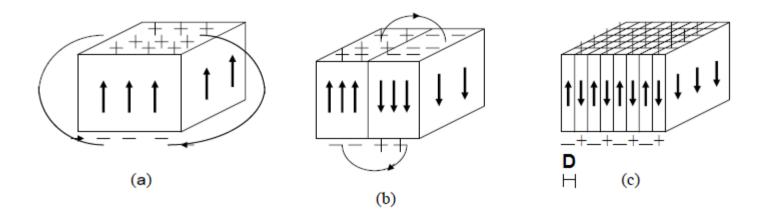
$$E_d = -\frac{1}{8\pi} \int_{all\ space} H_d^2 dV$$

where the second integral is to be performed over *all* space, both inside and *outside* the body.



For a uniformly magnetized macroscopic body the overall magnetostatic energy can be significant (large straw field)

This can be effectively reduced with the nucleation of *magnetic domains* of antiparallel magnetization such as those shown in the figure, cases (b) and (c):



Positive and negative magnetic poles at the sample surface become finely distributed, and the *external* field decreases.

A quick calculation: consider a thin slab of Co, with $M_s = 1.4 \times 10^3$ emu/cm³ aligned along z by crystal anisotropy. Taking $N_z \cong 4\pi$ one gets, in the single-domain configuration (a): $\varepsilon_d = M_s^2/2 = 1 \times 10^6$ erg/cm³. In the presence of regular domains of width D (c) one gets instead: $\varepsilon_d \cong 1 \times 10^6$ D which can be much smaller.

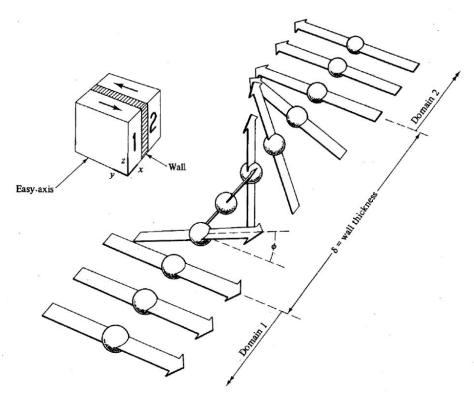
Of course, *D* cannot become equal to zero as suggested by the last formula: an intermediate region called *magnetic domain wall (DW)* must exist between two adjacent domains of antiparallel magnetization. Nucleation of a DW requires paying an energy cost, because DW's store both exchange and anisotropy energy.

Domain wall thickness and stored energy

Within a DW the magnetization points along a direction not corresponding to an easy axis *and* a quasi-continuous rotation of the **M** vector occurs there.

The wall thickness is the space length required for a full rotation of a given angle to occur.

The full rotation angle between domains of antiparallel magnetization is π (180° domain wall).

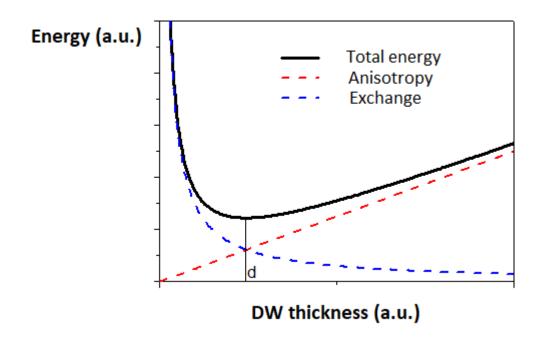


The DW «accumulates» exchange and anisotropy energy

These two energy terms are in direct competition:

- to minimize exchange energy the DW should be as thick as possible
- to minimize anisotropy energy the DW should be as thin as possible

Breakeven point at a DW wall thickness d. (*) There, the accumulated energy is still positive.

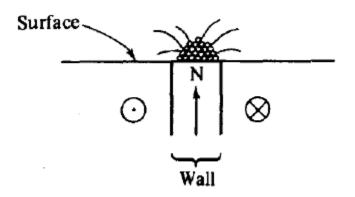


*insight nr. 2

Bloch walls vs. Néel walls

Across the thickness of a 180° DW there are virtually no magnetic poles (≡ inhomogeneities of the magnetization in a direction perpendicular to the wall).

