Crystal fields. Spin-Orbit Coupling Magnetic Anisotropy.



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- I. Introduction: origin and kinds of magnetic anisotropy.
- II. Crystal Field effects.
- III. Spin-Orbit coupling: origin of crystalline anisotropy.
- IV. Crystalline anisotropy (bulk). / Shape anisotropy: dipolar interactions,...
- V. Effects of anisotropy: SW model, dynamics, relaxation...
- VI. Surface anisotropy (nano): atomistic vs. effective models.

VII. Unidirectional anisotropy: exchange bias

VIII. Other anisotropy terms: magnetoelastic, induced,...

➢ In a (ANTI)FERROMAGNET:

$$E_{ij}^{\text{Exch}} = -J_{ij}\vec{S}_i \cdot \vec{S}_j \implies \text{Invariant with respect} \text{to coord. system} \stackrel{\text{Cooling}}{\text{below } \mathsf{T}_{e}} \qquad \text{Magnetization } \mathsf{M} \\ \text{can point in} \\ \text{any direction} \end{aligned}$$

$$\texttt{below } \mathsf{T}_{e} \qquad \texttt{below } \mathsf{T}_{e} \qquad \texttt{Spontaneous magnetization lies} \\ \texttt{along preferential} \\ \texttt{crystal field effects} \\ \texttt{so Coupling} \qquad \texttt{Energy depends on} \\ \texttt{the direction of } \mathsf{M} \qquad \texttt{Spontaneous magnetization lies} \\ \texttt{along preferential} \\ \texttt{crystallographic directions} \\ \texttt{(easy axes)} \end{aligned}$$

$$\texttt{Phenomenological description:} \\ \texttt{thermodynamic (Gibbs free energy)} \qquad \texttt{E}_{i}^{\text{Ani}} = f(\vec{M}_{i}) \qquad \bigstar \qquad \texttt{K}_{uni}, K_{cub}, K_{surf}, \ldots \\ \texttt{anisotropy constants (J/m^3,...)}$$





Magnetocrystalline

direction of M w.r.t. crystal axes, coupling between M and the lattice via SO interaction

Magnetostatic (shape)

direction of M w.r.t. shape axes, coupling between M and demagn. field via Zeeman int.

# Types of magnetic anisotropy



breaking of crystal lattice at surfaces and interfaces (Néel), increases @ small sizes

Exchange

proximity effects, coupling bw. FM/AFM,... loop shifts, Exchange Bias



Magnetoelastic

direction of M w.r.t. lattice, coupling between M and crystal strain (SO interaction)



by magnetic annealing (H+Heat), stress annealing, plastic defomation,...

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The Interaction Hamiltonian of magnetic ions in a solid is the sum of different terms:



- Notice that the Spin-Orbit coupling and Crystal Field interactions are generally much larger than Zeeman interaction.
- As a result, the magnetic moment is always a small perturbation on the electronic problem. The magnetic properties are solved by perturbation methods.

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# Relative size of interactions in solids



Central idea: The electron spin interacts with the crystal structure via the S-O Coupling

- The spin moment is coupled to the electron cloud (orbitals): S-O coupling.
- When an external field rotates the e<sup>-</sup> spins, the orbitals try to follow them: energy cost depends on the orientation relative to neighboring orbitals.
- If orbitals overlap along a given direction: additional energy cost due to Coulomb repulsion.
- Some orientations of the total magnetic moment are favorable: easy-axes.





#### I. Introduction

- > Spin distribution affects electronic wave-functions.
- > Different electronic wave functions have different Coulomb interactions.
- > Thus, spin distribution has an associated energy.
- > Spins "see" real space through the Pauli principle + Coulomb repulsion.

Magnetic anisotropy can be defined as the energy associated to a change in the orientation of the magnetic moments.





#### Crystal Field Theory

# II. Crystal fields



- Developed by H. Bethe (1929) and J.H. van Vleck (1935)
- > Influence of anions surrounding a magnetic cation.
- Coulomb interactions between 3d, 4f ion and cations.
- Both lattice environment and coordination matter.



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Charge and n of the metal ion.

Spatial distribution of ligands: Octah., Tetrah...

Orbital symmetry and occupancy.

- Main purpose: compute level splittings.
- Calculation of crystal field potential: Coulomb interaction due to anions.
- Energy splittings: perturbation theory, with V<sub>cf</sub>(r) as perturbation potential.

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# **CRYSTAL FIELD THEORY**

- > Only Coulomb interactions between TM cation and n.n. anions considered.
- > The hybridization of d TM orbitals with p orbitals of ligands (covalent bond) is neglected.
- > It is a 1-electron model.
- > Gives relative energy splittings, the order of magnitude is correct but not the values.



- Incorporates ligand orbitals through Molecular Orbital theory.
- > Uses group theory symmetries to derive level splittings.
- > It starts with the correlated multiplet states  ${}^{2S+1}L_{J}$  of the free ion.
- > The LF to correlation ratio gives the energy splittings. Dq,... as empirical parameters

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$$\frac{\mathscr{C}_{g} \text{ orbitals}}{C_{g} \text{ orbitals}}$$

$$\sim Y_{2}^{0} \qquad d_{z^{2}} = \sqrt{\frac{5}{16\pi}} \frac{3z^{2} - r^{2}}{r^{2}} R_{n2}(r) \qquad d_{xy} = \sqrt{\frac{15}{4\pi}} \frac{xy}{r^{2}} R_{n2}(r) \qquad \sim \frac{i}{\sqrt{2}} (Y_{2}^{-2} - Y_{2}^{2})$$

$$\sim \frac{1}{\sqrt{2}} (Y_{2}^{-2} + Y_{2}^{2}) \qquad d_{x^{2} - y^{2}} = \sqrt{\frac{15}{16\pi}} \frac{x^{2} - y^{2}}{r^{2}} R_{n2}(r) \qquad d_{xz} = \sqrt{\frac{15}{4\pi}} \frac{xz}{r^{2}} R_{n2}(r) \qquad \sim \frac{1}{\sqrt{2}} (Y_{2}^{-1} - Y_{2}^{1})$$

$$d_{yz} = \sqrt{\frac{15}{4\pi}} \frac{yz}{r^{2}} R_{n2}(r) \qquad \sim \frac{i}{\sqrt{2}} (Y_{2}^{-1} + Y_{2}^{1})$$

