Synchrotron Mössbauer Spectroscopy (SMS)

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Phenomenon to observation:

- The nucleus is not a point charge
  - internal dynamics \Rightarrow nuclear transitions
  - volume \Rightarrow isomer shift
  - spin \Rightarrow magnetic level splitting
  - quadrupole moment \Rightarrow quadrupole splitting

- SMS – Synchrotron Mössbauer Spectroscopy (a.k.a. NFS)
  - internal magnetic fields, electric field gradients, isomer shifts
  - applications include magnetic phase transitions, determination of spin & valence states, and melting studies

Recent reviews of Nuclear Resonant Spectroscopy:
R. Röhlisberger (Springer Tracts in Modern Physics, 2004)
W. Sturhahn and J.M. Jackson, GSA special paper 421 (2007)
Excitation of the $^{57}$Fe nuclear resonance:

fixed, isolated nucleus

14.4125 keV

$|e\rangle$

$|g\rangle$

4.66 neV

nucleus & electronic interaction or external fields

$|e,3/2\rangle$

$|e,1/2\rangle$

$|e,-1/2\rangle$

$|e,-3/2\rangle$

$|g,-1/2\rangle$

$|g,1/2\rangle$

$|g\rangle$

S(E)

$\approx \mu$eV

$nucleus & simple lattice excitation

$|e\rangle|2\rangle$

$|e\rangle|1\rangle$

$|e\rangle|0\rangle$

$|g\rangle|2\rangle$

$|g\rangle|1\rangle$

$|g\rangle|0\rangle$

$\approx 10$ meV

Mössbauer absorption

phonon side band

Synchrotron Mössbauer Spectroscopy — 3
Scattering channels:

\[ |\gamma_i\rangle |\Psi_i\rangle \rightarrow |\Psi_n\rangle \rightarrow |\gamma_f\rangle |\Psi_f\rangle \]

\[ |\chi_i\rangle \prod_j |\phi_j^{(i)}\rangle \quad |\chi_f\rangle \prod_j |\phi_j^{(f)}\rangle \]

lattice nucleus & core electrons

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NRIXS

incoherent

\[ |\phi_j^{(i)}\rangle \neq |\phi_j^{(f)}\rangle \]

SMS

(coherent inelastic)

\[ |\phi_j^{(i)}\rangle = |\phi_j^{(f)}\rangle \]

\[ |\chi_i\rangle \neq |\chi_f\rangle \]

(coherent elastic)

\[ |\Psi_i\rangle = |\Psi_f\rangle \]

G.V. Smirnov,

Nuclear level splitting:

<table>
<thead>
<tr>
<th>Irreducible tensor rank</th>
<th>0</th>
<th>1 parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>5 parameters</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3 parameters</td>
</tr>
</tbody>
</table>

**Isomer shift**

- Level scheme
- Energy spectrum
- All materials
- Electron density

**Electric field gradient**

- Magnetic field
- Atomic electrons
- Crystal field contribution
- Vanishes for cubic symmetry

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Synchrotron Mössbauer Spectroscopy — 5
SMS and traditional MB spectroscopy:

Traditional Mössbauer (MB) spectroscopy

Synchrotron Mössbauer Spectroscopy (SMS)

SMS advantages

➢ intensity and collimation
➢ control of polarization
➢ micro-focusing

SMS challenge

➢ accessibility
➢ spectra less intuitive

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### Table: SMS and Traditional MB Spectroscopy Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>SR</th>
<th>$^{57}$Co source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral flux</td>
<td>$3 \times 10^{12}$</td>
<td>$2.5 \times 10^{10}$ ph/s/eV</td>
</tr>
<tr>
<td>Brightness</td>
<td>$1 \times 10^{22}$</td>
<td>$2.5 \times 10^{13}$ ph/s/eV/sr</td>
</tr>
<tr>
<td>Spectral flux density</td>
<td>$5 \times 10^{12}$</td>
<td>$2 \times 10^{5}$ ph/s/eV/mm$^2$</td>
</tr>
<tr>
<td>(Focused)</td>
<td>$2 \times 10^{16}$</td>
<td>—</td>
</tr>
<tr>
<td>Typical beam size (mm$^2$)</td>
<td>$0.4 \times 2$</td>
<td>$10 \times 10$</td>
</tr>
<tr>
<td>Focused beam size (µm$^2$)</td>
<td>$6 \times 6$</td>
<td>—</td>
</tr>
<tr>
<td>Polarization</td>
<td>Linear or circular</td>
<td>Unpolarized</td>
</tr>
<tr>
<td>Best energy resolution (eV)</td>
<td>$4.7 \times 10^{-9}$</td>
<td>$9.4 \times 10^{-9}$</td>
</tr>
<tr>
<td>Energy range (eV)</td>
<td>$\approx 8 \times 10^{-5}$</td>
<td>$\approx 1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

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Origin of oscillations in time spectra:

SR pulse (all energies) + sample response (few energies)

\[\frac{\hbar}{\epsilon}\]

interference

E

\[E + \epsilon\]
Signatures in SMS time spectra:

- **single line:**
  - isomer shift only

- **two lines:**
  - electric field gradient, quadrupole splitting
  - two sites with different isomer shifts

