Nuclear Magnetic Resonance in ferromagnets: structural and magnetic properties investigations

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Outline of the talk

• NMR in ferromagnets: an analysis tool among others
• Basis of Nuclear Magnetic Resonance
  – Quantum description
  – Classical description
  – Spin Echo
• Particularities of NMR in ferromagnets
• Structural information by NMR
  • Local symmetry
  • Local chemical environment
• Magnetic information by NMR
  • Hyperfine field profile
  • Field and temperature dependent measurements
• Local magnetic susceptibility: 3D NMR in Ferromagnets
  • Restoring field
  • Magnetization reversal inhomogeneity
  • Magnetic anisotropy inhomogeneity
• Conclusion

NMR in ferromagnets: an analysis tool among others

• Volume
  – Xray Diffraction: XRD: Xtal Structure, Super-period, Texture, Interface roughness
  – Transmission Electron Microscopy: TEM: Stacking, Grain structure, Superlattice coherence, Misfit dislocations, Interface roughness, chemical analyses when combined with EELS/EDXS
  – Hyperfine techniques: Nuclear Magnetic Resonance, Mössbauer Spectroscopy: Chemical & Topological Short Range Order
  – Many other techniques: Neutron diffraction, Exafs, RBS…

• Free surface
  – Electron Diffraction: RHEED, LEED: Growth mode, 2D Surface structure, Orientations
  – Auger Spectroscopy: AES: Growth mode, Surface diffusion & segregation
  – Imaging: STM, AFM: Direct topological view

Bulk Structure

Xtal Structure
Xtal Orientation
Texture, Stacking Mosaicity
Grain Size

Extended defects, Grain boundaries
Impurities at defects
Point Defects, Impurities

Interface nanostructure

XRD
TEM
NMR
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Basis of Nuclear Magnetic Resonance

- Characteristics of nuclei:
  - Spin
    - Has to be non zero: from ½ (¹H) to 7 (¹⁷⁶Lu)
    - Odd number of neutrons or protons
  - Gyromagnetic ratio $\gamma$
    - The ratio of magnetic dipole moment to the angular momentum
      - $M = \gamma L$
      - Characterizes the motion in a magnetic field

Quantum mechanics: Resonant Absorption of Photon

$$\begin{align*}
\text{Spin } 1/2 & : H_0 = 0 \\
\text{Photon} & : H_1(\omega) \\
\text{Resonance: } \omega = \omega_L
\end{align*}$$

$H_0$: Static magnetic field: Zeeman Effect
$H_1$: Radiofrequency field: Resonant Absorption
Observable Elements & Sensitivity

**In practice:**
- Organic materials: H, F, P (17O, 14N, 13C)
- Metalloids: Ga, B, As, In (Si, Se, Te)
- Normal metals: Li, Na, Al (Be, K)
- Transition Metals: V, Mn, Co, Cu, Nb, La, Re (Y, Pt, Ta)
- Rare Earths: Pr, Eu, Tb, Ho (Nd, Gd)

**To increase sensitivity:**
- Low Temperature: NMR signal increases as $1/T$ (Curie law)
- High Field: NMR signal increases as $\omega^2 = \gamma^2 H^2$

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NMR Classical description

- Why is it possible to use a classical description.
  - NMR measurements are done simultaneously on a very large number of nuclei
- NMR processes much easier to explain

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Motion of a particle rotating about an axis

- We consider a particle moving about an axis
- The Newton’s second law:

  $$\sum \vec{F} = \frac{d\vec{p}}{dt}$$

- If we multiply both sides by the cross product with the position vector we obtain:

  $$\vec{r} \times \sum \vec{F} = \vec{r} \times \frac{d\vec{p}}{dt}$$

  $$\sum \vec{\tau} = \vec{r} \times \frac{d\vec{p}}{dt}$$

  $$\sum \vec{\tau} = \frac{d(\vec{r} \times \vec{p})}{dt}$$
Motion of an object rotating about an axis

\[ \vec{L} = \vec{r} \times \vec{p} \]

It is called the angular momentum of the particle.

So we can write:

\[ \sum \vec{\tau} = \frac{d\vec{L}}{dt} \]

The sum of the torques is equal to the time derivative of the angular momentum.

This is the rotational analog of the Newton’s second law.

The case of a nuclear spin

Now consider a nuclear spin of magnetic moment \( M \) in a magnetic field.