Magnetic poles are created at the top and bottom of the wall on opposite surfaces of a bulk material, where the DW terminates; positive and negative poles are however separated by a macroscopic distance, and the associated magnetostatic energy is negligible.

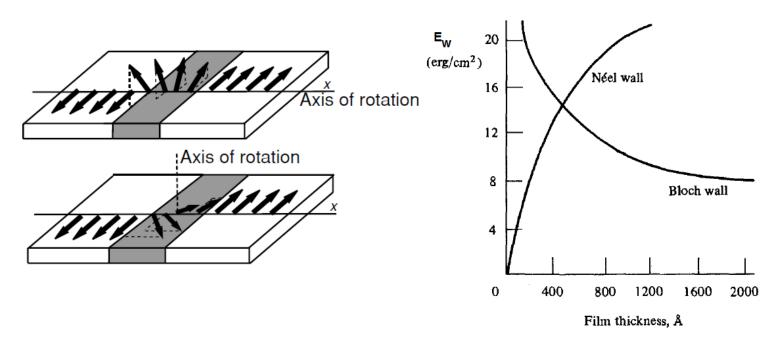


Magnetic poles appear at the surface in correspondence of a 180° DW

(The stray field generated by the poles provides a way to visualize the DW by observing the magnetic micropowders accumulated there)

Bloch walls vs. Néel walls

In thin films, the magnetostatic energy would significantly increase as a result of free poles at film surfaces. In order to reduce the energy, the moments inside the wall may rotate **in the plane.** Such a wall is called a Néel wall.

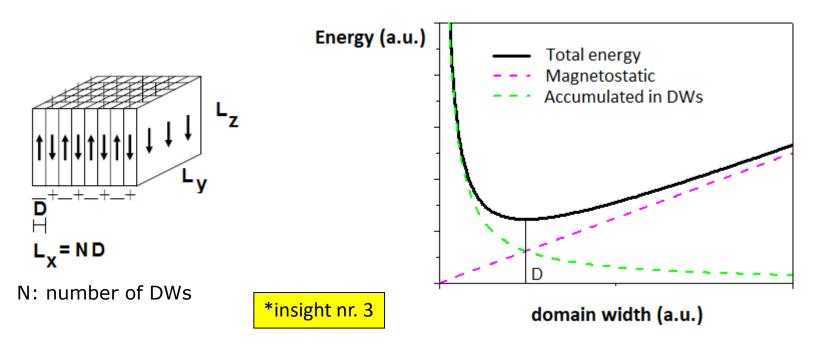


Néel wall (below) becomes more stable than Bloch wall (above) below some critical film thickness (data refer to Permalloy [a soft NiFe alloy]).

Magnetic domains reduce the magnetostatic energy; however, each pair of adjacent domains requires a DW between them - which accumulates magnetic energy.

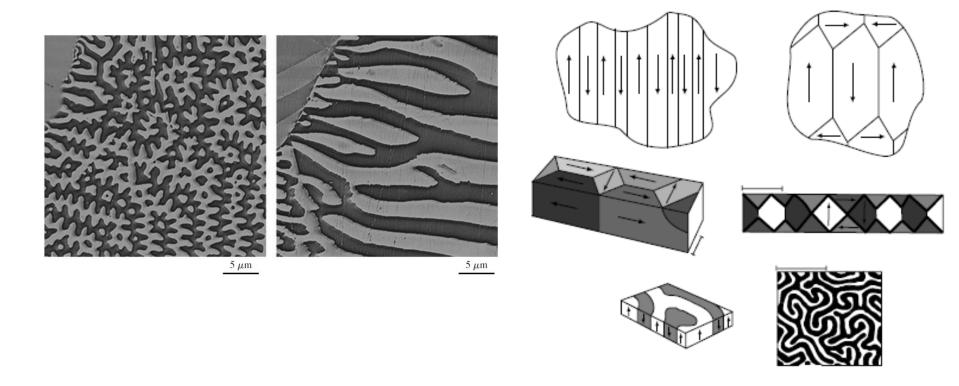
There is another pair of competing energies and a breakeven condition (*):