## II. Crystal fields

### > Crystal field effects: calculation example for the d<sup>1</sup> configuration

# Coulomb potential due to all <u>6 anions</u>

$$V_{oct}(\vec{r}) = \sum_{i=1}^{6} \frac{-Ze}{4\pi\varepsilon_0 r_i}$$

Coulomb potential due to one anion @ (a,0,0)

$$V_1(\vec{r}) = \frac{-Ze}{4\pi\varepsilon_0 a} \left\{ 1 - \frac{2x}{a} + \frac{r^2}{a^2} \right\}^{-1/2}$$

#### Expansion for small r/a....

$$V_1(\vec{r}) \simeq \frac{-Ze}{4\pi\varepsilon_0 a} \left\{ 1 - \frac{1}{2} \left[ -\frac{2x}{a} + \frac{r^2}{a^2} \right] + \frac{3}{8} \left[ \frac{4x^2}{a^2} - \frac{4xr^2}{a^3} + \frac{r^4}{a^4} \right] - \frac{5}{16} \left[ -\frac{8x^3}{a^3} + \frac{12x^2r^2}{a^4} \right] + \frac{35}{128} \frac{16x^4}{a^4} \right\}$$
 e.g.: O<sup>2-</sup>

Summing over all 6 anions and using symmetries...

$$V_{oct}(\vec{r}) = -D(x^4 + y^4 + z^4) - \frac{3}{5}r^4) + Ct. \qquad D = \frac{35Ze}{16\pi\varepsilon_0 a^5} \qquad V_{oct}(\vec{r}) \sim Y_0^4 + \sqrt{\frac{5}{14}}(Y_4^4 + Y_{-4}^4)$$

# (a) Calculation of energy level splittings: example with orbital dxz

$$\begin{split} \Delta T_{2g} &= \langle d_{xz} | V_{Oct} | d_{xz} \rangle = D \int d\Omega \int dr r^2 (d_{xz})^2 \left( x^4 + y^4 + z^4 - \frac{3}{5} r^4 \right) \qquad |d_{xz}\rangle = \sqrt{\frac{15}{4\pi}} \frac{xz}{r^2} R_{n2}(r) \quad x = r \sin \theta \cos \varphi , . . \\ &= D I_{rad} \int d\Omega \frac{15}{4\pi} (S_{\theta} C_{\varphi} C_{\theta})^2 (S_{\theta}^4 C_{\varphi}^4 + S_{\theta}^4 S_{\varphi}^4 + C_{\theta}^4 - 3/5) \qquad I_{rad} = \langle r^4 \rangle = \int_0^\infty dr r^2 r^4 R_{nd}^2(r) \end{split}$$

q=Ze

# II. Crystal fields

Performing the angular integrals...

$$\Delta T_{2g} = DI_{rad} \left( \frac{15}{21} - \frac{3}{5} \right) = -DI_{rad} \frac{8}{105} \qquad D = \frac{35Ze}{16\pi\varepsilon_0 a^5}$$

(b) Calculation of energy level splittings: Example with orbital  $d_{z^2}$ 

$$\Delta E_g = \langle d_{z^2} | V_{Oct} | d_{z^2} \rangle = + DI_{rad} \frac{12}{105}$$

Finally, it is customary to use the following notation for the difference in energy splittings:

$$\Delta E_g = 6Dq = \frac{2}{5}\Delta_0$$
  

$$\Delta T_{2g} = -4Dq = -\frac{3}{5}\Delta_0$$
  

$$\Delta_0 \equiv 10Dq = \Delta E_g - \Delta T_{2g}$$
  
with  $q \equiv \frac{2}{105}$ 

$$e_{g} \qquad e_{g} \qquad e_{g$$

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q=Ze

- Overlap of the  $e_g$  orbitals with the ligands ( $\sigma$  bonding) is stronger than for the  $t_{2g}$  orbitals ( $\pi$  bonding)
- $t_{2g}$  orbitals have lower overlap with neighb. anions  $\Rightarrow$  less electrostatic repulsion  $\Rightarrow$  decrease in energy. ۲
- $e_g$  orbitals have higher overlap with neighb. anions  $\Rightarrow$  strong electrostatic repulsion  $\Rightarrow$  increase in energy.



- The situation is reversed in tetrahedral symmetry (4 anions):
- $e_g$  orbitals have lower overlap with neighb. anions  $\Rightarrow$  less electrostatic repulsion  $\Rightarrow$  decrease in energy.
- $t_{2g}$  orbitals have higher overlap with neighb. anions  $\Rightarrow$  strong electrostatic repulsion  $\Rightarrow$  increase in energy.
- Calculations show that the crystal field splitting is smaller than for the octahedral case.

$$\Delta_t = \left(\frac{16}{9} + \frac{8}{3}\right) Dq = \frac{4}{9} \Delta_o$$





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TM orbitals that point more toward the ligand positions are higher in energy Symmetry properties of the anions determine the splittings and degeneracies.



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- What happens when the ionic charge of the cation is varied: d<sup>n</sup>, n=1,...10?
- Remember Hund's rules...



What determines if an ion will be HS or LS?

Coulomb interaction U leading to Hund's 1<sup>st</sup> rule (maximize S) is greater than or less than the CF splitting

For the  $d^4-d^7$  configurations, the electron filling of the 10 possible d spin–orbitals leads to two distinct ground states, depending on the relative size of the electron correlation energy relative to the LF splitting:

- If the electron **correlation** energy is larger (or "**high**"), the ground state has **high-spin**.
- If the electron correlation energy is smaller (or "low"), the ground state has low-spin.