From the magnetic field results a torque:

\[ \vec{\tau} = \vec{M} \times \vec{H} \]

And its magnetic moment is defined through its gyromagnetic ratio \( \gamma \)

So the spin equation of motion becomes

\[ \sum \vec{\tau} = \frac{d\vec{L}}{dt} \]

\[ \gamma \vec{M} \times \vec{H} = \frac{d\vec{M}}{dt} \]

Motion of an object rotating about an axis

The case of a nuclear spin

The direction of the motion is perpendicular to the plan defined by \( M \) and \( H \).

This is a precession motion.
• How to give a classical description of this quantum process?

We need to consider 2 fields:

- $H_0$: Static magnetic field: Zeeman Effect (OK with what we know)
- $H_1$: Radiofrequency field: Resonant Absorption

NMR Classical description

- A rf field is the sum of 2 fields rotating in opposite directions

NMR - Macroscopic Viewpoint

In a frame rotating at the same angular velocity $\omega_L$ as the spin, the spin looks static.

In the frame rotating at velocity $\omega_L$ the apparent static magnetic field is ZERO

Pulsed $H_1$

- Pulse Duration: $\tau$
- Particular Turn Angles
  - $\pi/2 : \Rightarrow M_n \perp H_0$
  - $\pi : M_n$ Reversal

At Resonance

- $H_0 - \omega/\gamma = 0$
- Turn Angle: $\omega_1 \tau$
What is the NMR signal?

The component of the nuclear magnetization in the xy plane

NMR signal is maximum when the turning angle is $\pi/2$

A way to measure the NMR signal: Spin Echo

Classical (Hahn) Spin Echo Pulse Sequence

Free Induction Decay

Spin Echo

Dephasing (Spread of $\omega$)

Rephasing

Magnet (H scan)

Sample coil

RF pulse (µS) 1 to 1000 MHz ($\omega$ scan)

Absorption

Emission

NMR Induction Signal

H or $\omega$ field or Frequency Scan NMR

Free Induction Decay in Time Domain

Fourier transform NMR

Field or Frequency Scan NMR

Pulsed NMR Setup

NMR – Relaxation times

• After a spin echo; the spin system has to go back to equilibrium:
  • 2 relaxation processes:
    • vanishing of the nuclear magnetization in the xy plane
    • Reorientation of the magnetization towards the Z axis.

Relaxation along the laboratory Z direction:
  spin lattice relaxation time $T_1$ (10 ms)

Relaxation into the xy plane:
  spin-spin relaxation time $T_2$ (10 µs)
Outline of the talk

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  - Local chemical environment
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  - Magnetic anisotropy inhomogeneity
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NMR in ferromagnets: Particularities

In ferromagnets the magnetic field $H_0$ is the field inside the material on the nuclei sites (for example, 20 Tesla for Cobalt nuclei in bulk Co).

- It is called the Hyperfine Field (HF)
- The HF strength depends on the local symmetry and local chemical environment of the probed nuclei

An NMR spectrum in a ferromagnet is measured by frequency sweeps:
- it is a number of atoms versus a resonance frequency.

Among the “traditional” ferromagnets (Fe, Co and Ni),
- Co has the highest sensitivity (10^4 time larger than Fe for example)

NMR Frequency and Local symmetry: Bulk Co

Pure samples: Frequency is the fingerprint of the atom site local symmetry
**Standard - Bulk Cobalt - fcc & hcp**

Stacking faults in fcc/hcp structures

- **fcc base**
  - (111)
  - ABCABCABCABC
  - cccccccccccc

- **hcp base**
  - ABABABABABAB
  - hhhhhhhhhhh

- **1 fault**
  - ABCABCBABCAC
  - cccccchccccccc

- **2 faults**
  - ABCABCBABCAC
  - cccccchccccccc

- **h in c / c in h**
  - ABABABCACACA
  - hhhhhccchhhh

**Bulk Structure of electrodeposited Co Thin Films**

Quantitative analysis

- **Stacking faults:** 3% 30%

![Graph showing fcc and hcp fractions](image)

Electrodeposited on very flat Au film

Initial growth mostly hcp (<20%fcc)
Then fcc + SF

AFM Imaging: Change of structure correlated to change of film morphology:
First stage: flat layers
Second stage: Columns

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**NMR frequency and Chemical environment**

- **Co$_{0.90}$Cu$_{0.10}$**
  - 1 Cu
  - 2 Cu

- **Co$_{0.90}$Ru$_{0.10}$**
  - 1 Ru
  - 2 Ru
  - 3 Ru

- **Co$_{0.90}$Fe$_{0.10}$**
  - 0 Fe
  - 1 Fe
  - 2 Fe
  - 3 Fe

*Alien atoms as nearest neighbor of the probed atom shifts the resonance frequency. The value and sign of the shift depends on the nature of the neighboring atom. (Cu: -16 MHz; Ru: -25 MHz; Fe: +10 MHz)*
NMR frequency and Chemical environment: quantitative analysis

Decomposition of NMR spectrum with Gaussian lines.

