Refresher lecture in Magnetism

Virginie Simonet virginie.simonet@neel.cnrs.fr

Institut Néel, CNRS & Université Grenoble Alpes, Grenoble, France Fédération Française de Diffusion Neutronique

IntroductionAtomic magnetic momentAssembly of non interacting momentsMagnetic moments in interactionLocalized versus itinerant electronsFrom microscopic to macroscopicApplicationsModern trends in research





Introduction

Magnetic materials all around us : the earth, cars, audio, video, telecommunication, electric motors, medical imaging, computer technology...







Introduction

Magnetism:

science of cooperative effects of orbital and spin moments in matter

→Wide subject expanding over physics, chemistry, geophysics, life science.

Large variety of behaviors: dia/para/ferro/antiferro/ferrimagnetism, phase transitions, spin liquid, spin glass, spin ice, skyrmions, magnetostriction, magnetoresistivity, magnetocaloric, magnetoelectric effects, multiferroism, exchange bias...

in different materials: metals, insulators, semi-conductors, oxides, molecular magnets,.., films, nanoparticles, bulk...

Inspiring or verifying lots of model systems (ex. Ising model)

Magnetism is a quantum phenomenon but phenomenological models are commonly used to treat classically matter as a continuum





 \checkmark An electric current is the source of a magnetic field B

✓A magnetic moment is equivalent to a current loop

$$\vec{\mu}_{\ell} = \vec{I}.\vec{S} = \frac{-ev}{2\pi r}\pi r^2 \vec{n} = \frac{-evr}{2}\vec{n}$$

creating a dipolar magnetic field















Consequences:

- ✓ Magnetic moment and angular momentum are antiparallel
- ✔ Calculations with magnetic moment using formalism of angular momentum





Magnetism in quantum mechanics:

Distribution of electrons on atomic orbitals, which minimizes the energy: Building of atomic magnetic moments

The electronic wavefunction $\Psi_{n\ell m_\ell}$ is characterized by 3 quantum numbers

 $\begin{array}{l} n : \text{electronic shell} \\ \ell : \text{orbital angular momentum quantum number} \quad 0 < \ell < n-1 \\ \hline \begin{array}{c} \ell & 0 & 1 & 2 & 3 \\ \hline & s & p & d & f \end{array} \end{array}$

 m_ℓ : magnetic quantum number $-\ell < m_\ell < +\ell$





Magnetism in quantum mechanics: quantized orbital angular momentum



The magnitude of the orbital momentum is $\hbar\sqrt{\ell(\ell+1)}$

The component of the orbital angular momentum along the z axis is $\,\hbar m_\ell$





Magnetism in quantum mechanics: spin angular momentum of pure quantum origin

$$\hat{s}_Z \Psi_s = \hbar m_s \Psi_s$$
$$\hat{s}^2 \Psi_s = \hbar^2 s (s+1) \Psi_s$$

With the quantum numbers :

$$s = 1/2, m_s = -1/2, +1/2$$



The magnitude of the spin angular momentum is $\hbar\sqrt{s(s+1)} = \hbar\sqrt{3/4}$

The component of the spin angular momentum along the z axis is $\hbar m_s$





Magnetism in quantum mechanics:

Magnetic moment associated to 1 electron in the atom Two contributions: spin and orbit

> Magnetic moments $\hat{\mu}_{\ell} = -g_{\ell}\mu_{B}\hat{\ell}$ $\hat{\mu}_{s} = -g_{s}\mu_{B}\hat{s}$



With
$$g_{\ell} = 1$$
 and $g_s = 2$
and the Bohr magneton $\mu_B = \frac{\hbar e}{2m_e}$





Magnetism in quantum mechanics: several e- in an atom

$$\hat{L} = \sum_{ne-} \hat{\ell} \qquad \hat{S} = \sum_{ne-} \hat{s}$$

Combination of the orbital and spin angular momenta of the different electrons: related to the filling of the electronic shells in order to minimize the electrostatic energy and fulfill the Pauli exclusion principle