## II. Crystal fields

The electronic structure of the TM ions has different possibilities *depending on the relative magnitudes of the crystal field splitting energy*  $\Delta$ *, and the exchange energy*  $J_{ex}$ .

- If Δ > J<sub>ex</sub>, the ground state configuration is obtained by filling the orbitals completely, starting with the lowest t<sub>2g</sub> energy levels.
- If  $\Delta < J_{ex}$ , then the ground state is obtained by filling the orbitals singly such that the spins are all parallel.



TM oxides have high spin states with  $Co^{3+}$  (d<sup>6</sup>), Ni<sup>3+</sup> (d<sup>7</sup>), and Ru<sup>4+</sup> (d<sup>4</sup>) being notable exceptions.

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Competition between crystal field and S-O coupling:

 $\begin{array}{l} \Delta \mathsf{E}_{\mathsf{cf}} << \Delta \mathsf{E}_{\mathsf{so}} \ \ \textit{Hund's rules are applicable.} \\ \Delta \mathsf{E}_{\mathsf{cf}} >> \Delta \mathsf{E}_{\mathsf{so}} \ \ \textit{Only lowest levels are occupied.} \end{array}$ 

**High Spin state** 

Electrons occupy  $t_{2g}$  and  $e_g$  levels according to Hund's rules.

## Low Spin state

Electrons accommodate first in the lower  $t_{2g}$  levels and pair up to 6 e's. Then eventually occupy the  $e_g$  levels.



Examples: Verwey transition in magnetite, Jahn-Teller effect, oxy-deoxy transition.

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#### II. Crystal fields

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Crystal Field stabilization energy: difference in electron energies in presence and absence of splitting

$$CFSE_{Oct} = E_{in \ LF} - E_{iso}$$





## **II.** Crystal fields

#### Jahn-Teller effect

- > If a crystal gives rise to a degenerate ground state for the TM ion, it will distort itself in a form that removes this degeneracy.
- Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a

system of lower symmetry and lower energy, thereby removing the degeneracy.



- Example  $Mn^{3+}$ : high spin configuration: 1 e<sup>-</sup> in upper e<sub>g</sub> state.
- Lower its energy by a tetragonal distortion  $\Rightarrow$  level splitting  $\Rightarrow$  lowering of 1 e<sub>g</sub> state ( $d_{z^2}$ ).
- Filled lower t<sub>2g</sub> states also split (no net change in energy).



- Tetragonal elongation:  $d_{\chi z, y z, z^2}$  lower their energy.
- Tetragonal contraction:  $d_{xy,x^2-y^2}$  lower their energy.

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> If a crystal gives rise to a degenerate ground state for the TM ion, it will distort itself in a form that removes this degeneracy.

> A system with a single electron (or hole) in a degenerate level will tend to distort spontaneously.



- Example  $Mn^{3+}$ : high spin configuration: 1 e<sup>-</sup> in upper e<sub>g</sub> state.
- Lowers its energy by a tetragonal distortion  $\Rightarrow$  level splitting  $\Rightarrow$  lowering of 1 e<sub>g</sub> state ( $d_{z^2}$ ).
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- Tetragonal elongation:  $d_{xz,yz,z^2}$  lower their energy.
- Tetragonal contraction:  $d_{xy,x^2-y^2}$  lower their energy.



# Weak J-T effects: t<sub>g</sub> orbitals unevenly unoccupied)



Stronger J-T effects



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> Odd number of electrons in  $e_g$ -orbital: gain in stabilization energy  $\Rightarrow$  J-T distorsion

 $\blacktriangleright$  Even number of electrons in e<sub>g</sub>-orbital: no net change in energy  $\Rightarrow$  No distorsion

# Competition between elastic distortion and orbital occupancy (1939)



- Energy cost to move an atom of mass M away from equil. position, characterized by Q. Associated to a particular vibrational mode of freq. ω.
- Total energy is raised/lowered by the local distortion of orbitals:



Rising or lowering the orbital energy level (linear to 1<sup>st</sup> order)

**Elastic deformation** 

- Two energy minima at  $Q_0 = \pm A/(M\omega^2)$  with Emin=  $-A^2/(2 M\omega^2)$
- Result: if one of these orbitals is occupied, the system saves energy by distorting spontaneously.
- J-T theorem does not tell which distortion will occur.

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What happens if an e- can occupy one out of 2 degenerate orbitals?



There is ALWAYS a distortion that removes the degeneracy





## Origin of S-O interaction:

Coupling between spin moment (S) and orbital moment (L) of e-'s (classical approach).

Dirac equation for relativistic QM (in non-relativ. limit of Pauli)  $\Rightarrow$  relativistic origin.

Responsible for Hund's 3<sup>rd</sup> rule.

More important for heavy elements and inner shells (4f vs 3d).

 $\lambda$  varies as Z<sup>4</sup> (inner electrons), of the order of: 8 K (Li),..., 60 K (3d elements), 160 K (actinides)

For an electron 
$$\mathcal{H}_{so} = \frac{-e}{2m_e^2 c^2} \frac{dV}{dr} \hat{\boldsymbol{\ell}} \cdot \hat{\mathbf{s}} \Longrightarrow \mathcal{H}_{so} = \frac{Ze^2 \hbar^2 \mu_0}{8\pi m_e^2 r^3} \hat{\boldsymbol{\ell}} \cdot \hat{\mathbf{s}} \equiv \xi_{n\ell}(r) \left( \hat{\boldsymbol{\ell}} \cdot \hat{\mathbf{s}} \right)$$
$$V(r) = \frac{Ze}{4\pi\varepsilon_0 r}$$

Multielectronic atom

$$\mathcal{H}_{so} = rac{\Lambda}{\hbar^2} \, \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \qquad \Lambda = \pm rac{\lambda}{2S}$$

S-O coupling at the origin of:

- Magnetocrystalline anisotropy.
- Magnetostriction.
- Anisotropic magnetoresistance.
- Anomalous planar and spin Hall effect.