- **many lines:**
  - magnetic field
  - several sites with different line positions

**Effective thickness:**

\[ D_{\text{eff}} = F_{LM} \sigma_0 \rho D \]

- \( F_{LM} \) : Lamb-Mössbauer factor
- \( \sigma_0 \) : resonant cross section
- \( \rho \) : nuclei per area
- \( D \) : geometric thickness

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Mössbauer spectroscopy

SMS

- undisturbed line shape, \( D_{\text{eff}} = 1 \)
- line broadening, \( D_{\text{eff}} = 50 \)
Interpretation of SMS spectra:

- Nuclear resonant contribution to the index-of-refraction

\[ \delta n(E) = \frac{\Gamma}{4k} F_{LM} \sigma_0 \rho \sum_{mm'} \frac{W_{mm'}}{E_{mm'} - E - i\Gamma/2} \]

- Time spectrum

\[ \frac{dI}{dt} = \left| \int \left[ e^{ikD\delta n(E)} - 1 \right] e^{-iEt/h} \frac{dE}{2\hbar} \right|^2 \]

- Mössbauer transmission spectrum

\[ T(E) = \int \text{Trace} \left[ e^{-kD\text{Im}[\delta n(E')] \right] L(E - E') dE' \]

Thickness effects:

- Distortions of time or energy spectra by thickness effects are often unwanted and complicate data evaluation and interpretation.

- Time spectrum expanded

\[
\frac{dI}{dt} = \left| \sum_{n=1}^{\infty} D_{\text{eff}}^n \int g^n(E) e^{-iEt/h} \frac{dE}{2\hbar} \right|^2
\]

with

\[
g(E) = i \frac{\Gamma}{4} \sum_{mm'} \frac{W_{mm'}}{E_{mm'} - E - i\Gamma/2} \]

- Higher order terms (n>1) become important if

\[
D_{\text{eff}} \max_E |g| \approx 1 \quad \Rightarrow \quad D_{\text{eff}} \approx \frac{2}{\max_{mm'} |W|}
\]
Experimental setup for SMS:

- x-ray pulses must be sufficiently separated in time
- detectors must have good time resolution and excellent dynamic range
- monochromatization to meV-level required to protect detector
- energy is tuned to the nuclear transition
Target applications:

➢ perfect isotope selectivity & complete suppression of nonresonant signals
➢ excellent sensitivity ($10^{12}$ nuclei in the focused beam)

☆ magnetism

☆ materials under high pressure

☆ nano-structures
Magnetism:

- Magnetism is of great importance in science and technology.

- Magnetism is inseparable from the electronic state of matter.

- High pressure, temperature, composition are basic parameters to modify the electronic state and thus affect magnetism.
Some experimental methods:

- **Spatially coherent, snapshot in time**
  - magnetic neutron diffraction
  - magnetic x-ray diffraction

- **Local in space, snapshot in time**
  - polarization-dependent x-ray absorption such as XMCD
  - x-ray emission spectroscopy (XES)

- **Coherent in space and time**
  - nuclear resonant scattering (SMS)
Diamond anvil cells for Mbar pressures:

A force applied to the diamond anvils can produce extreme pressures in a small sample chamber.
Re-entrant magnetism in Fe$_2$O$_3$:

- Canted anti-ferromagnet at low pressures ($\alpha$–Al$_2$O$_3$ structure)
- Loss of magnetic order at intermediate pressures (Rh$_2$O$_3$–II structure)
- Complex magnetic order at high pressures (post-perovskite structure)

(schematic by S.H. Shim, ASU)
Re-entrant magnetism in Fe$_2$O$_3$:

☆ low-spin Fe at intermediate pressures (XES measurements)

☆ complex magnetism at high pressures is stabilized by high-spin Fe

☆ but the actual magnetic structure has not been determined yet

Spin wave in a Fe/Cr multilayer:

Improving energy resolution:

- Extending the time range improves the energy resolution

APS hybrid mode

E.E. Alp et al. (unpublished)

bcc-Fe, B⊥ polarization

best possible resolution with traditional Mössbauer spectroscopy
SMS in the DAC with Laser heating:

- challenges
  - stability during data collection time (few minutes)
  - chemical reactions
  - quality of thermal insulator surrounding the sample

Melting under high pressure:

\[- \ln F_{LM} = k^2 \langle u^2 \rangle\]

\[\gg 1/k^2 \text{ for liquids}\]

**best fit with MINUTI software**

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*Earth Planet. Sci. Lett. 362 (2013)*

*Earth Planet. Sci. Lett. 447 (2016)*
In conclusion:

➢ **Synchrotron Mössbauer Spectroscopy (SMS)**

☆ coherent elastic scattering of x-rays
☆ neV resolution over μeV range
☆ internal magnetic fields, electric field gradients, isomer shifts
☆ extreme environmental conditions

➢ **Application of SMS**

☆ unique method to study magnetism in targeted layers
☆ determination of magnetic field magnitude and direction
☆ identify Fe(II), Fe(III) and their spin states in minerals
☆ melting under extreme pressure
☆ reliable software required for evaluation of SMS time spectra
☆ some suitable resonant isotopes are $^{57}$Fe, $^{119}$Sn, $^{151}$Eu, $^{161}$Dy