Spin-orbit coupling:
$$\lambda \hat{L} \cdot \hat{S}$$

Total angular momentum $\hat{J} = \hat{L} + \hat{S}$
A given atomic shell (multiplet) is defined by 4 quantum numbers :
L, S, J, M_J with $-J < M_J < J$





Magnetism in quantum mechanics: several e- in an atom

Hund's rules for the ground state 1st rule $S = M_S = \sum_{ne^-} m_s$ maximum 2nd rule $L = M_L = \sum_{ne^-} m_\ell$ maximum in agreement with the 1st rule 3rd rule from spin-orbit coupling

 $J = |L - S| \qquad \qquad J = |L + S|$

for less than $\frac{1}{2}$ filled shell for more than $\frac{1}{2}$ filled shell





Application of Hund's rule : L and S are zero for filled shells

Example of unfilled shell Tb³⁺ is 4f⁸, 8 electrons to put in 14 boxes ($\ell = 3$)



so L=3 and S=3

The spin-orbit coupling applies for more than $\frac{1}{2}$ filled shell so J=6 and -6 < M_J < 6

The ground state is 13-fold degenerate





Total magnetic moment of the unfilled shell

$$\hat{\mu} = -\mu_B(\hat{L} + 2\hat{S})$$
$$\mu = g_J \mu_B \sqrt{J(J+1)}$$

$$\mu_J = -g_J \mu_B J$$

With the Landé g_J -factor

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$







Magnetism is a property of unfilled electronic shells: Most atoms (bold) are concerned but 22 are magnetic in condensed matter



Atom in matter:

✓ Chemical bonding \rightarrow filled e- shells : no magnetic moments







Atom in matter:

✓ Chemical bonding \rightarrow filled e- shells : no magnetic moments, except for:



4f electrons: inner shell3d electrons: outer shell (more delocalized)





Atom in matter:

✓ Influence of surrounding charges → crystal field (CEF)







Atom in matter:

✓ Influence of surrounding charges → crystal field (CEF)

4f electrons
spin-orbit >> CEF
Partially filled electronic shells : non-spherical 4f charge distribution
+ CEF → selects some orbitals (lift degeneracy)
+ spin-orbit → anisotropy J: alignment of magnetic moments along some directions







Summary

Magnetism is a quantum phenomenon

Magnetic moments are associated to angular momenta

Orbital magnetic moment and spin magnetic moment

Localized magnetic moment in 3d and 4f atoms with different behaviors

Orbital and spin moments can be coupled (spin-orbit coupling)

Importance of environment, crystal field:

- quenching of orbital moment in 3d
- magnetocrystalline anisotropy in 4f atoms





Measurable quantities:

Magnetization : magnetic moment per unit volume derivative of the energy w. r. t. the magnetic field

$$M = -\frac{\partial F}{\partial B}$$

Susceptibility: derivative of magnetization w. r. t. magnetic field, alternatively, ratio of the magnetization on the field in the linear regime

$$\chi = \mu_0 \frac{\partial M}{\partial B} \approx \mu_0 \left(\frac{M}{B}\right)_{lin}$$







Zeeman energy: coupling of total magnetic moment with the magnetic field Diamagnetic term: induced orbital moment by the external magnetic field





N atomic moments in a magnetic field B

Calculation of magnetization and susceptibility Thermal average (Boltzmann statistics) + perturbation theory

$$M_{\alpha} = \frac{N}{V} \sum_{j} -\frac{\partial E_{j}}{\partial B_{\alpha}} \frac{\exp(-\beta E_{j})}{\sum_{j} \exp(-\beta E_{j})} \quad \text{with} \quad \beta = k_{B}T$$





Energy:
$$\hat{W}_B = \mu_B(\vec{\hat{L}} + 2\vec{\hat{S}}).\vec{B} + \frac{e^2}{8m_e}\sum_{ie-}(\vec{\hat{R}}_i \times \vec{B})^2$$

