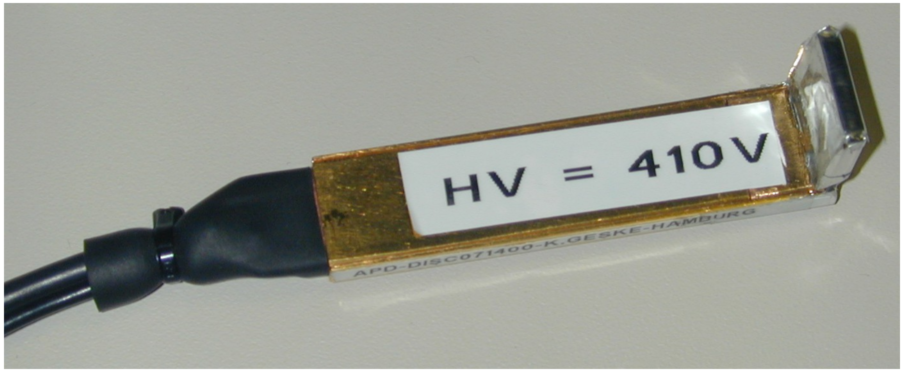
Synchrotron Mössbauer Spectroscopy (SMS)



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Phenomenon to observation:

- The nucleus is not a point charge

  - ✰ internal dynamics ⇒ nuclear transitions
  - ✰ volume ⇒ isomer shift
  - ✰ spin ⇒ magnetic level splitting
  - ✰ quadrupole moment ⇒ quadrupole splitting

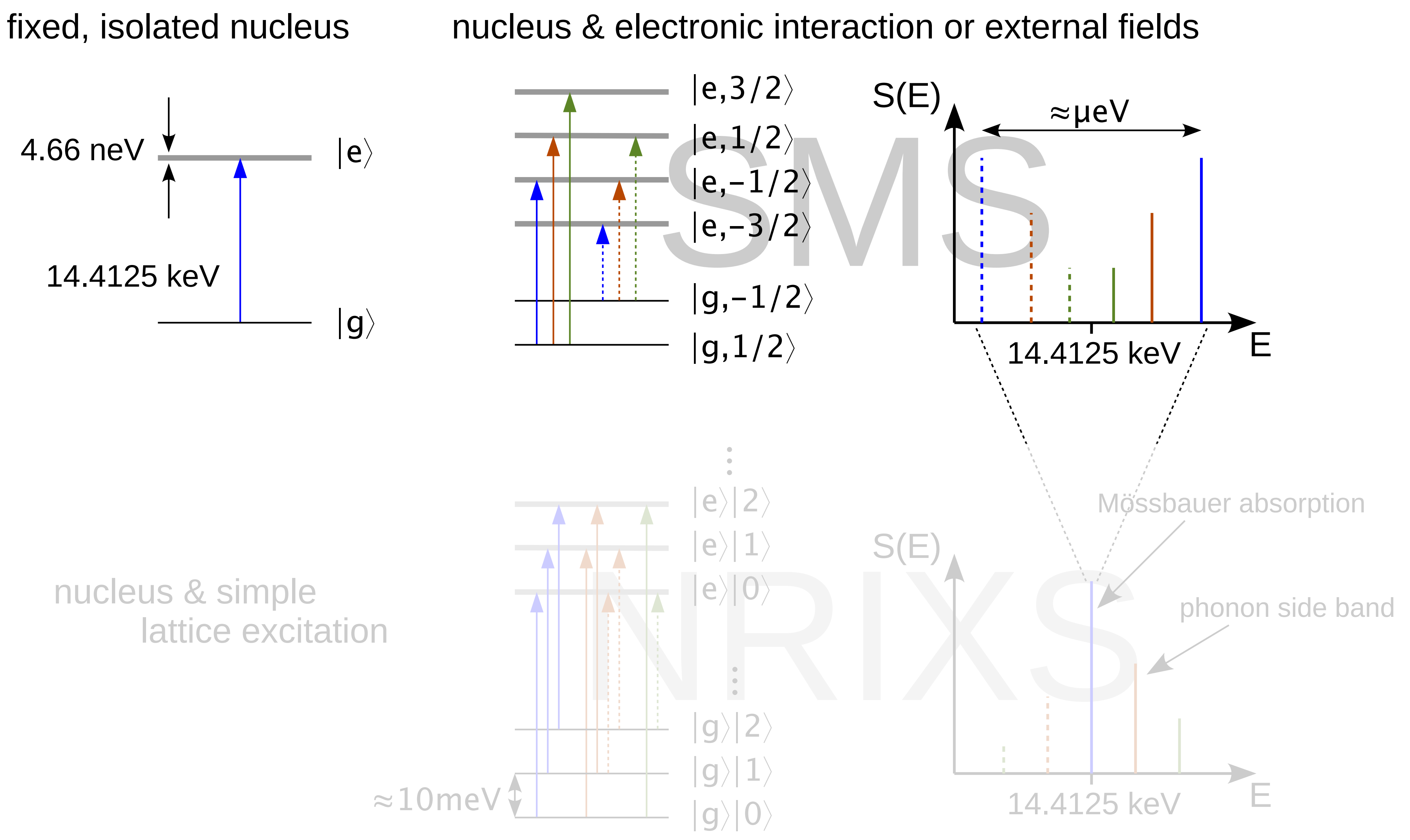
- SMS – Synchrotron Mössbauer Spectroscopy
  (a.k.a. NFS)

  - ✰ 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:

E. Gerdau and H. deWaard, eds., Hyperfine Interact. 123-125 (1999-2000)
W. Sturhahn, J. Phys.: Condens. Matt. 16 (2004)
R. Röhlsberger (Springer Tracts in Modern Physics, 2004)
W. Sturhahn and J.M. Jackson, GSA special paper 421 (2007)

Excitation of the ^{57}Fe nuclear resonance:



Scattering channels:

initial state → intermediate state → final state

$$|\gamma_i\rangle|\Psi_i\rangle \;\rightarrow\; |\Psi_n\rangle \;\rightarrow\; |\gamma_f\rangle|\Psi_f\rangle$$

$$|\gamma_i\rangle|\Psi_i\rangle = |\chi_i\rangle\Pi_j|\phi_j^{(i)}\rangle \qquad |\gamma_f\rangle|\Psi_f\rangle = |\chi_f\rangle\Pi_j|\phi_j^{(f)}\rangle$$

lattice — nucleus & core electrons

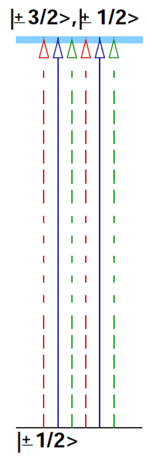
NRIXS	(negligible)	SMS
incoherent	coherent inelastic	coherent elastic
$\lvert\phi_j^{(i)}\rangle \neq \lvert\phi_j^{(f)}\rangle$	$\lvert\phi_j^{(i)}\rangle = \lvert\phi_j^{(f)}\rangle$, $\lvert\chi_i\rangle \neq \lvert\chi_f\rangle$	$\lvert\Psi_i\rangle = \lvert\Psi_f\rangle$

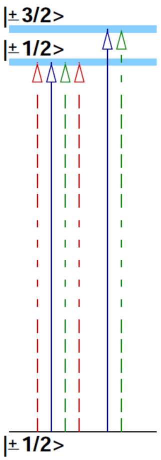
G.V. Smirnov, Hyperfine Interact. 123-124 (1999)