#### III. Spin-Orbit Coupling

#### S-O Coupling: semi-classical derivation



In atoms 10-100 meV for 3d's	
$\xi_{n\ell}^{1,000}$ $\xi_{n$	Kl) $^{10^{-1}}$
Atomic number Z	Atomic number (Z)
$\mathbf{J}=\mathbf{L}+\mathbf{S}$	L-S coupling scheme
$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} (\mathbf{J}^2 + \mathbf{L}^2 - \mathbf{S}^2)$	$ L, S, J, M_J\rangle$

$$\langle n, \ell, m | \, \hat{\mathcal{H}}_{so} \, | n, \ell, m \rangle = \frac{Z^4 \alpha^2}{2n^3} \frac{J(J+1) - L(L+1) - S(S+1)}{2L(L+1/2)(L+1)}$$

**Table 4.5.** Spin-orbit coupling constants for ionsin the 3d and 4f series, in kelvin.  $\Delta \varepsilon$  is the energyof the first excited multiplet

	Ion	$\xi_{n\ell}$	Λ	$\Delta \varepsilon$
3d <sup>1</sup>	Sc <sup>2+</sup>	124	124	310
3d <sup>2</sup>	Ti <sup>2+</sup>	176	88	264
3d <sup>3</sup>	$V^{2+}$	246	82	205
3d <sup>4</sup>	Cr <sup>2+</sup>	340	85	85
3d <sup>6</sup>	Fe <sup>2+</sup>	656	-164	656
3d <sup>7</sup>	Co <sup>2+</sup>	818	-272	1224
3d <sup>8</sup>	Ni <sup>2+</sup>	987	-494	3948
$4f^{1}$	Ce <sup>3+</sup>	920	920	3220
$4f^{2}$	Pr <sup>3+</sup>	1080	540	2700
$4f^{3}$	Nd <sup>3+</sup>	1290	430	2365
$4f^{4}$	Pm <sup>3+</sup>	1540	380	1900
$4f^{5}$	Sm <sup>3+</sup>	1730	350	1225
$4f^{6}$	Eu <sup>3+</sup>	1950	330	330
$4f^{8}$	Tb <sup>3+</sup>	2450	-410	2460
$4f^{9}$	Dy <sup>3+</sup>	2730	-550	4125
$4f^{10}$	Ho <sup>3+</sup>	3110	-780	6240
$4f^{11}$	Er <sup>3+</sup>	3510	-1170	8775
$4f^{12}$	Tm <sup>3+</sup>	3800	-1900	11400
$4f^{13}$	Yb <sup>3+</sup>	4140	-4140	14490

 $\Lambda = \pm \frac{\lambda}{2S}$ 

## III. Spin-Orbit Coupling

#### Quenching of orbital moment

# Magnetic moments of ions in a solid: 3d TM and 4f RE

<b>Table 4.6.</b> The 4 <i>f</i> ions. The paramagnetic moment $\mathfrak{m}_{eff}$ and the saturation moment $\mathfrak{m}_0$ are in units of $\mu_B$									
$4f^n$		S	L	J	g	$m_0 = gJ$	$m_{eff} =$	$g\sqrt{J(J+1)}$	$m_{e\!f\!f}^{exp}$
1	Ce <sup>3+</sup>	$\frac{1}{2}$	3	$\frac{5}{2}$	$\frac{6}{7}$	2.14	2.54	${}^{2}F_{5/2}$	2.5
2	Pr <sup>3+</sup>	1	5	4	$\frac{4}{5}$	3.20	3.58	${}^{3}H_{4}$	3.5
3	Nd <sup>3+</sup>	$\frac{3}{2}$	6	$\frac{9}{2}$	$\frac{8}{11}$	3.27	3.52	$4I_{9/2}$	3.4
4	Pm <sup>3+</sup>	2	6	4	$\frac{3}{5}$	2.40	2.68	${}^{5}I_{4}$	
5	Sm <sup>3+</sup>	$\frac{5}{2}$	5	$\frac{5}{2}$	$\frac{2}{7}$	0.71	0.85	${}^{6}I_{5/2}$	1.7
6	Eu <sup>3+</sup>	3	3	0	0	0	0	$^7\dot{F_0}$	3.4
7	$\mathrm{Gd}^{3+}$	$\frac{7}{2}$	0	$\frac{7}{2}$	2	7.0	7.94	$^{8}S_{7/2}$	8.9
8	Tb <sup>3+</sup>	3	3	6	$\frac{3}{2}$	9.0	9.72	$^7F_6$	9.8
9	Dy <sup>3+</sup>	$\frac{5}{2}$	5	$\frac{15}{2}$	$\frac{4}{3}$	10.0	10.65	${}^{6}H_{15/2}$	10.6
10	Ho <sup>3+</sup>	2	6	8	$\frac{5}{4}$	10.0	10.61	${}^{5}I_{8}$	10.4
11	Er <sup>3+</sup>	$\frac{3}{2}$	6	$\frac{15}{2}$	$\frac{6}{5}$	9.0	9.58	${}^{4}I_{15/2}$	9.5
12	Tm <sup>3+</sup>	1	5	6	$\frac{7}{6}$	7.0	7.56	${}^{3}H_{6}$	7.6
13	Yb <sup>3+</sup>	$\frac{1}{2}$	3	$\frac{7}{2}$	$\frac{8}{7}$	4.0	4.53	${}^{2}F_{7/2}$	4.5

Good agreement between  $m_{ef}$  and experimental value. RE's ions behave in the solid as isolated ions\*\*.

$$\mu_{\text{eff}} = 2g_J \mu_B \sqrt{J(J+1)} \qquad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