Diamagnetic term for N atoms:

$$\chi = -\frac{N}{V}\mu_0 \frac{e^2}{4m_e} < R_{\perp}^2 >$$
 perpendicular to the field

due to the induced moment by the magnetic field

→ negative weak susceptibility, concerns all e- of the atom, T-independent





$$\text{Energy:} \quad \hat{W}_B = \boxed{\mu_B(\vec{\hat{L}} + 2\vec{\hat{S}}).\vec{B}} + \frac{e^2}{8m_e}\sum_{ie-}(\vec{\hat{R}}_i \times \vec{B})^2$$

Paramagnetic term for N atoms:

$$M = \frac{N}{V} g_J J \mu_B B_J(x) \quad \text{ with } \quad x = \frac{g_J J \mu_B B}{k_B T}$$

and the Brillouin function:

$$B_J(x) = \frac{2J+1}{2J} \operatorname{coth}\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \operatorname{coth}\left(\frac{x}{2J}\right)$$





Paramagnetic term







Paramagnetic term

$Limit x << 1 i.e. k_BT >> H$



It works well for magnetic moments without interactions and negligible CEF: ex. Gd^{3+} , Fe^{3+} , Mn^{2+} (L=0)





Summary of magnetic field response of non-interacting atomic moments

At small H/k_BT : linear regime







Dipolar interaction:

$$E = \frac{\mu_0}{4\pi r^3} [\vec{\mu}_1 \cdot \vec{\mu}_2 - \frac{3}{r^2} (\vec{\mu}_1 \cdot \vec{r}) (\vec{\mu}_2 \cdot \vec{r})]$$

 $\mathcal{H} = -\sum \mathrm{J}_{\mathrm{ij}} ec{S}_i . ec{S}_j$

Much too weak to account for the ordering of most magnetic materials

Exchange interaction:

Origin: electrostatic and Pauli exclusion principle Many-electron wavefunctions must be antisymmetric through the exchange of two electrons

H

Heisenberg Hamiltonian

J: exchange coupling constant J > 0 ferromagnetic J < 0 antiferromagnetic

Simonet, Meeticc 2018, Banyuls sur mer



Region of constructive interference

Region of destructive interference

Exchange interaction

•Direct exchange: usually weak \rightarrow overlap between magnetic orbitals

•Superexchange: in insulators, indirect mediated by non-magnetic atoms Depends on geometry of the bonds. Most often antiferromagnetic. Explains the magnetism in transition metal oxides.



From paramagnetic state at high temperature to ordered state at low temperature: phase transition













Molecular field model

Calculation of magnetization and susceptibility for interacting magnetic moments

The interactions are represented by a fictitious field from neighboring moments

$$\begin{split} \mathcal{H} &= -\sum_{ij} \mathbf{J}_{ij} \vec{S}_i . \vec{S}_j + g\mu_B \sum_j \vec{S}_j . \vec{B} \\ \mathcal{H} &= g\mu_B \sum_i \vec{S}_i . (\vec{B} + \vec{B}_{mf}) \text{ with } \vec{B}_{mf} = -\frac{2}{g\mu_B} \sum_j \mathbf{J}_{ij} \vec{S}_j \end{split}$$





Molecular field model

Ferromagnetic case:

Calculation of the susceptibility in the low field, high temperature limit

$$\vec{B}_{mf} = \lambda \vec{M}$$
$$M = \frac{(g_J \mu_B)^2 J (J+1)}{3k_B T} (B + \lambda M) = \frac{C}{T} (B + \lambda M)$$
$$\chi = \frac{C}{T - \lambda C} = \frac{C}{T - T_C}$$

 $T_C = \lambda C$ the Curie temperature

•At $T_{\rm C}$, χ becomes infinite : the system becomes spontaneously magnetized

•Below T_C , the moments can be aligned by the internal molecular field without *B*