NMR intensity increase as:
1 NN: grows as C,
2 NN: grows as C^2,
3 NN: grows as C^3,
C: Concentration in alien atoms.

Random distribution of the alien atoms among the nearest neighbors (NN) of Co.

The line intensity follows a binomial law.

Problem - Bulk Not Understood

CoPt alloys:
- 2 sets of satellites
  - narrow upwards
  - broad downwards
- Related to position of the nearest neighbor among the 12 NN?
- Long range interactions between Pt impurities?
- Second neighbor shell?

Frequency Shifts in Co based Alloys

Frequency shift due to impurities in the nearest neighbor shell
Nearly proportional to the number of impurities

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Phase</th>
<th>Al</th>
<th>Si</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Ge</th>
<th>Nb</th>
<th>Ru</th>
<th>Re</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency Shift / Imp. NN (MHz)</td>
<td>fcc</td>
<td>-22</td>
<td>-16</td>
<td>-40</td>
<td>-40</td>
<td>-37</td>
<td>+9</td>
<td>-7</td>
<td>-16</td>
<td>-16</td>
<td>-47</td>
<td>-50</td>
<td>≈0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frequency Shift / Imp. NN (MHz)</td>
<td>hcp av*</td>
<td>low</td>
<td>-32</td>
<td>-22</td>
<td>-32</td>
<td>-41</td>
<td>-53</td>
<td>-10</td>
<td>-17</td>
<td>-16</td>
<td>-25</td>
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<td></td>
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</tr>
<tr>
<td>Frequency Shift / Imp. NN (MHz)</td>
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</tr>
<tr>
<td>Frequency Shift / Imp. NN (MHz)</td>
<td>bcc</td>
<td>+11</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
</tbody>
</table>

Note

* In anisotropic hcp alloys, the shift value depends whether the impurity neighbor is in the same (001) plane as the Co atom or in the adjacent planes: Two satellites (low & high) are observed for very diluted alloys. In more concentrated alloys (>2%) the two satellites merge into an average one (av) because of the broadening due to long range disorder.
Examples: Magnetic multilayers

- Frequency fingerprint of Chemical/Xtallographic Environment
- Frequency Ranges correspond to Different Sample Parts

Co/Cu multilayer

Modeling of Interface Spectra

Monoatomic Step Defects

Simulated Spectra

Interface Model

Parameters of the model:
- \( d \): Average distance between steps
- \( l \): Average length of straight parts

Application: small roughness

Average distance between steps: 2.8 at.d.
Average straight length: 1.6 at.d.
Modeling of Interface Spectra
Diffuse Interface

Simulated Spectra
- 3 Mixed Planes
- 6 Mixed Planes
- 1 Mixed Plane
- 2 Mixed Planes
- 3 Mixed Planes

Parameters of the model:
Concentrations in each plane
(Concentration profile)
Example: Linear profile
Application: Large admixture >2ML.

Interface Model

Cross section view

.../Cr/Co/Cr/... Largely Mixed Interfaces

Spin Echo Intensity
Frequency (MHz)
50           100          150           200          250
[Co_{16Å}/Cr_{8Å}]

Cr concentration at.%

Hyperfine Field (% of bulk)

Mg/Zr/Co multilayers for applications in optics: Asymmetric Co interfaces

Mg/Zr/Co experiment
Mg/Zr/Co simulation
Mg/Zr/Co interfaces

Spin Echo Intensity
Frequency (MHz)
50           100          150           200          250

Almost perfect Mg/Co interfaces

Mg/Co/Zr experiment
Mg/Co/Zr simulation

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Magnetic information: Hyperfine Field Profile

Interface Model:

Concentration profile

Side output:

Average HF in each atomic plane

Average HF an estimate of Co magnetic moment at interfaces

<table>
<thead>
<tr>
<th>NMR</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>HF/HF_{bulk}</td>
</tr>
<tr>
<td>0.0</td>
<td>1.00</td>
</tr>
<tr>
<td>0.99</td>
<td>1.03</td>
</tr>
<tr>
<td>0.94</td>
<td>0.97</td>
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<td>0.75</td>
<td>0.89</td>
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<tr>
<td>0.63</td>
<td>50</td>
</tr>
<tr>
<td>0.13</td>
<td>75</td>
</tr>
</tbody>
</table>

Co clusters in matrices

- Magnetic properties depend on the size of the clusters:
  - Large clusters: multi-domain
  - Small clusters: single domain and depending on temperature, the magnetic moment direction is blocked (at low temperature) or rotating randomly in any direction (at high temperature)

Domain structure and blocking temperature is determined by the magnetic anisotropy of the material and by the size of the clusters. To understand the magnetic properties we need to know the size (distribution) of the clusters and the magnetic anisotropy.