<b>Table 4.7.</b> The 3 <i>d</i> ions. $\mathfrak{m}_{eff}$ is in units of $\mu_B$									
$3d^n$		S	L	J	g	$\begin{array}{l} m_{e\!f\!f} = \\ g \sqrt{J(J+1)} \end{array}$	$m_{eff} = g\sqrt{S(t)}$	$\frac{1}{(S+1)}$	$m_{e\!f\!f}^{exp}$
1	${ m Ti}^{3+}, { m V}^{4+}$	$\frac{1}{2}$	2	$\frac{3}{2}$	$\frac{4}{5}$	1.55	1.73	${}^{2}D_{3/2}$	1.7
2	$Ti^{2+}, V^{3+}$	1	3	2	$\frac{2}{3}$	1.63	2.83	${}^{3}F_{2}$	2.8
3	$V^{2+}, Cr^{3+}$	$\frac{3}{2}$	3	$\frac{3}{2}$	$\frac{2}{5}$	0.78	3.87	${}^4F_{3/2}$	3.8
4	$Cr^{2+}, Mn^{3+}$	2	2	0			4.90	$^{5}D_{0}$	4.9
5	$Mn^{2+}, Fe^{3+}$	$\frac{5}{2}$	0	$\frac{5}{2}$	2	5.92	5.92	85/2 5 D	5.9
6	Fe <sup>2+</sup> , Co <sup>3+</sup>	2	2	4	$\frac{3}{2}$	6.71	4.90	$^{-}D_{4}$ $^{4}E_{-}$	5.4
7	Co <sup>2+</sup> , Ni <sup>3+</sup>	$\frac{3}{2}$	3	$\frac{9}{2}$	$\frac{4}{3}$	6.63	3.87	$\frac{1.9/2}{3}F_{A}$	4.8
8	Ni <sup>3+</sup>	1	3	4	$\frac{5}{4}$	5.59	2.83	$^{2}D_{5/2}$	3.2
9	Cu <sup>2+</sup>	$\frac{1}{2}$	2	$\frac{5}{2}$	$\frac{6}{5}$	3.55	1.73	${}^{1}S_{0}$	1.9

Experimental value agrees with spin only contribution It is as if L was zero or *quenched*.

$$\mu_{\rm eff} = 2\mu_B \sqrt{S(S+1)}$$



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## III. Spin-Orbit Coupling

#### Quenching of orbital moment

# Magnetic moments of ions in a solid: 3d TM and 4f RE

 $\Pi$ 



Good agreement between  $m_{ef}$  and experimental value. RE's ions behave in the solid as isolated ions\*\*.



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# Role of wave functions



4f orbitals much less extended, are more localized. 4f's are screened by (lie beneath) 5s, 5p's. Crystal field less important than S-O coupling. 3<sup>rd</sup> Hund's obeyed.



3d orbitals extend further from the nucleus, more delocalized. 3df's less screened (only by 4s). Crystal field more important than S-O coupling.

### III. Spin-Orbit Coupling

#### Quenching of orbital moment

# In the presence of crystal fields (in the solid):

- Spherical harmonics Y<sub>I</sub><sup>m</sup> are no longer eigenstates of the Hamiltonian as for a free atom.
- We have seen that the w.f. contains mixtures of  $m_e$  states.
- L and  $m_{\ell}$  are no longer good quantum numbers.
- Eigenstates are real spherical harmonics:  $p_x$ ,  $p_y$ ,  $p_z // d_{x^2-y^2}$ ,  $d_{z^2}$ ,  $d_{xy,...}$





$$\hat{L}_{z} = -i\hbar \frac{\partial}{\partial \varphi} \quad \begin{cases} \bullet \text{ Purely imaginary.} \\ \bullet \text{ Hermitian: real} \\ \text{ expect. values} \end{cases} \quad \begin{cases} p_{\alpha} \rangle & \text{Real w.} \\ |d_{\alpha} \rangle & \text{functions.} \end{cases} \implies \langle \hat{L}_{z} \rangle_{\alpha} = 0 \end{cases}$$

$$\begin{cases} \hat{L}_z |d_{xz}\rangle = \frac{\hbar}{\sqrt{2}} (-Y_2^{-1} - Y_2^1) = i |d_{yz}\rangle \\ \langle d_{xz} | \hat{L}_z |d_{xz}\rangle = \frac{i}{\sqrt{2}} (\langle 2, -1| - \langle 2, 1|)(|2, -1\rangle + |2, 1\rangle) = 0 \end{cases}$$

Expectation value of L is zero for all p and d orbitals.

**ORBITAL MOMENT IS QUENCHED (by the CF)** 

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## III. Spin-Orbit Coupling



P. Bruno (1989)

What is called magnetocrystalline anisotropy energy?

It is the energy it takes to rotate the magnetization from an easy to a hard direction.

The energy involved is related to S-O coupling:

$$\Delta E_{\rm so} = \langle H_{\rm so} \rangle_{\rm hard} - \langle H_{\rm so} \rangle_{\rm easy} = \zeta \left[ \langle \boldsymbol{L} \cdot \boldsymbol{S} \rangle_{\rm hard} - \langle \boldsymbol{L} \cdot \boldsymbol{S} \rangle_{\rm easy} \right] > 0$$

Very small for TM, typical values: 1-10  $\mu$ eV/atom in bulk !! (Compare to J ~ 1-10 meV)



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Exchange interaction: creation of  $\vec{m}_s$ 

Ligand fields (symm.+strength): responsible for anisotropic orbital  $\vec{m}_o$ 

S-O coupling effect: partially remove the quenching of L.

S-O coupling: link between  $\vec{m}_s$  and  $\vec{m}_o$ , responsible for "lattice talking to spin".

i.