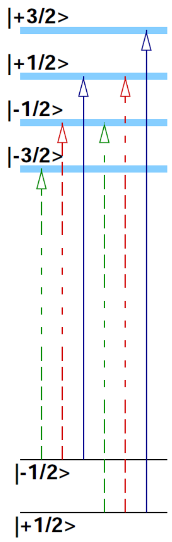
Nuclear level splitting:

irreducible tensor rank	0 1 parameter	2 5 parameters	1 3 parameters
	isomer shift	**electric field gradient**	**magnetic field**

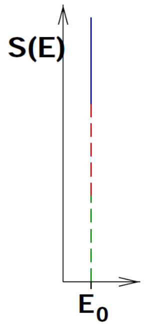
level scheme

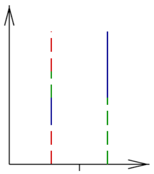


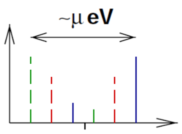




energy spectrum





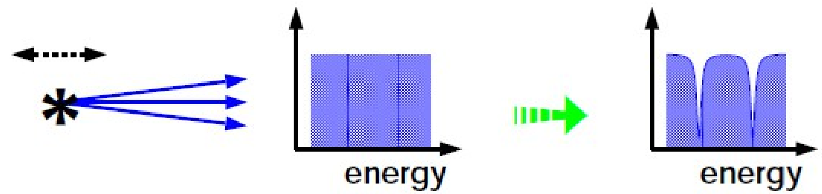


- all materials
- electron density

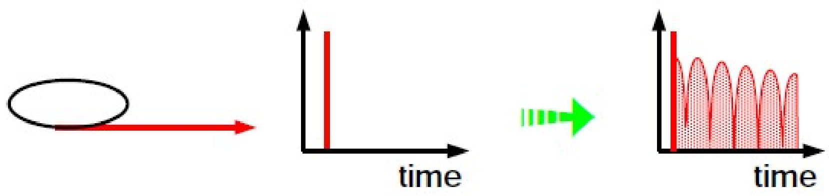
- atomic electrons
- crystal field contribution
- vanishes for cubic symmetry

- magnetic ordering

SMS and traditional MB spectroscopy:



traditional Mössbauer (MB) spectroscopy



Synchrotron Mössbauer Spectroscopy (SMS)

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

W.Sturhahn, J.Phys.: Condens.Matt. 16 (2004)

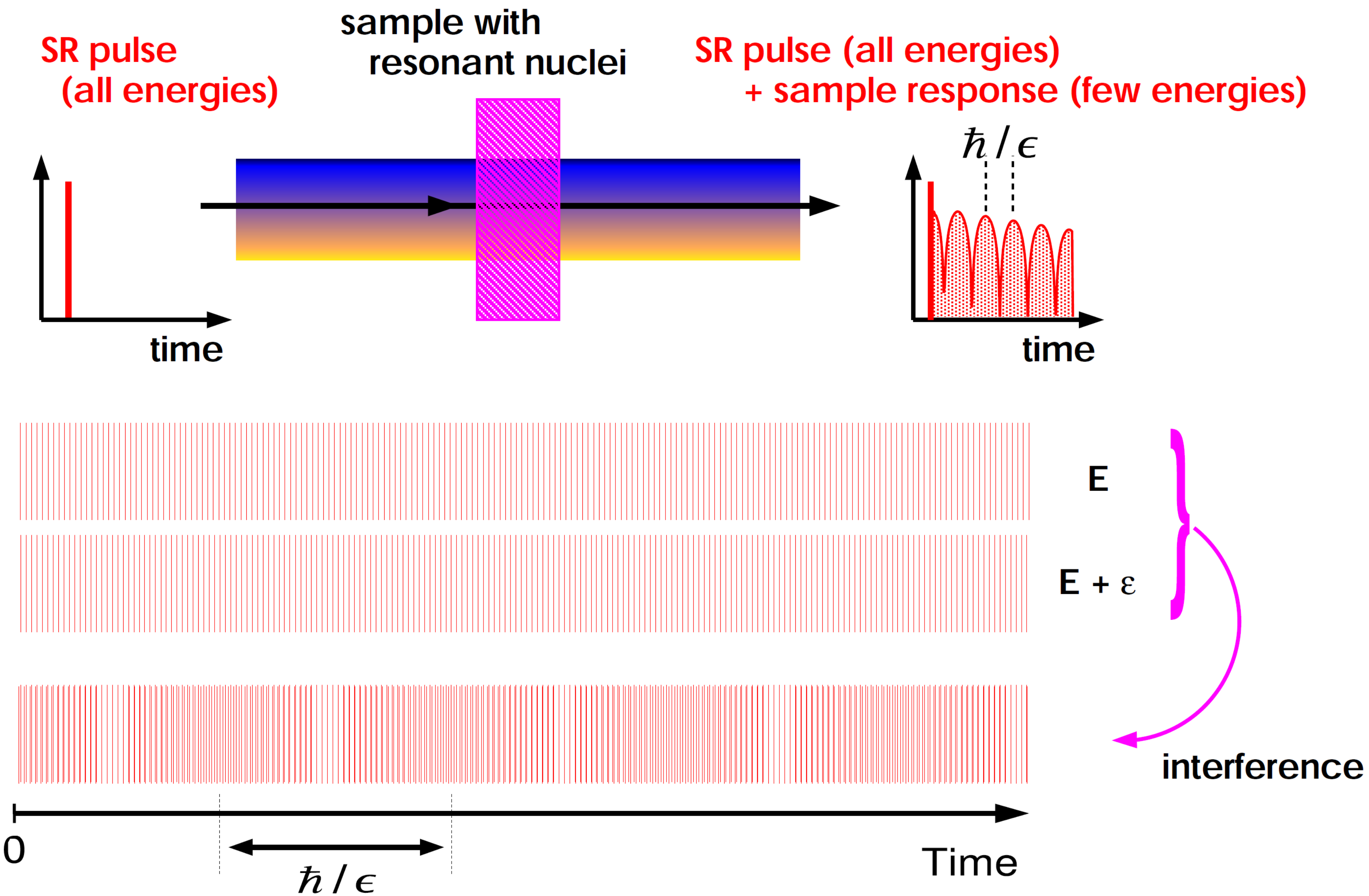
SMS advantages

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

SMS challenge

- accessibility
- spectra less intuitive

Origin of oscillations in time spectra:



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:

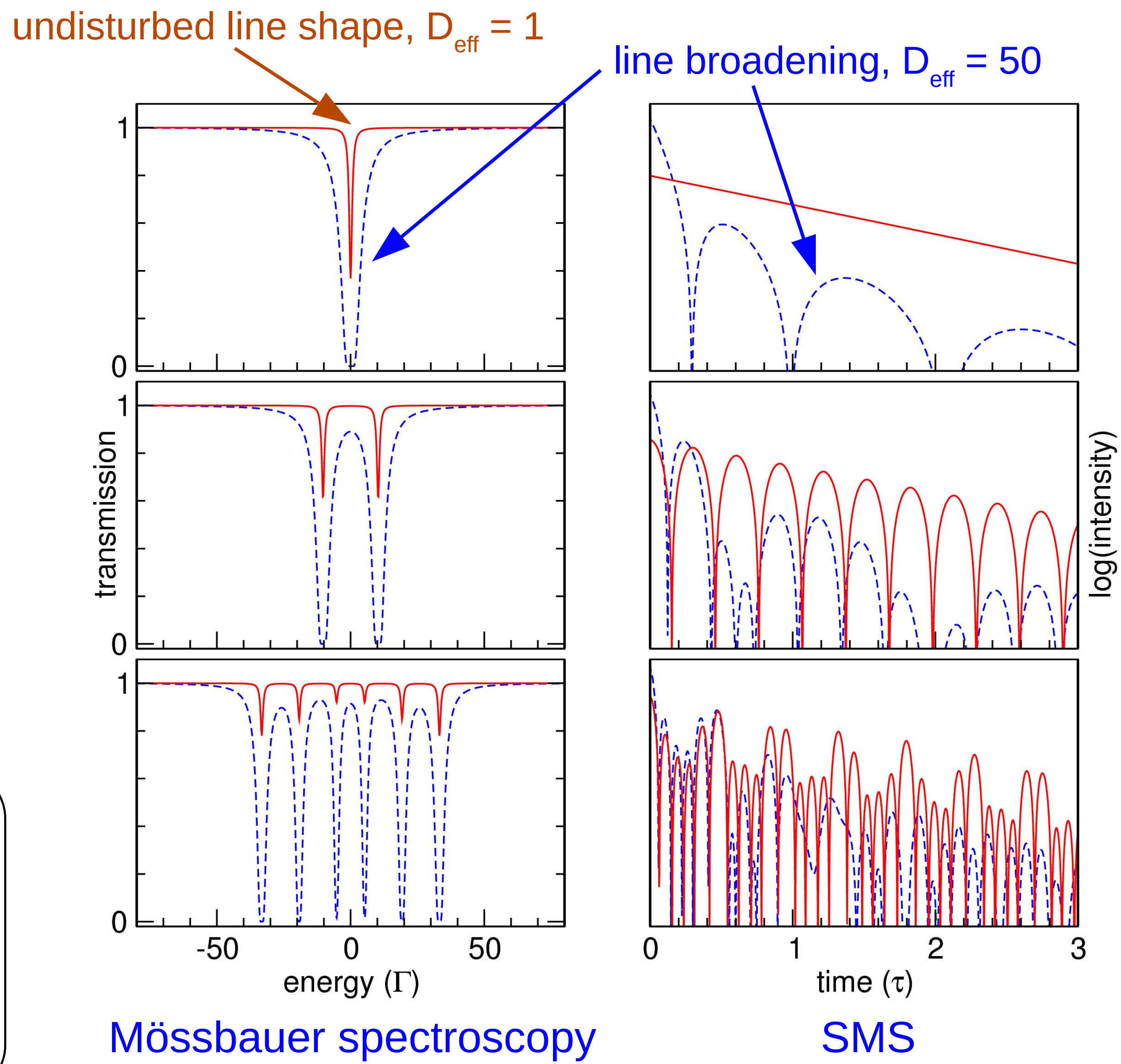
$D_{eff} = F_{LM}\, \sigma_0\, \rho\, D$

Lamb-Mössbauer factor

resonant cross section

nuclei per area

geometric thickness



Interpretation of SMS spectra:

- Nuclear resonant contribution to the index-of-refraction

$$\delta\mathbf{n}(E) = \frac{\Gamma}{4k} F_{LM} \sigma_0 \rho \sum_{mm'} \frac{\mathbf{W}_{mm'}}{E_{mm'} - E - \mathrm{i}\Gamma/2}$$

- Time spectrum

$$\frac{\mathrm{d}\mathbf{I}}{\mathrm{d}t} = \left| \int \left[\mathrm{e}^{\mathrm{i}kD\delta\mathbf{n}(E)} - 1 \right] \mathrm{e}^{-\mathrm{i}Et/h} \frac{dE}{2h} \right|^2$$

- Mössbauer transmission spectrum

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

W.Sturhahn, J.Phys.: Condens.Matt. 16 (2004)

Thickness effects:

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

- Time spectrum expanded

$$\frac{\mathrm{d}\mathbf{I}}{\mathrm{d}t} = \left| \sum_{n=1}^{\infty} D_{\mathrm{eff}}^{n} \int \mathbf{g}^{n}(E)\, \mathrm{e}^{-\mathrm{i}Et/h} \frac{dE}{2h} \right|^2$$

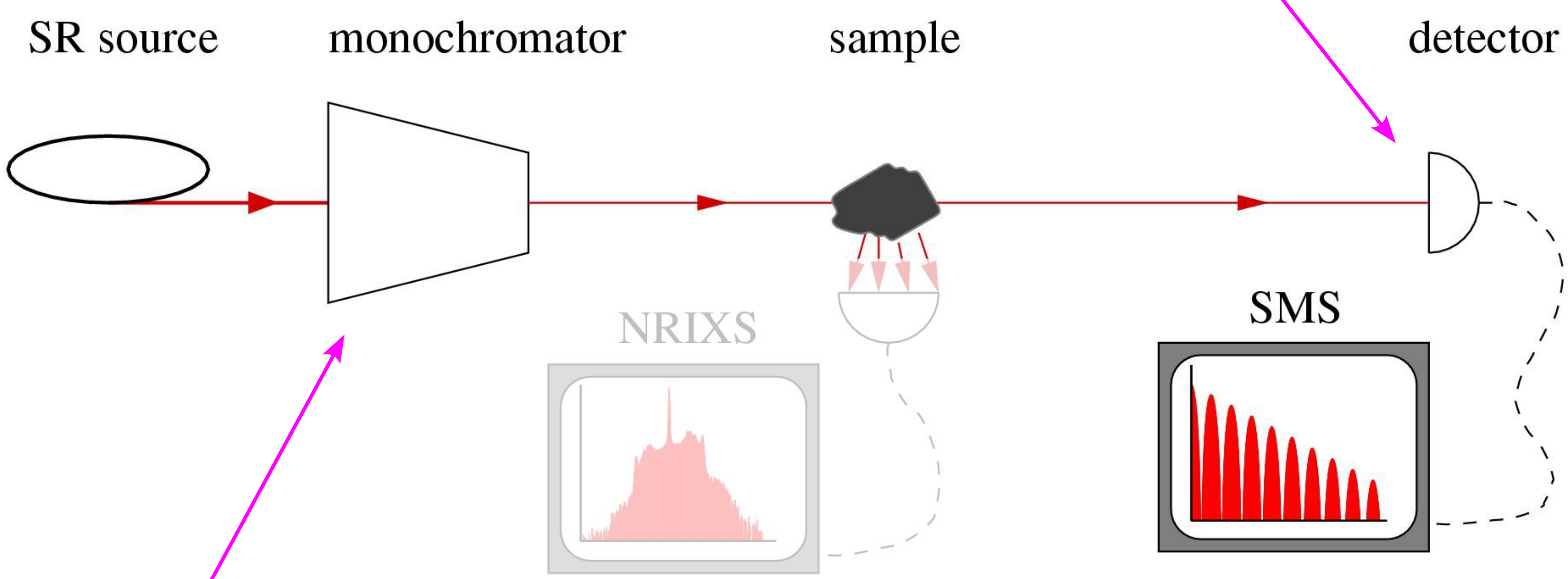
with $$\mathbf{g}(E) = \mathrm{i}\,\frac{\Gamma}{4} \sum_{mm'} \frac{\mathbf{W}_{mm'}}{E_{mm'} - E - \mathrm{i}\Gamma/2}$$