Magnetic Properties by NMR

With additional external static magnetic field

Co clusters in Silica

**Lower frequency line**

Large Co clusters, multidomain, fcc:
- No demagnetizing field (217 MHz)
- Presence of Bloch walls (no shift in low field)

**Upper frequency line**

Small Co clusters, single domain, fcc:
- Not hcp, no HF anisotropy (no broadening with H_{ext})
- Demagnetizing field -6 kOe (223 MHz)
- No Bloch wall (shift \( -\gamma H_{ext} \))

When Co Clusters are superparamagnetic:

No NMR signal

**Lower frequency line**

Large Co clusters ferromagnetic:
- Constant intensity

**Upper frequency line**

Small Co clusters superparamagnetic:
- Loss of intensity with increasing temperature
- Large distribution of blocking temperatures

Large distribution of sizes:
Coexistence of small single domain clusters and of large multidomain clusters
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NMR - Macroscopic Viewpoint

Laboratory frame

Rotating frame (ω)

Pulsed $H_1$

Particular Turn Angles

$\pi/2 : \Rightarrow M_{n} \perp H_0 \ \ \pi : M_{n} \text{ Reversal}$

Measured NMR signal is proportional to the magnitude of the nuclear magnetization in the XY plane: Maximum when turn angle $\omega_1 \tau = \pi/2$

Enhancement factor & Restoring Field

Restoring Field

$H_{\text{res}} = \frac{2 \omega_1 \tau}{\pi} \text{Hopt(ferro)}$

related to:

- Anisotropy field (single domain behavior)
- Coercive field (domain nucleation or domain wall stiffness)
- Exchange bias, Coupling field (coupling energy between layers/grains)
3D NMR spectra in ferromagnets

How to visualize inhomogeneities

**NMR Intensity vs**
- Frequency: Structural NMR
- RF Field: Magnetic stiffness

The larger the strength of the \( H_1 \) field we need to apply, the stiffer the part of the sample under investigation.

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Structure & Magnetic Stiffness

Frequency = environment
- High frequency, bulk Co: Co atoms surrounded by other Co atoms
  - The frequency gives the local symmetry (fcc or hcp Co)
- Low frequency, interface: Co atoms by Co and Cu atoms
- Radiofrequency strength vs frequency:
  - Shows how magnetically stiff each environment is

Coupling Oscillations

Excitation mode for Ferromagnetic coupling
- Interface planes partly decoupled from inner planes
  - Softer than bulk (usual)
  - More sensitive to AF coupling (expected)
- AF coupling only partly transferred to inner planes

Excitation mode for Anti-Ferromagnetic coupling
- Interface planes partly decoupled from inner planes
  - Softer than bulk (usual)
  - More sensitive to AF coupling (expected)
- AF coupling only partly transferred to inner planes
Magnetization Process Homogeneity

Discriminates between
• Inhomogeneous magnetization process
And
• Coherent rotation of a net remanent magnetization e.g. Biquadratic Coupling

Co/Cu Multilayers

Co15ÅCu9Å
AF + F coupling

Co15ÅCu15Å
Ferromagnetic coupling

Co10ÅCu10Å
Biquadratic coupling ?

Inhomogeneities of Co Dispersion, Inhomogeneities of Magnetic Anisotropy: Co clusters in Cu

FC ZFC Measurements: 2 different blocking temperatures:
-Usual interpretation: 2 populations with different typical diameter.
The NMR viewpoint:

Evidence for the existence of two phases with different magnetic anisotropies

Conclusions

NMR allows to get specific information about of the structural and magnetic properties in different parts of the sample

Bulk Co
• Structure of the bulk of the layers and their respective magnetic stiffness
  Small grains lead to soft layers because of an increased number grain boundaries

At interfaces
• Morphology of the Interfaces
• Magnetization profile.
• Magnetic stiffness depends on interface disorder and defects

Between layers
• Coupling strength
• Discriminates between coherent and incoherent magnetization process.

In granular systems
• Distribution of sizes, magnetic anisotropy, superparamagnetism.

Ref:
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P. PANISSOD, C. MENY