#### > Origin of magnetocrystalline anisotropy

 $|^{2}$ 

$$E_{so} = \frac{\xi_{so}^2}{4} \sum_{nm} \frac{|\langle n, s | H_{so} | m, s' \rangle|^2}{E_{n,s} - E_{m,s'}} \quad \langle L_{\alpha}^n \rangle = \zeta \sum_m \frac{|\langle d_n^+ | L_{\alpha} | d_m^+ \rangle}{\Delta_{nm}}$$
$$E_{so}^{\alpha} = \xi_{so}^2 \sum_{nm} \frac{|\langle n, \uparrow | L_{\alpha} | m, \uparrow \rangle|^2}{\Delta_{nm}}$$
$$m_o^{\alpha} = -\mu_B \langle L_{\alpha} \rangle = -\mu_B \xi_{so} \sum_{nm} \frac{|\langle n, \uparrow | L_{\alpha} | m, \uparrow \rangle|^2}{\Delta_{nm}}$$



$$\begin{split} \langle H_{\rm so}^{\alpha} \rangle &= \frac{\zeta^2}{4} \sum \frac{|\langle \phi_n^j | L_{\alpha} | \phi_m^j \rangle|^2}{\Delta_{nm}} + \sum \frac{|\langle \phi_n^j | H_{\rm so}^\alpha | \phi_l^{j'} \rangle|^2}{\Delta_{nl}} = E_{jj}^{\alpha} + E_{jj'}^{\alpha} \\ \\ \text{Calculation involves 2^{nd} order perturb. theory.} \\ \text{Anisotropy energy is a 2^{nd} order effect.} \\ \\ \text{Cubic crystals: go to 4^{th} order.} \\ \\ \\ \text{K}_{\text{uni}} \sim \xi^2 / \text{w} , \text{K}_{\text{cub}} \sim \xi^4 / \text{w}^3 . \end{split}$$





#### Phenomenology $\succ$

<111>

 $\infty$ 

500

600

Ο

10

# How do we notice magnetic anisotropy?

Magnetization curves, experimental results in BULK material

 $\Pi$ 







Lecture II: Magnteic anisotropy

In a (ANTI)FERROMAGNET:





**Neumann's Principle**: if a crystal is invariant with respect to certain symmetry operations, any of its physical properties must also be invariant with respect to the same symmetry operations, or otherwise stated, the symmetry operations of any physical property of a crystal must include the symmetry operations of the point group of the crystal.



> Symmetry arguments:

• Time reversal  $\Rightarrow$  m  $\rightarrow$  -m  $\Rightarrow$  no odd terms

$$E_{\text{Ani}} = b_0 + \sum_{ij} b_{ij} \alpha_i \alpha_j + \sum_{ijkl} b_{ijkl} \alpha_i \alpha_j \alpha_k \alpha_l + \dots$$

 $b_0, b_{ij}, b_{ijkl}$ : anisotropy constant tensors

$$E_{\text{Ani}} = \sum_{\ell, \text{even}} \sum_{m=-\ell}^{m=+\ell} \kappa_{\ell}^{m} Y_{\ell}^{m}(\theta, \varphi)$$

 $\kappa_{\ell}^m:~\ell^{\rm th} {\rm order}$  anisotropy coefficients

• Point and space groups of the crystal lattice: reduce the number of terms and constants to be considered.

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Rotational symmetry along c axis (hexagonal crystals)

$$E_{\text{Ani}} = b_0 + K_1(\alpha_1^2 + \alpha_2^2) + K_2(\alpha_1^2 + \alpha_2^2)^2 + \dots$$

$$E_{\rm Ani} = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \dots$$

(no  $\phi$  dependence)

- > Usually, only the first order contribution is needed.
- $\succ$  For an easy axis oriented along the direction  $\hat{n}$  , we can also write:

$$E_{\rm Uni} = -K_u (\hat{m} \cdot \hat{n})^2$$



 $\succ$  For a nanoelement or NP with atomic moments  $\vec{m_i} = \mu_i \hat{S_i}$ , it is the sum of of single-site terms:

$$E_{\rm Ani,T} = -\sum_i K_i (\hat{S}_i \cdot \hat{n}_i)^2$$

i.



Lowest order terms: 
$$\kappa_2^{\pm 2}, \kappa_2^0 : Y_2^{\pm 2}, Y_2^0 \implies 2$$
 anis. constants  
 $E_{Ani} = K_1 \sin^2 \theta + K_1' \sin^2 \theta \cos(2\varphi)$   
For Trigonal, hexagonal, tetragonal:  $K_1'=0$   
Higher order terms needed:

> Tetragonal: 
$$E_{Ani} = K_1 \sin^2 \theta + (K_2 \sin^4 \theta + K_2' \sin^4 \theta \cos(4\varphi)) + \dots$$

> Trigonal: 
$$E_{\text{Ani}} = K_1 \sin^2 \theta + (K_2 \sin^4 \theta + K_2' \sin^3 \theta \cos \theta \cos(3\varphi)) + \dots$$

> Hexagonal:  $E_{\text{Ani}} = K_1 \sin^2 \theta + (K_2 \sin^4 \theta) + (K_3 \sin^6 \theta + K'_3 \sin^6 \theta \cos(6\varphi))$ 

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$$E_{\text{Ani}} = b_0 + \sum_{ij} b_{ij} \alpha_i \alpha_j + \sum_{ijkl} b_{ijkl} \alpha_i \alpha_j \alpha_k \alpha_l + \dots$$

Invariance of {b\_{ij}} under several symmetry operations given by a matrix  ${\cal R}$ 

> [111] 120° rotation:

$$\mathcal{R}_{120^{\circ}} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \implies B = \begin{pmatrix} a & c & b \\ b & a & c \\ c & b & a \end{pmatrix} \implies$$

$$B = \mathcal{R}^T B \mathcal{R}$$
$$B = \{b_{ij}\} = \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{11} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix}$$