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

$$D_{\mathrm{eff}} \max_{E} |\mathbf{g}| \approx 1 \quad \Rightarrow \quad D_{\mathrm{eff}} \approx \frac{2}{\max_{mm'} |\mathbf{W}|}$$

Experimental setup for SMS:

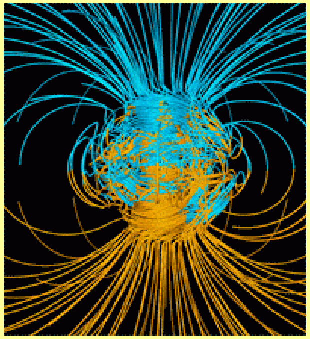
- x-ray pulses must be sufficiently separated in time
- detectors must have good time resolution and excellent dynamic range



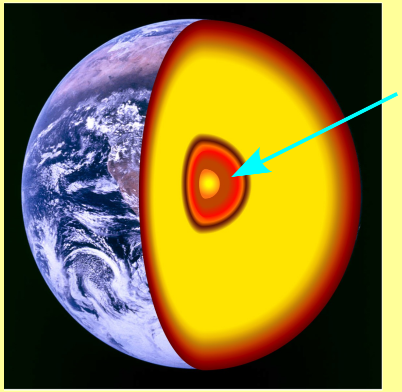
- monochromatization to meV-level required to protect detector
- energy is tuned to the nuclear transition

Target applications:

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

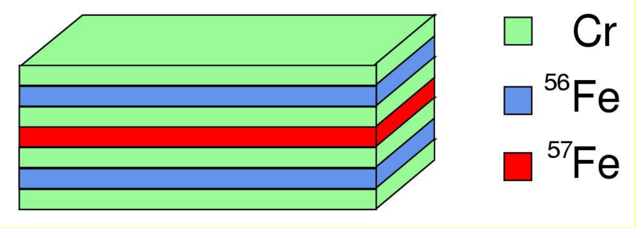


✰ magnetism



P > 1Mbar

✰ materials under high pressure

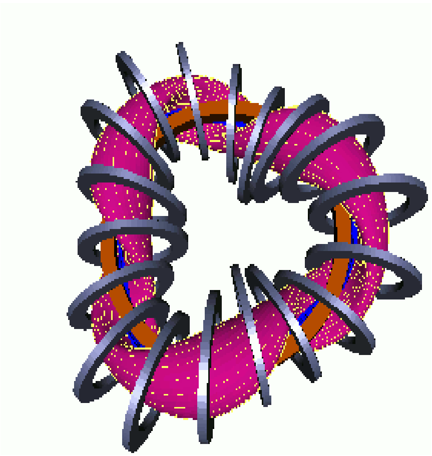


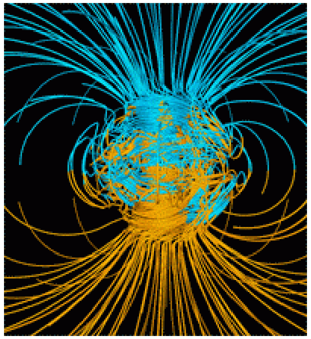
✰ nano-structures

Magnetism:

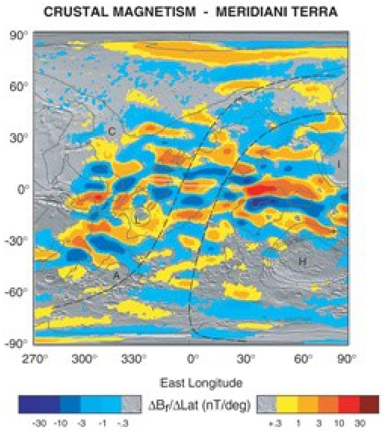
- magnetism is of great importance in science and technology.

magneto-hydrodynamics

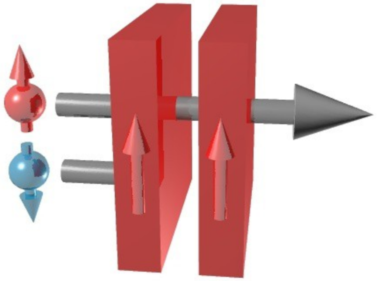




planetary magnetism & magnetic records



storage devices



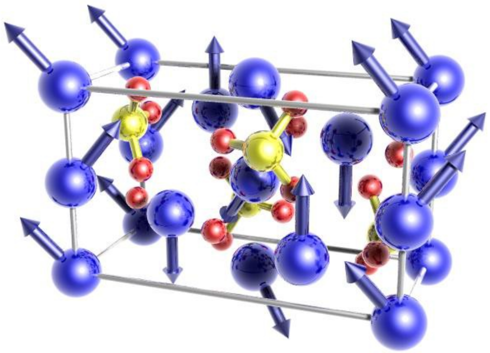
spintronics

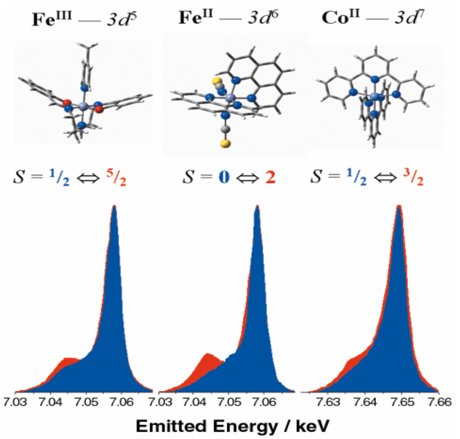
- magnetism is inseparable from the electronic state of matter.

- high pressure, temperature, composition are basic parameters to modify the electronic state and thus affect magnetism.

Some experimental methods:

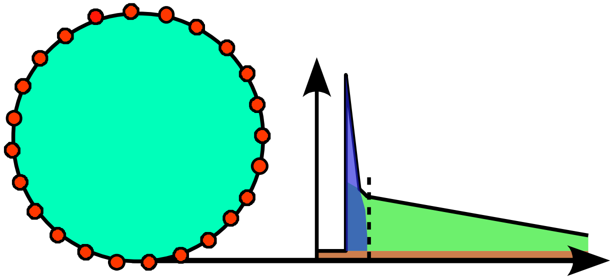
- spatially coherent, snapshot in time
  - ✫ magnetic neutron diffraction
  - ✫ magnetic x-ray diffraction



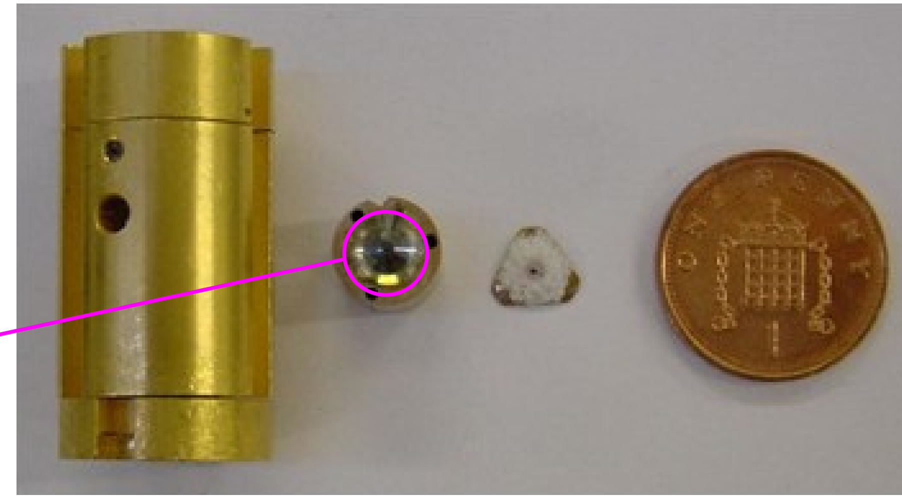


- local in space, snapshot in time
  - ✫ polarization-dependent x-ray absorption such as XMCD
  - ✫ x-ray emission spectroscopy (XES)