Molecular field model $x = \frac{g_J \mu_B J (B + \lambda M)}{k_B T}$ Ferromagnetic case: **Calculation of the magnetization below Tc** 1.0 $T > T_c$ $T = T_c$ $T < T_c$ \rightarrow Solve simultaneously 2 equations for B=0 M M_S $M = g_J \mu_B J B_J(x)$ No solution for $T > T_C$ One solution for $T < T_C$ Spontaneous magnetization 2^{nd} order phase transition at T_C 6 X



Molecular field model

Ferromagnetic case: summary paramagnetic Ferromagnetic $\chi = \frac{C}{T - T_C}$ $M_{1.0}$ M_S 1/x

C

 T_C 0 susceptibility magnetization Simonet, Meeticc 2018, Banyuls sur mer UNIVERSITÉ Grenoble

Molecular field model

Antiferromagnetic case: same analysis but for each of the 2 sublattices

Spontaneous magnetization below the Néel temperature T_N

Molecular field model

Other types of magnetic states (non collinear, disordered)

Complex magnetic structures or disordered ground states due to magnetic frustration

• Lattice geometry: ex. triangle of magnetic moments antiferromagnetically interacting

Other types of magnetic states (non collinear, disordered)

Other types of magnetic states (non collinear, disordered)

• Example of $Ba_3NbFe_3Si_2O_{14}$ insulator, helix + 120° arrangement, chiral compound

Magnetic excitations

Perfect order at T=0 At T≠0, order disrupted by spin waves Allow entropy gain without losing too much in exchange energy

Magnetic excitations

Dispersion relation for a cubic crystal Probed by inelastic neutron or resonant X-ray scattering: information on the ground state Hamiltonian

Ferromagnet J>0

Antiferromagnet J<0

 $E(k) = -4\mathrm{J}S|\sin(ka)|$

Localized versus itinerant electrons

Hubbard model

$$H_{\text{Hubbard}} = -\sum_{i,j} t_{i,j,\sigma} c_{i,\sigma}^{\dagger} c_{j,\sigma} + \sum_{i} U n_{i,\uparrow} n_{j,\downarrow}$$

- Metal state due to hopping term t (gain in kinetic energy from Heisenberg uncertainty principle) \rightarrow measure of band width
- Coulomb energy U: cost of putting 2 e⁻ on the same lattice site (Pauli exclusion principle) \rightarrow measure of electron correlations

- → Half filling, 1 e⁻ per site and $U=\infty$: insulator
- → Half filling, U large and >> t: antiferromagnetic Mott insulator Heisenberg Hamiltonian with $-J = 4t^2/U$
- $\rightarrow U \approx t$ metal-insulator transition
- \rightarrow t >> U metallic ferromagnetic

Localized versus itinerant electrons

Magnetism in metals

Starting point: the free electron model, properties of Fermi surface, electronic band structure, then add correlations

For a non-magnetic metal: same number of spin \uparrow and \downarrow electrons at Fermi level

Pauli paramagnetism Bands split by magnetic field Temperature independent > 0 Enhanced by e⁻ correlations

$$\chi_P = \mu_0 \mu_B^2 N(E_F)$$

Landau diamagnetism Orbital response of e⁻ gas to magnetic field Temperature independent < 0

$$\chi_L = -\frac{m_e}{m^*}^2 \frac{\chi_P}{3}$$

Localized versus itinerant electrons

Magnetism in metals

➔non-integer magnetic moment

and more: generalized susceptibility, spin-density wave instabilities, Kondo effect...