- to minimize the magnetostatic energy the number of domains should be as large as possible (and the domain width as low as possible)
- to minimize the DW energy the number of DWs should be as low as possible (and the domain width as large as possible)



Domain walls patterns

In actual materials, there is a wide variety of equilibrium magnetic domain patterns; domain shape and width is dictated by the complex interplay of different magnetic energies



Magnetization processes in macroscopic bodies

Fundamental aspects of macroscopic ferromagnetism

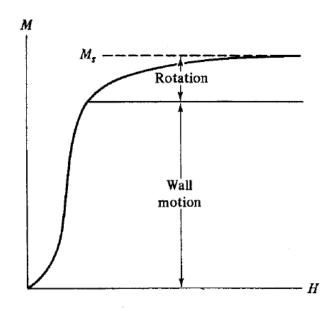
- The technical magnetization process
- Magnetic losses
- An introduction to coherent magnetization dynamics

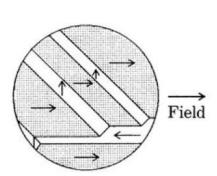
The "technical" magnetization process in bulk ferromagnetic materials

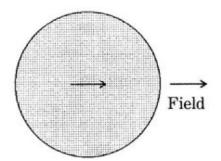
A ferromagnetic body in the absence of applied magnetic field is spontaneously divided into many domains .

The initial *macroscopic* magnetization of the body is zero (or close to zero) because of the mutually compensating contributions from antiparallel domains.

An applied field modifies the starting configuration and a net magnetization of the material is measured.



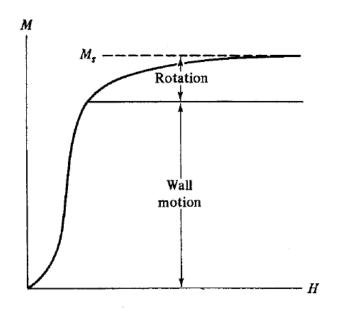


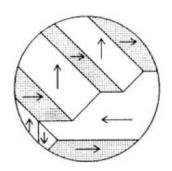


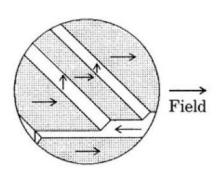
The "technical" magnetization process in bulk ferromagnetic materials

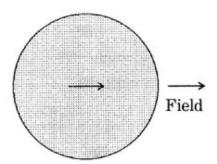
Al low fields, favorable domains (those whose local magnetization is closest to the applied field direction) **grow** at the expenses of the unfavorable ones according to a sort of principle of "survival of the fittest".

At higher fields, the magnetization rotates coherently towards the field direction (if needed).

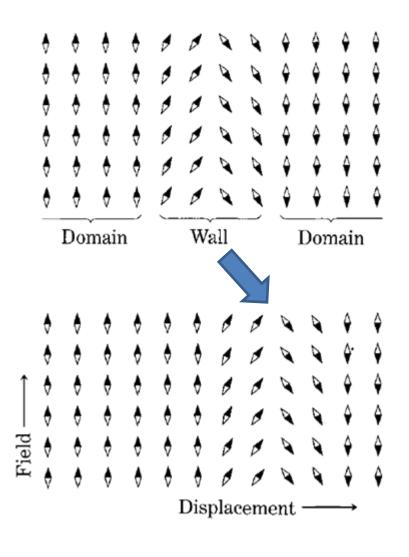








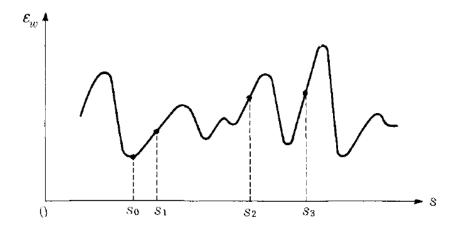
Domain wall displacement



DW displacement occurs because of the force (pressure) exerted by the external field and involves a continuous rotation of local magnetization with time.