- coherent in space and time
  - ✫ nuclear resonant scattering (SMS)

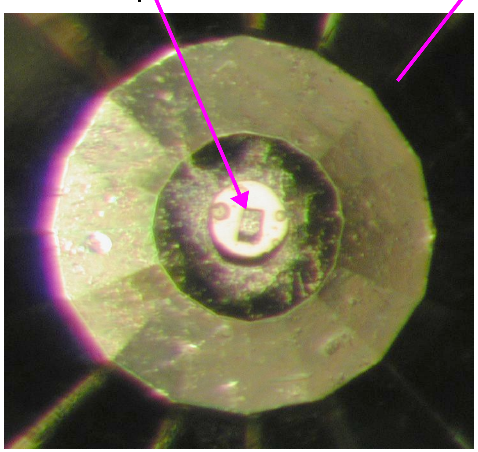


Diamond anvil cells for Mbar pressures:



- ✰ A force applied to the diamond anvils can produce extreme pressures in a small sample chamber.

sample



100 μm

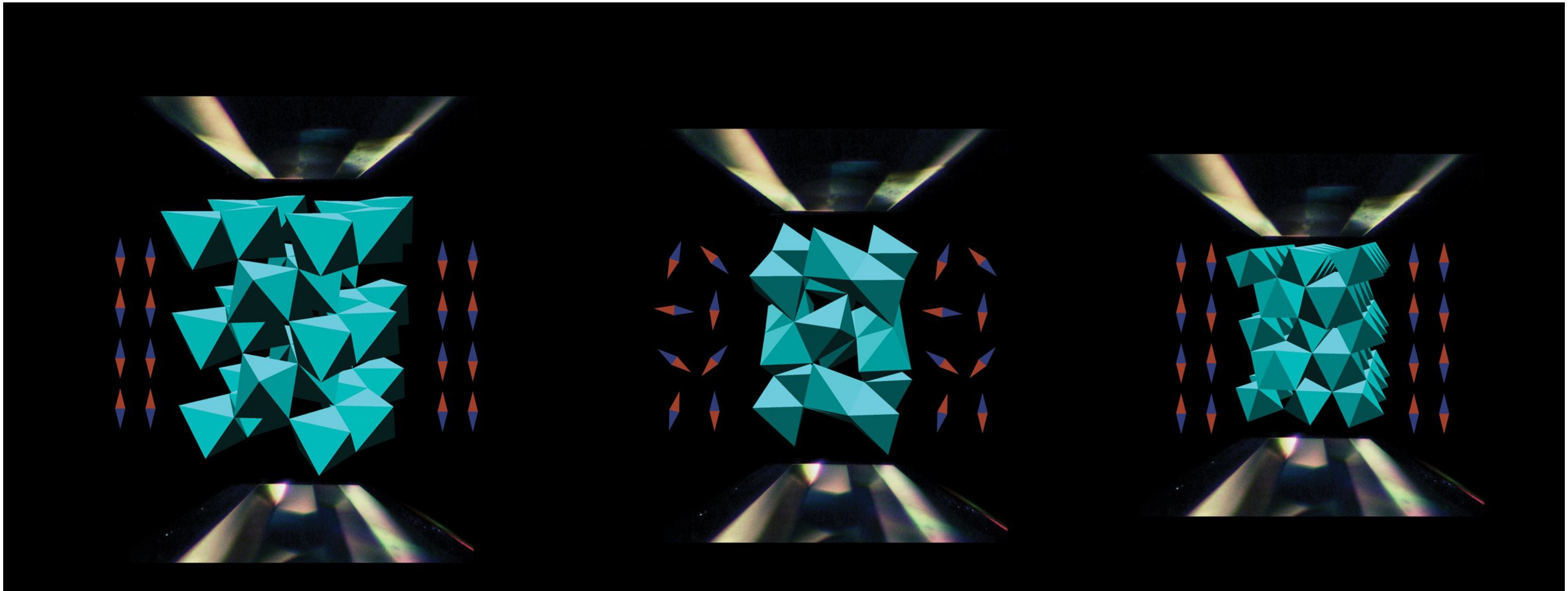
50 mm

Re-entrant magnetism in Fe_2O_3:

☆ canted anti-ferromagnet at low pressures (α–Al_2O_3 structure)

☆ loss of magnetic order at intermediate pressures (Rh_2O_3–II structure)

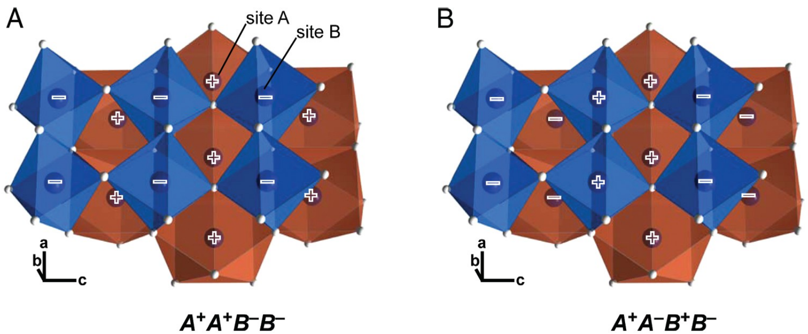
☆ complex magnetic order at high pressures (post-perovskite structure)



(schematic by S.H. Shim, ASU)