Macroscopic behavior of magnetization, a compromise between 4 mechanisms:

Exchange interaction: favors uniform magnetization. Very strong but short-ranged

✓ Dipolar interaction:

tends to avoid the formation of magnetic poles. Weak but long-ranged

✓ Magnetocrystalline anisotropy:

orients the magnetic moments along privileged directions

✓Zeeman energy:

interaction with an external magnetic field

 \rightarrow alignment of the magnetic moments along the field

for a homogeneous ferromagnetic material, minimization of the energy:

$$F_T = F_{ex} + F_{dip} + F_{an} + F_H$$

Magnetocrystalline anisotropy

→ Magnetic moments prefer to align along certain crystallographic directions (stronger for 4f than for 3d atoms)

Magnetization variation against anisotropy in ferromagnets

Dipolar energy

$$E = \frac{\mu_0}{4\pi r^3} [\vec{\mu}_1 \cdot \vec{\mu}_2 - \frac{3}{r^2} (\vec{\mu}_1 \cdot \vec{r}) (\vec{\mu}_2 \cdot \vec{r})]$$

Minimizing the demagnetizing field produced by the material

- \rightarrow shape anisotropy
- → formation of magnetic domains with magnetization // anisotropy directions

→Explains zero macroscopic magnetization in ferromagnetic materials below T_C if they have not been submitted to a magnetic field

Magnetic domains

Fe-Si

NdFeB

Cost in exchange and anisotropy energies at the boundaries between domains: domain walls

Width of the wall: balance between exchange and anisotropy energy

Coercitivity represents the magnetization ability to resist reversal against applied magnetic field

Coercive field for coherent rotation → Stoner-Wolfarth model:

 $E = K\sin^2\theta + \mu_0 M_s H\cos\theta$

Uniaxial anisotropy Zeeman term

Coercitivity represents the magnetization ability to resist reversal against applied magnetic field

Coercive field for coherent rotation → Stoner-Wolfarth model:

> $E = K \sin^2 \theta + \mu_0 M_s H \cos \theta$ Uniaxial anisotropy

Zeeman term

- As long as $H < 2K/\mu_0 M_s$, $\theta = 0$ and $\theta = \pi$ are two minima separated by an energy barrier
- When $H = 2K/\mu_0 M_s$, the barrier flattens and the magnetization can rotate to the minimum $\theta = \pi$

Stoner-Wohlfarth model works well for nanoparticles

The coercive field $H_c = 2K/\mu_0 M_s$

But $H_c \ll 2K/\mu_0 M_s$ for most systems

In macroscopic materials, influence of defects: Rotation occurs by nucleation on defects and propagation of domain walls

Simonet, Meeticc 2018, Banyuls sur mer

Activation

volume

Hysteresis cycle of a ferromagnet

Applications

Applied research \rightarrow lots of applications, concerns mostly ferromagnetic materials Hard magnetic materials: reasonable value of remanence, high coercitivity Soft magnetic materials: high remanence, low coercitivity Materials for electronics: operate at high frequencies

Recording and reading

Research in magnetism: modern trends

- Magnetic frustration: complex magnetic (dis)ordered ground states
- Molecular magnetism: photoswitshable, quantum tunneling
- Mesoscopic scale (from quantum to classical) \rightarrow quantum computer
- Multiferroism: coexisting ferroic orders (magnetic, electric...)
- Quantum phase transition (at T=0)
- Low dimensional systems: Haldane, Bose-Einstein condensate, Luttinger liquids
- Iridates and topological matter
- Magnetism and superconductivity
- Nanomaterials: thin films, multilayers, nanoparticles
- Spintronics: use of the spin of the electrons in electronic devices
- Skyrmionics
- Magnetoscience: magnetic field effects on physics, chemistry, biology ...

200 Å

Further reading

- "Magnetism in Condensed Matter" by Stephen Blundell, Oxford University press (2003)
- "Introduction to magnetism" by Laurent Ranno, *collection SFN 13, 01001 (2014), EDP* Sciences, editors V. Simonet, B. Canals, J. Robert, S. Petit, H. Mutka, free access DOI: <u>http://dx.doi.org/10.1051/sfn/20141301001</u>
- "Magnetism and Magnetic Materials" by J.M.D. Coey, Cambridge Univ. Press (2009)
- "Magnétisme" by Trémolet de Lacheisserie, EDP Sciences (2000)
- Any questions: virginie.simonet@neel.cnrs.fr