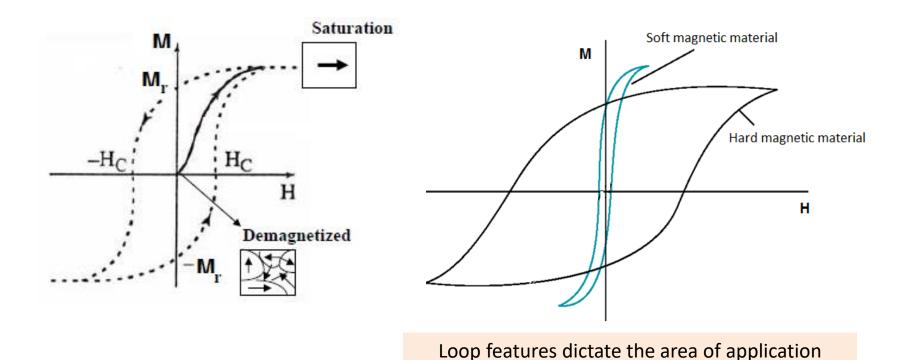
The displacement is *hindered* by defects (point defects, dislocations, inclusions, stress centers,...).

The wall moves in a complex, multivalley "potential energy landscape" which is the source of intrinsic irreversibility of this motion.



In general, both magnetization mechanisms, i.e., DW displacement and coherent rotation of the vector \mathbf{M}_s are **stochastic** in nature and display intrinsic **irreversibility**.

As a consequence, if the magnetization process is done under an alternating magnetic field, *magnetic hysteresis* appears. The hysteresis loop's area has the meaning of the energy (per unit volume) **dissipated by the material in the magnetic loop.** (*)



*exercise nr. 6

Magnetic losses have a strong impact on world economy!

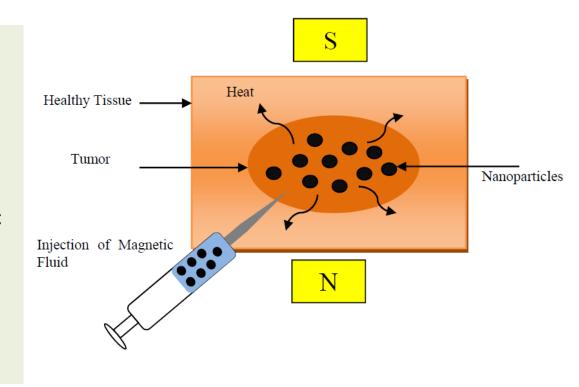
- Total worldwide transformer loss per year \cong 285 TWh (as of 2011)
- Average worldwide cost of 1 kWh of electrical energy \cong 0,19 \$ (as of 2011)
- Total worldwide cost of transformer losses in 2011 ≅ **5.4** x **10**¹⁰ (**54** billion !!) \$ Gross domestic product of Croatia (2017) ≈ 53 billion \$

Electrical energy is dissipated as **heat** during the cyclic magnetization process.

This may have beneficial effects too.

E.g.: cyclic magnetization of magnetic nanoparticles results in controlled heating of living tissues

(hyperthermia: see subsequent lecture)



Microwave magnetization dynamics (propaedeutic to ferromagnetic resonance)

Under a magnetic field \mathbf{H} applied along \mathbf{z} , the **non-collinear** magnetization vector $\mathbf{M}_{\mathbf{s}}$ is expected to freely precess around the field axis according to:

$$\frac{d\mathbf{M}_{s}}{dt} = -\gamma \mathbf{M}_{s} \times \mathbf{H}$$
gyromagnetic ratio \rightarrow $|\gamma| = \frac{g_{J}\mu_{B}}{\hbar}$

The solution is:

$$\begin{cases} M_{sx} = m\cos\omega_0 t \\ M_{sy} = m\sin\omega_0 t \\ M_{sz} = const \end{cases}$$

 $M_{sz}=const$ ω_{0} = γ H being the Larmor frequency, m is the projection of M_{sx} , M_{sy} on the z axis.

H//z

 ω_0

In a ferromagnetic material the internal field (exchange field) is of the order of several hundred kOe. Therefore $\omega_0 \approx 1.1 \times 10^5 \times 1 \times 10^5 \approx 10^{10} \text{ s}^{-1}$ (f₀ $\approx 10^9 \text{ Hz}$).

The magnetization vector will eventually *relax* towards the field direction on the time scale of magnetometer measurement – because of **dissipation** processes.