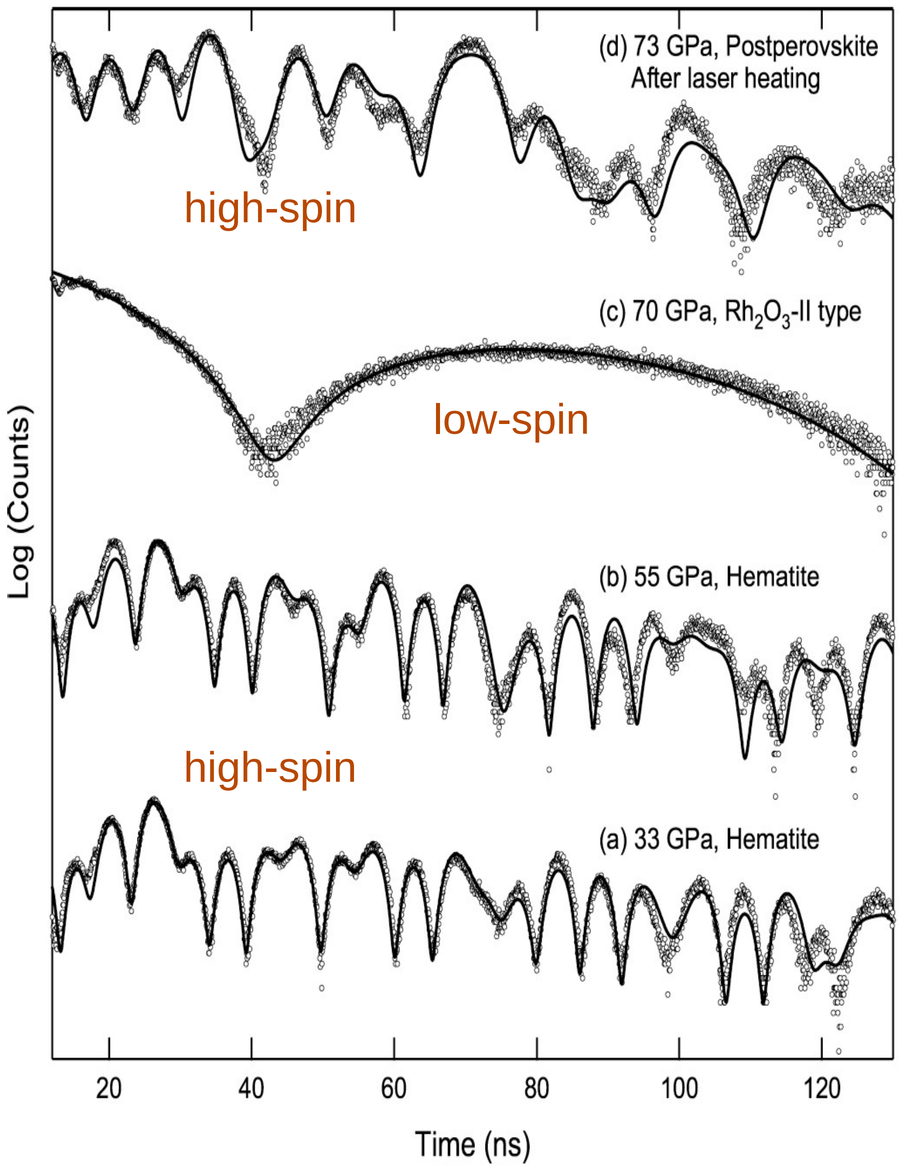
Re-entrant magnetism in Fe_2O_3:

- ✰ low-spin Fe at intermediate pressures (XES measurements)
- ✰ complex magnetism at high pressures is stabilized by high-spin Fe

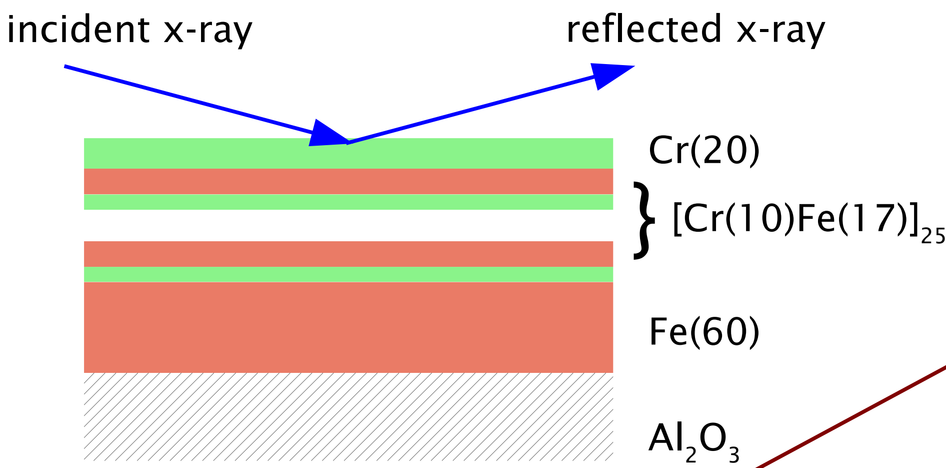


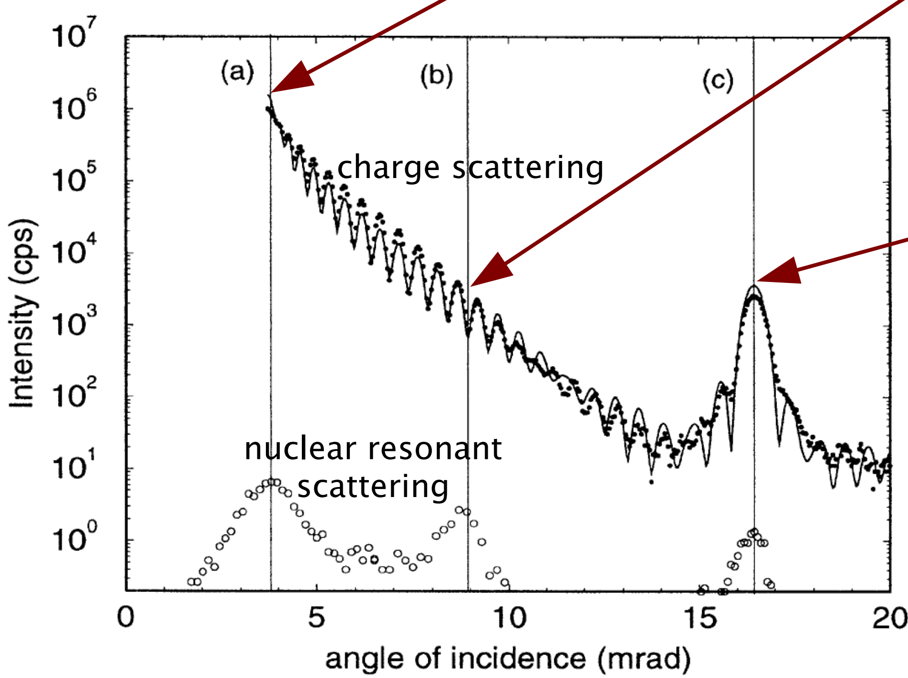
- ✰ but the actual magnetic structure has not been determined yet

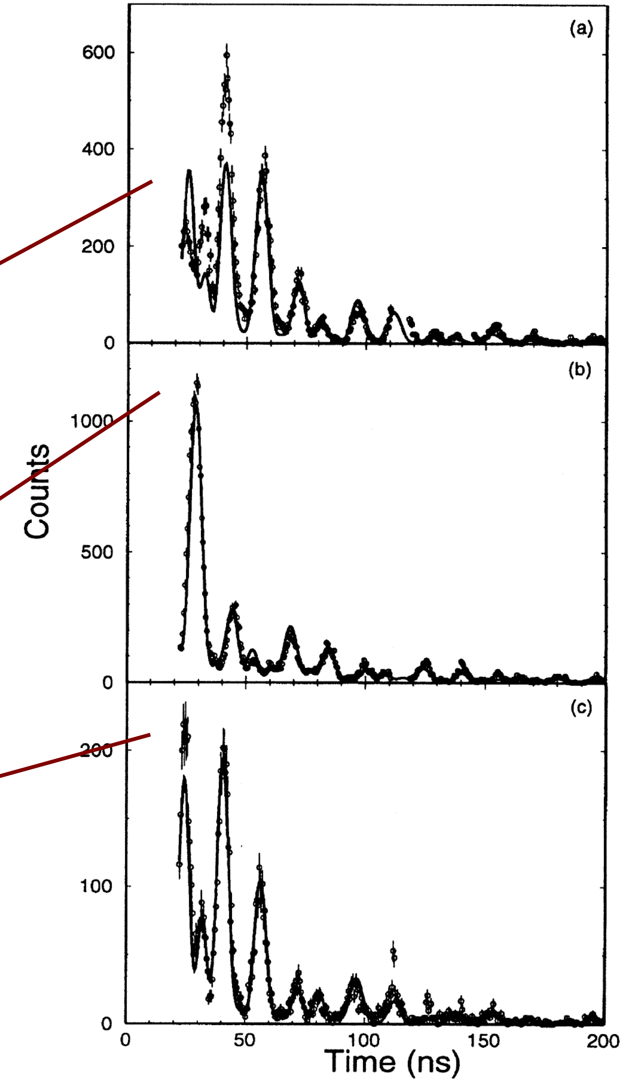
S.-H. Shim, A. Bengston, D. Morgan, W. Sturhahn, K. Catalli, J. Zhao, M. Lerche, V. Prakapenka, Proc. Natl. Acad. Sci. 106 (2009)