3 independent constants  $\{b_{11}, b_{21}, b_{31}\} = \{a, b, c\}$ 

# > [001] 90° rotation:

$$\mathcal{R}_{90^{\circ}} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \implies B = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix} \implies 1 \text{ independent constant } b_{11} = b_{22} = b_{33} \equiv a$$

$$\sum_{ij} b_{ij} \alpha_i \alpha_j = a(\alpha_1^2 + \alpha_2^2 + \alpha_3^2) = a = \text{constant} \qquad \longleftrightarrow \begin{cases} \alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_2^2 \alpha_1^2 & \alpha_1^4 + \alpha_2^4 + \alpha_3^4 \\ \alpha_1^4 + \alpha_2^4 + \alpha_3^4 & = 1 - 2(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_2^2 \alpha_1^2) \end{cases}$$

$$Possible \ 4^{th} \text{ order terms}$$

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$$E_{Ani} = b_0 + \sum_{ij} b_{ij} \alpha_i \alpha_j + \sum_{ijkl} b_{ijkl} \alpha_i \alpha_j \alpha_k \alpha_l + \dots \implies E_{Ani} = K_0 + K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_2^2 \alpha_1^2) + K_2 (\alpha_1^2 \alpha_2^2 \alpha_3^2) \dots$$
Symmetry relations...

Alternatively, the 1<sup>st</sup> term can be expressed in terms of spherical angles as:

$$E_{\rm Ani} = K_1 (\sin^4 \theta \cos^2 \varphi \sin^2 \varphi + \sin^2 \theta \cos^2 \theta) = \frac{1}{4} \left( \sin^4 \theta \sin^2 (2\varphi) + \sin^2 (2\theta) \right)$$

Or in terms of spherical harmonics and anisotropy coefficients as:

$$E_{\text{Ani}} = \kappa_0 + \kappa_4 (\alpha_1^2 \alpha_2^2 + \alpha_1^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2 - 1/5) + \kappa_6 \left[ \alpha_1^2 \alpha_2^2 \alpha_3^2 - \frac{1}{11} (\alpha_1^2 \alpha_2^2 + \alpha_1^2 \alpha_2^2 + \alpha_3^2 \alpha_1^2 - 1/5) \right] - \frac{1}{105} + \dots$$

> Usually, only the first anisotropy constant is relevant, and we can write:

$$E_{\rm Cub} = K_c (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_2^2 \alpha_1^2)$$

Room Temp.	Fe (bcc)	Ni (fcc)	Co (hcp)	Fe <sub>3</sub> O <sub>4</sub>	CoFe <sub>2</sub> O <sub>4</sub>
K <sub>1</sub> (J/m³)	4.72 x 10 <sup>4</sup>	-5.7 x 10 <sup>3</sup>	4.53 x 10 <sup>5</sup>	-1.1 x 10 <sup>4</sup>	2.0 x 10 <sup>5</sup>
K <sub>2</sub> (J/m³)	-1.0 x 10 <sup>3</sup>	-2.3 x 10 <sup>3</sup>	1.44 x 10 <sup>5</sup>	-	-

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> Uniaxial anisotropy energy

K<sub>1</sub>, K<sub>2</sub>>0 (Co)

# $E_{\rm Ani} = K_1 \sin^2 \theta + K_2 \sin^4 \theta$

0

-0.2

-0.4

-0.6

-0.8

-1.0

π



0

-0.2

-0.4

-0.6

-0.8



 $\frac{\pi}{2}$ Ø

*Easy plane anisotropy* 

Easy-axes:

Basal plane

Hard axis:

[001]

50

 $K_0 = 0, K_1 = -1, K_2 = 0, K_3 = 0$ 

 $\frac{3\pi}{4}$ 



θ

2

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> Uniaxial anisotropy energy: higher orders

3

51

0.4

0.6 0.8 1.0

 $1/t_{co} (nm^{-1})$ 

$$E_{\text{Ani}} = K_1 \sin^2 \theta + (K_2 \sin^4 \theta) + (K_3 \sin^6 \theta + K'_3 \sin^6 \cos(6\varphi)) \qquad \textbf{K_1<0, K_2>0}$$

$$K_0 = 0.5, K_1 = -1, K_2 = +1, K_3 = 0$$



In-plane

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 $1/t_{co} (nm^{-1})$ 

0.6 0.8 1.0

0.4

# > Cubic anisotropy energy

# K<sub>1</sub>>0 (Fe)





 $K_0 = 1, K_1 = 2, K_2 = 0$ 





 $K_0 = 1, K_1 = -2, K_2 = 0$ 











## > Mixed anisotropies: sum of two uniaxial directions

Competing anisotropies:

- Uniaxial crystalline
- Shape anisotropy

Who will win?

$$E_{\text{Ani}} = K_a \sin^2 \theta + K_b \sin^2 (90^\circ - \theta)$$
$$= K_b + (K_a - K_b) \sin^2 \theta$$



#### From bulk to nano... $\succ$







#### Demagnetizing factors and effective shape anisotropy $\geq$

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$$E_{dem} = -\frac{\mu_0 V M^2}{2} \left( \mathcal{N}_x \alpha_1^2 + \mathcal{N}_y \alpha_2^2 + \mathcal{N}_z \alpha_3^2 \right)$$



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Favors in-plane M.