Assuming that the rate of relaxation is proportional to the amount by which the moment is out of equilibrium, addition of the loss term results in:

$$\frac{dM_{sz}}{dt} = -\gamma (\mathbf{M}_s \times \mathbf{H})_z - \frac{M_{sz} - M_s}{\tau_1}$$

 τ_1 is the *longitudinal relaxation time*. Similarly, the transverse components relax to zero, but with a different (transverse) relaxation time:

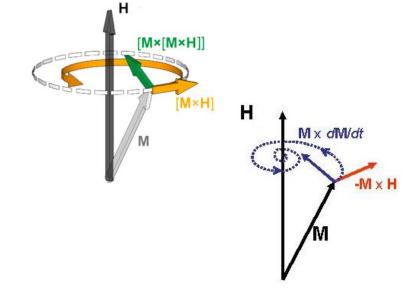
$$\frac{dM_{sx,y}}{dt} = -\gamma (\mathbf{M}_s \times \mathbf{H})_{x,y} - \frac{M_{sx,y}}{\tau_2}$$

These are the phenomenological Bloch equations.

The Bloch equations are compatible with a general equation of motion containing a phenomenological damping term. Two expedient expressions, due to Landau -Lifschitz and Gilbert respectively, are:

$$\frac{d\mathbf{M}}{dt} = -\gamma (\mathbf{M} \times \mathbf{H}) + \gamma \frac{\lambda}{M} \mathbf{M} \times \mathbf{M} \times \mathbf{H}$$

$$\frac{d\mathbf{M}}{dt} = -\gamma (\mathbf{M} \times \mathbf{H}) + \frac{\alpha}{M} \mathbf{M} \times \frac{d\mathbf{M}}{dt}$$



 α is the Gilbert damping, which is of the order 0.01-0.1; with $\omega_0 \approx 10^{10}$ s⁻¹, τ_1 is the of the order of the nanosecond at room temperature.

→ Damping is overcome by "pumping" energy into the system

See subsequent lectures on magnetic resonances and spintronics

There and back again

Just a glimpse to the Nanoscale

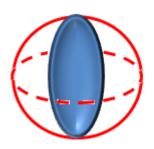
- •When fine magnetic particles become single-domain?
- A Langevin-function revival
- Magnetic forces on fine magnetic particles

Magnetic domains disappear in fine particles

Magnetic domains have a typical width; they do not develop in a ferromagnetic body of sufficiently small size.

Which is the critical size below which a particle no longer exhibits multiple domains $(\rightarrow i.e.$, it becomes a *single-domain particle*)? This is important for applications of fine particles in permanent magnets, recording media, healthcare.

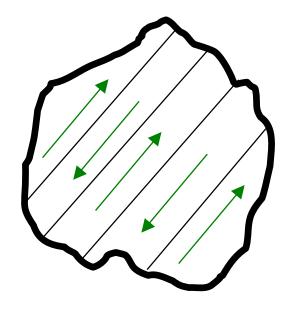
For the *single-domain state* to be stable, the energy needed to create one domain wall spanning a spherical particle of radius r , $E_{wall} \pi r^2$, must exceed the magnetostatic energy $E_d = 4\pi/3 \ M_s^2 V$ (the demagnetizing factor being $4\pi/3$ in this case):

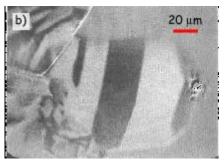


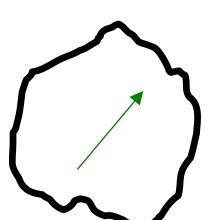
$$E_{DW}\pi r^2 > \frac{4\pi}{3} M_S^2 \frac{4\pi}{3} r^3$$

$$r_{crit} \cong \frac{9}{16\pi} \frac{E_{DW}}{M_s^2}$$

For Co, $r_{crit} \cong 15$ nm; for SmCo₅ with very large K_u (1×10⁷ J/m³), $r_{crit} \cong 1$ μm .