Spin wave in a Fe/Cr multilayer:



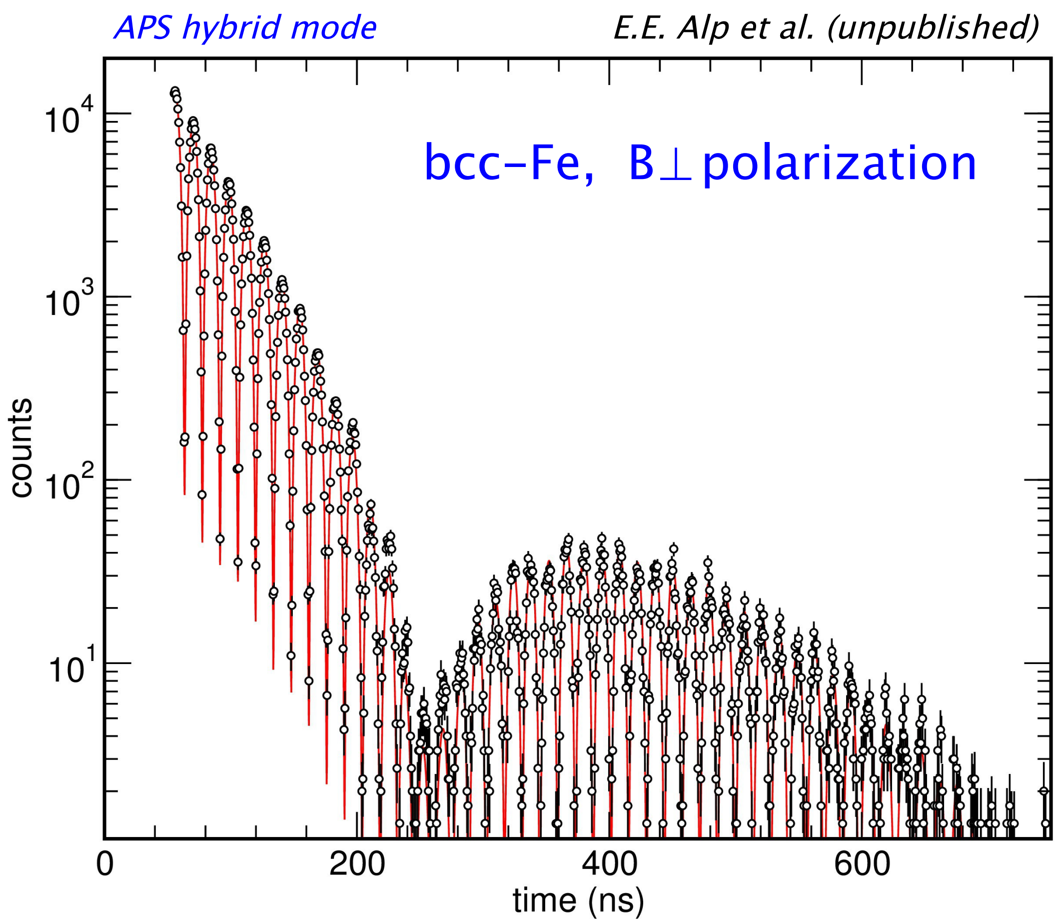


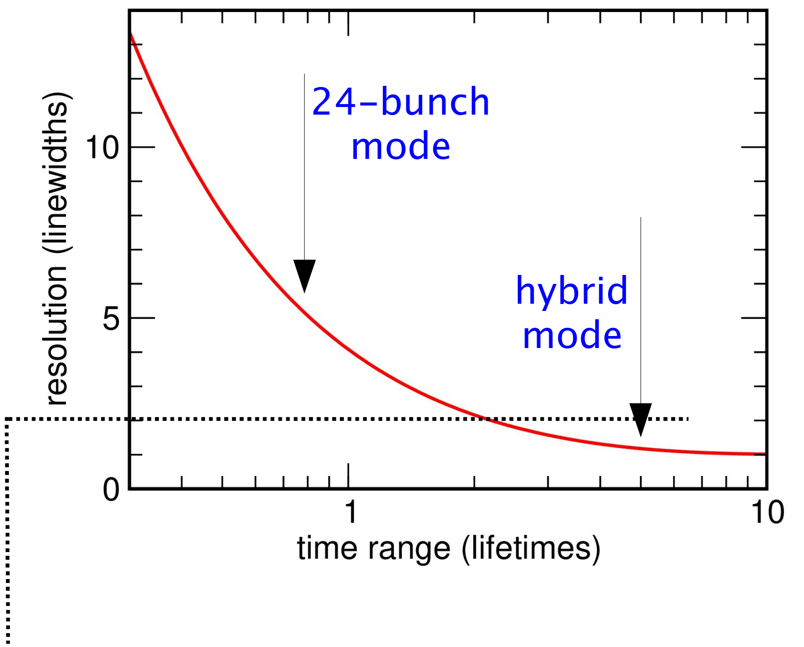


T.S. Toellner, W. Sturhahn, R. Röhlsberger, E.E. Alp, C.H. Sowers, E. Fullerton, Phys. Rev. Lett. 74 (1995)

Improving energy resolution:

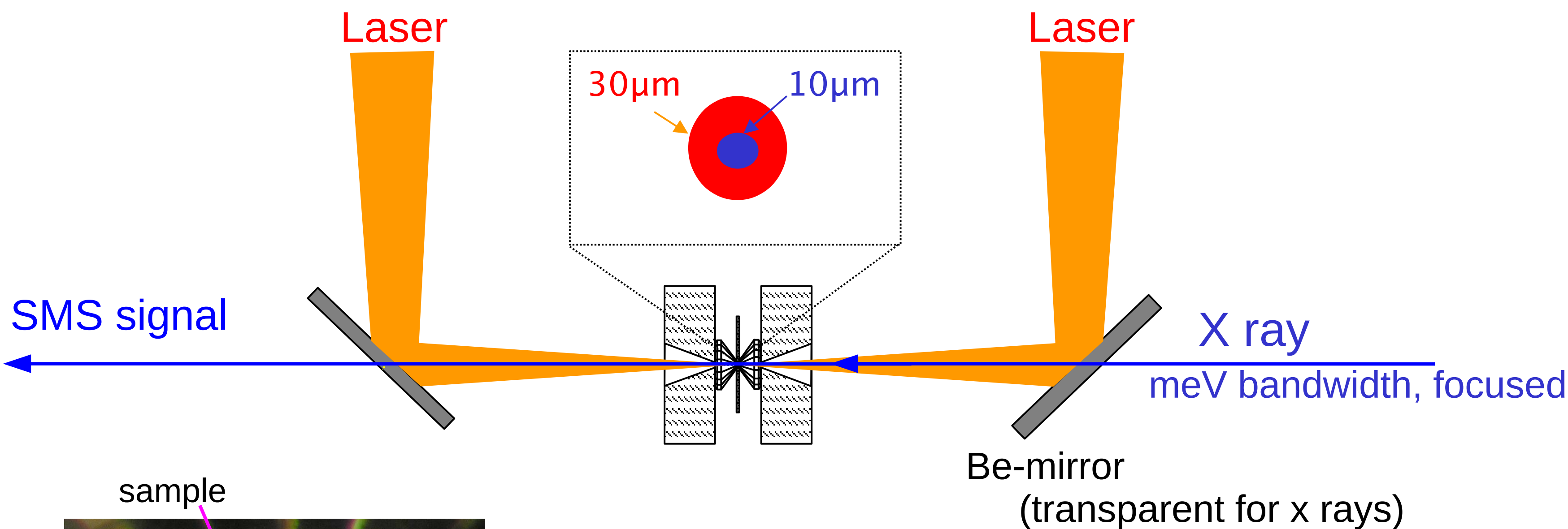
- Extending the time range improves the energy resolution