#### > Influence of invdidual NP properties on SAR



# **Shape Matters**





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#### Lattices of magnetite NPs: HL area vs assembly geometry

Random assemblies with increasing concentration

# Macrospin models: dipolar + Aligned easy-axes

# **Shape Matters**

# SC lattice with increasing heights H



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# V. Effects of Anisotropy

Stoner-Wohlfarth Model

 $E = g(\theta, \phi) - \mu_0 \mathbf{M} \cdot \mathbf{H}$ 

- Single domain NP represented by: Macrospin M= M<sub>s</sub> S
- > Uniaxial anisotropy:  $E_{ani} = g(\theta) = K_u V \sin^2 \theta$

$$E_T = K_u V \sin^2 \theta - \mu_0 M_s H \cos(\theta - \psi)$$

Reduced field

 $H_{\rm K} = \frac{2K_u}{\mu_0 M_s V} \qquad h = \frac{H}{H_{\rm K}}$ 

$$\varepsilon_T = \sin^2 \theta - 2h \cos(\theta - \psi)$$

Equilibrium magnetization directions:

$$\frac{\partial \varepsilon_T}{\partial \theta} = 2\sin\theta\cos\theta - 2h\sin(\theta - \psi) = 0$$

$$\frac{\partial^2 \varepsilon_T}{\partial \theta^2} = 2\cos 2\theta + 2h\cos(\theta - \psi) > 0$$

- For  $\psi$ =0 (aligned NP): 2 minima only for h < 1, H < H<sub>k</sub>
- For  $\psi \neq 0$  (non-aligned NP): 2 minima only for h< h<sub>c</sub>( $\alpha$ )





# For $\psi = 0$ (aligned NP)

 $\succ$ 



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# $\varepsilon_T = \sin^2 \theta - 2h \cos(\theta - \psi)$

For  $\psi$ =0 (aligned NP): 2 minima only for h < 1, H < H<sub>k</sub>

For  $\psi \neq 0$  (non-aligned NP): 2 minima only for h< h<sub>c</sub>( $\psi$ ) < 1



# Critical field $h_c(\psi)$

# At zero temperature:

- Magnetization points along energy minima.
- Irreversible jump @ the critical field:  $h = h_c(\psi)$
- For  $\psi$ = 90°: linear and reversible.

$$m = \frac{M}{M_s} = \cos(\theta - \psi)$$

# Hysteresis Loops



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# Hysteresis Loop for an assembly of randomly oriented NPs

García-Otero et al. JMMM 203, 268 (1999)



 $h_c = 0.479, \ M_r = 0.5$ 

# Cubic anisotropy



 $K > 0: h_c = 0.321, M_r = 0.831$  $K < 0: h_c = 0.189, M_r = 0.866$ 





M. Jamet, PRL 86, 4676 (2001)

# SW Astroid at finite T for one 3 nm Co NP.





Wernsdorfer et al. JAP 81, 5543 (1997)



D. Schmool, H. Kachkachi et al. SSP 301 (2015)

Josephson junctions

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# V. Effects of Anisotropy

### > Influence of anisotropy: time scales



# **Thermal activation**



Monte Carlo simulation

Phenomenological models





#### Phenomenology



$$K_{eff} = K_V + K_S \frac{S}{V}$$



Size dependence of the effective anisotropy constant in Co NPs, the line represents the fit to the expression.

0.75

 $1/D (nm^{-1})$ 

1.00

1.25

1.50

D (nm)

2

0.50

F. Luis, Phys. Rev. B 65, 094409

### Phenomenology



## **VI. Surface anisotropy**



#### Surface anisotropy : Holllow Maghemite NPs

Ò Iglesias et al. PRB 79, 094419 (2009) Nanomaterialls, 6 221 (2016)





- •Hollow NPs, D= 8nm
- Polycrystalline structure.

# Varying the shell thickness



# Contribution of inner and outer surfaces



Surface anisotropy: distinguishing in from out

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IN

## VI. Surface anisotropy

#### Effective One Spin Model



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# **VI. Surface anisotropy**

#### Effective One Spin Model





R. Yanes, O. Fesenko et al. PRB 40, 2140 (2007) JPD 42, 055013 (2009)

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## Basics



J. Nanoscience and Nanotechnology 8, 2761 (2008)

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Exchange Bias in Magnetic Systems

## Exchange Bias in Iron oxide based nanoparticle Systems M.-H. Phan, O. Iglesias et al. Nanomaterials 6, 221 (2016)

W. H. Meiklejohn and C. P. Bean Phys. Rev. 102, 1413 (1956); 105, 904 (1957)



FIG. 3. Hysteresis loops of fine oxide-coated particles of cobalt taken at  $77^{\circ}$ K. The dashed lines show the hysteresis loop when the material is cooled in the absence of a magnetic field. The solid lines show the hysteresis loop when the material is cooled in a saturating magnetic field.







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# **VII. Exchange Bias**

COLOR CODE: dark blue  $\Rightarrow$  core, green  $\Rightarrow$  shell

yellow (cyan) / shell (core) interfacial spins



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# **VII. Exchange Bias**

#### Exchange Bias : Results: ZFC-FC Loops

AF Interface Coupling  $J_{Int} = -0.5 J_{C}$ **0.6** (a) 0.4 FC 0.2 -0.4 ZFC (c) 0.1 ZFC Int  $\mathbf{M}_{\mathbf{Sh}}$ 

O. Iglesias et al., PRB 72, 212401 (2005)

= -0.5

= -0.5, J<sub>Int</sub> :

S

Non-uniform core reversal

Loop after FC is displaced towards negative field direction with respect to ZFC loop.

-1

0

h (K)

> Notice also the vertical shift of the shell magnetization.

Shell behavior is dictated by coupling with the core through J<sub>int</sub>.

 Changing the sign of the interface coupling influences the net magnetization at the interface.





Atomic details @ interface matter!!

Influence of interface roughness.

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-0.2

-3

-2

FC

3

2

1


## MAGNETIC ANISOTROPIES COME INTO MANY FLAVOURS !!

- 1. Macroscopic description of anisotropy dictated by symmetries and values (signs) of anis. constants.
- 2. At the nanoscale, anisotropy terms of different origin compete with each other.
- 3. Anisotropy influences energy barriers, reversal modes, hysteresis loops, time dynamics...
- 4. In general, simulation methods implementing atomistic description needed. Theoretical models can be set up to simply the description of NP assemblies, going beyond mascrospin models.



More info at: http://www.ffn.ub.es/oscar http://nanomagn.blogspot.com













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