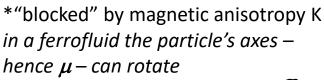


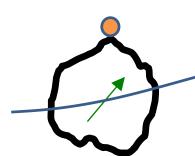
Fine particle with ferromagnetic domains

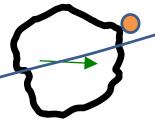
 $D^{\sim} 10^2 \text{ nm} \div 10^5 \text{ nm (depends on material)}$

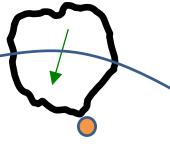
Single-domain fine particle (magnetically blocked* state)

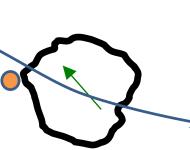
D~ 10 nm ÷ 10³ nm (depends critically on material & temperature)







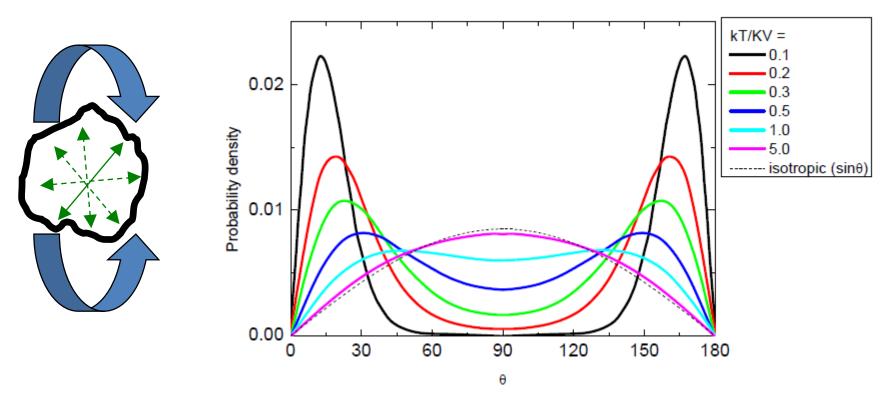




In very small particles (KV << k_BT) the local anisotropy energy (which scales with V) is not enough to resist to thermal disorder

Superparamagnetic regime: direction of magnetization can be pictured as continuously modified by thermal disorder

D ~ 3 ÷ 15 nm (depends critically on material & temperature)



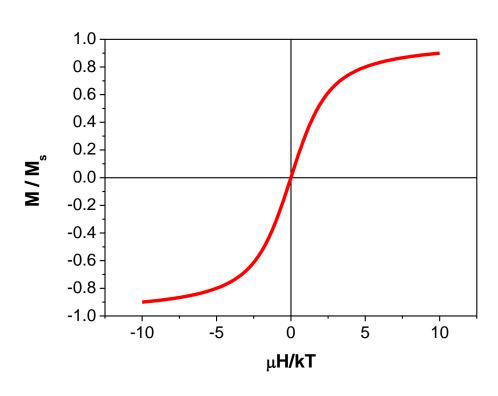
Directional probability of a macrospin. If KV $<< k_BT$, μ takes all directions over the sphere

Langevin's function revival

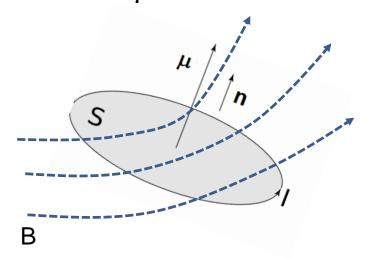
- M(H,T) is obtained adapting the procedure developed for paramagnetism of localized non-interacting magnetic moments (see Vleck's paramagnetism)
- However, macrospins behave classically
- Langevin's approach to paramagnetism applies $\Rightarrow \frac{M}{M_S} = L\left(\frac{\mu H}{k_B T}\right) = coth\left(\frac{\mu H}{k_B T}\right) \frac{1}{\left(\frac{\mu H}{k_B T}\right)}$
- M(H): slowly saturating, anhysteretic

But beware!!