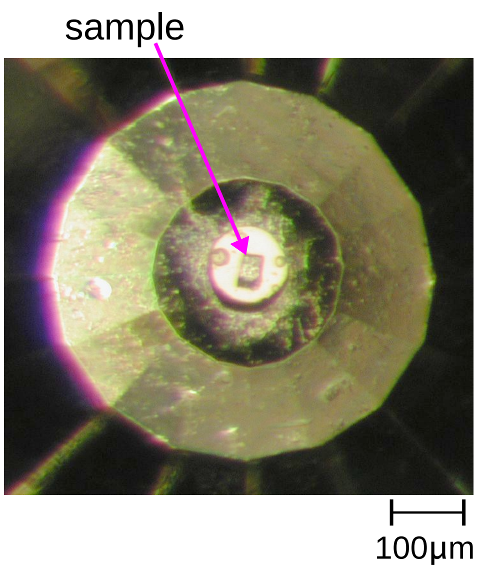




best possible resolution with traditional Mössbauer spectroscopy

SMS in the DAC with Laser heating:





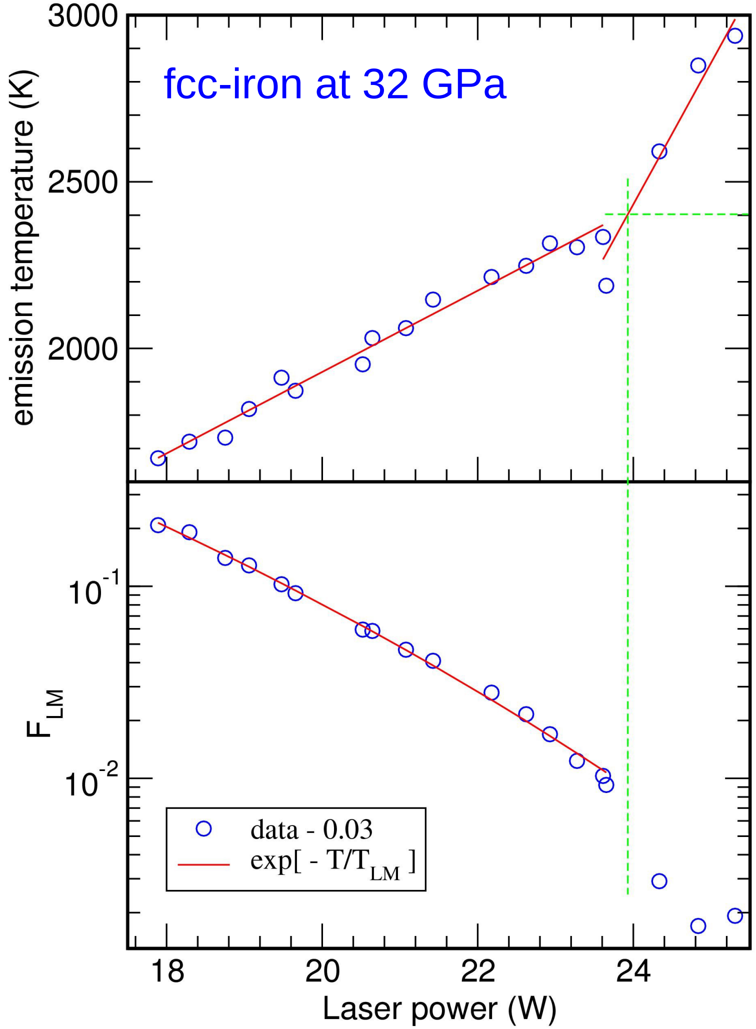
- challenges
  - ☆ stability during data collection time (few minutes)
  - ☆ chemical reactions
  - ☆ quality of thermal insulator surrounding the sample

J.M. Jackson, W. Sturhahn, M. Lerche, J. Zhao, T.S. Toellner, E.E. Alp, S. Sinogeikin, J.D. Bass, C.A. Murphy, J.K. Wicks Earth Planet. Sci. Lett. 362 (2013)

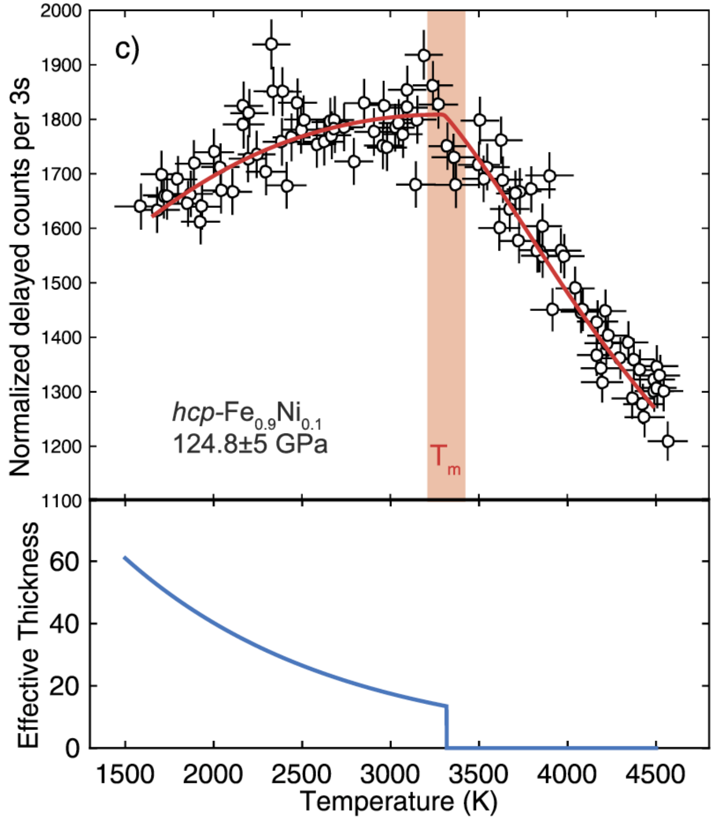
Melting under high pressure:

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

$$\gg 1/k^2 \quad \text{for liquids}$$



best fit with MINUTI software



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D. Zhang, J.M. Jackson, J. Zhao, W. Sturhahn, E.E. Alp, M.Y. Hu, T.S. Toellner, C.A. Murphy, V.B. Prakapenka 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