Virtually no *real* magnetic nanoparticles actually follow this «pure superparamagnetic» law (even at high temperatures)



Consider an ideal, classical magnetic dipole μ first. This can thought of as a tiny circular coil bearing a steady current I and lying on a plane identified by the normal unit vector \mathbf{n} . Remember that $\mu = IS\mathbf{n}$



If the coil is placed in the flux lines of an external field **B**, the potential energy is:

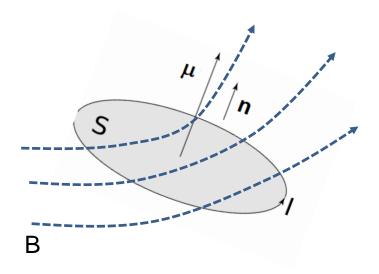
$$U = -\boldsymbol{\mu} \cdot \boldsymbol{B}$$

and the force on the dipole is: $\boldsymbol{F} = -\boldsymbol{\nabla} U$

This magnetic force is expressed as:

$$\boldsymbol{F} = \boldsymbol{\nabla}(\boldsymbol{\mu} \cdot \boldsymbol{B}) = \frac{\partial}{\partial x} \left(\mu_x B_x + \mu_y B_y + \mu_y B_y \right) \boldsymbol{i} + \frac{\partial}{\partial y} (\mu_x B_x + \cdots) \boldsymbol{j} + \frac{\partial}{\partial z} (\mu_x B_x + \cdots) \boldsymbol{k}$$

This expression can be cast in the equivalent form: $F = (\mu \cdot \nabla)B + \mu \times (\nabla \times B)$



When $\nabla \times \mathbf{B} = 0$ (magnetostatics; no free currents), the last expression (which becomes exact if the coil's radius \rightarrow 0) reduces to

$$F = (\mu \cdot \nabla)B$$

where the scalar operator within brackets has meaning:

$$\mu_x \frac{\partial}{\partial x} + \mu_y \frac{\partial}{\partial y} + \mu_z \frac{\partial}{\partial z}$$

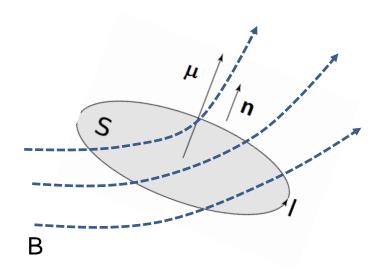
For instance, the force along x-direction is:

$$F_x = \mu_x \frac{\partial B_x}{\partial x} + \mu_y \frac{\partial B_x}{\partial y} + \mu_z \frac{\partial B_x}{\partial z}$$
 (and so on)

Note: if **B** is uniform, the force on μ is zero

A strong magnetic-field **gradient** is needed to have a strong magnetic force acting on *a* magnetic dipole moment

The same field produces on the μ vector a torque τ whose general espression is:



$$\tau = r \times F + \mu \times B$$

F is the force defined in the previous slide.

If **B** is uniform, **F**=0 and the torque reduces to:

$$\tau = \mu \times B$$

The previous expressions can be applied to magnetic nanoparticles (NP) when these are supposed to be **stable point dipoles**.

Actually, they aren't -

- multi-domain particles: B acts to change the NP magnetic domain pattern
- single-domain particles: **B** acts to modify magnetization at NP surface

A more correct expression (using the cgs system where $B \equiv H$) takes into account that the moment on a NP of volume V is:

$$\boldsymbol{\mu} = \boldsymbol{M}_0 V + \chi \boldsymbol{H} V$$

where \mathbf{M}_0 is the spontaneous magnetization of the NP when \mathbf{H} =0 and $\chi\mathbf{H}$ is the increase by effect of field (an effective susceptibility χ is used, and one makes the hypothesis that the effect of \mathbf{H} is linear). Therefore:

$$F = (\mu \cdot \nabla)B = v[(M_0 \cdot \nabla)B + \chi(H \cdot \nabla)B]$$

Finally, note that the above expressions apply for **small** (strictly speaking, **pointlike**), **rigid** particles only. For instance, if a magnetized body extends over a macroscopic volume V_{macro} the following (much more complex) integral expressions should be used:

$$\mathbf{F} = \int_{V_{macro}} (\mathbf{M} \cdot \mathbf{\nabla}) \mathbf{B} \ dV \qquad \qquad \mathbf{\tau} = \int_{V_{macro}} [\mathbf{r} \times (\mathbf{M} \cdot \mathbf{\nabla}) \mathbf{B} + \mathbf{M} \times \mathbf{B}] dV$$